RARE EARTH ELEMENTS IN COAL—THE CASE FOR RESEARCH AND DEVELOPMENT INTO CO-PRODUCTION WITH COAL

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1 INTRODUCTION

In FY2012, the National Energy Technology Laboratory (NETL) tasked Leonardo Technologies Inc. (LTI) with assessing the potential value represented by rare earth elements (REEs) found in coal deposits. REEs historically exhibited some price volatility but around 2009 the prices began to rise sharply as demand greatly increased due a growing demand in modern electronics and in renewable energy technologies. China was, and remains, the largest supplier and has been described as having "market power" (ref. 1-1). The initial work on rare earth elements began as part of PPM Contract Task: Technology Options for Reducing Environmental Impact and Improving Productivity of Domestic Coal Mining. This effort included several elements related to rare earth elements: assess evaluation of the resource potential of rare earth oxides and metals in coal seams and coal by-products within the United States based on available data; evaluation of commercially available technology for extracting rare earth oxides and metals from coal and coal by-products; and development of an advanced resource extraction concept. This work resulted in five key findings:

1. REEs associated with some coal deposits are enriched compared to crustal averages and may be found in some coal byproducts at levels that can approach the levels found in other sources of REE being evaluated for their commercial potential.

2. Data compiled during the 1970s to 1990s that explored trace elements in coal provide limited insight into the fate of REEs from coal mining and coal preparation.

3. Reports examining the occurrence of REEs in association with coal suggests that most REEs are found as minerals (i.e., an inorganic constituent), but some papers suggested that some portion of the REEs (particularly heavy REEs) may be found associated with both organic and inorganic constituents.

4. Research data focusing on hazardous trace elements evaluated elemental partitioning during conventional coal preparation and the fate of ash produced during combustion as it passed through particulate collection devices. Data suggest that REE would be found concentrated in coal preparation wastes and collected in the particulate removal devices found at power plants.

5. Fly ash and bottom ash impoundments present complex targets for reprocessing; coal blending practices may dilute or further enhance the average concentration of REEs being fed to a power plant. Unmined portions of coal seams or coal mine wastes might expose portions of an original deposit that are highly enriched in REEs.

New tasking in FY 2013 included work on an Extraction of REE from Coal Process Concept. Under this tasking, support was provided to evaluate the potential for extracting REEs from coal. REE found associated with coal might provide an accessible source assuming that they could be produced at competitive costs. The planned work included:

1. Evaluate if existing coal mining activities or coal waste reprocessing operations are beneficial sources of rare earth elements.
2. Collect data on rare earth concentrations in coal seams and coal wastes.
3. Assess the efficacy of separation techniques as applied to as-mined coal, coal preparation wastes, and combustion wastes.
4. Develop conceptual designs for separating rare earths from coal.
5. Develop an updated database of REE in coal and produce a report documenting the potential viability of the program concept.

Work performed included actions to assess the potential and ability of extracting REE from coal and coal waste streams:

- Assessed the potential annual production and resource data by gathering readily available data and actual samples to be submitted for third-party analysis.
- Gathered new coal and coal waste data by a focused field campaign tied to current production.
- Assessed the efficacy of separation techniques currently applied to as-mined coal, coal preparation wastes, and combustion wastes.
- Produced the conceptual system design for widespread characterization and production, including assessment of methods for analysis of REEs, R&D needs focused on in-line monitoring for REE, and physical and chemical processing.

- Reported results in a framework that would allow for an independent cost/benefit assessment through a generic case study and a comparison to other undeveloped REE sources in the United States.
- Completed a revised data base of elevated REE concentrations associated with coal deposits. Developed an early version of an information, data, and literature clearinghouse to be operated at NETL. Search tools and knowledge mapping (that is, how the information would be structured for ease of use) should be limited to readily available tools within the IT framework at NETL.
- Prepared a conference presentation and an online article reporting on resource mapping.

The work for FY13 was to include a limited campaign to gather samples from a few operating sites to link measured REE values to the current coal industry footprint. The data source used in the earlier work included a substantial amount of data from samples taken several decades ago.

Field work was delayed until late calendar year (CY) 2013. In early CY 2014, Congress appropriated funds for an REE from coal program that required preparation of a Report to Congress by the end of CY 2014. The legislative language set forth in the Consolidated Appropriations Act, 2014, which was included in the final legislation (H.R. 3547, Public Law 113-76), states:

> *Within NETL Coal Research and Development, the agreement includes $15,000,000 to perform an assessment and analysis of the feasibility of economically recovering rare earth elements from coal and coal byproduct streams, such as fly ash, coal refuse, and aqueous effluents. The Department is directed to report its findings and, if determined feasible, to outline a multi-year research and development program for recovering rare earth elements from coal and coal byproduct streams to the Committees on Appropriations of the House of Representatives and the Senate not later than 12 months after enactment of this Act.*

The original work plan was subsumed into the Office of Fossil Energy (FE) and NETL efforts to respond to this charge from Congress. FY 2014 tasking and subsequent modifications (Table 1) to that tasking reflected these changes. The activities included concluding any

remaining field work that was originally planned; developing and funding an expanded program by external organizations to collect samples representing both a broad variety of source types (coal, coal preparation plant samples, coal combustion wastes, mining wastes, and waters associated with coal processing) and coal regions; testing a handheld X-ray fluorescence (XRF) device to perform field measurements of REEs; continued collection of data on REE concentration and extraction, and support for development by FE Headquarters (HQ) and NETL of the Report to Congress. Subsequent task orders followed in FY 2014 and FY 2015. The effort ended in May of 2015. See Figure 1 for a simple representation of the flow of the work.

This report is a summary of the work performed on the topic of REEs associated with coal. Emphasis is placed on work from the start of FY 2013 forward. In addition, work results will not be presented in a strictly chronological order but rather key findings which may have been developed after a number of samples had been taken and analyzed, will be presented in sections dealing with field samples. Two separate efforts were made to assess resources—one by LTI early in the project and another more structured study by Tetra Tech completed in time to be used in the Report to Congress—which will be discussed together.

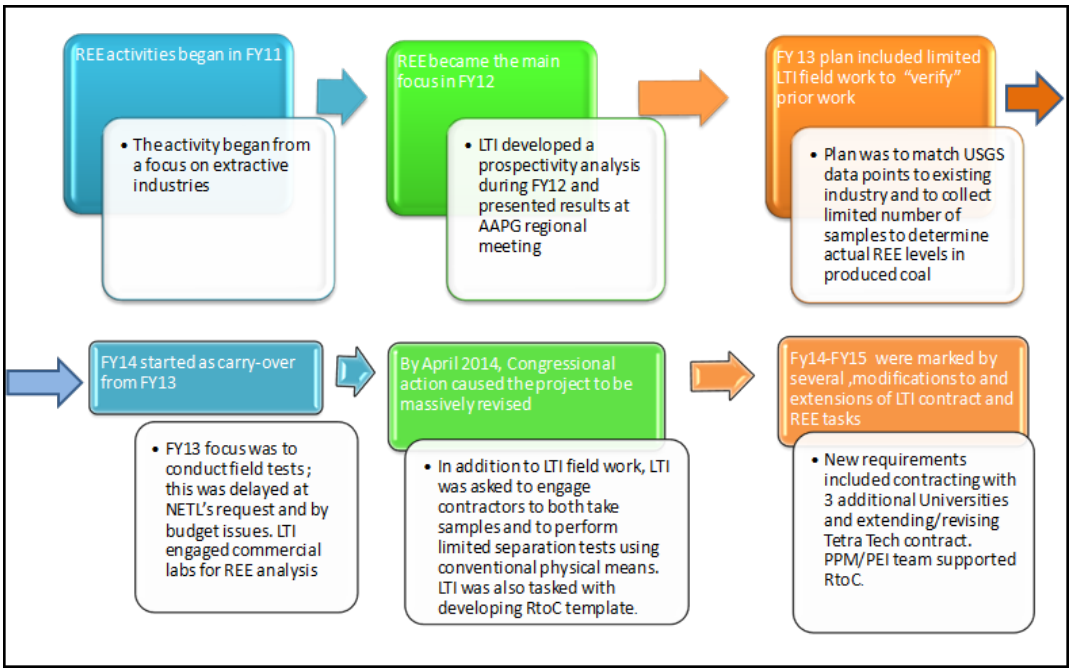


Figure 1. Work Flow within Task 150.02 Focused on REEs

Table 1. Summary of LTI Contract

Contract	Scope	Date
Task 04002.150.02.01	Technology Options for Reducing Environmental Impact and Improving Productivity of Domestic Coal Mining	10/1/2011-9/30/2012
Mod B added 150.02.03	Extraction of REE from Coal—Process Concept	Extended through 11/15/2013
Mod C extending 150.02.03	Extraction of REE from Coal—Process Concept	Extended through 4/30/2013 and added: • LTI field program • Develop collaboration • Presentation/publication

Mod D extending 150.02.03	Extraction of REE from Coal—Process Concept	Extended through 11/15/2014 and added: • Subcontracts to conduct field sampling and pilot separations focused on CAPP and SAPP • Improve on resource estimates from Mod C • Evaluate field devices (i.e., XRF) • Processing report • Develop preliminary cost information at plant or plant complex level • Interact and coordinate with the ESAP Contractor performing cost study
Mod E	Extraction of REE from Coal—Process Concept	Maintained 11/15/2014 date but added: • Subcontracts to conduct field sampling and pilot separations focused on NAPP, Alaska, and other western coal fields • Develop preliminary cost information as in Mod D • Compare REE concentration values and costs with current commercial practices for producing REE concentrates
Mod F extending 150.02.03	Extraction of REE from Coal—Process Concept	Extended through 1/31/2015 and added: • Support for Report to Congress • Support to EDX site development • Data upload for results from all sources • XRF calibration report • XRF transfer plan

2 ARGUMENTS FAVORING EVALUATION OF REE'S IN COAL AS A NATIONAL RESOURCE

The work during FY11 and FY12 focused on assessing the amount and distribution of various REEs in U.S. coal formations. There was considerable data in the literature detailing concentrations of REEs found in coal beds (usually by seam or formation). (ref. 2-1 to 2-5) A significantly smaller body of work was reviewed that reported on REEs found in coal produced by coal preparation or as a combustion byproduct. (ref. 2-6 to 2-8) Many of these were from outside the United States (China, Russia, etc.) However, these reports typically focused on individual sources of coal. The LTI work sought to develop an estimate for resources on a national basis and to highlight a few coal regions that might contain REEs in sufficiently elevated concentrations to make them an alternative, commercially-viable source for REEs.

Many of the prior studies of trace elements (including REEs) in coal, coal combustion ash, and other coal-derived wastes found that a number of rare/precious metals and critical energy elements can be found in coal in concentrations that varied from formation to formation and within the extent of an individual formation. An additional consideration in assessing the impact of REE extraction from coal-based sources is that extraction of many of the trace metals might improve the potential to reuse combustion wastes or reduce the cost of disposal for any remaining solid materials. This benefit would accrue due to removal of hazardous trace elements and could complement any value stream arising from extraction of commercially-important metals.

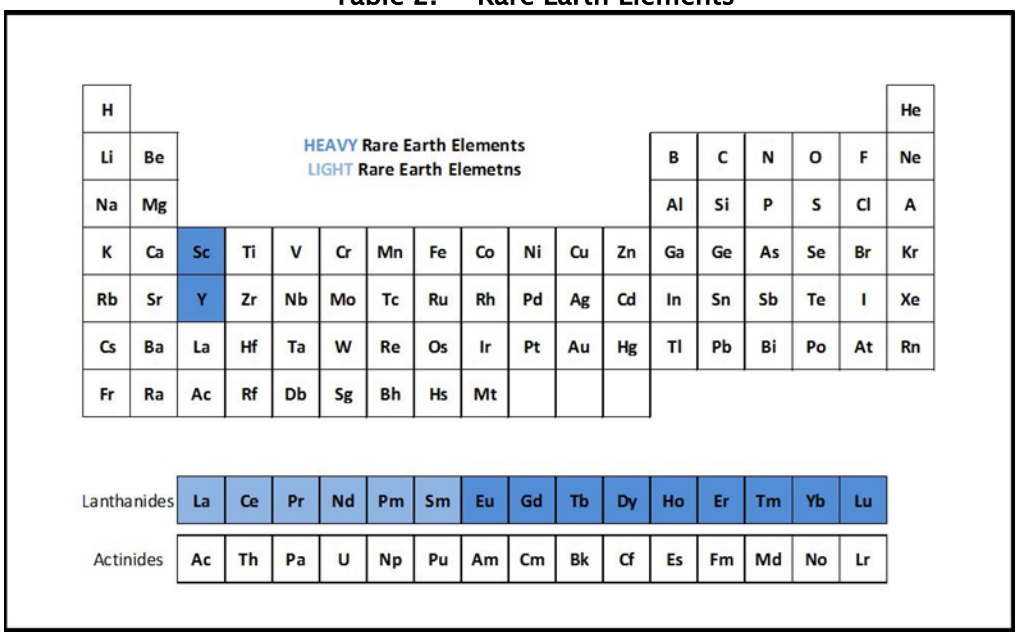
2.1 CO-PRODUCTION AND OUTSOURCED PROCESSING VERSUS DEDICATED MINES WITH VERTICALLY INTEGRATED PROCESSING

The logic for evaluating coal as a source arises from both the concentration values discussed above and from the fact that active coal mines have already absorbed the costs for developing the mine and much of the up-front extraction, size reduction, and gravity separation that is also found in REE production schemes. Many observers of rare or precious metal markets (see Table 2) argue that co-production is a crucial element of successful development and sustainable operation.(ref. 2-9 and 2-10) Some of the active REE mining operations (Bayan Obo in China is primarily a source of iron ore) and many of the projects currently under development are co-production projects (such as Kvanefeld [see: ref. 2-11

Greenland Minerals and Energy Ltd.] and Nechalacho Basal [see: ref. 2-12 Avalon Rare Metals Inc.]).

The Mountain Pass mine was part of a larger vertically integrated scheme that involved partial processing in the United States and final processing in China. A central question that has yet to be answered for REEs is whether vertical integration within a company focused almost exclusively on REEs is a better path to a sustainable commercial future or would horizontal integration targeting several different types of rare metals (that relies on others to refine the products) would serve as a hedge against volatility within a particular group of rare metals (such as REEs).

Table 2. Rare Earth Elements



A number of studies were reviewed (ref. 2-1 through 2-8) at the beginning of this work. In general, the papers focused on a detailed examination of one or a few sites, typically in a single coal body, and developed information relevant to the dispersal of REEs across the formation, the fate of REEs when any of these coals were cleaned, and the presence of REEs in combustion byproducts. The results cited in these papers are generally consistent with the results developed by all participants in this project.

Researchers also sought to correlate concentration patterns with other geologic events. This subject will be discussed later in this document.

2.1.1 Typical REE Price Volatility vs. Fluctuations in Price Due to Market Power

Rare mineral prices (not just for REEs) often demonstrate significant volatility (ref. 2-13: Ecorys report to EU). Rare earth prices had not been historically volatile until 2008. However, those data covered a period when the light rare earths (primarily Ce and La) were the target and the uses for these rare earths were well-established and stable (alloys, glasses, dopants, and catalysts). As the demand for REEs shifted to include other REEs (Praseodymium (Pr), Neodymium (Nd), Dysprosium (Dy), Samarium (Sm), Europium (Eu), Terbium (Tb), and Yttrium (Y)), supply constraints became an important issue. In addition, the only current, commercial source of the heavier REEs is from the lateritic clay deposits in southern China. Prices spiked alarmingly in 2008 and 2009 but began to drop for most REE that are routinely available. However, prices have remained elevated for a few REEs (which coincide with the critical REEs in the USDOE Critical Materials report-ref. 2-14).

During the period when REE prices were undergoing a steep rise, many new projects were planned. A significant number were co-production projects for which the concentration of total rare earth oxides was less than 0.3 percent (3,000 ppm). Many analysts have argued that co-production projects spread the financial risk over several products and reduce the financial risk compared to REE-only candidates. The total rare earth oxide (TREO) concentration for many of these projects was low but they were co-production opportunities in which other rare metals or commercial commodities were also present. Many of these same projects focused on sites that contained higher amounts of the heavier REEs. However, as of today, China had and still maintains market power over rare earth element supplies and prices, particularly as demand rises. The section on cost studies will provide further information about economic studies performed under this project and other recent analyses.

2.1.2 Other Rare/Precious Metals or Critical Energy Elements Found in Coal

Rare earth elements are principally associated with uncommon varieties of igneous rocks. Above average concentrations of REE-bearing minerals are also found in placer deposits which are residual deposits formed from deep weathering of a number of igneous rocks, pegmatites (an igneous rock with extremely large crystals), iron-oxide copper-gold deposits, and marine phosphates. The alkaline rocks in which REEs are often found may be the result of a geologic process that extracts and concentrates elements that do not fit into the structure of the common rock-forming minerals. The resulting magmas are unusually

enriched in elements such as zirconium, niobium, strontium, barium, lithium, and the rare earth elements (ref. 2-15).

Weathering of all types of rocks yields sediments; depending on the source of the erosion products, certain rare earth element-bearing minerals, such as monazite and xenotime, can be concentrated along with other heavy minerals. Another type of REE deposit, the ion-absorption type, is formed by the leaching of rare earth elements from seemingly common igneous rocks and fixing the elements onto clays in soil. Trace amounts of rare earth elements have also been identified in magnetite-apatite replacement deposits. The same can be said for marine phosphate deposits, which can contain as many as 0.1 percent REE oxides (ref. 2-16). Recovery of rare earth elements as a byproduct of phosphate fertilizer manufacture or from phosphate wastes has been considered.

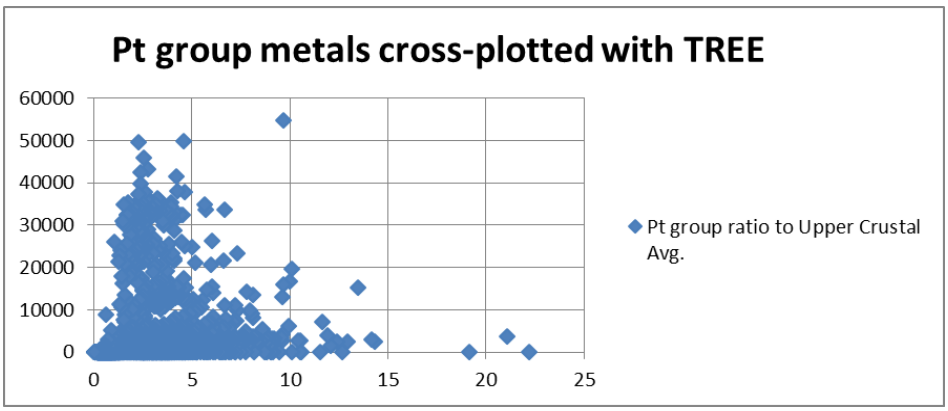
The ores of rare earth elements are mineralogically and chemically complex and commonly radioactive. The principal deleterious impurity in REE-bearing minerals is thorium. The cost of handling and disposing of radioactive material is a serious impediment to the economic extraction of the more radioactive REE-rich minerals, in particular monazite, which typically contains considerable amounts of thorium. (ref. 2-15).

2.2 REE'S FOUND IN COMMERCIAL DEPOSITS OF OTHER COMMODITY MATERIALS

Rare earth elements are often found in deposits mined to extract other valuable minerals. The most common occurrence is in deposits being evaluated for uranium and/or thorium. The Mountain Pass site was originally explored as a source of uranium (U) ore (ref.2-16). The black sand placers in North Carolina were mined in the past to extract thorium (Th) (ref.2-16). These two elements, which are part of the actinide series, have similar atomic structures and bonding characteristics to the rare earths (the lanthanide series) which may account for the fact that they are often found together. The Bayan Obo mine in China was originally developed as an iron ore mine.

As part of the work in FY12 and FY13, cross plots were developed of normalized concentrations for both REEs and other rare elements (the full list of energy critical elements includes: Lithium (Li), Cobalt (Co), Gallium (Ga), Indium (In), and Tellurium (Te); ref. 2-14) were developed to see if these elements might routinely be found in a single deposit. (See Figure 2) A limited number of coal deposits appear to be enriched (when calculated on an ash-only basis) in some rare metals and energy critical elements

(particularly Li, Co, and Ga). For instance, there appear to be a number of samples with enrichment, on an ash-only basis, for platinum group metals (typically with Iridium (Ir)>Osmium (Os)> Platinum (Pt) > Ruthenium (Ru) > Rhodium (Rh) >Palladium (Pd)) by ten thousand to fifty thousand times while the total REE (TREE) enrichment is five to ten times the crustal average value (ash-only basis). Similarly, the ratio between U + Th and REEs indicates that coals with elevated levels of REEs do not have similarly elevated levels of uranium and thorium. Given the small concentration values that were measured and used in the calculation of each ratio (numerator and denominator), the potential significance of any of these relationships can only be evaluated by further research.



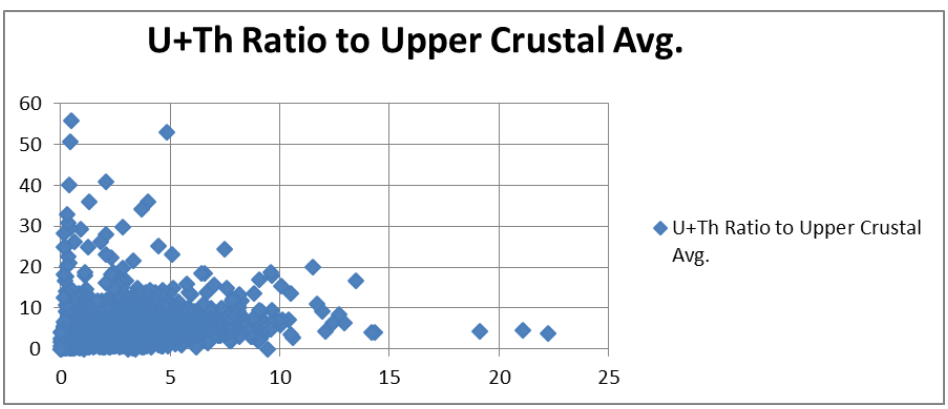


Figure 2. Cross Plot of Measured Values, Normalized by Crustal Averages of Each Element for Other Rare Elements Found Associated with Some Coals

Top: Cross plot of the normalized platinum group metal values (Sum of Pt + Ir + Os + Ru + Pd + Rh) to the normalized value of the sum of all REEs. In general, Ir>Os>Pt>Ru>Pd>Rh for the coal samples tested. Bottom: Cross plot of the normalized uranium plus thorium values (U + Th) to the normalized value of the sum of all REEs. In general, Th>U in the coal samples tested.

Many of the prior studies (late 1970s through the late 1980s) of trace elements (including REEs) in coal, coal combustion ash and other coal-derived wastes reported that a number of rare/precious metals and critical energy elements can be found in coal in concentrations that varied from formation to formation and within the extent of an individual formation. These studies were primarily focused on tracing the fate of hazardous trace elements and in evaluating whether coal cleaning could be effective in reducing or eliminating the health risks posed by these hazardous elements. Given that REEs are not considered hazardous, the data that was developed does not typically include a thorough characterization of rare earths. In addition, at the time of these studies, many of the individual concentrations of the heavy rare earth elements challenged the resolution of the analytical techniques employed.

Deep coal cleaning techniques were studied at that time, including a range of chemical coal cleaning approaches, to essentially remove all hazardous trace elements and nearly all of the mineral matter. These techniques included both physical approaches (fine grinding) and chemical approaches in combination to achieve the desired results. At that point in time, these techniques were shown to not be cost effective and other post-combustion technologies were used as the basis for regulations. However, an additional consideration in assessing the impact of REE extraction from coal-based sources is that extraction of many of the trace metals might improve the potential to reuse combustion wastes or reduce the cost of disposal for any remaining solid materials. New interest in legislation addressing solid wastes from coal processing and coal combustion may impose significant costs on those organizations managing legacy wastes. This benefit would accrue due to removal of hazardous trace elements and could complement any value stream arising from extraction of commercially-important metals. (ref. 2-8, 2-17, 2-18)

2.3 USGS COALQUAL DATABASE AS A MEANS TO ASSESS "NATIONAL OPPORTUNITY"

For the initial prospectivity analysis, the U.S. Geological Survey (USGS) COALQUAL database (ref. 2- 19 USGS COALQUAL Database, version 2) served as the source for data for all U.S. coal basins and was utilized to identify potential coal basins and seams. Version 2 of this database included results from over 7,400 total samples, many with very low ash concentrations. The sample data contained within the USGS COALQUAL is based on assembled cores for which all partings >4" had been removed. In the USGS database the

REE concentration data are reported on a whole coal basis using a methodology developed by Swanson and Huffman. (ref. 2.20)

Conceptually, this approach produced results equivalent to those for a commercial coal (8-10 percent ash). If the samples analyzed are restricted to those with ash concentrations exceeding ≈5 percent, the number of samples drops below 5,000. In actual deposits and for as-mined coal, the values are likely to differ substantially from the USGS approach for any sample not subjected to the same process of removal of large partings. For example, eastern, underground mines typically process coal with 40-50 percent mineral matter through preparation plants.

The USGS COALQUAL was utilized because it appeared to be the most comprehensive database of coal point-source and major-, minor-trace-element content available. In addition to this information the database also contains chemical data, geodetic locations, field observations, sample analyses, bed thickness; lithology; depth of burial, moisture, ash, sulfur content, and heating value data for collected samples.

For the LTI work, the whole coal numbers were converted back to ash-only numbers as the measurement technique (ref. 2.21) for REE determinations requires that the sample be ashed in a particular way before the measurement is made. This database was never intended to represent an accurate statistical sample of all coal regions in the United States. Many of the samples were contributed by individual state geological surveys (or equivalent state agencies). The number of samples per coal region varied and, due to the time period when this information was being compiled, certain coal regions are under-represented.

In the early phases of this work, simple criteria for evaluating whether a coal-based source might be attractive in some way as a source of REEs were used. A measured concentration value of total REEs (on an elemental basis, not as oxides) over 1,000 ppm on an ash basis served as a threshold value. Clusters of core samples that met this criterion were used to identify "hot spots"—formations or seams with a substantial number of individual measurements exceeding 1,000 ppm (ash only). Not all coal formations that met this criterion were used in determining the initial resource values that were developed as a consequence of this analysis. Sets of high-valued samples had to come from commercially-significant coal seams or formations to be considered. This screening involved the use of U.S. Energy Information Administration (EIA) data as reported in the Annual Energy Outlook (ref. 2-22) and compiled in the "Annual Coal" report (ref.2-23).

Using the data found in the USGS COALQUAL database (version 2), clusters of higher REE concentration data (as reported on an ash-only basis) were grouped to identify basins of interest. The results are summarized in Figure 3.

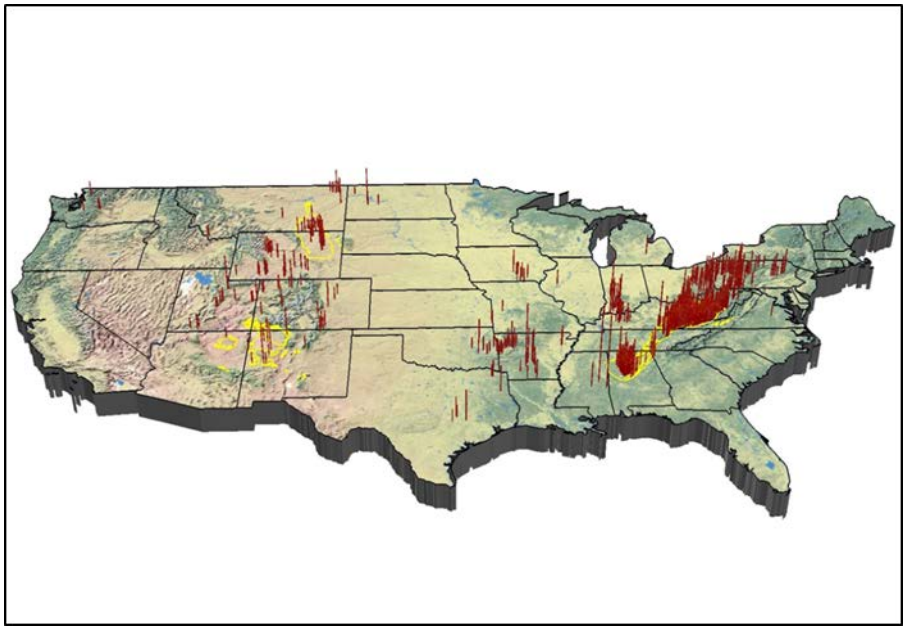


Figure 3. Basins of Interest

The height of each bar (each representing a single data point) is proportional to the total REE concentration for that sample. These results were used as input to the preliminary resource assessment although the data available were not fully representative of typical coal production in the United States in recent decades.

The data found in the USGS COALQUAL data base were used to plot concentration of each individual rare earth element found in the selected coal beds as seen in Figure 4. This figure also includes data for the typical upper crustal average of REEs, and concentration data typical of both the Mountain Pass deposit in the United States and of lateritic clay deposits in China. These latter three sets of concentration data are from the literature. (ref. 2-24) The Mountain Pass site was, at that time, the major U.S. source of REEs, primarily the commercially important light REEs (Lanthanum (La), Cerium (Ce), and Neodymium (Nd). The Chinese lateritic clay deposits are the primary global source of commercially important heavy REEs (Yttrium (Y), Terbium (Tb), Dysprosium (Dy) and Erbium (Er)).It should be noted that global demand for these two groups of elements is shifting from the light REEs toward

the heavy REEs. This topic will be discussed further later in this report. Note that all of the coal sources shown on this figure are found in three of the regions shown on the map in Figure 3.

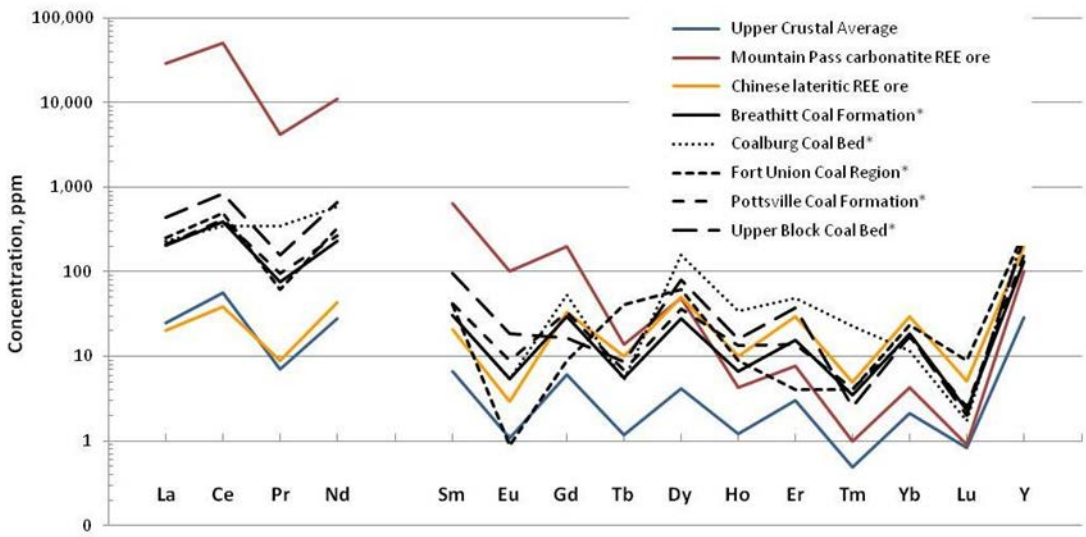


Figure 4. Concentration of Individual REEs in Selected Coal Bed

The ash-only, coal-sourced, values would certainly be typical of coal fly ash and bottom ash derived from the high REE locations found within these particular sources. Note that these concentrations for the coal samples are far lower in light REEs but are similar in value to the Chinese lateritic clays and approach or exceed the concentrations reported for this particular set of data for Mountain Pass from element gadolinum and higher.

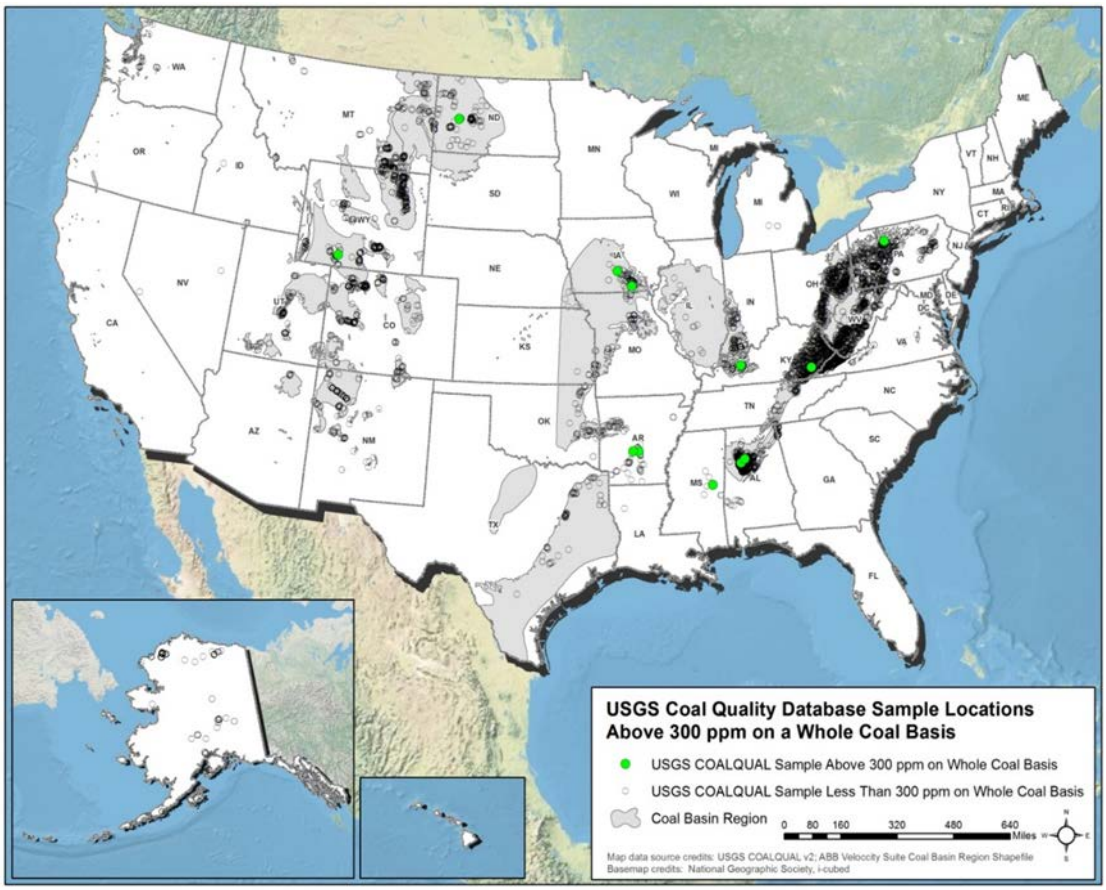


Figure 5. USGS Coal Quality Database Sample Locations

The USGS COALQUAL database has served as a means to assess a "National Opportunity", in which rare earth elements may be recoverable from coal and coal-related materials. This national database included 7,430 borehole coal samples, in which 136 parameters are recorded, including data on location and sample description, analytical data from ASTM tests, and USGS tests for major-, minor- and trace elements. Figure 5 depicts location of individual coal core samples across the United States. A concern regarding this database is its age. It is necessary to realize that these data were collected nearly 30 years ago (in some cases) and analyzed using the analytical tools available at that time. The performance of various analytical techniques for measurement of some or all rare earth elements was evaluated by USGS who conducted a round-robin study amongst their laboratories. (ref. 2-25). A number of methods were used to make determinations of various rare earth elements; Inductively coupled plasma mass spectrometry (ICP-MS) and Inductively coupled

plasma atomic emission spectroscopy (ICP-AES) were both judged to provide reasonable values and to be capable of measuring various REEs when present in very low concentrations.

2.4 CONCEPT OF PROSPECTIVITY

Through data mining efforts it was discovered that in various USGS samples collected throughout all U.S. coal basins, concentrations of REEs in coal were significantly greater than the crustal average. The discovery was recognized as a national opportunity and led to a "Prospectivity Analyses." The term "prospectivity" is one that is frequently used, but has no real definition. For the purposes of this report, prospectivity analyses are considered a requirement of determining a real interest. That is, should a substantial enough field sampling be implemented to determine that recovery of REEs from coal and coal-related materials is a real issue (or opportunity), as contrasted with speculative, abstract, hypothetical, or moot issues. Thus, this prospectivity analyses was conducted to determine if further research is justified (e.g., identifying resource locations and reserves on a national scale and if an economical separations methodology can be developed).

Coupled with Prospectivity Analyses is "Prospectivity Mapping." Prospectivity mapping is also known as mineral prospectivity mapping or mineral potential mapping. There are three approaches to prospectivity mapping; data-driven, knowledge-driven, and hybrid mix-driven and are explained in the following:

- *Data-Driven:* In areas with significantly known mineralization, a data-driven approach can be adopted in which known deposits are analyzed in relation to the surrounding geology. A number of parametric and non-parametric statistical tests can be used to determine if identified spatial relationships are considered statistically significant. Important relationships are then spatially quantified over the entire region of interest. Ultimately multiple quantified relationships are combined, typically using a "Geographical Information System, (GIS), into a single prospectivity map.

- *Knowledge-Driven:* In areas with little known mineralization, a knowledge-driven approach can be implemented in which a mineral-systems approach is used in which theories about the formation of the deposit are identified, spatially quantified and then combined using a GIS.

- *Hybrid Mix-Driven:* Prospectivity mapping can be constructed using a mix of data-driven and knowledge-driven components and these are often referred to as hybrid prospectivity maps.(https://en.wikipedia.org/wiki/Prospectivity_mapping and (ref. 2-26 Porwal and Kreuzer, Introduction to the Special Issue: Mineral prospectivity analysis and quantitative resource estimation, Ore Geology Reviews 38 (2010) 121-127)

The data-driven approach (using the USGS data) was employed to map REEs within specific coal seams, albeit due to limited hole spacing additional drilling would be needed to improve statistical results. Yet these data were able to depict a unique fingerprint for each coal seam, such that it can be observed that rare earth elements are not uniformly distributed throughout a coal seam. Prospectivity mapping of USGS data uniquely shows areas or zones or "hot spots" within all (individual) coal seams to have elevated REEs of varying concentrations, which has led to theories relative to how the REEs were deposited within the coal at the time of formation.

The prospectivity mapping approach was modified later in the project to include those life-cycle processes associated with post-coal extraction. The processes in which raw coal passes through to reach final disposal include: coal cleaning and power generation. In this aspect of the project, the schematics of the coal cleaning and coal burning processes were used as "base prospectivity maps" with sampling occurring throughout the various process steps. The prospectivity mapping as applied to process scenarios was a knowledge-driven approach. Due to modern coal blending practices, little is known about mineralization in the coal entering either cleaning or burning operations. Thus, sound theories related to process separations and densities of materials were applied.

Lastly, due to budget and time limitations and the relative scale, prospectivity mapping of waste disposal sites (coal refuse piles, ash piles, slurry impoundments) was not pursued. However, a limited amount of surface sampling of waste disposal sites was performed. A future prospectivity mapping will require a hybrid mix-driven approach, such that modern regulatory data relating to the construction, material sources, dates, and locations within a pile should be obtainable. The knowledge-based approach will include the application of that knowledge gathered from the COALQUAL database, in which particular coal seams depicted higher REE concentrations than others. Thus, it is likely that known (approximate) locations of those wastes (within the piles) suspected of having higher REE concentrations would be targeted for drilling or excavation.

The greatest practical issue in GIS-based mineral prospectivity analysis is the availability of relevant data sets to which these sophisticated computer-driven methods can be applied. This is probably the primary reason why GIS-based prospectivity analysis has not been applied more widely. There are two critical requirements for the ideal data set. It must (a) be an unbiased sample of the area of interest, and (b) have uniform coverage of this area. Any departure from these ideal criteria inevitably results in a biased data set and all the inherent problems that stem from such bias. The performance of any prospectivity analysis technique ultimately depends on two factors: (a) accuracy, precision and consistency of the input spatial proxies, and the fidelity with which they represent the mineralization processes, and (b) degree of conceptual understanding of the underlying mineral system. The section on recommended improvements to adding enhanced information about the occurrence of REEs in coal can be found in Section 7.

2.5 PRELIMINARY RESOURCE ASSESSMENT (BASED ON LIMITED REGIONAL ESTIMATES)

To assess resources that could later be qualified as reserves, the coalbeds listed in the USGS database were mapped onto the EIA list (ref. 2-27) of the top 25 producing coal seams in the United States. Several of these coalbeds (or in some cases coal formations) trend across two or more states and the coalbed name changes with the transition. The top 25 coalbeds were matched to rare earth concentration data and ten coalbeds or formations were found to exhibit a significant share of the higher measured REE concentrations.

Calculations to estimate the amount of rare earth elements that might be actively mined today were developed. Based on data largely available in USGS reports, the estimated recoverable reserves was used to provide an estimate of the total tonnages of rare earth elements that exists in these coalbeds and coal formations. These ten coalbeds or formations currently yield approximately one-half all coal mined in the U.S. The concentration values used in the calculations are not restricted to only the ones that would report as REE+Y>700 but included all coal samples listed in the USGS Coal Quality database for the subject coalbed or coal formation.

For instance, the Stockton-Lewiston coal is represented by 22 total samples out of 1,708 samples covering the Central Appalachian Basin. Similarly, the Coalburg (Peach Orchard) coal is represented by 72 samples from that same data set, Winifrede by 13, Hazard#4 (Fire

Clay/Chilton, Phillips and Windrock) by 38, and Williamson (Amburgy, and Lower Splint) by 22.

For the other three basins, total numbers of samples are much smaller. The Southern Appalachian coals are represented by 35 samples from the Mary Lee group (Blue Creek coal and Mary Lee coal are both in this group). Wyodak—Anderson is described by 31 samples while the Fruitland #8 is represented by only 10 samples and the Menefee by only 3. The Central Appalachian basin data are far more extensive than any of the other three regions highlighted. The question of representation is an important one that would need to be addressed in going forward with the analysis of the potential to extract REE from mineral matter associated with coal deposits. (ref. 2-28)

The summary information from that work developed the following estimates:

- 10 of top 25 producing seams in 2010 are in regions (ref. 2-29a: EIA) identified with elevated REE concentrations.
- Production estimates use average value for all samples of that coal seam, not just>700 PPM for each coal seam.
- "Unintended production." Total tonnages of REE+Y associated with coal mined in 2010 exceeds 40,000 tons annually.
- "Unintended production" of heavy rare earth elements and yttrium may exceed 10,000 tons annually.
- Estimated recoverable resources for total REE+Y may exceed 2 million tons for the identified coalbeds and coal formations. Heavy REE+Y may exceed 500,000 tons (based on USGS National Coal Resource Assessment (ref. 2-29b).
- Approach was a compromise between estimating percentage of a coal bed exhibiting the higher concentrations of rare earth elements versus using best resource data available. This highlights the need for additional data to further assess whether these deposits could have economic value in terms of REE.

3 DISCUSSION OF PRELIMINARY ASSESSMENT

3.1 PROSPECTIVITY ANALYSIS AND PURSUIT OF SUPPORTING DATA

As discussed above, based on the initial screening that was performed on the USGS data, LTI developed the estimates described above. These results appears to suggest that coal and coal residues (either from mining and preparation or post-combustion) could contain a significant amount of REEs. For total REE+ Y, the estimated recoverable resource was found to exceed 2 million tons for the identified coalbeds and coal formations. The corresponding value for heavy REE+Y may exceed 500,000 tons. The amount associated with coal mining (described as unintended recovery) may be on the order of 40,000 tons (annually) of REE+Y. The corresponding quantity for heavy REEs + Y could have exceeded 10,000 tons. The fate of the amount that had been historically extracted by mining was not explored in the initial work. Nor was an estimate made for legacy materials that could be found in ash piles or ash ponds.

However, work was performed under the field campaign by the University of Kentucky that profiled 14 operating coal preparation plants. Data collected on total REEs that were found in the coal that entered the coal preparation plant totaled 9993 tons per year. Of the nearly 10,000 tons entering the plant, 1,557 left with the clean coal while the rest was found in the coarse or fine refuse. (ref. 3-1)

3.2 OVERLAYS OF ACTIVE SITES FROM COAL SECTOR

To develop maps that could be used to suggest high-value areas for further sampling, the USGS COALQUAL database (converted to an ash-only basis) was incorporated into ESRI ArcGIS software for spatial modeling and analyses. Preliminary assessments using spatial modeling were not based on 3-D imaging so only “suggested” key locations were identified.

Various interpolation tools available in the ArcGIS software were then utilized as a means to predict and identify preferred areas to test. Iso-concentration maps and overlay data such as mines, preparation plants and power plants were used to identify potential test sites, as shown in Figure 6. Because the bulk of the USGS samples were located in the eastern United States, the initial focus was in the Central Appalachian region, Figure 7. In addition, although Iso-concentration maps assisted in predicting preferred areas to sample, access to the identified locations still needed to be secured.

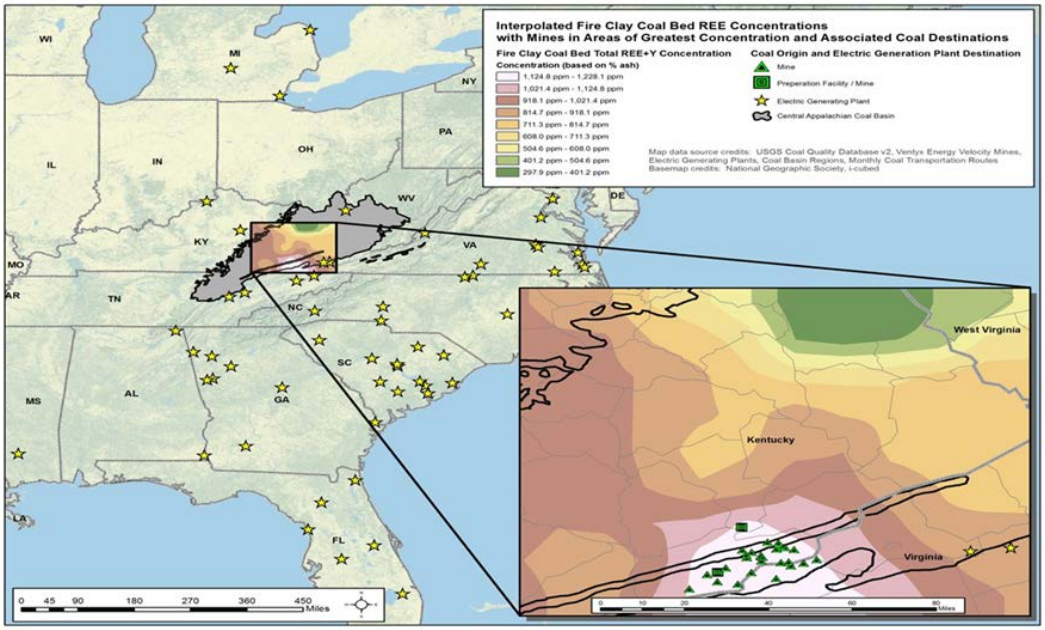


Figure 6. Kriging Analysis Results Used to Identify Potential Test Sites

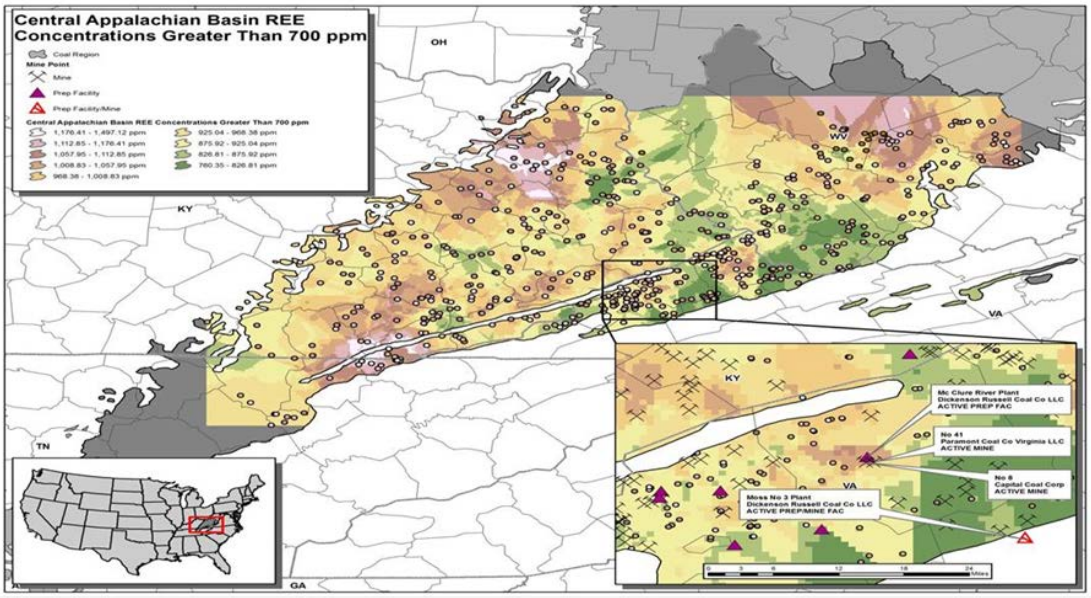


Figure 7. Overlay Concentration Map with Active Facilities for a Basin
(data mapped on an ash-only basis)

In Figures 8 and 9, respectively, the Kriging and nearest-neighbor interpolation techniques are compared. The sample locations have been symbolized using a color gradient to show the approximate concentration range of total REE, based on whole coal for the Lower Kittanning coal bed. Although default parameter were selected for each interpolation method, note the discrepancy between the ranges of concentration values between the two interpolated layers. Additional research into the spatial modeling interpolation techniques should be considered as a way to improve results.

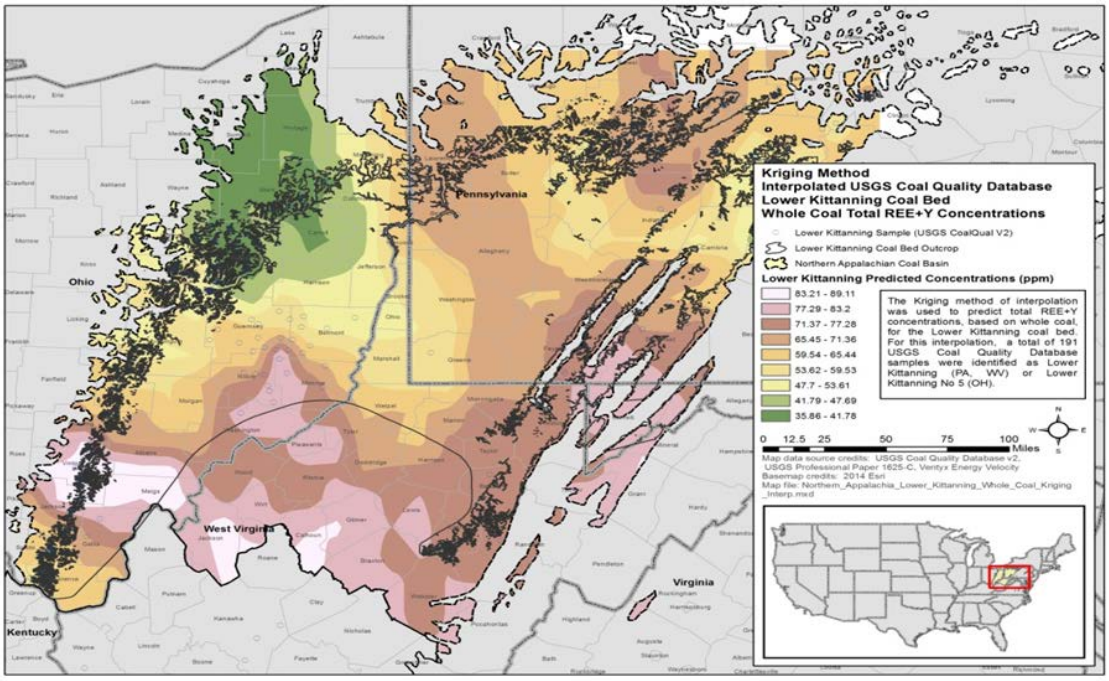


Figure 8. Lower Kittaning Seam Concentrations Based on Kriging Analysis
(values expressed on whole coal basis)

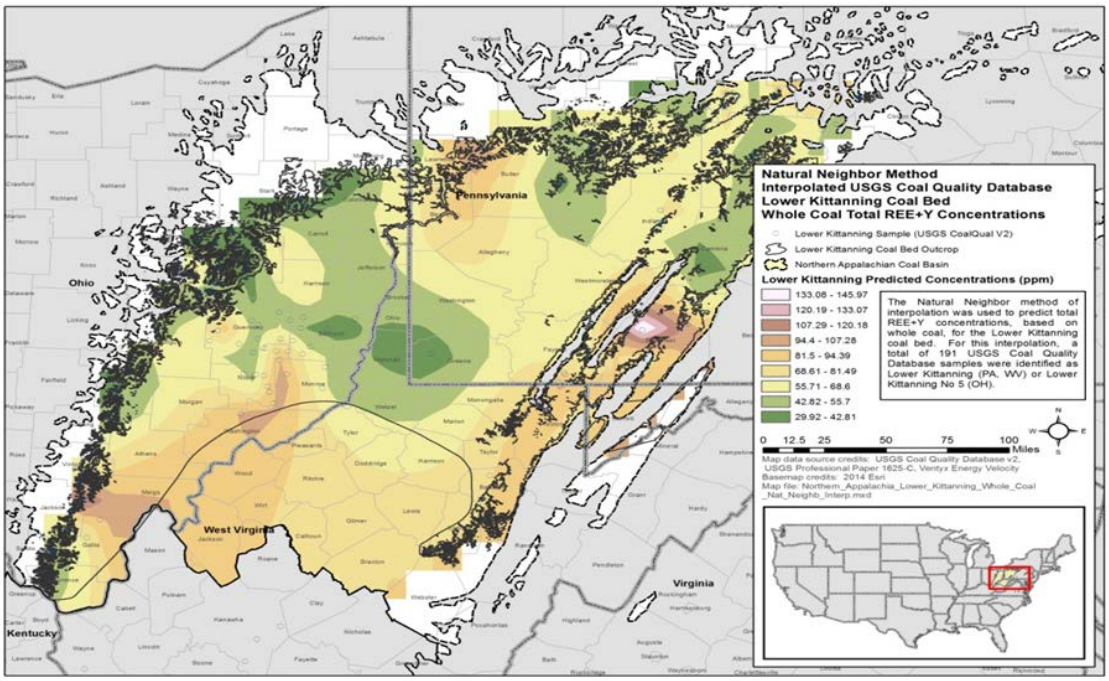


Figure 9. Lower Kittaning Seam Concentrations Based on Nearest Neighbor Analysis

Using the data found in the USGS COALQUAL database, clusters of higher REE-concentration data (as reported on an ash-only basis) were grouped to identify basins of interest.

The prospectivity analysis relating to REEs in coal deposits is largely dependent upon the USGS Coal Quality Database v2. The analyses of these data, does indeed, demonstrate that the concentrations of REEs in portions of all U.S. coal seams can significantly exceed crustal concentrations. Consequently, the feasibility of exploiting these, and other critical energy elements, for economic development and national security purposes currently exists. The significant challenge, however, is to locate the areas containing bulk materials containing high concentrations of REEs. These areas include in situ coal, and waste disposal operations associated with coal cleaning operations (refuse) and power plant usage (ash products), Figure 6, 7, and 10 respectively. Later in the project, new data derived from samples provided by WVGES were plotted to identify candidate sites that might have higher in-situ concentrations of rare earth elements, Figure 10 is a plot of some of these data.

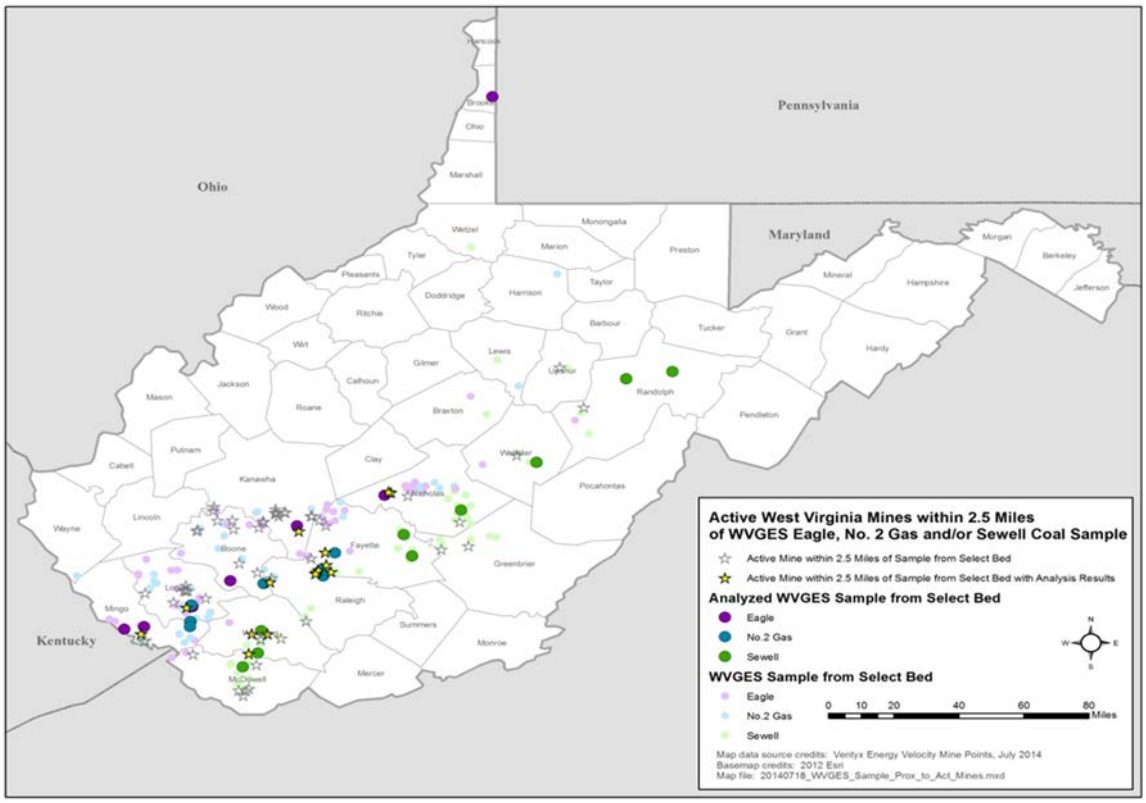


Figure 10. Active Mines Near Select Seam Data from WVGES Samples

Initial efforts began with the spatial interpolation of the in situ (coal) data found in the USGS Coal Quality Database v2. Interpolation is an estimate of a variable at an unmeasured location from observed values at surrounding locations. Kriging, which is based on regression against observed z values of the surrounding data points and are weighted according to spatial covariance values was determined to be the optimal interpretation approach. The nearest-neighbor interpolation approach was considered, but this algorithm selects the value of the nearest point and does not consider the values of neighboring points at all, and thus was not selected (Figure 9).

All interpolation algorithms (inverse distance squared, splines, radial basis functions, triangulation, etc.) estimate the value at a given location as a weighted sum of data values at surrounding locations. Almost all assign weights according to functions that give a decreasing weight with increasing separation distance. Kriging assigns weights according to a (moderately) data-driven weighting function, rather than an arbitrary function, but it

is still just an interpolation algorithm and will give very similar results to others in many cases (Isaaks and Srivastava, 1989). (ref. 3-2)

In particular:

- If the data locations are fairly dense and uniformly distributed throughout the study area, you will get fairly good estimates regardless of interpolation algorithm.
- If the data locations fall in a few clusters with large gaps in between, you will get unreliable estimates regardless of interpolation algorithm.
- Almost all interpolation algorithms will underestimate the highs and overestimate the lows; this is inherent to averaging and if an interpolation algorithm didn't average we wouldn't consider it reasonable.

Some advantages of kriging:

- Helps to compensate for the effects of data clustering, assigning individual points within a cluster less weight than isolated data points (or treating clusters more like single points).
- Gives estimate of estimation error (kriging variance), along with estimate of the variable, Z, itself (but error map is basically a scaled version of a map of distance to nearest data point, so not that unique).
- Availability of estimation error provides basis for stochastic simulation of possible realizations of (u).

Conventional mining exploration of coal reserves involves drilling boreholes on specific spatial grids to establish a confidence level relative to the presence of coal. A demonstrated coal reserve from cores and outcrop observations is direct evidence of its presence and inferred coal is near demonstrated coal deposits. The demonstrated coal reserves involves to sub-categories, measured and indicated. The spatial distances between bore holes for measured and indicated reserves are ¼ mile and ¾ mile centers, and for inferred coal the distance is 3 miles.

The coal quality database, known as the National Coal Resources Data System (NCRDS), was to contain information on the quantity and quality of our domestic coal resources. A major objective was to locate, measure, and characterize all of the nation's coal resources, without

regard to bed thickness, depth, location, or quality. An initial goal of the project was to obtain and characterize at least one sample per coal bed from every geographic quadrangle (approximately 50 square miles) underlain by coal. This order of magnitude in borehole spacing has significant impact on the weighting of values associated with the spatial interpolation of these data, such that confidence levels are much lower than those associated with conventional coal mining exploration.

It is important to note, that this study focused on commercial coal seams or coal seams thick enough for economical extraction and did not focus on the thin, unmineable coal seams. Consequently, although a 50 mile grid (or quadrangle approach) was utilized by the USGS, bore holes in areas in which specific coal seams that have been previously extracted could not provide a data point for the extrapolation of spatial data of that particular coal seam. As the result, distances between sampling points (with data) within a specific coal seam doubles (100 miles), and again, detrimentally impacts the weighting operations associated the spatial interpolations discussed above.

Lastly, and also important to note, it is estimated that over half of all U.S. coal reserves (commercially mineable) in the U.S. (with exception of Alaska) have already been extracted over the past 150 years. As a general result, data for most commercial coal seams is clustered, as shown in Figure 11 and again as described above, has a detrimental impact on all interpolation approaches. Thus based on discussions presented above, kriging was selected as best option for performing a spatial interpolation of REE data from USGS database.

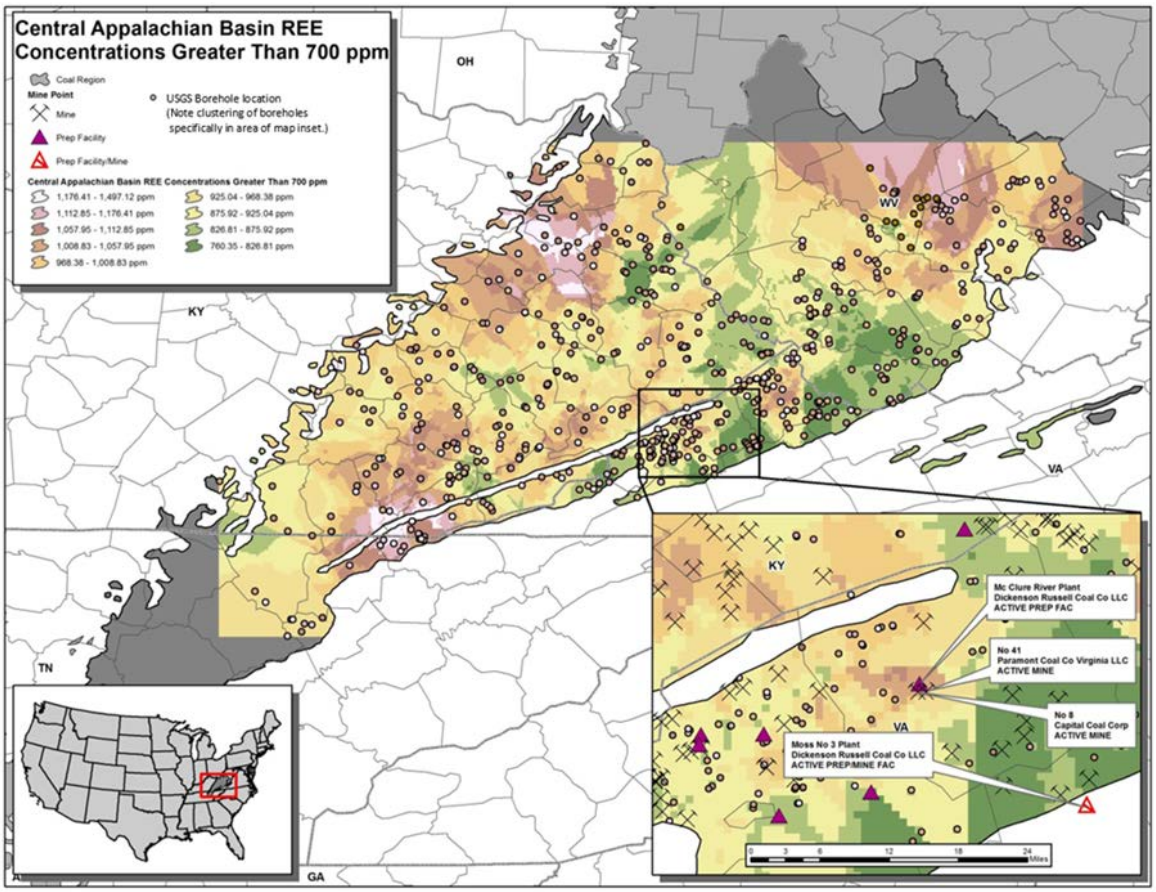


Figure 11. Clustering of USGS Wellbores

3.3 VERIFICATION STUDIES

3.3.1 LTI Field Work

Under Mod D, LTI was tasked with completing a limited field sampling effort that was designed to better understand both targets of interest and issues to be addressed in designing a larger field sampling effort. Sampling targets included coal mines, coal preparation plants, industrial units utilizing coal (including fluidized- bed units), electricity generating units, and associated waters. LTI developed approaches as to the sort and minimum quantity of samples to be collected, established a clear, unique labeling system to enhance sample tracking, contracted for laboratories qualified to perform the required ASTM methods and worked with the NETL Chemical Handling Facility (CHF) to ensure that all rules for shipping, receiving, and storing any samples taken were followed.

LTI reached out to a number of coal companies and power generating facilities to seek permission to conduct sampling campaigns at one or more of their sites. These discussions lead to development of a series of non-disclosure agreements that granted LTI access to various sites, which defined which elements could be measured and reported through our analyses, and what could be used in reports to NETL or published in the open literature. Identification of the companies by name in any document that could become public was specifically excluded. Although the field campaign was designed to be completed before any outside contractor was sought for additional sampling work, delays outside of the control of either NETL or LTI caused completion of this effort to overlap with the university-led campaigns.

LTI also contacted the West Virginia Geologic and Economic Survey (WVGES) as a means to acquire additional samples (taken in a manner similar to those of the USGS samples) for analysis. A similar request would be made through the Kentucky Geologic Survey (KGS) under the contract to the University of Kentucky (discussed below) to gather a limited number of samples from the Central and Southern Appalachian basins, from the Gulf Coast Province and from the Illinois basin.

Prior to initiating field sampling operations, data from the USGS and samples from the West Virginia Geologic and Economic Survey (WVGES) (which were frequently one and the same) was analyzed to identify those coal seams which reported the highest REE concentrations (on an ash basis) and to target them as potential candidate sites for field sampling. The coal seams identified with the highest REE concentrations were the Eagle, No. 2 Gas, and Sewell seams. Targeting candidate sampling locations is one thing, it is quite another matter to gain access to those locations. Companies were willing to collaborate with LTI as long as a mutually agreeable non-disclosure agreement (NDA) was in place. Negotiation of these NDA's incurred some delays. As a result, and to begin the process of developing field sampling procedures and protocols, field sampling began on ash piles created from coal seams of lesser known REE concentrations, rather than those of high REE concentrated coals seams identified in Figure 11.

Field efforts required introductory meetings and site visits, which also typically included an NETL representative. LTI's sampling program involved the assemblage of field equipment including: highly accurate Global Positioning System (GPS) equipment, sampling containers (which varied based on site conditions, analytical requirements, and subsequent storage issues at NETL), camera, container labeling supplies, hand tools, and a variety of safety

equipment (hard hats, steel toed shoes, hearing protection, safety glasses, etc.). It should be noted that sample sizes that LTI used included: 55 gallon drums, 5 and 1 gallon buckets, and gallon and half gallon plastic bags, Figure 12. A sample form was developed for LTI use and was also utilized, in part, by LTI's subcontractors. This form included the name of the mining operation, coal seam, address of the facility, names of the LTI and coal company personnel involved with sampling, a discreet alpha-numeric sample ID, sample description and location, including GPS coordinates, and tracking numbers for photographs.

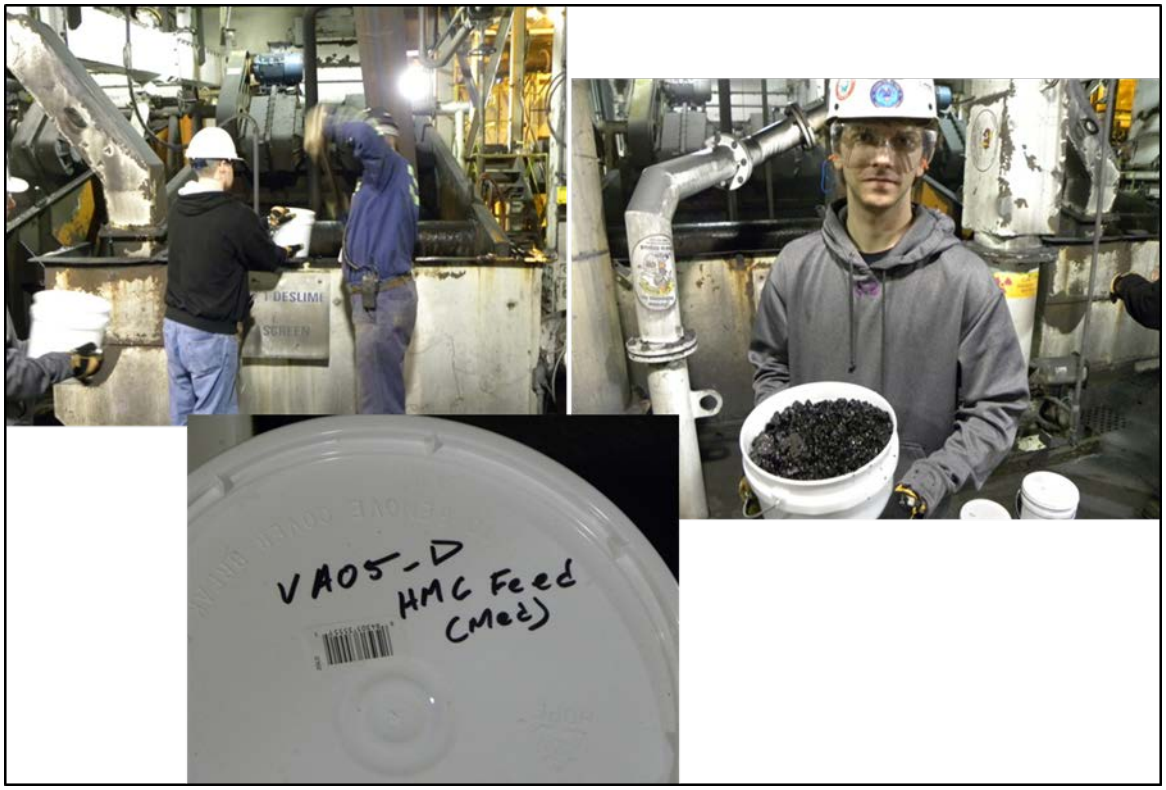


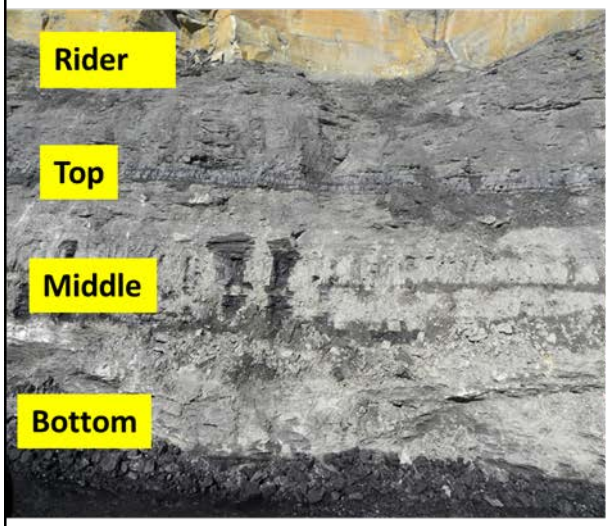
Figure 12. LTI Field Samples

Field sampling procedures and protocols were developed to encompass the entire lifecycle of coal. Consequently, three basic sampling scenarios were developed: surface outcrops and piles (raw coal, coal refuse and ash byproducts), coal preparation plants (various circuits and processes within), and coal-fired power plants (various circuits and processes within) It should be noted that several raw coal samples were collected from underground at the working face (Figure 13). However, these samples were collected either by the coal company or, later, by the University of Kentucky personnel due to the lack of the mandatory

40-hour MSHA underground safety training course by LTI personnel. Furthermore, only one set of underground samples provided the GPS coordinates relative to the working face at the time of collection. All other underground raw coal samples were collected at the surface load-out points and the exact position of the working face was unknown.

Figure 13. Typical Mine—Fire Clay Coal

Sampling at the Surface Sites—Field sampling on the surface included extracting sample materials from coal outcrops (Figure 14) and various piles of raw coal, refuse (Figure 15) and ash byproducts (Figure 16). Throughout a significant portion of the project life, field sampling was mostly conducted without the availability of any sort of concentration screening tool, although the use of handheld X-ray florescence technology was attempted near the end of the project and is discussed in a later section of this report.



Whole coal = w.c.
Ash-only = a.o.)

Coal Bench	Thickness	Ash	Sulfur	BTU/lb
No. 7 Rider		18.0	2.25	11,200
No. 7 Top	20 - 22 in	11.5	0.73	12,200
No. 7 Middle		10.0	0.72	12,400
No. 7 Bottom "Junk"		20.0	0.70	11, 000
No. 7 Bottom		10.5	0.70	12,400

Coal bench	REE content (w. c.)	REE content (a. o.)
No. 7 Rider	98	596
No. 7 Rider (2nd sample)	43	491
No. 7 Top	125	520
No. 7 Bottom "Junk"	67	609

Figure 14. Sample from Coal Outcrop

The surface piles of ash and refuse resulting from the various processing operations were massive in size, and decades in the making. It is estimated that these piles typically were comprised of millions to 10s of millions cubic yards of material. Only surface samples were gathered, no excavation, drilling or auguring activities were involved. The depth or thickness of these piles is estimated to range from about 50 to over a hundred feet or more. Inquiries were made, with the coal company personnel, relative to the source coal seams and age of the materials. Typically, these piles were older than the coal company personnel and only a relatively limited amount information could be obtained.

Figure 15. Coal Refuse Pile

The need to blend coals for power plants in order to meet atmosphere emissions requirements, which dates back to the Clean Air Act, has had a trickle-down effect relative to mixing of the resulting waste materials (ash byproducts and coal refuse) and their subsequent surface disposal over the past several decades. It is common practice for coal preparation plants to clean multiple sources (or seams) of coal in order to create a product that meets the requirements imposed by a particular power plant. Furthermore, a power plant will purchase a defined product from multiple preparations plants. Consequently, the waste piles currently being constructed are a blend of multiple coal seams and multiple REE concentrations. What is not known is whether or not these blends enhanced concentrations of REE materials or diluted them, only further prospecting will tell.

Figure 16. Collecting Samples at Power Stations

Sampling of these waste piles typically involved sampling at the base of a side of the pile, the top of pile, and in the middle if safely accessible, such as the presence of a bench or gradual slope (Figure 16, bottom left). This approach allowed for materials of differing age and (likely) source to be collected. The top surface of these piles, generally flat from the benching involved with the construction of the pile, was uniformly divided with samples representing the entire area of the top surface. The number of samples that could be taken and analyzed was limited by available analytical funding.

Lastly, field sampling at surface mines typically involved gathering raw coal samples from relatively small piles located within the mine pit (Figures 14 and 15). Lastly, pit cleanings or raw unprocessed wastes were randomly gathered, also within the operating mine pit. Furthermore, only a limited number of outcrop, bench or highwall samples were gathered at any surface mine due to safety reasons (Figure 14 for example).

Sampling at Coal Preparation Plants—Field sampling at coal preparation plants is better defined as process sampling. Figure 17 depicts a schematic for the processes typical of general preparation plant. Samples were collected from all the process streams identified in the schematic identified above. Consequently, samples of solid materials (coal and refuse) (Figure 18) of various sizes and samples of liquids (slurries) were collected (Figure 19). Additional safety issues, relative to surface sampling, were also encountered relative to the prep plant due moving machinery and materials and a significant noise factor that typically required communication by hand signals or the written word. Lastly, sample management differs significantly from that of surface sampling and requires additional safety precautions. Raw coal typically enters a prep plant at the top (which is roughly equivalent to a 10-story building), via conveyor belt, and is gravity fed to various internal processes which occur on about five different levels or floors within the plant. Consequently, sampling takes place on each of the levels, and transporting the empty and full containers (approximately 30-50 pounds in weight) of samples requires hand transport through and around moving machinery, tight locations, and up and down numerous steps connecting each level.

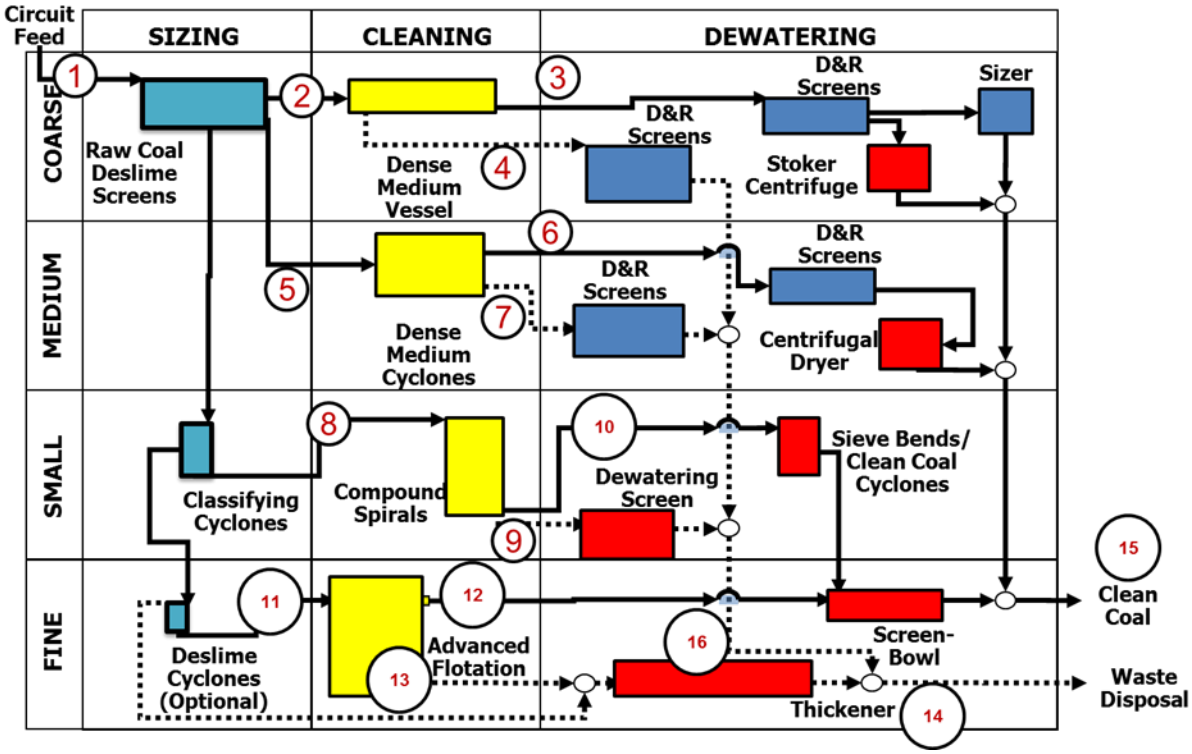


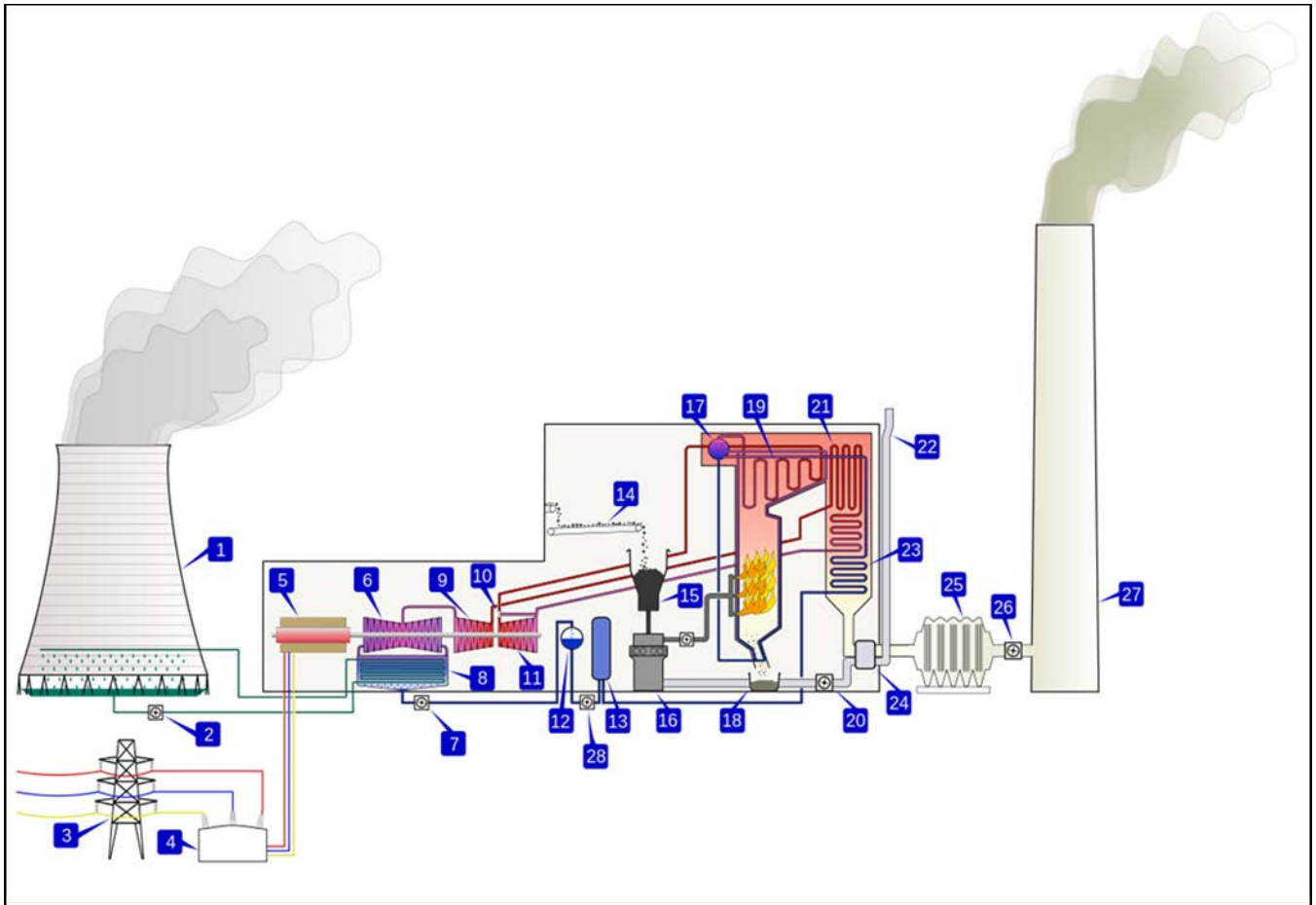
Figure 17. Generic Preparation Plant Schematic

Figure 18. Coal Samples

Figure 19. Liquid (slurry) Samples

As mentioned above, it is common practice for coal preparation plants to process multiple sources of coals (and seams). Furthermore, one collaborating coal company put forth a special effort, since they had enough material to supply a whole shift, to run a single source of coal to provide enough time to sample the entire plant with a single source of coal passing through the various processes. Albeit, it is not known what impact that the materials from the previous processing shift located in small amounts throughout the plant may have had. This effort was based on the assumption that REE content was somewhat uniform and to determine if concentrating of REE would occur at some specific process with in the plant. All sampling at preparation plants included raw coal entering and clean coal exiting, as well as the various processes from within.

Sampling at Power Plants—Sampling of the various processes associated with power plants is analogous to that of sampling coal preparation plants. Such that there are numerous processes associated with the burning of coal, including clean coal hopper, coal pulverizer, bottom ash hopper, economizer, and precipitator. See Figure 20 for a typical diagram of a coal-fired thermal power plant. (ref. 3-3)



1. Cooling tower. 2. Cooling water pump. 3. Transmission line (3-phase). 4. Unit transformer (3-phase). 5. Electric generator (3-phase). 6. Low pressure turbine. 7. Condensate extraction pump. 8. Condensor. 9. Intermediate pressure turbine. 10. Steam governor valve. 11. High pressure turbine. 12. Deaerator. 13. Feed heater. 14. Coal conveyor. 15. Coal hopper. 16. Pulverised fuel mill. 17. Boiler drum. 18. Ash hopper. 19. Superheater. 20. Forced draught fan. 21. Reheater. 22. Air intake. 23. Economiser. 24. Air preheater. 25. Precipitator. 26. Induced draught fan. 27. Chimney stack. 28. Feed pump

Figure 20. Typical Coal-Fired Power Plant

LTI gathered samples as they were delivered and oversaw the process of logging them into the CHF. Smaller portions of most samples were drawn and submitted for analysis by one of our laboratory analysis contractors for determination of the REE concentrations (element by element) along with several additional key "pathfinder" elements. The pathfinder elements were chosen to be either elements typically found in association with REEs (thorium), elements or mixtures typically tracked in studies of coal cleaning or combustion

(for example, ash, calcium) and finally a partial list of other energy critical elements (platinum-group metals for example). A standard set of elements were measured for all the sites covered by NDAs and for all the samples collected by the University of Kentucky during their filed collection activities. The main exception to this approach was for a power company that asked LTI to add several energy critical elements, at fluidized bed power stations for which we routinely requested that the calcium content of the ash be measured, and for the samples provided by WVGES for which a larger set of trace metals were added.

In all, samples were gathered from sites owned and operated by ten different companies. These ten included:

- A coal mining company operating in the Northern Appalachian coal basin (NAPP)
- LTI accessed and sampled at four sites including coal preparation facilities and an ash haul-back site
- A company operating a waste repository for Pittsburgh seam coal fines
- A coal mining company that made available sites in the Central Appalachian basin (CAPP)
- LTI accessed a surface mine, and two mine/preparation plant complexes
- A power generating company burning a number of coals from both the CAPP and the NAPP
- LTI sampled at three combustion units and several ash ponds
- A second mining company that made available samples from the CAPP
- Four companies that operate fluidized bed units in Pennsylvania burning both high-ash bituminous and anthracite coals

Under Mod D, the University of Kentucky was separately tasked with collecting additional samples from operating field sites—mines, preparation plants, power stations, industrial sites, and ash or other waste ponds. In addition, they were tasked with collecting no less than 75 samples from various state geological agencies in Kentucky, Virginia, Alabama, Mississippi, Louisiana, and Texas. The sites sampled in both the Central Appalachian basin

and in other basins are listed in Table 3. Similarly, samples were taken at a number of sites in the Southern Appalachia basin, the Illinois basin, and the Powder River basin, Table 4.

The university delivered a preliminary list of possible sampling locations with justifications for their selection to LTI; discussions were held as to which candidates should be pursued. Once permission was granted for the university to access the approved sites and they had obtained the necessary permission from the site owner, the sampling effort began.

More than 125 geologic survey samples were collected but only 75 were analyzed. The rest are being held at NETL pending a future opportunity to measure the REE content and other elemental concentrations. All the field samples have been analyzed and appear in the "Combined sample spreadsheet" on the NETL Energy Data eXchange platform (EDX) (http://www.netl.doe.gov/research/coal/rare-earth-elements/ree-edx).

Table 3. Central Appalachian Sampling Locations by Type

Sample Source	Unit	Coal Seam	Sampled	Shipped to LTI
1. Two Coal Preparation Plants	Redacted	West Kentucky No. 13	X	X
		Mary Lee	X	X
2. Two Power Plants		Illinois Basin Blend	X	X
		West Kentucky Blend	X	X
3. Channel Samples		West Kentucky No. 13	X	X
		Mary Lee	X	X
4. Surface Mine		West Kentucky 11, 13a & 13b	X	X
5. Fluidized Bed		3 August splits	X	X
6. Industrial Facilities		Powder River Basin	X	X
		San Juan Basin	X	X
		Powder River Basin	X	X
7. Ash Disposal Sites		Illinois Basin	X	X
		West Kentucky Blend	X	X
		Gulf Coast	X	X
8. Geologic Survey Samples		25 coal seams	X	X
		14 coal seams	X	X
		8 coal seams	X	X
		28 coal seams	X	X

N	Not Started
P	In Progress
X	Completed

Table 4. Other Basin Sampling Locations by Type

Sample Source	Unit	Coal Seam	Sampled	Shipped to LTI
1. Two Coal Preparation Plants	Redacted	Fireclay	X	X
		Eagle	X	X
2. Two Power Plants		Fireclay	X	X
		Fireclay	X	X
3. Channel Samples		Fireclay	X	X
4. Surface Mine		Upper Elkhorn No. 1	X	X
5. Fluidized Bed		Central Appalachian	X	X
6. Industrial Facilities		Central Appalachian	X	X
		Blue Gem	X	X
7. Ash Disposal Sites		Central Appalachian	X	X
		Central Appalachian	X	X
		Fireclay	X	X
8. Fifty Geologic Survey Samples		30 seams	X	X
		20 seams	X	X

N	Not Started
P	In Progress
X	Completed

In addition, the University of Kentucky was tasked under a separate contract with collecting and sizing six samples determined by mutual agreement with LTI. These six samples were to represent mined coal, coal from a preparation plant, a fine, cleaned coal sample from a waste pile, and a parting from a Texas lignite mine. These samples, once ground to the required size, were to be subjected to a series of bench-scale preparation tests. All bench-scale testing results have been analyzed and appear in the University of Kentucky final report (PSU report ref) on the EDX site.

Mod E was intended to broaden the reach of the sample collection and bench-scale separation testing effort. Three universities were brought under subcontract—Pennsylvania State University, the University of Utah, and the University of Alaska, Fairbanks. PSU was tasked with collecting samples and performing bench-scale tests on rock and mineral samples collected from selected sites in Pennsylvania. These included, weathered material from the overburden (roof rock) in an open pit coal mine in central Pennsylvania, screen rejects from a coal blending yard, and ash from an operating fluidized bed power plant (clinkers, bottom ash, fly ash, etc. Preparation plant refuse material (15 samples) was also collected.

The collected samples were prepared using standard mineral processing procedures and subjected to the following separations procedures and characterization analyses:

- Gravity separation (float-sink/washability tests)
- Magnetic separation methods
- Electrostatic separation methods
- Ion exchange based leaching methods

The collected samples and their derivatives from various separation/enrichment methods were analyzed for REE concentrations by multiple analytical techniques. In addition, the samples were also subject to proximate analysis. All of the samples were sent to LTI to be analyzed at one of the two contract laboratories engaged by LTI to perform the REE analyses.

The University of Alaska, Fairbanks (UAF) collected samples from Healy coal (No.4 coal bed) in the Suntrana formation. The Wishbone Hill district belongs to Matanuska field and is in Southern Alaska-Cook Inlet region. The Matanuska coal

field is the most important Paleocene coalfield in Alaska because it contains high-rank minable coal beds. The Wishbone Hill sample used in our test program was from Jonesville coal zone and was handpicked from the exposed oblique-slip fault outcrop. Furthermore, samples were also collected from UAF power plant of fly-ash, bottom ash and cinders. Float-sink tests were conducted for coarse sizes at the different specific gravities between 1.30 and 2.0. The fine fraction (-100 mesh) was later subjected to flotation and magnetic separation tests. Final reported REE values were taken from measurements made by ALS in Vancouver. (ref. 3-4)

Based on preliminary geologic assessment, discussions with LTI and initial screening for REE content, 36 different samples from 7 different states were selected for analysis. All acquired samples were sampled, prepared, and analyzed according to ASTM (American Society for Testing and Materials) standards. In addition to raw coal samples, a number of partings/reject/refuse samples were collected and analyzed. Particle classification, density separation (float-sink/washability analysis), flotation, and wet magnetic separation were employed. Through this task, effectiveness of existing/conventional technologies to concentrate REE+Y+Sc from different coal and coal waste materials is evaluated. All raw samples and split fractions obtained through physical separation tests were analyzed for their REE, yttrium, and scandium contents using ICP-MS. Final reported values were taken from measurements performed by SGS. Furthermore, the proximate analysis was performed to obtain information about the ash, moisture, fixed C, volatile matter, S, and Btu contents of all raw samples and selected split fractions. (ref. 3-5)

Observations and comments will be summarized in Section 3.4 through 3.6.

3.3.2 Tetra Tech

Tetra Tech contracted to perform more formal resource assessment. Results of their analysis is discussed in section 3.6. The final report of this analysis is available on the EDX site.

3.3.3 XRF Device—Field Data, Calibrations, Correlations (and limitations)

XRF Discussion

As mentioned above, a large portion of the initial field sampling effort was conducted based on the analysis done using the USGS COALQUAL data. The sample collection was straightforward with no special requirements other than placing material in containers and

preventing any cross-contamination issues, with all analytical preparations being conducted in the laboratory. This approach is limited. The LTI sampling was aimed at developing an initial set of data including some that overlay the sampling points in the USGS database. We also sought to gather samples from actual operating facilities rather than to collect core samples from locations not currently involved in actual production. Are coals with higher REE contents (whether on an ash-only or whole coal basis) being mined and fed to preparation plants? Are these same coals reaching power stations? It was not within the means of the project – either based on cost or time available – to sample a very large number of sites and to subject the samples to an expensive analytical process – to guide the search. An alternative means was needed.

Given the apparent need to improve field capabilities by developing a means of being selective (or screening) in the field, an alternative instrumental method was selected for evaluation. This means took the form of a new state-of-the-art X-ray fluorescence technology in the form of new handheld instrument that utilized an alternative means (rather than an isotopic source) to generate the X-rays. Although this instrument had been previously proven in other hard rock mining application, it had not previously been applied to coal and coal-related material prior to LTI's efforts.

After receiving the handheld X-ray fluorescence spectrometer, during the latter part of the project according to the original schedule, it was deployed into the field for its first evaluation. Initial results were unsatisfactory and with some further investigation, it was determine by LTI and the manufacturer that there was a factory related calibration problem with the instrument. The instrument was returned to the manufacturer along with three field samples of differing composition (raw coal, fly ash, and refuse) to be used in the factory re-calibration of the instrument. Subsequent applications of the instrument on potential materials containing REEs produced results which were still considered questionable.

A need existed to validate the performance of this new instrument using a variety of material substances. As a part of the extensions to the project, LTI contracted with Tetra Tech, Inc., which owned the identical instrument to conduct a comparative study of the two instruments utilizing the same sample materials (coal, refuse, ash, and National Institute of Standards and Technology (NIST) samples. Side-by-side comparisons were conducted and a collaborative report was generated, which was titled "Study on the Utilization of Portable Handheld XRF Spectroscopy as a Screening Tool for Rare Earth Elements in Coal

and Coal Waste Products." The results of this comparative study of instruments were somewhat positive, yet there were inconsistencies associated with measurements taken of NIST samples. Details of this report can be found on EDX. A key finding is summarized in Figure 21.

Study on the Utilization of Portable Hand-Held XRF Spectroscopy as a Screening Tool for Rare Earth Elements in Coal and Coal Waste Products

- By Dr. Rex C. Bryan, Dr. Dave Richers, Dr. H.T. Andersen, Mr. Terry Ackman, and Mr. Tom Gray, P.E.
- Results of study when testing selected samples available in the Collected Samples spreadsheet

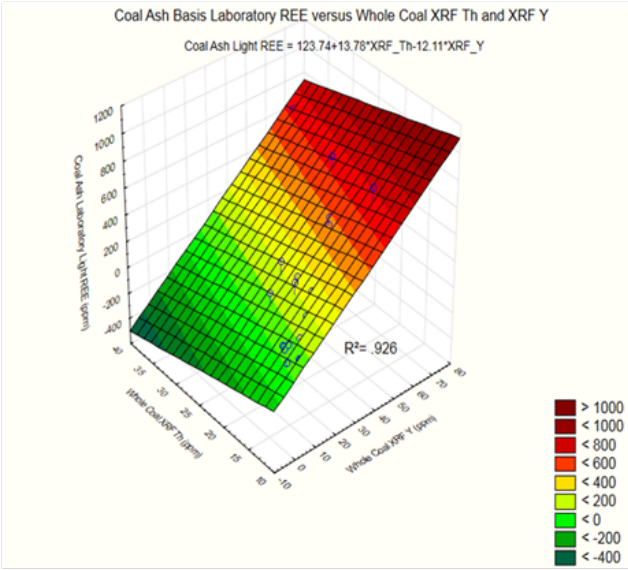


Figure 21. XRF Measurements of Th and Y Can Be Correlated to Laboratory Measurements of Light REEs+Y

It is recommended that further laboratory testing of the XRF be completed prior to further field applications. This further lab testing should include the preparation of laboratory designed samples, the use if NIST samples, field samples of know composition, and a close collaborative effort alongside the manufacturer relative to their ability to tweak the instrument's factory calibrations using various (custom) types and sizes of coal-related materials (raw coal, ash products, and refuse). It is further recommended that an isotope based portable system, with a higher energy source, be reviewed as a potential alternative or companion instrument to the XRF discussed above, which may provide additional capabilities relative to identifying the heavy REEs. It is recognized that such an instrument would require additional safety training and specialized handling and storage.

XRF calibration - open items

- Study based on measurements using two similar XRF devices of REE samples that LTI collected and had analyzed in labs.
- Tetra Tech device did not have the same set of calibrations as did LTI device so sensitivity to REEs might differ.
- Tetra Tech did not extend applicability of XRF measurements beyond light REEs (La, Ce, Pr, Nd) plus Y.
- The correlation shown on the previous slide was derived from the data; a correlation with Y was also developed between measured Y and total REE (with R^2=0.878).
- Important discrepancies seen: neither agreed for several elements in NIST std.; Nd values differed between instruments.

Figure 22. XRF Open Items

Lastly, the use of an XRF in the field will require significant modifications to the approach in which field samples are collected and processed. As discussed in Appendix 3—XRF Field Analytical Protocol, which is located in the report mentioned above, sample thickness, density, moisture, matrix, and size impacts the capability and reliability of the handheld instrument. Consequently, a small, portable field laboratory (powered by a field generator) that is capable of sizing and dewatering samples in the field will be required to obtain the optimum performance from the XRF. Although this approach adds some additional burden on field sampling efforts, it should produce more reliable results in the field. Furthermore, more effective sampling in the field will result in minimizing sample load, which in turn reduces analytical costs. These savings in analytical costs should overshadow the relatively minimal costs associated with the development of a portable field lab.

3.4 SUBCONTRACTED FIELD WORK

Each of the four university contracts mentioned above was unique in terms of the number and types of samples processed; the coal basins that served as the focal regions; the scale of the experiments that were performed; and the test methods employed. The University of Kentucky included a mineral release study; Pennsylvania State University did a number of leaching studies and primarily focused their work on mining wastes. Each study was focused on a limited set of coal basins and on important coal formations or seams as evidenced by the fact that samples were largely recovered from active commercial operations (mining, preparation, and combustion). The basin-level focus, types of samples gathered, and separation tests performed are given in Table 5.

Table 5. Summary of Locations and Measurements Performed in the Various Field Campaigns

Coal Basin	Primary Analyses : Sample Type	Separation Tests Performed	Notes
CAPP	REE composition (total ppm & distribution) in: coal reserves, ROM coal, preparation plants, power plant feed, fly ash, bottom ash, mine wastes, combustion by-products	• Washability • Mineral Release • HGMS • flotation; • electrostatic separation	• Wide range of sample types collected • Prep plant mass balances • ~12 prep plants "surveyed" • Bench-scale Separations Tests
NAPP	REE composition (total ppm & distribution) in: coal reserves, ROM coal, preparation plants, power plant feed, fly ash, bottom ash, mine wastes, combustion by-products, aqueous effluents	• Washability • HGMS • flotation • electrostatic separation • Ionic Liquids	• Aqueous effluents • Bench-scale Separation tests focused on roof rock & partings/ Mine refuse • Several preparation plants "surveyed"
IL	REE composition (total ppm & distribution) in : coal reserves, ROM coal, preparation plants, power plant feed, fly ash, bottom ash, mine wastes, combustion by-products	• Washability • HGMS • flotation • electrostatic separation	• Prep plant Mass Balances • Washability characterized • Wide range of Sample Types Collected
SAPP	REE composition (total ppm & distribution) in: coal reserves, ROM coal, preparation plants	• Washability	• Prep plant Mass Balance • Core and channel samples
Gulf Coast Lignite	REE composition (total ppm & distribution) in: coal reserves, , power plant feed, fly ash, bottom ash, and mine wastes	• Washability • HGMS • flotation electrostatic separation	• Power plant feed, fly ash and bottom ash • Partings sample subjected to bench-scale separations tests
PA Anthracite	REE composition (total ppm & distribution) in: power plant feed, fly ash, and bottom ash	• total of three samples tested	• Power plant feed, fly ash and bottom ash
Rocky Mtn.	REE composition (total ppm & distribution) in: ROM coal	• samples tested for REE composition	• ROM coal and outcrop samples
Powder River Basin	REE composition (total ppm & distribution) in: coal reserves, power plant feed, fly ash, bottom ash, mine wastes (inc. AML)	• Washability • HGMS • flotation electrostatic separation	• Coal and pit cleanings tested • AML site REE composition tested
Alaska	ROM coal, Fly ash	• Washability • HGMS • Flotation	• Two different coal regions included • Fly ash and Bottom ash samples for one coal

Exceptions to that approach included the samples from a large, fine coal repository that were tested by the University of Kentucky and samples from outcrops in Montana that did not represent current mining activities (Sand Coulee and Belt) that were analyzed as part of the University of Utah effort.

The outcrop samples from Montana were taken given the historical data presented in Figure 23 shown below. The data suggests that different benches within the sample contained significantly different concentrations of Y (which was used to estimate total REE content). This location is no longer being mined. However, outcrops in that region are available for sampling. LTI coordinated discussions focused on gaining permission to access sites in that region that involved Tetra Tech, the University of Utah, and the Montana Department of Environmental Protection. Photographs of the sampling locations are reproduced from the University of Utah final report and shown in Figures 24 and 25.

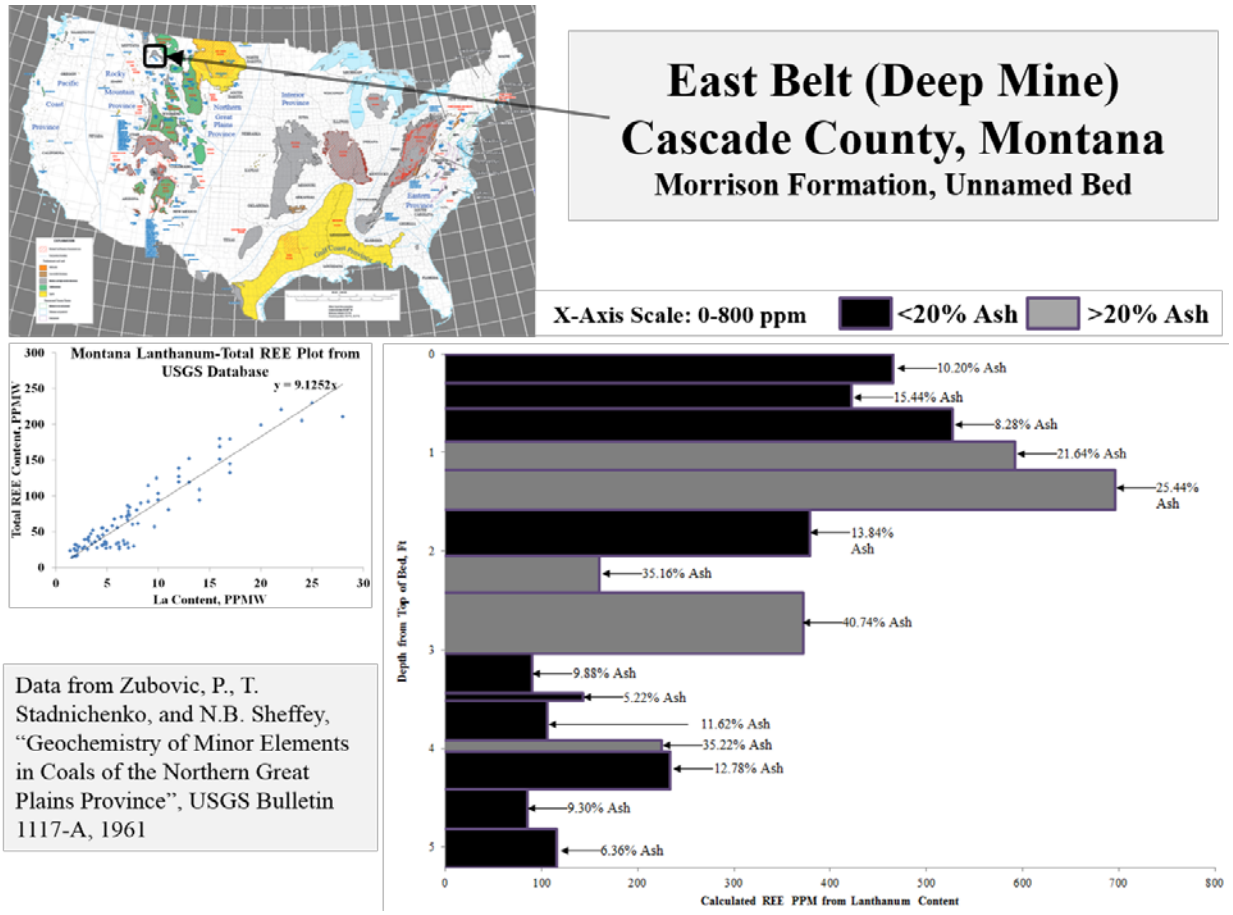


Figure 23. Bench Sample Data from East Belt Deep Mine

Figure 24. Pictures of the Sand Coulee Outcrop Sampling Site

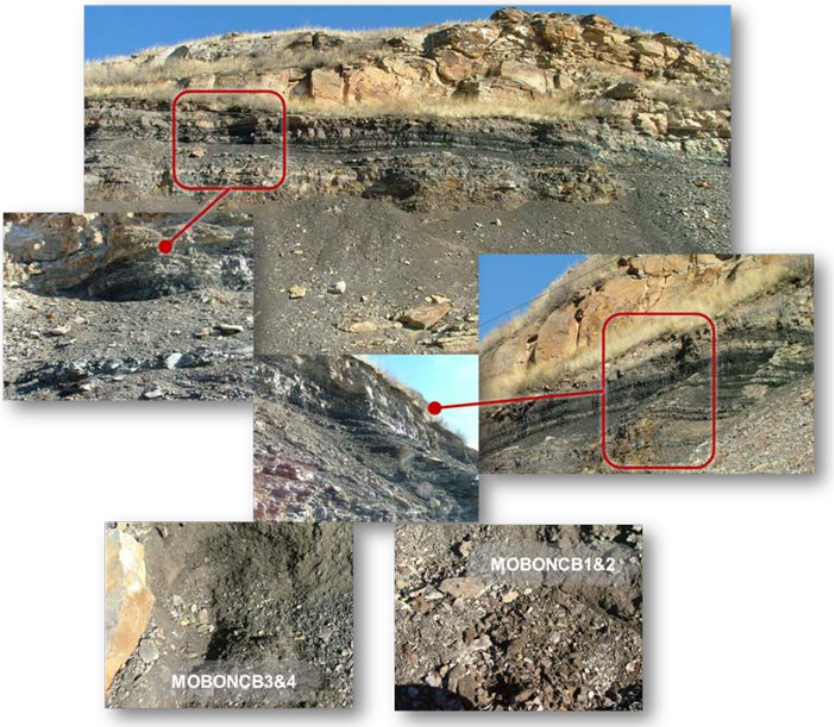


Figure 25. Pictures of the Belt Outcrop Sampling Site

The MOSONCB3 sample exhibited a REE+Y+Sc concentration exceeding 380 ppm. Most of the higher-valued REE samples (whole coal or ash only basis) came from the two locations.

University-Led Field Campaign—The sampling and conventional separations studies performed by the four Universities were executed under two separate contract modifications. The contracts were issued so that each project recovered samples from different coal regions. The field campaign rolled out in two segments—an initial effort that was defined under Mod D focused on the Central Appalachian basin, the Illinois basin, and the Southern Appalachian basin. The University of Kentucky was selected to perform sample collection in conjunction with Virginia Polytechnic Institute and State University. Sampling targets included coal mines, coal preparation plants, industrial units utilizing coal (including fluidized- bed units) and electricity generating units. LTI specified the sort of samples to be collected, required a clear, unique labeling system to enhance sample tracking, and provided guidance on shipping the samples to locations selected in concert with NETL (initially the NETL Chemical Handling Facility was specified). These samples were gathered as they were delivered. LTI reviewed the samples we received to ensure that they met the required criteria. LTI then sent the samples to one of our laboratory analysis contractors for determination of the REE concentrations (element by element) along with the key "pathfinder" elements discussed earlier.

A second subcontract was awarded under Mod D also to the University of Kentucky to perform a limited series of pilot-scale preparation tests on six samples (along with smaller, preliminary studies to better establish test conditions for the pilot-scale work, coal washability tests in particular). They were tasked with performing a series of typical tests used to evaluate the separation of individual elements under physical cleaning. The university was specifically excluded from research into novel separations techniques or the evaluation of new flotation agents. The university was also tasked with getting whatever REE concentration determinations that they felt were necessary at a laboratory of their choosing. However, LTI specified the type of samples to be collected for five of the samples and provided the sixth from material gathered during the earlier LTI -lead field work. LTI also specified the analytical protocol that was to be followed. Results of these subcontracts will be discussed later in this section.

The second set of subcontracts were issued under Mod E and responded to a request from NETL to broaden the field sampling effort. The universities involved were the University of Utah, the University of Alaska, Fairbanks, and the Pennsylvania State University. Each

respondent was required to collect samples from one or more specified coal region. They were given the option of having the REE analyses performed through NETL or at a laboratory of their choosing. If a different laboratory from those contracted by LTI was chosen, the analytical methodology was to be the one stipulated by LTI (or an equivalent method pending review and approval by LTI). Both the University of Utah and the University of Alaska, Fairbanks chose to use other laboratories at more convenient locations to each campus. Pennsylvania State University elected to send their samples to LTI.

Each of these three subcontracts included not just sample gathering but small-scale tests to evaluate the response of the samples to physical coal cleaning technologies including froth flotation. All results have been made available at a public website.

3.4.1 Sample Gathering for REE Measurements

The EDX REE Portfolio public website contains an inventory of collected samples, analysis results, data, and technical reports. An introduction and overview of the REE study is also provided (Figure 26).

Figure 26. EDX REE Public Website Home Page

(EDX REE portfolio public website link: https://edx.netl.doe.gov/ree/)

Data pertaining to sampling is available for download under the Data and Resources heading, then Sample Analysis (Figure 27). The focus of the sampling effort was to characterize the concentration, elemental composition, and mineralogy of rare earth elements in coals, mineral matter associated with coal, fly ash, bottom ash, and post-processing/post-use materials. Aside from the REE concentrations, only limited other chemical measurements were made. The files under Sample Analysis include those that summarize or synthesize data collected from multiple sources or that involve different organizations in planning, acquiring, and analyzing each sample. These datasets are available in Excel file format. The university data sets found under each listed university that participated in the NETL study efforts are also available here and is also available for review in the context of the university's study in the form of a comprehensive downloadable pdf reports available within NETL Technical Reports under Research Products (Figure 28) within the EDX REE Portfolio.

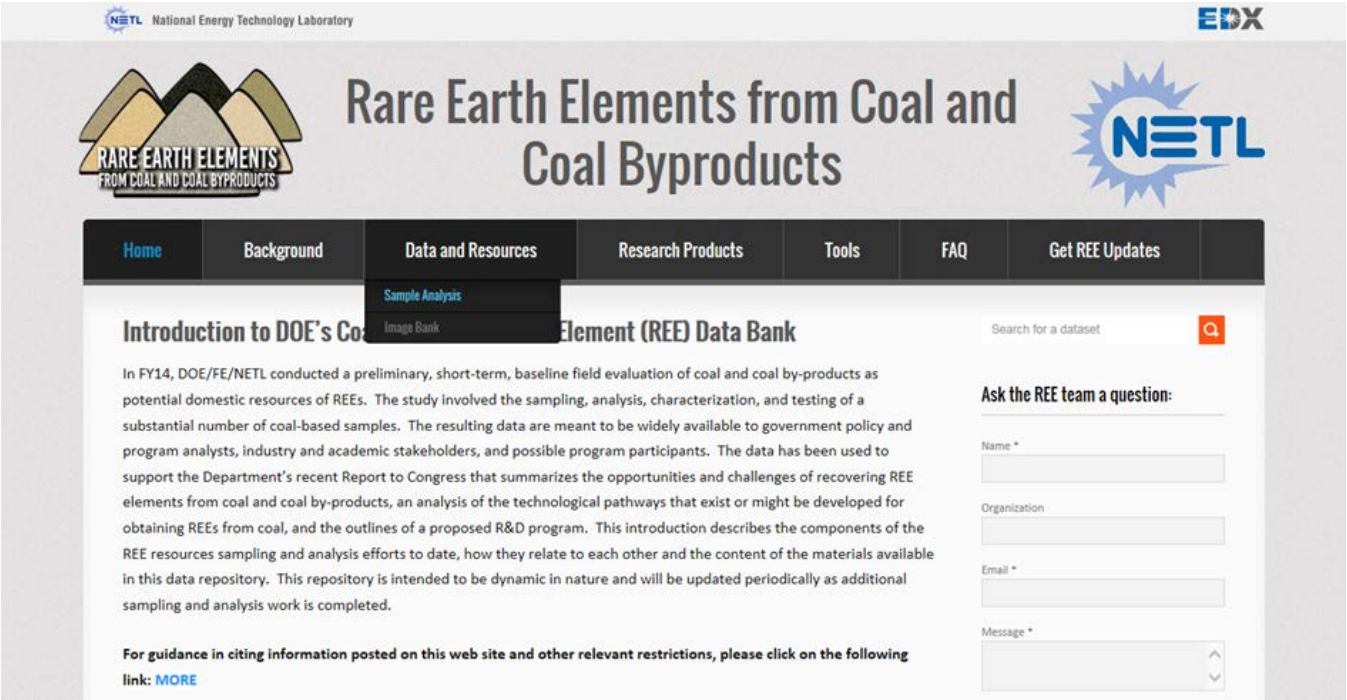


Figure 27. EDX REE Public Website—Sample Analysis

Figure 28. EDX REE Public Website NETL Technical Reports

3.4.2 Geographic Coverage versus Initial Studies

There are a large number of coal basins in the United States; a limited number continue to be mined for a significant amount of coal. Figure 29 provides an overview of the coal provinces (several basins may be found within a province). For example, the Appalachian Province includes the Northern Appalachian basin (NAPP), the Central Appalachian basin (CAPP), and the Southern Appalachian basin (SAPP). The Northern Great Plains Province includes the Powder River Basin and a lignite basin primarily of commercial interest in North Dakota.

The differences between coal rank are based on the degree of coalification; higher ranked coals are generally thought of as older in geologic age. They are further along in the coalification process (largely a displacement of moisture then of bound hydrogen) until they are nearly pure carbon. From the figure below, the oldest coals are found in the Appalachian Province and in the Interior Province. The Rocky Mountain and Pacific Coast Provinces are dominated by coals of intermediate age while the youngest coals (more recent deposits of organic sedimentary materials) are found in the Northern Great Plains Province and the Gulf Province.

The presence or absence of rare earth elements and other commercially significant metals can probably be connected to other geologic events occurring at the same time as the sedimentary basins that became major coal formations were filing with organic materials.

Based on the USGS concentration data for Central and Southern Appalachian coals, coals dating from approximately 320 million years ago plus or minus 20 million years show a

larger percentage of samples with higher values for total rare earth element concentrations than other coals in these basins. This window of time coincides with a time when the African plate was colliding with the North American plate then receding toward its present location. The collision caused an uplift that became the present-day Appalachian Mountains and likely resulted in significant volcanic activity.

Comparing the age of these coal bodies with the geologic information about when the sedimentary basin were filling with organic material; and when major geologic events - volcanism, mountain-building, etc.—were occurring, there does appear to be a coincidental association. Whether there is a direct connection or not will be explored at a later point in this report.

A similar review of geologic events suggests the western coals with higher REE levels are also from time periods marked by volcanism and mountain building.

Specific coal basins, specific formations within those basins, and important commercial coal seams, were targeted as candidates for the university sample gathering work. Universities within or nearby to those specific coal regions were tasked, as described above, to gather samples. The number of samples and the specific targets varied. The University of Alaska Fairbanks was tasked only with Alaskan coals. The University of Utah and the University of Kentucky both had broader charters, although each typically focused on gathering samples so that there was little overlap. Utah primarily collected samples in the Rocky Mountain Province and the Northern Great Plains Province while Kentucky focused on the Central and Southern Appalachian basins and the Interior Province (primarily the Illinois basin). Pennsylvania State University focused on coals from the Northern Appalachian basin.

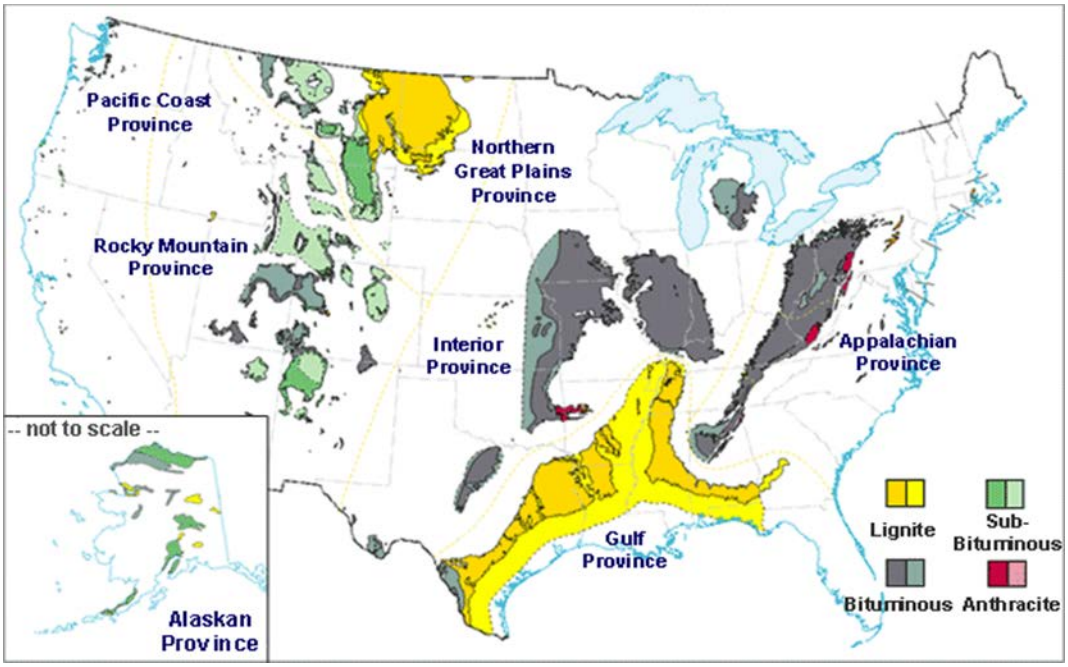


Figure 29. Overview of U.S. Coal Provinces and Enclosed Basins

The results of the field work are compiled on the EDX site. Contributions of each of the separate activities are presented in one or a series of files. Work by each university is listed by university and the final reports are also available. The information is available in files that can be downloaded and analyzed by anyone with an interest in this topic. The main thrust of the discussion of results in this report will be focused on data across the all the samples that were gathered. Our intent is to identify common trends and to highlight differences that bear further analysis.

3.5 DATA GATHERING AND ANALYSIS

The following combines data from the field work conducted by LTI alone and from the results obtained by the Universities and analytical laboratories engaged by LTI: the University of Kentucky and Virginia Polytechnic Institute and State University (for the physical separation samples tested and for the results for the 14 commercial coal preparation facilities), and by the University of Alaska, Fairbanks, Pennsylvania State University, and the University of Utah.

3.5.1 Identification of Potential Source Streams

The aim of the sample gathering and mineral separation analyses was neither to specifically find the highest whole coal REE concentration samples—such a goal was considered to be too hit or miss given the percentage of highest REE coal samples (when ranked by the whole coal value and by the ash only value) in the USGS database (≈15 percent) and given the total time available for the sample collection and testing. Nor was it intended to find physical separation methods that would concentrate REEs near to commercially significant levels. The separation tests were intended to establish whether a case could be made for more research and to profile samples from a number of coal provinces and their enclosed basins. It was also targeted at establishing a baseline for rare earth concentrations as found for samples from active mining, in ashes from power generation at a number of types (large pulverized coal fired units, fluidized bed boilers, and industrial boilers—often stoker units) and finally from various types on mine waste (partings separated at the mine site), coal preparation waste, liquid runoff from some of the sites evaluated, and reject streams within power plants (such as pulverizer rejects).

3.5.2 Initial Data

Based on these sample categories, data was collected from all engaged organizations and data was entered on the EDX site in searchable databases. The final reports from each university are also posted on the EDX site. The intent of this approach was to allow open access to data so that interested parties could download a single data file or a group of these files and perform comparative analyses amongst the results.

A chart appears on the EDX site (Figure 30, below) that captures the value chain and identifies possible recovery opportunities.

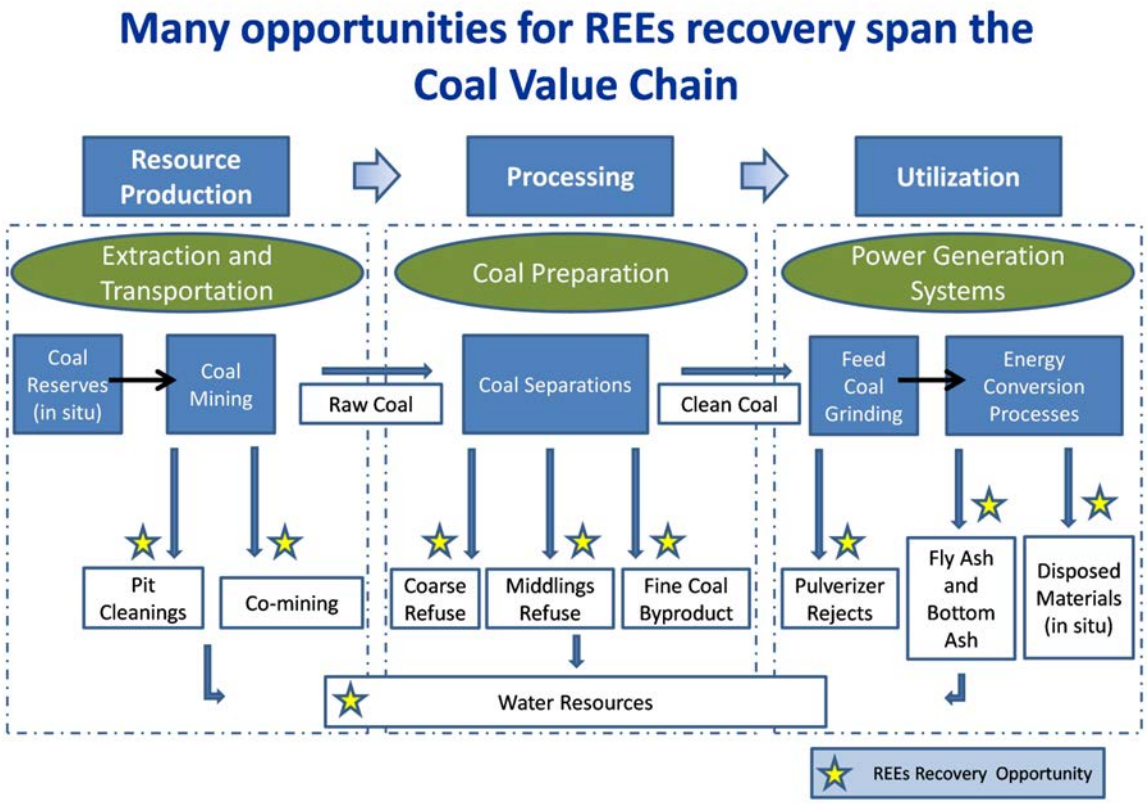


Figure 30. REE Recovery Opportunities from the Coal Value Chain

The large body of data complied profiles results for coals from within particular regions but none of the data gathering efforts focused on data integration. Observations from across all researchers engaged are summarized in section 3.6. There seem to be differences in the patterns of both the LREE/HREE ratio amongst coal deposits and there may also be differences when comparing specific gravity fractions from washability study or the results from actual coal preparation plants.

It should be noted that the various Universities and LTI were working with analytical samples drawn from field samples of varying sizes. In a few cases, we had a number of drums of one particular stream from within a coal preparation plant. In other cases, as with some of the geological survey samples that were gathered in a manner consistent with the Swanson and Huffman paper cited earlier, we were dealing with hundreds of grams. The samples collected by Utah and Alaska were large enough for laboratory-scale washability

tests and were intermediate in size to the other two categories. Details of sampling procedures and test procedures can be found in each final report.

A series of simple figures have been prepared based on averages for either the all of a particular sample type or for all of a particular coal deposits. These are discussed in the next subsection.

3.5.3 Insights into Data

One of the interest facts that seem to be supported by the data are that the LREE/HREE ratio varies depending upon the point within the coal value chain where it is taken. Figure 31 combines all the data (from all sources) by the type of sample. The Utilization group of samples, with the exception of the two Utilization, Feed coal (which is the coal fed into a power plant) data sets, show lower LREE/HREE rations suggesting that the process of cleaning the coal for sale in power generation selectively concentrates the HREEs. The sample group descriptions are consistent with the figure above. The range of values for the Utilization group, without the feed coal data, ranges from ≈26 percent HREE in the sample to ≈40 percent HREEs in the sample. For the two Utilization, feed coal, sets, the range is from ≈21 percent HREE to ≈26 percent. The Resource Production data sets show a range of values from ≈24 percent HREE up to ≈32 percent. Finally, the Processing samples group ranges from ≈16 percent HREE up to 26 percent.

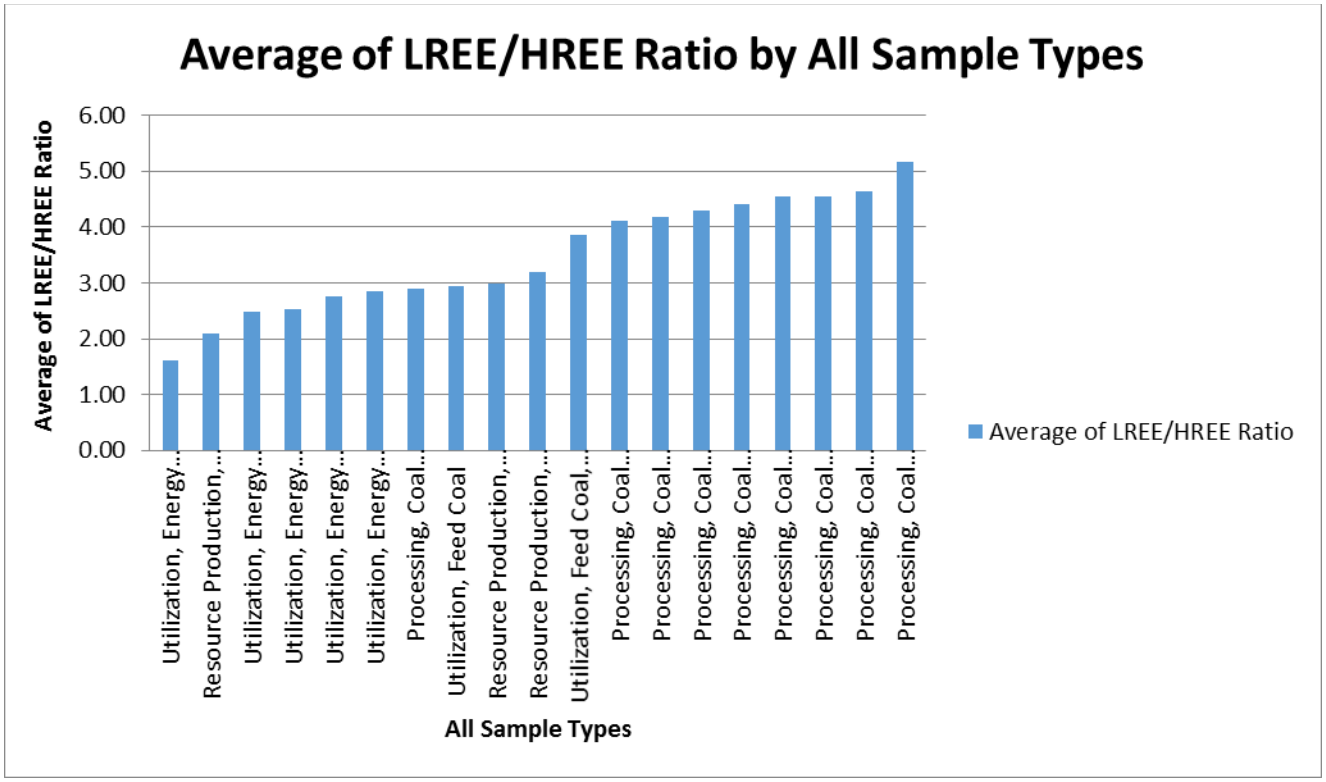


Figure 31. Average LREE/HREE Ratios by Sample Type

The following two figures (Figure 32 and 33) are focused solely on one basic sample type, utilization wastes and coal preparation refuse streams. Note that the high-valued LREE/HREE result came from samples of in-plant rejects, a measure taken to screen out material that might cause operational problems within the plant. These materials should make-up only a small percentage of the total shipments to a coal-fired power plant. Note that the LREE/HREE ratio varies from approximately 1.5 (≈40 percent HREE) to more than 5.0 (≈17 percent).

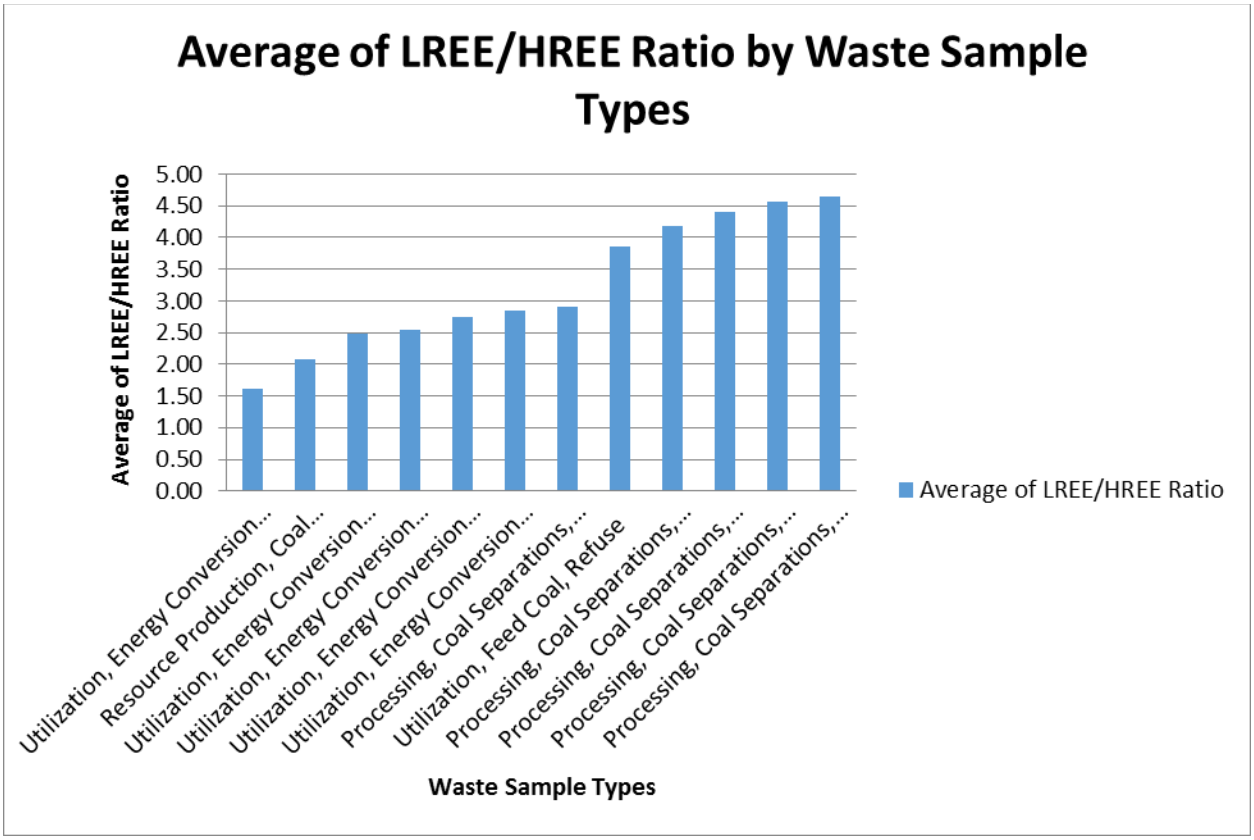


Figure 32. Average LREE/HREE Ratio for Waste Samples Only

Figure 33 is a similar plot of only those samples that could be described as raw coal, feed coal to a preparation plant, or feed coal to a boiler of any kind. Note that the LREE/HREE ratio varies from approximately 1.5 (≈40 percent HREE) to almost 4.5 (≈18 percent). Table 6 lists the number of samples included to arrive at the average values for each bar in the chart.

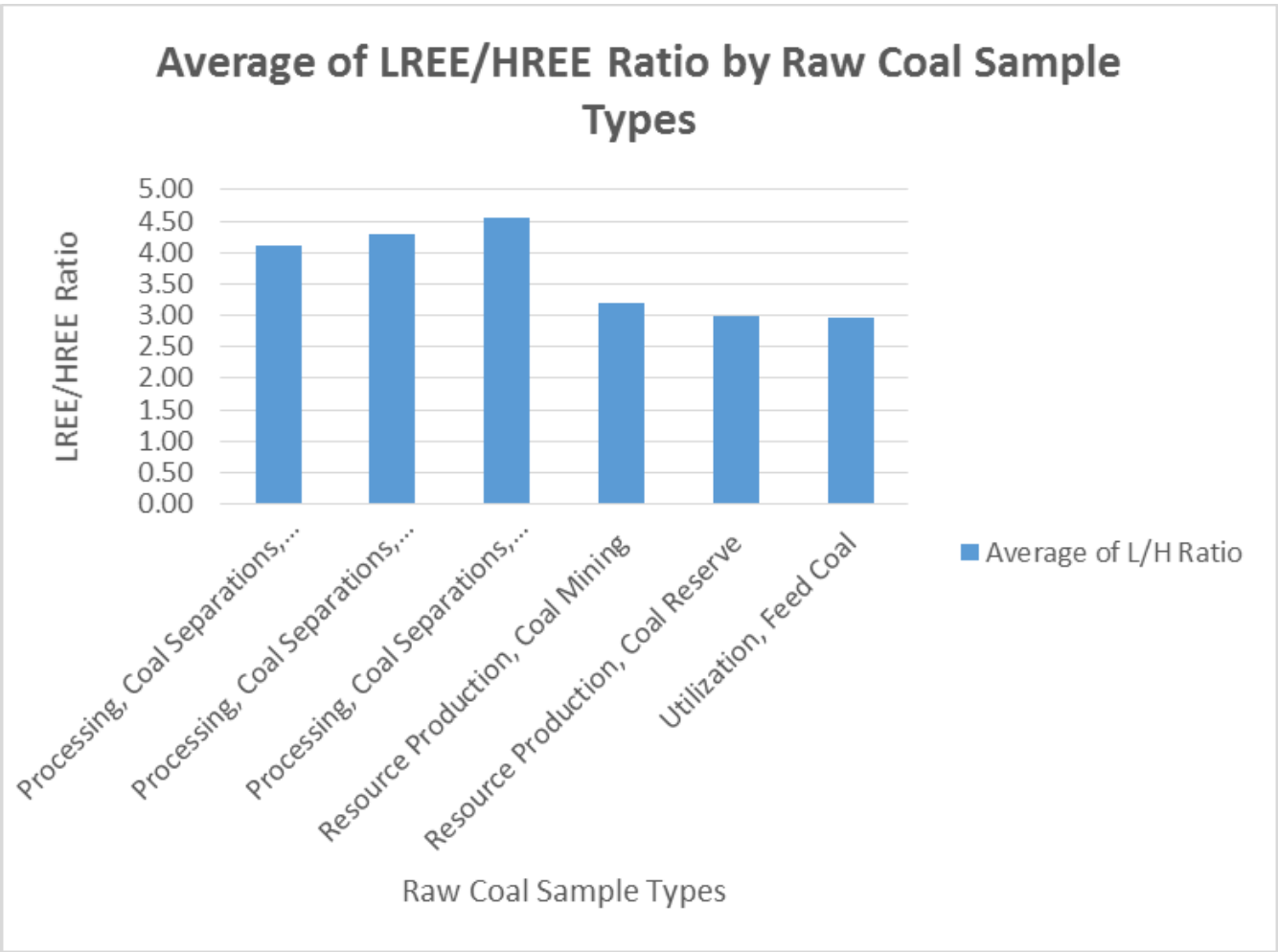


Figure 33. Average LREE/HREE Ratio for All Coal Samples

Table 6. Sample Sizes Averaged Together

Clean Coal Sample Types	Average of L/H Ratio	Sample Count
Processing, Coal Separations, Clean Coal	4.12	276
Processing, Coal Separations, Feed Coal	4.29	17
Processing, Coal Separations, Raw Coal	4.55	184
Resource Production, Coal Mining	3.20	185
Resource Production, Coal Reserve	2.99	78
Utilization, Feed Coal	2.95	45

The next plot (Figure 34) combines data for waste samples by the coal basin or coal province of origin. In some cases, no samples or very small sample numbers, corresponding to a category (such as Processing, Coal separations) were available to enter data by coal basin or samples were only available in small numbers (1-5) so an arbitrary cut-off was made at three. These data show similar that the highest values (i.e., least amount of HREEs in the samples) vary to some extent across the three basins with the largest number of samples. The Gulf Coast samples appear to contain the highest relative amount of HREEs followed by Alaska samples and the Central Appalachian samples. The limited number of Anthracite ash samples showed values close to those calculated for the refuse samples for the three basins represented by the largest number of samples.

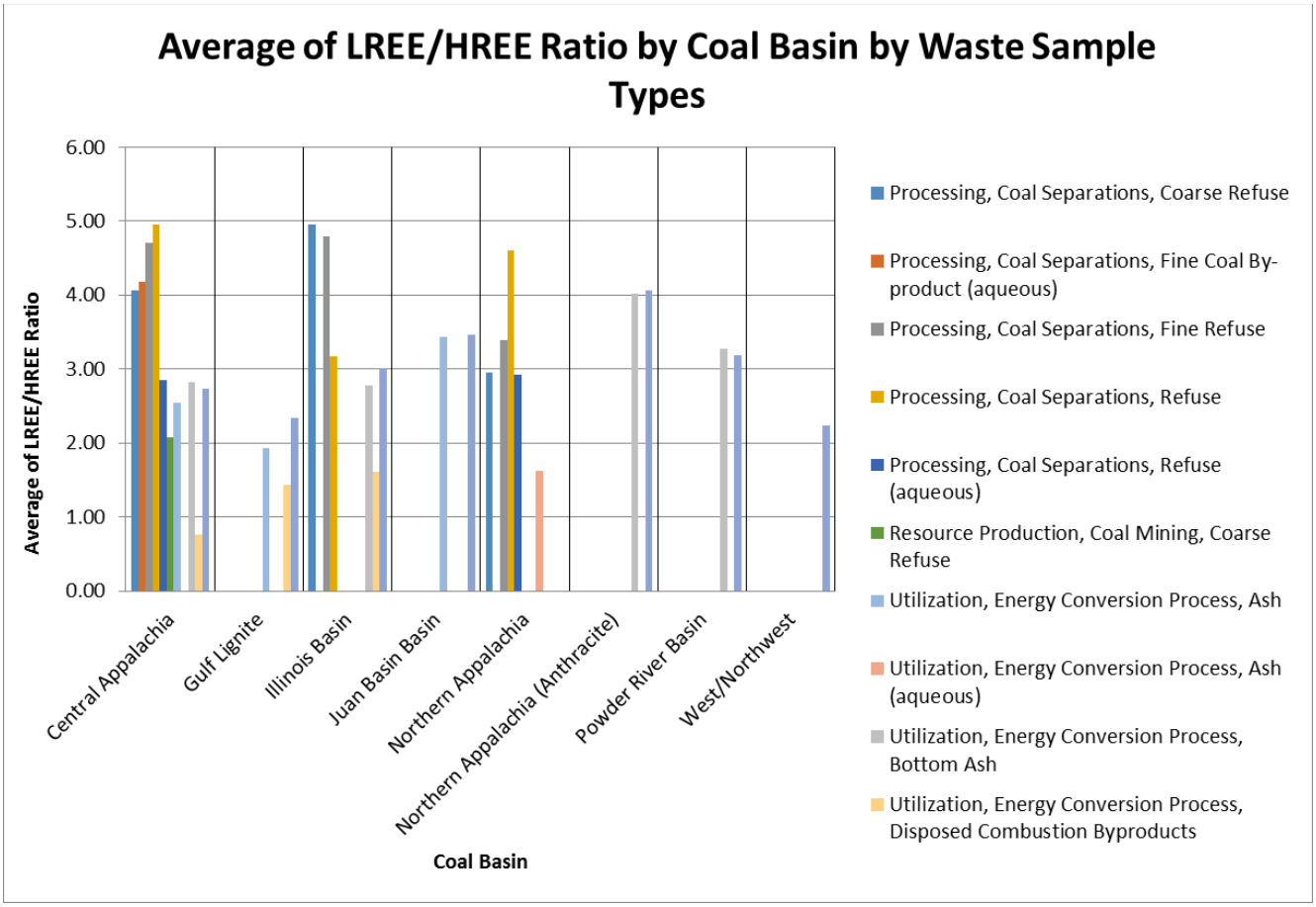


Figure 34. LREE/HREE Ratio by Coal Province or Basin

Although all ratios calculated for a sample set range between ≈0.8 (or 56 percent HREE for a limited set of Central Appalachian bottom ash samples) to a high of ≈5.0 (or 17 percent for a set of Coal Refuse for a strip mine site samples for Central Appalachian coals). The spread is four-fold when translated into the relative share of HREEs in the total sample. There do appear to be variations between basins and certainly within the types of samples as a whole.

Another worthwhile comparison amongst the sample types and the basins is to calculate the ratio between total rare earth element values TREE (including Y) and some of the potential indicator elements (Y, Th and La). Lanthanum has long been used as a predictor for total REE concentrations (ref. 3-6). Data taken in historic reports examined in this study developed correlations based on the known crustal distribution of the rare earth elements and lanthanum. Lanthanum, cerium, yttrium were often the only REEs reported. Similarly,

due to their co-occurrence with thorium, the presence of thorium has often been suggested as an indicator as to the presence of REEs. And finally, due to the focus in this work on the HREEs, we included yttrium in the ratios that were plotted. The six figures below suggest that the use of La, Y, and Th appear to decrease the range of the multiplier one would need to use to match the measured total REE data on both a sample type basis and by coal basins. For the ratios constructed using the sum of the lanthanum, yttrium, and thorium values, the ratios between highest and lowest ration for both the sample types and the basins is approximately two. For the ratios constructed using the sum of the yttrium and thorium values, the ratio between the highest and lowest values by sample type is 5.5 while than on a basin basis was 2.8. The value by sample type for yttrium alone ranged over a factor of 19. Details of the data sets used in developing Figures 38 and 39 are given in tables 7 and 8.

The correlation shown in Figure 21 relates measured values of LREEs to both the thorium and yttrium concentrations as measured by the XRF device tested in this study. The samples used in that testing effort were primarily waste samples.

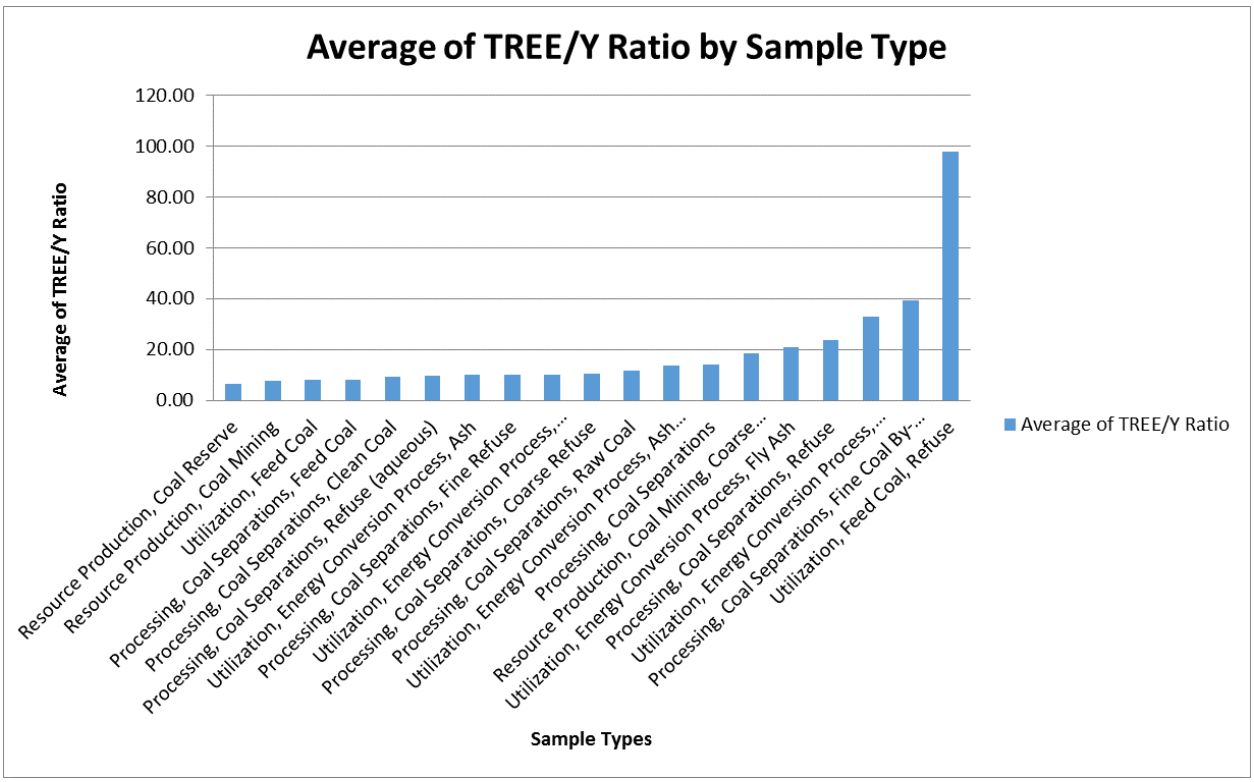


Figure 35. Average Value of TREE to Yttrium Ratio by Sample Category

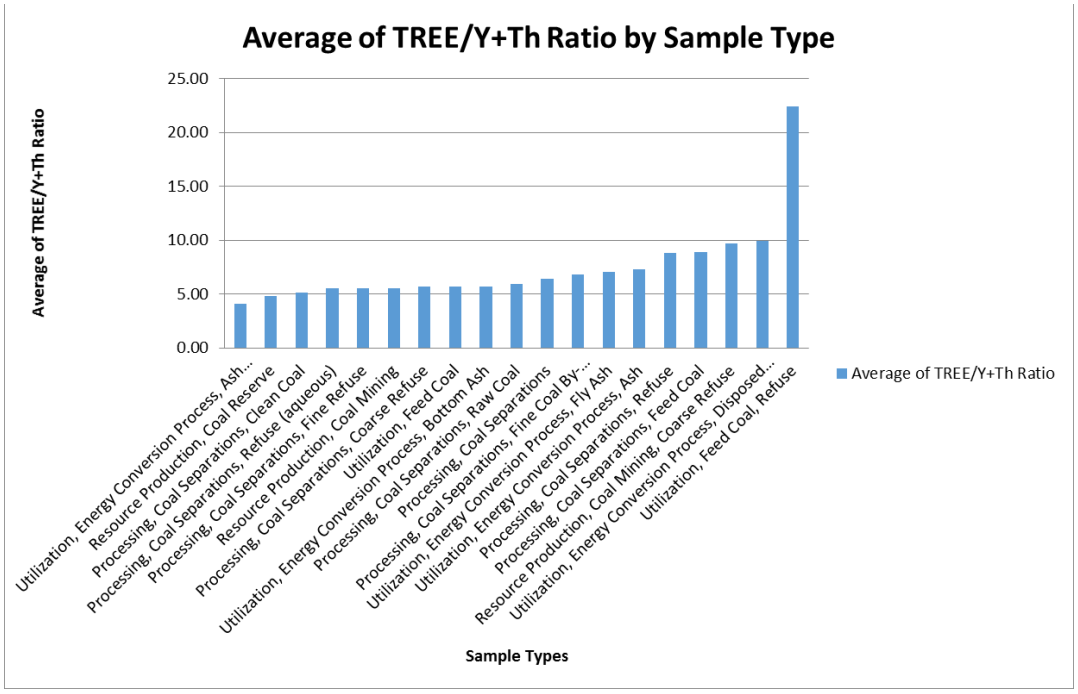


Figure 36. Average Value of TREE to Y + Th Ratio by Sample Types

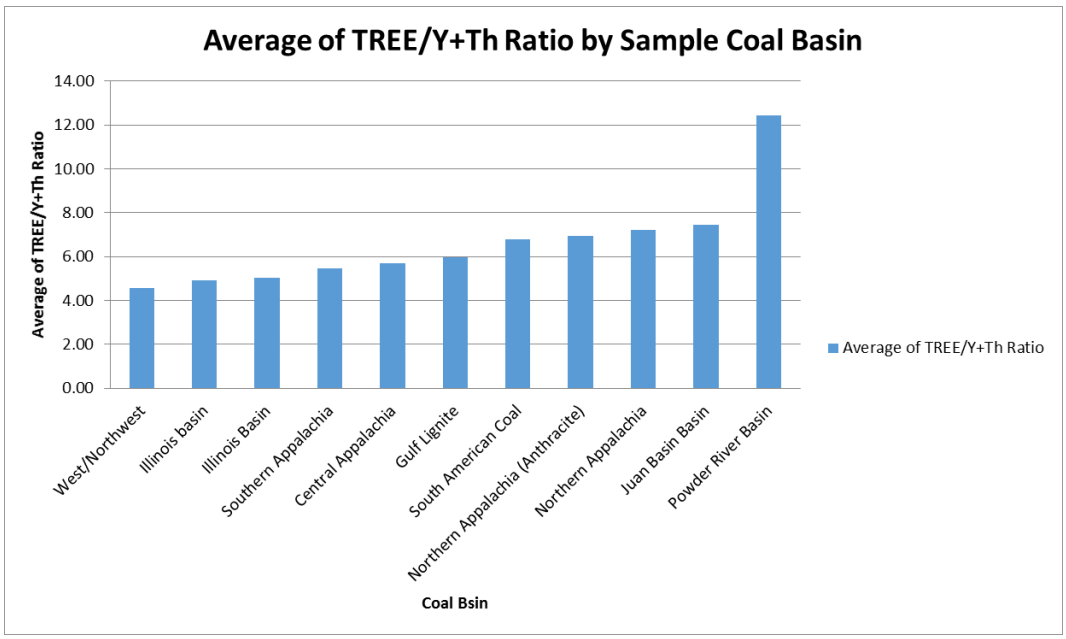


Figure 37. Average Value of TREE to Yttrium Plus Thorium Ratio by Coal Basin

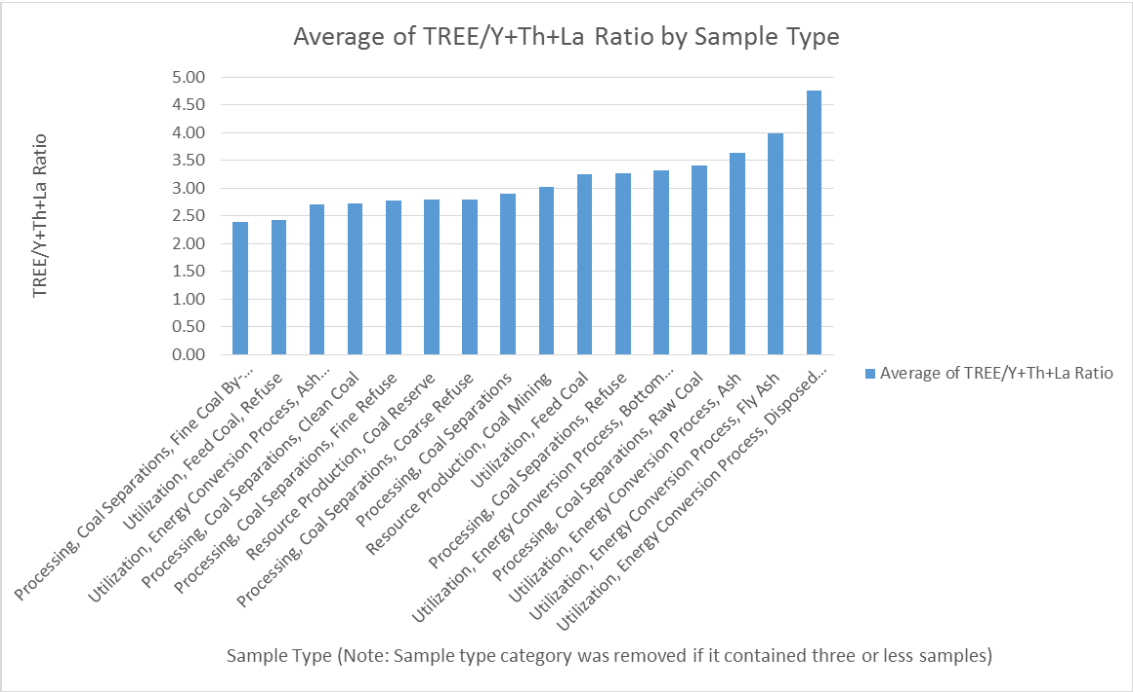


Figure 38. Average Value of TREE to Yttrium Plus Thorium Plus Lanthanum Ratio by Sample Types

Table 7. Sample Sizes Averaged Together

Row Labels	Average of TREE/Y+Th+La Ratio	Sum of Count
Processing, Coal Separations	2.90	66
Processing, Coal Separations, Clean Coal	2.73	41
Processing, Coal Separations, Coarse Refuse	2.79	37
Processing, Coal Separations, Fine Coal By-product (aqueous)	2.40	7
Processing, Coal Separations, Fine Refuse	2.77	31
Processing, Coal Separations, Raw Coal	3.41	52
Processing, Coal Separations, Refuse	3.27	43
Resource Production, Coal Mining	3.03	68
Resource Production, Coal Reserve	2.79	78
Utilization, Energy Conversion Process, Ash	3.64	22
Utilization, Energy Conversion Process, Ash (aqueous)	2.70	4
Utilization, Energy Conversion Process, Bottom Ash	3.31	21
Utilization, Energy Conversion Process, Disposed Combustion Byproducts	4.76	10
Utilization, Energy Conversion Process, Fly Ash	3.98	40

Utilization, Feed Coal	3.25	45
Utilization, Feed Coal, Refuse	2.43	4
Grand Total	**3.12**	**574**

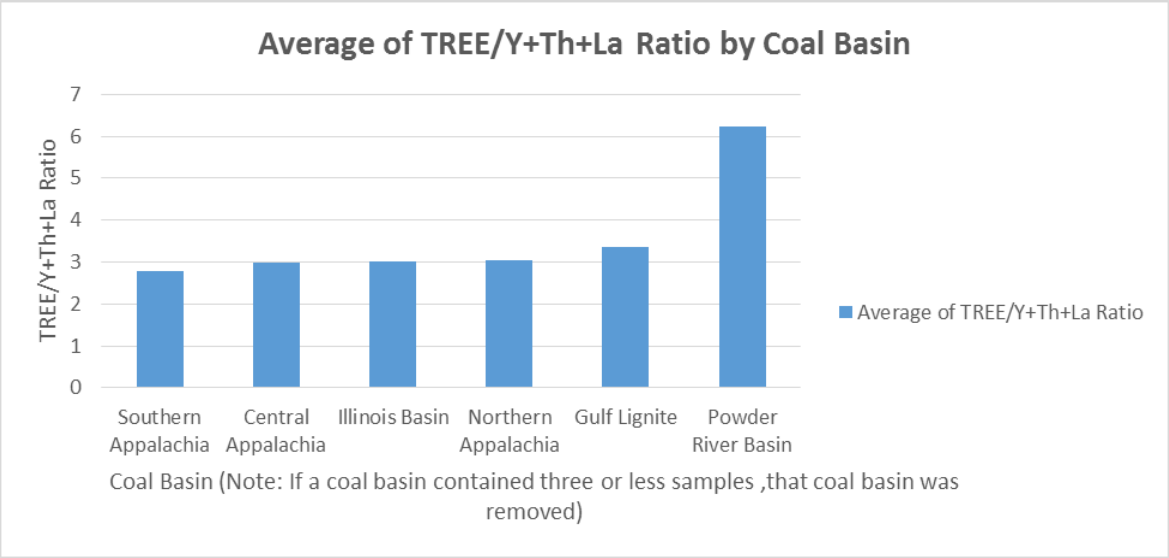


Figure 39. Average Value of TREE to Yttrium Plus Thorium Plus Lanthanum Ratio by Coal Basin

Table 8. Sample Sizes Averaged Together

Row Labels	Average of TREE/(Y+Th+La)Ratio	Sum of Count
Southern Appalachia	2.777593358	4
Central Appalachia	2.982731129	227
Illinois Basin	3.014522011	33
Northern Appalachia	3.051267153	62
Gulf Lignite	3.34785283	14
Powder River Basin	6.22965478	7

This table includes data from 347 independent samples.

Mass flow calculations were made for several coal preparation plants tested in this study. One example is given below. These data are based on drum sized samples that were then processed (ground to a standard size then separated into smaller samples) prior to withdrawing representative samples that were submitted for analysis. The results, presented on both a whole coal basis (total) and as ash-only values show that the clean coal samples has a low total mass content of REES but the REE concentration of that sample, when ashed, contains an REE concentration of ≈1,700 ppm (which is likely to be the REE content of a fly ash produced from burning this coal as a sole feed coal). The total amount of REEs represents approximately 30 percent of the total that was feed into the coal preparation plant.

In contrast, the total mass percentage of REEs found in the coarse refuse was ≈63 percent. The splits by the specific gravity fractions evaluated for each portion of the sample are also listed. The 1.6 float values for TREEs are high in both the clean coal and the fine refuse samples. The coarse coal sample shows the highest REE concentration is the 1.6-22.4 float cut.

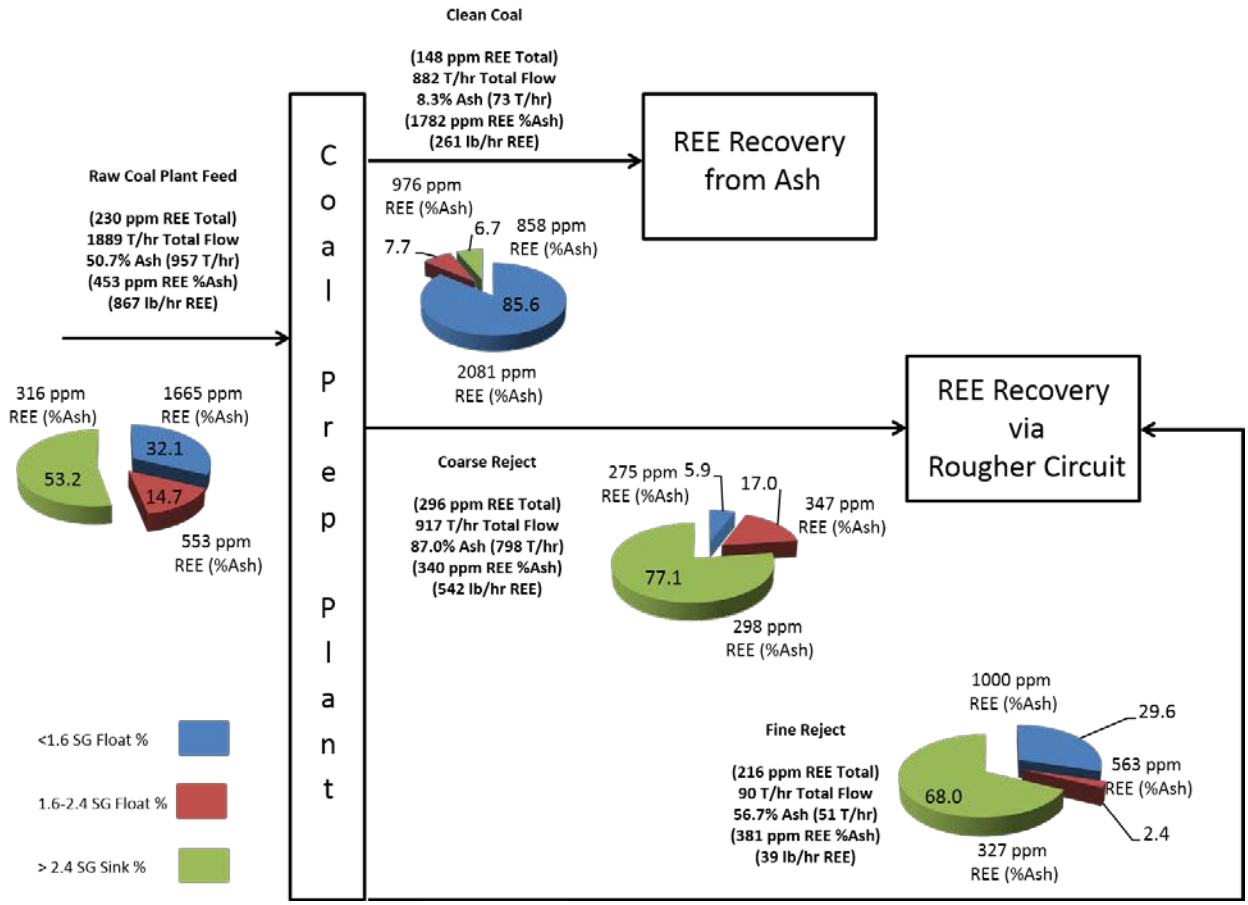


Figure 40. Mass Split of REEs Within a Preparation Plant

Mass balances for other preparation plants sampled suggest that the 30/70 split for this plant is higher than many. The range in the ratio of the clean coal REE mass fraction to the coarse refuse mass fractions ratio ranges from ≈0.15/0.85 to ≈0.30/0.70 for the limited set of plants for which such data are available. The amount of the REE reporting to the fine refuse is generally less than 10 percent although the ash-only concentration of REEs is ≈1,000 ppm.

3.6 SUMMARY

OBSERVATIONS FROM SAMPLES GATHERED ACROSS ALL BASINS

The LTI-lead field studies took samples at a limited number of facilities. The number and coverage was never intended to be comprehensive. However, several observations are worth discussing. Findings and recommendations will be presented in Section 7.

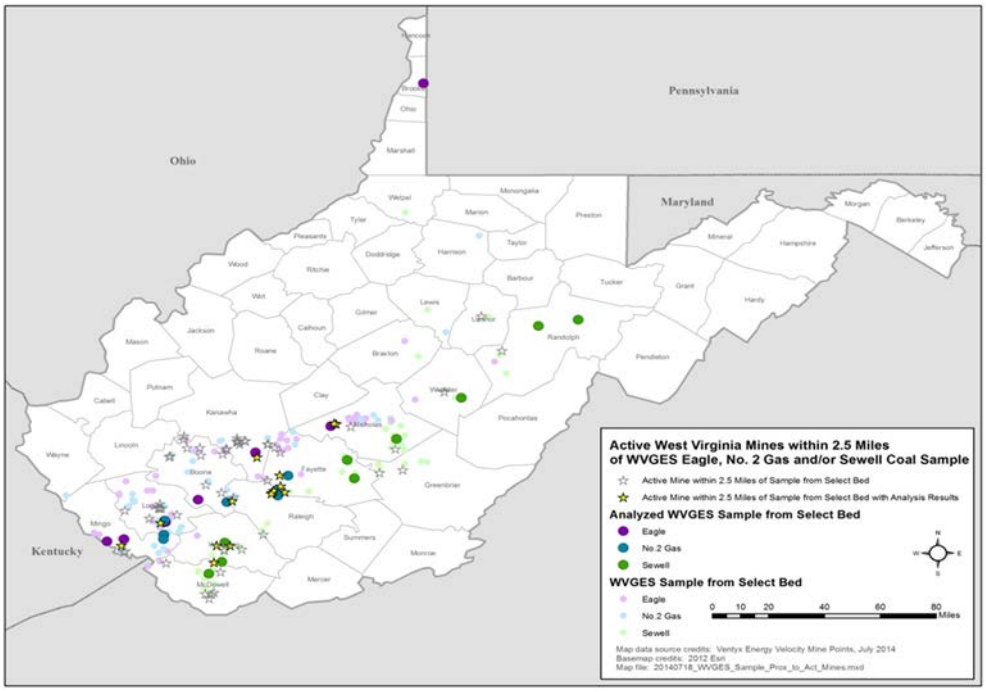


Figure 41. WVGES Sample Data

- One of the uses of the WVGES samples was to identify promising coal seams and promising locations for additional sample taking. Figure 41 shows a number of the WVGES samples that were then plotted alongside active mines and preparation facilities in order to identify a site from which to collect samples for the bench-scale preparation tests.
- Current mining and coal cleaning practices result in coals from several mines, not always from the same seam, being cleaned together to produce a product stream with a mineral matter content between 8 and 10 percent. This practice means that a high REE-bearing seam may be mixed with a lower concentration stream on a belt on the way into a preparation plant.
- Power stations similarly burn blends of blends in an effort to manage (simplify) environmental compliance.
- Although the clean coal coming from a preparation plant can have, depending upon the source coal, over 1,000 ppm total REEs on an ash basis, this represents a modest

percentage of the total REEs entering the preparation facility. The bulk of the mass of REEs is found in the coarse refuse.

- Individual reject streams within the preparation plant boundary appear to have differing percentages of the total REE mass and may represent an opportunity to begin concentrating REEs.
- Individual seams or benches (including larger partings) may be recoverable at surface mines and may represent easier targets for concentrating the REEs found within.
- The ratio of HREE to LREE (HREE/LREE) is different in coal and coal wastes that it is in other, commercial deposits.
    - The elemental analysis of raw samples revealed a wide range of LREE/HREE ratio. The ratio was found to be in the range from 2.67 for NDBMFUB1 sample to 13.43 for NMSJMSJB1 sample as defined in this report. The University of Utah chose to include the Y concentration amongst the LREEs. Other studies, including those by LTI, list Y with the HREEs. (ref. 3-9)
- The heaviest of the HREE appear to be enriched in coals that have passed through the cleaning process. (Is it only in the clean coal fraction?)
- Developing ratios of TREE to indicator elements such as Th, Y, etc., appear to be useful means to estimate total REE concentration using devices such as the XRF device tested in this study.
- Developing 3-D images of the deposits and using a full array of data (core samples, natural gas and petroleum well logs, magnetic surveys) would result in a substantial improvement in prospectivity studies.
    - During the course of the project, it was suggested by LTI that examination of magnetic surveys and other similar geophysical surveys could yield significant insight into areas worth exploring;

The Tetra Tech study mentioned in Section 3.3.2 investigated the association of coal and REEs by assessing the geophysical makeup of coal basins (i.e., using gravity/magnetics to assist in mapping basement features), determining what geologic relationships might exist between REE occurrences in the various coal basins, cataloging elevated REE occurrences

in coal and non-coal entities within the basins, and identifying likely sources of REE in select coal basins in the eastern and western United States. In addition, geostatistical methods were employed to provide a statistically valid interpretation of REE relationships with geology as a means of predicting which coal basins could be viable targets for REE exploration. (ref. 3-7). Tetra Tech developed maps that showed an overlay of the REE content of coals (derived from the USGS COALQUAL database) and other potentially relevant geologic features (see Figure 42).

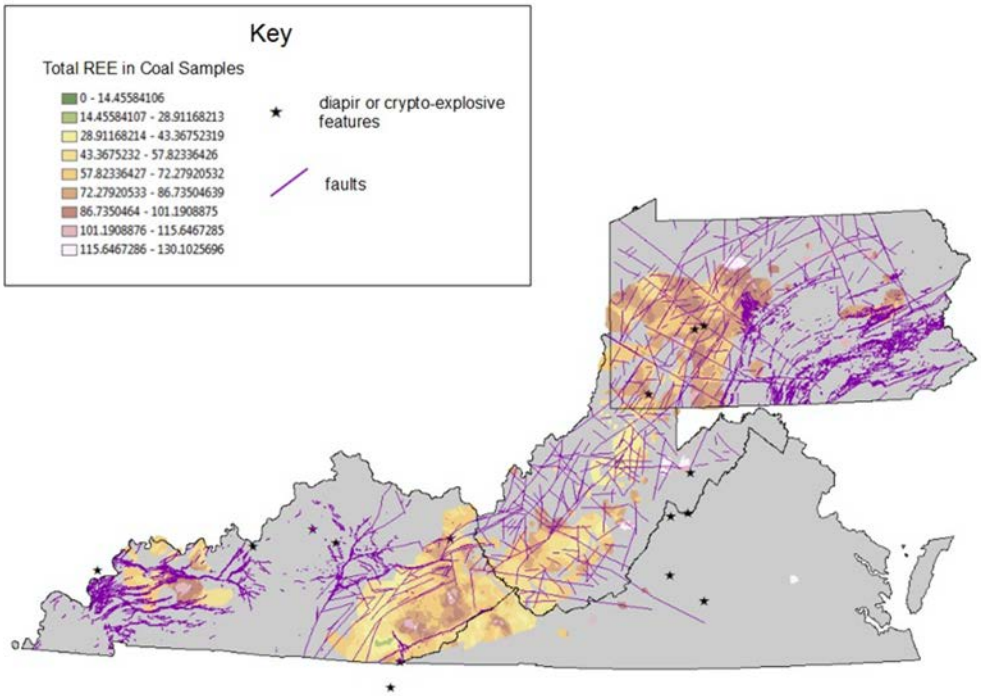


Figure 42. Overlay of USGS Data with Other Geological Features

FE HQ suggested that oil and gas well logs might provide useful data. At LTI's direction, Tetra Tech explored that possibility. Their work focused on the Arco well #1 in Perry County, Kentucky. The ARCO Well #1 in Perry County has LAS well logs that were developed along a well bore that penetrated the Pennsylvanian section. This site is located in that portion of Perry County that had several coal beds. Logs were made that included Density Porosity, Caliper, Gamma-Ray, Density, and Neutron Porosity. Figure 43 shows these traces

for the entire well as well as a more detailed view of the Pennsylvanian and upper Mississippian sections of the well.

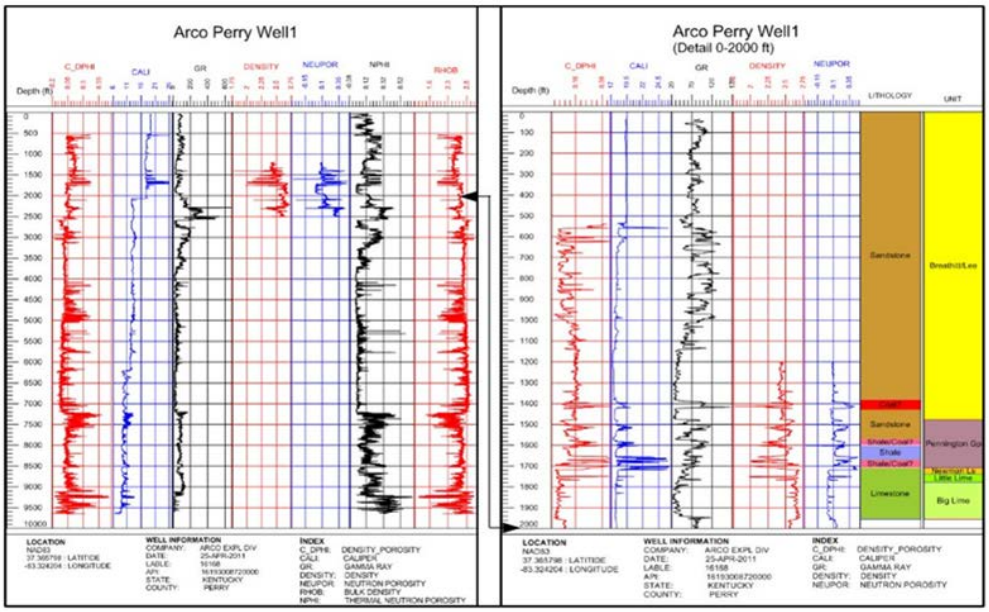


Figure 43. Geophysical Well Log of the ARCO Well #1

The location of this well does confirm that two coal seams (Amburgy and Fire Clay Coal, respectively) are penetrated by this well. Further, kriged total REE coal data (Figure 44) indicates that this region of Perry County contains elevated amounts of REE associated with the coal seams as defined in this study.

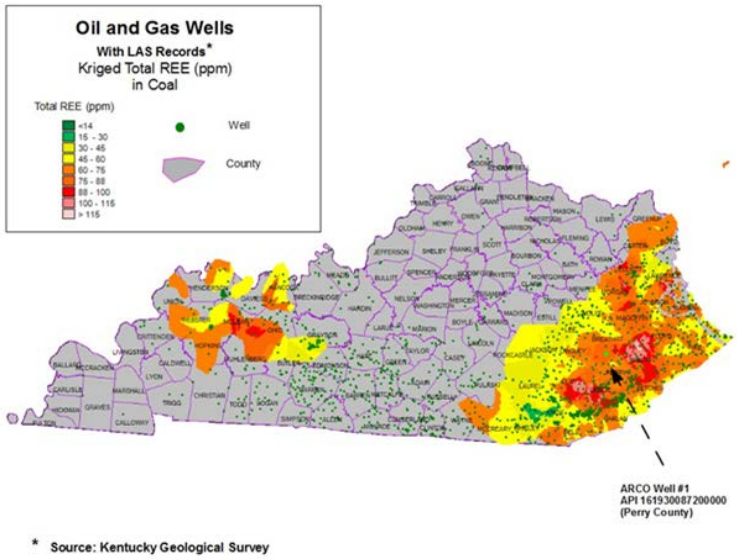


Figure 44. Distribution of Kriged Total REE in Relation to the ARCO Well #1 in Eastern Kentucky

These results, by no means comprehensive, suggest an additional path forward. A considerable amount of similar information is available in fossil resource-rich areas. An exploration of how to organize and recover relevant information tied to REEs associated with coal could limit the need for extensive field studies that might involve expensive exploratory techniques. However, these approaches do not address the potential that large, waste repositories, pit cleanings, coal preparation waste, fly ash ponds and piles, might hold as readily available sources for REE containing materials.

- Differences were found amongst coal samples; higher TREE values were seen in ≈20 percent. A review of the age of each coal in relationship to other tectonic events (including volcanism) appears to support the idea that such an explanation is a useful screening tool to locate promising coal formations.
    - The REE content of the Wishbone Hill coal was higher than that of Healy coal. HREE and LREE report to higher density fractions. The REE content of both coals correlate well with the total amount of ash. Both the bottom ash (BA) and fly ash (FA) from the University power plant had similar contents of both LREE and HREE when adjusted for the volatiles content. (ref. 3-8)

- Only a small number of the measured samples were found to contain elevated REE+Y+Sc concentrations—9 samples (ash samples excluded) had REE+Y+Sc concentrations over 150 ppm (whole coal basis). This amounts to ≈23 percent of the samples tested. Across all received samples, the results of elemental analysis revealed a particularly wide range of REE+Sc+Y concentrations within 34 samples analyzed. Of the 34 samples, 30 samples were found to contain an REE+Y+Sc concentration exceeding 150 ppm (ash only basis). (ref. 3-9)
- For the MOSONCB3 sample, ICP-MS analysis found REE+Y+Sc concentrations of 382 ppm. However, no REE bearing minerals detected within over six million pixels analyzed using the QEMSCAN method. We could speculate as to why this occurred but in order to better understand REE distribution in coal and coal waste samples, a further comprehensive mineralogical analysis using microprobe, Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), and/or nano-computed tomography (CT) should be performed in the future. The findings of this analysis will be critical for development and optimization of new REE concentration technologies. (ref. 3-9)
- The samples from the Fort Union Basin, Powder River Basin, and North Central Basin demonstrated highest REE+Y+Sc concentrations. The North Central Basin samples, including Sand Coulee outcrop and Belt outcrop samples, contain over 200 ppm of REE+Y+Sc expressed per whole sample basis. (ref. 3-9)
- A mineralogical study was conducted on selected samples from the pre-concentration studies involving the use of SEM-EDS and ToF-SIMS. A portion of the samples were prepared using a low temperature ashing unit to remove the carbon while maintaining the structure of the mineral matter. The mineralogical findings are: (1) the REEs exist as a mineral dispersed within coal in the form of monazite, xenotime and bastnaesite as well as an element substitute in clay; and (2) the RE mineral particle size is in the range of 1-10 micrometers and smaller. (ref. 3-10)

- Difference source coals showed differences in responses to the physical separation techniques that were employed. This may be a consequence of the particular

equipment employed (for example magnetic field strength, flotation reagents tested, etc.) or it may relate to the particular trace elemental composition of the coals that were tested.

- Wet high intensity magnetic separation tests on -100 mesh fractions showed that Wishbone Hill fines contain higher Sc in non-magnetics than that of Healy coal. LREE elements are similarly distributed between magnetics and non-magnetics for Wishbone Hill fines except Sc, Sm and Gd which were richer in magnetics. This trend is valid for the HREE content of the Wishbone Hill in that HREE elements appear to be preferentially reporting to magnetic fractions. In addition, flotation tests on -100 mesh fines revealed that both LREE and HREE concentrated more in tailings than float fractions. This finding is more pronounced for Wishbone Hill fines. This follows the same trend as indicated in the washability tests that the inorganic part of these Alaskan coals is much richer in rare earth elements than those of organic material. (ref. 3-8)

- Most of the separation methods evaluated showed little effect for the size ranges tested. Density-based separation showed the most REE+Y+Sc concentrated density fractions of coal were found to be within the intermediate densities tested, or from 1.4 to 1.8 SG—the REE concentration in density fractions curve shows a quadratic trend. This general trend was found to be true for most of the samples analyzed but varies in magnitude for coals of different type. The REE recovery in intermediate density fractions was found to be larger for finer particle sizes. The REE could be concentrated using density-based mineral concentration methods, and the recoveries could be increased using finer particle sizes. The improvement of current and development of new fine particle density-based concentration technologies will be necessary to overcome the limitations of currently available technologies. (ref. 3-9)

- The roof rock sample contained the largest concentration of total REEs on a whole material basis and responded best to gravity separation and ion exchange leaching techniques. The pit cleaning sample exhibited low potential to ion exchange treatment methods. The pit cleanings sample did show a marked response to magnetic enrichment but it is to be noted that this was a sample with lower bulk REE content. However, it is a coal product with

a fair amount of combustible material and the combustion of carbonaceous material typically results in the REEs remaining in the combustion ash, and at a higher concentration in the ash. Among the two refuse materials, one of the samples (PSU #8) showed a very clear separation and enrichment behavior under electrostatic separation while the other refuse sample (PSU#10) showed no significant discriminatory behavior under any tests. (ref. 3-11)

- Recommendation: It is recommended to continue with leaching tests on the ashed material of pit cleanings and one of the refuse materials for further enrichment. The roof rock material has a higher REE content to begin with so further leachability tests are recommended and process optimization for leachability with ammonium sulfate should be further investigated. (ref. 3-11)

- The potential for pre-concentrating REEs using density-based separators was found to be minimal which can be explained by the ultrafine grain sizes of the RE minerals. The REE content of the ash-producing mineral matter increased substantially as the specific gravity was reduced. For example, the REE content in the ash material produced from the Fire Clay coarse refuse increased from 455 ppm in the feed to 1,485 ppm in the 1.6 SG float fraction which is an increase of 326 percent. A similar trend was realized from each sample evaluated in the study including those from the 20 coal preparation plants. Based on this finding, bottom ash material was collected from a utility that uses Fire Clay seam coal as fuel. The total REE was around 800 ppm for the three bottom ash material and the washability data suggested equal distribution across all specific gravity fractions. (ref. 3-10)

- Froth flotation was found to be the only method of the six evaluated that could be exploited to pre-concentrate REEs. For thickener underflow material collected at a processing plant cleaning Eagle seam coal, the total REE content was increased from 172 ppm (whole coal basis) in the feed to 367 ppm in the flotation concentrate, which is an increase of 213 percent, using a common collector for rare earth mineral flotation. It should be noted that this performance is not an optimum result given that only five tests were performed on the single sample tested. (ref. 3-10)

- An REE mineral release and concentration study was conducted on a sample collected from the middlings stream of an operating preparation plant treating the Fire Clay seam coal. Crushing the material to a particle size smaller than 6 mm (1/4-inch) and conducting a float-sink test using a 1.5 SG medium resulted in a near 200 percent increase in the REE content in the sink fraction. The 1.5 SG float material was ground to a mean particle size of 10 micrometers and subjected to froth flotation using fuel oil as the collector. The REE content increased from 118 ppm in the feed to 565 ppm in the tailings of the flotation process. This finding indicates that the finely dispersed, high REE mineral matter can be liberated and concentrated. (ref. 3-10)

4 SAMPLE TRACKING AND COAL STRATIGRAPHY

4.1 VALUE IN UNIFYING STRATIGRAPHIC RECORD IN EASTERN COAL PROVINCES TO BETTER TRACK RESOURCES AND TO ESTIMATE RESERVES

The COALQUAL database clearly demonstrated, through prospectivity mapping that some coal seams contained areas of higher concentrations of REEs than other coal seams. Consequently, these coals and their associated wastes, whether it is: in-situ, in process, or in waste site, are the logical targets for further field investigations. This is a cradle-to-grave approach, however, and implies that specific (regulatory and industry) stratigraphic, production and disposal records of particular coal seams (nation-wide) will be essential to develop a means to track REE resources and estimate reserves during future field operations.

Field data gathering activities will cross various political boundaries (e.g., state, county), thus presenting the challenge of coordinating data from on both sides of the boundary since variability of data, format, and nomenclature can and does exist. For example, a single coal seam that underlies six states in within the central Appalachian basin has 6 different names. Table 9 lists EIA's initial effort to address this issue of alternative coal seam names and includes only the top 25 producing coalbeds, there are many more coal seams which cross specific boundaries and have multiple names in which the EIA has not addressed. Furthermore, the coalbed names listed in the EIA table are the names most commonly used in the particular state having the greatest production from that coalbed.

Table 9. Different Names by State or County for Important Coal Seams

Rank	EIA Bed ID	Bed name	State	Alternate Coal Bed Name(s) and State Located										Formation
1	1699	Wyodak	MT/WY											
2	0212	Pittsburgh												
3	0489	No. 9	W. KY	No. 5	IL	No. 5	IN							
4	0484	Herrin (Illinois No. 6)	IL	No. 11	W. KY									
5	0036	Pittsburgh	PA											
6	0111	Coalburg	WV	Peach Orchard	E. KY									Kanawha (WV)
7	1696	Anderson-Dietz 1-Dietz 2												
8	0084	Lower Kittanning	WV	No. 5	OH									Princess (WV)
9	1787	Roland	WY											
10	1569	Beulah-Zap	ND											
11	1701	Smith												
12	0151	Upper Elkhorn No. 3	E. KY	Jellico	TN	Taggart	VA	Cedar Grove	WV					Kanawha(KY); Wise (VA)
13	0103	Stockton-Lewiston	WV											
14	1570	Hagel												
15	0168	Lower Elkhorn	E. KY	Imboden	VA	No. 2 Gas	WV	Pond Creek	??					Kanawha (KY); Wise (VA)
16	0344	Pocahontas No. 3												Pocahontas (WV)
17	0121	Winifrede	WV	Quakertown	PA									Kanawha (WV)
18	1808	Rosebud	MT											
19	0280	Blue Creek	AL											Allegheny (WV)
20	0071	Upper Freeport	PA											Allegheny (WV)
21	0176	Eagle	WV	Middle Eagle	WV									Kanawha (WV)
22	1750	Wadge	CO											
23	0480	Danville No. 7												
24	0157	Alma	WV	Windrock	TN	Phillips	VA	Chilton	WV	Elkhorn No. 1	E.KY	Rich Mountain	TN	
25	0135	Hazard No. 4	E. KY	Fire Clay	??	Hyden	KY							Kanawha(WV); Breathitt (KY)

This issue of non-unified stratigraphic naming nomenclature is still wide-spread throughout the various U.S. coal basins. The issue of alternate seam names has been relatively recently and adequately addressed in the western coal province of the Powder River Coal Basin by the USGS (ref. 4-1). Problems in the mapping of named coal beds from one area to another in the PRB arose when USGS geologists used Montana coal-bed names to identify Wyoming coal beds. Furthermore, in the Wyoming part of the PRB, splitting and merging of coal beds also complicated local and regional mapping (ref. 4-2 through 4-5). The USGS was able to accomplish this daunting task as the result of coalbed methane (CBM) development in this particular basin. CBM development has provided unprecedented drilling with as many as 16 wells per square mile. This closely spaced stratigraphic data had permitted regional correlations of coalbeds in the PRB.

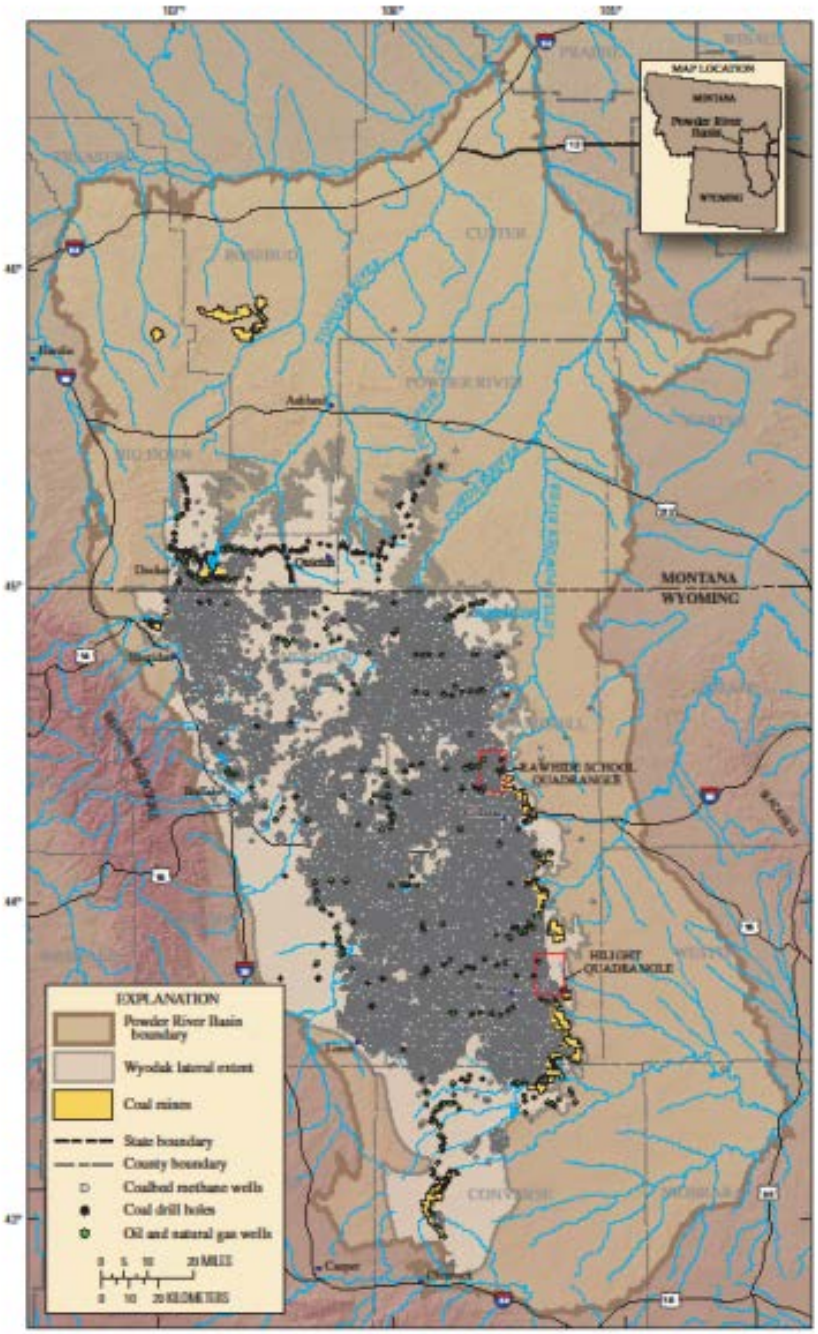


Figure 45. Powder River Basin Coal Bed Methane Wells

In the eastern coal provinces the mapping of coalbeds has similar nomenclature issues although the geology may differ. Furthermore, the eastern coal provinces do not have the

extraordinary number of coalbed methane wells as exhibited in Figure 45 above. However, the eastern coal provinces do have an active natural gas industry at present, which is drilling through all coal strata to reach the deeper natural gas reserves. These drilling data have yet to be explored and may provide significant value in unifying the stratigraphic records. Lastly, the modern-day option of directional/horizontal drilling (within coal seams) has yet to be explored as a means of identifying REEs on a seam-by-seam basis.

4.2 NOTIONAL HYPOTHESIS DEVELOPED TO EXPLAIN INCIDENCE OF HIGHER-THAN-NORMAL REES AND TO IMPROVE PROSPECTIVITY APPROACH

As mentioned above, the COALQUAL database clearly demonstrated, through prospectivity mapping, that some specific coal seams contained areas or "hot spots" of higher concentrations of REEs than other coal seams. Furthermore, it has also been observed that the REE concentrations within these targeted (hot spots) can vary significantly on a seam-by-seam basis. Lastly, these areas of high REE concentrations do not spatially correlate (or line-up vertically) with near-by coal seams, either above or below. Consequently, a notional hypothesis has been developed as an attempt to explain the incidences of higher-than-normal REEs and improve a prospectivity approach.

An overview of the notional hypothesis is presented in the following. Since the REEs are found in varying concentrations within the coal deposits, it has to be assumed that they were deposited during the early stages of the formation of the coal itself. It is generally accepted, through the study of plate tectonics, which earths' continents were in different locations when the formation of today's coal began. One of the more standard explanations of how coal created is as follows: '

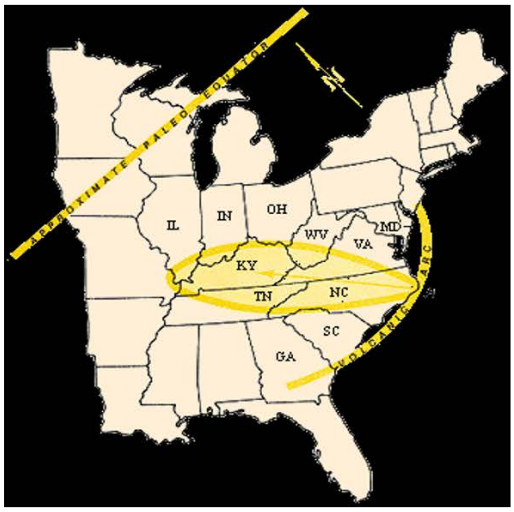
"At various times in the geologic past, the Earth had dense forests in low-lying wetland areas. Due to natural processes such as flooding, these forests were buried underneath soil. As more and more soil deposited over them, they were compressed. The temperature also rose as they sank deeper and deeper. As the process continued the plant matter was protected from biodegradation and oxidation, usually by mud or acidic water. This trapped the carbon in immense peat bogs that were eventually covered and deeply buried by sediments. Under high pressure and high temperature, dead vegetation was slowly converted to coal. As coal contains mainly carbon, the conversion of dead vegetation into coal is called carbonization (ref. 4-6)."

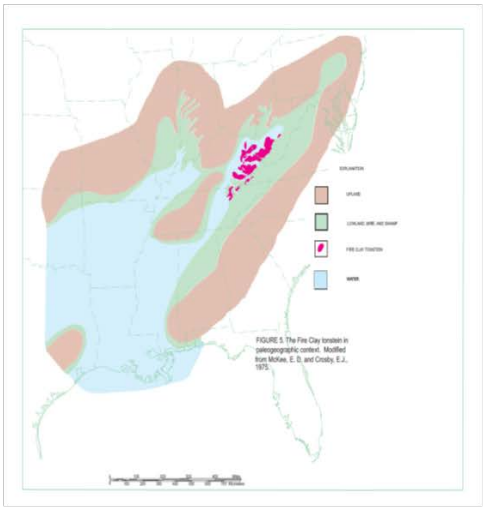
This hypothesis expands upon or clarifies the "natural processes" discussed above. Although flooding is accepted as a primary process, volcanism (i.e., super volcano[s]) was also prevalent at the time of coal formation. Thus, the deposits of REEs found today in the various coal seams were the result of repeated volcanic ash depositions that are known to have occurred in the geologic past. It is considered very likely, in this hypothesis, that volcanic ash that had been deposited on the land surface was both integrated (by airborne deposition) with the vegetation and subjected to hydraulic transport at the same time in the geologic past. Consequently, it is feasible that the large majority of this surface deposited REE-bearing ash was transported to the lowest lying areas of the topography at the time by hydraulic transport (streams, rainfall, storm runoff, etc.). As the result, this suggests that the zones or areas of high REE concentrations found in today's coal mines were the lowest lying areas in the surface topography at the time of deposition.

Two studies that focused on the eastern coal fields made a strong case for the influence of volcanism. They are summarized in Figure 46 (ref. 4-7 and 4-8). Both authors proposed volcanic activity as the likely cause of elevated REE levels in coals in the Pennsylvania period, approximately 300–325 million years ago (MYA). The note at the bottom includes a quote (ref. 4-9) about the one of a series of mountain building events that created the Rocky Mountains. The occurrence of elevated levels of REEs in western deposits loosely follows this sequence of orogenies.

Why Do We Find REEs Where We Do?

- Eastern US - Central App volcanism 300 -325 MYA?





Western US - Laramide Orogeny ~ 40 - 80 MYA? Series of mountain making, as well as basin-producing events. Extensive eastward thrust faulting accompanied by block faulting and metamorphism. Minor and sporadic extrusive volcanism and batholith formation.*

*http://capone.mtsu.edu/mabolins/WesternUS.htm

Figure 46. Eastern U.S.—Central Appalachian Volcanism

Further investigations will be needed to expand upon the hypothesis described above. One such approach would be to evaluate the elevation contours of the rock beneath (and supporting) the coal seam, rather than coal thicknesses. The assumption is that when the coal was formed, and pressure from the overburden increased with time, the coal/vegetative matter was squeezed from above by varying degrees depending upon geological occurrences (e.g., mountains, plate tectonics, etc.) and ultimately has had an impact upon the coal thickness as we know it (see Figure 47). However, in this approach, the assumption is that the host or supporting rock beneath the coal formation would not yield from load pressure as easily as the vegetative matter and that elevation contours of this sub-strata (mine floor) may be indicative of the low lying areas where the volcanic ash deposits had originally drained. This approach appears most reasonable for "relatively flat lying coal seams." Additional efforts would be required to address those tabular coal seams that are sloping to some degree (such as those typical of the Anthracite fields in

Pennsylvania and bituminous coals in Utah), a means to correct for elevation changes relative sea level would be required. Regardless of approach, a means to identify the low topographical areas within the coal seam when it was formed is necessary to prove the hydraulic transport and REE deposition theory.

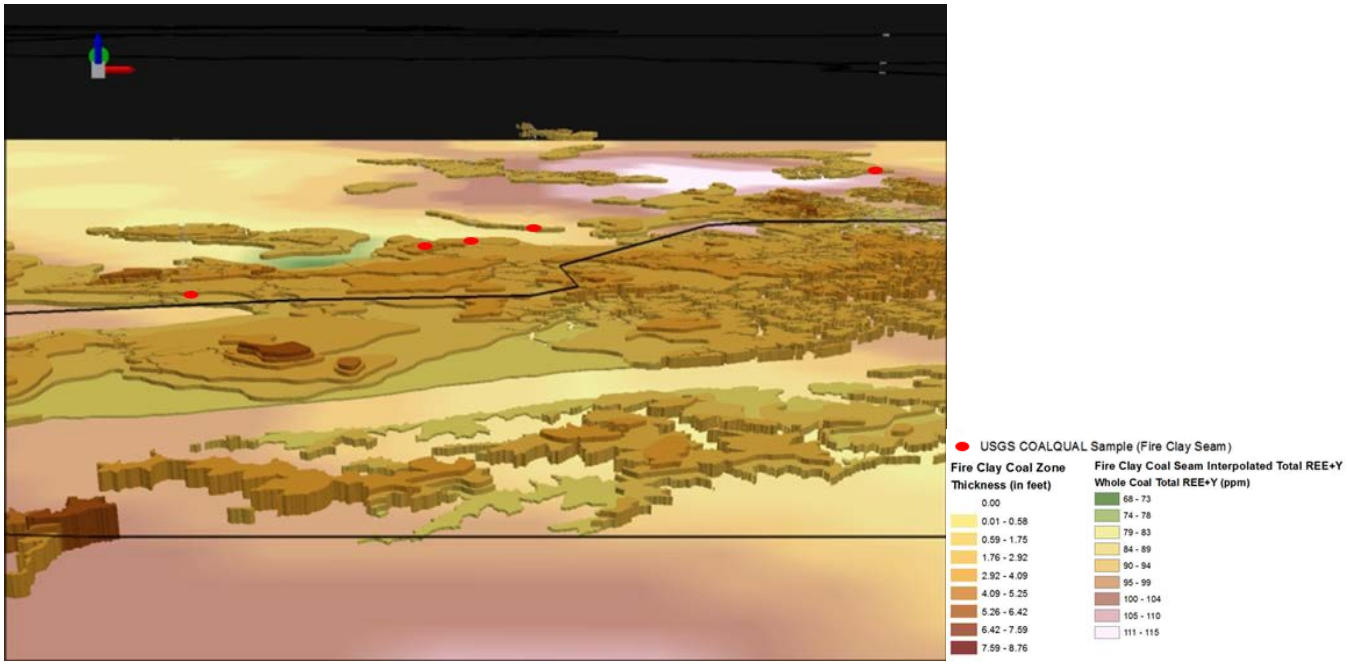


Figure 47. Three-Dimensional Representation of the Fire Clay Coal

4.3 INSIGHTS THAT MIGHT AID ADDITIONAL FIELD WORK

The future success of recovering REEs from our nation's coal and coal-related materials relies upon two critical needs: (1) the ability to economically and accurately identify and quantify specific REEs and their geographic locations, whether it be in-situ or re-located or in-process; and secondly, (2) is the critical need to develop an economical and effective process to separate the REEs from their typical mineral matrix. The future REE recovery will not be successful without both critical needs being satisfied. The following discussions will address the first critical need, prospecting and defining recoverable reserves of REEs in the field on a national basis.

4.3.1 Insights—Prospecting in the Field

Locating and quantifying U.S. REE reserves and their REE content is a matter of national interest. The relationship between REEs and U.S. coals on a national basis was identified and recently demonstrated through this prospectivity analysis. It has been determined that the only manner to identify how much and where our REE resources may become REE reserves is to follow the lifecycle of coal, starting with in situ REEs in unmined coal seams, following through the coal cleaning and power generation processes, and ending at waste disposal sites. Consequently, prospecting for REEs will encounter two different, yet fundamental settings; one is underground, and the other is on surface.

A prospecting or exploration plan would be of great value prior to engaging into a meaningful and major field sampling campaign. REEs are known to be present in multiple field settings including: in-situ coal, refuse material (piles and those being processed in coal cleaning plants), ash products (piles and those being processed in power generation plants). Addressing these field scenarios from the perspective of having effective tools (e.g., XRF) and supplies to ensure safety, minimize excessive sampling and expensive laboratory costs, had been previously discussed within the XRF and sampling sections above. The prospecting approaches and plans for field sampling for each of these varied field settings need to be addressed prior to engaging in field activities to ensure that field sampling is effective, yet not excessively costly in laboratory costs.

Underground Prospecting—The conventional approach to prospecting or exploration for in-situ coal is surface drilling. This approach was used in the national drilling effort by the USGS to identify remaining U.S. coal reserves and is also used by the coal industry to measure and prove reserves. This conventional exploration approach is a proven and reliable approach. Surface drilling will likely require many additional wells or boreholes on a national scale to supplement the existing data and obtain a reasonable confidence level of an in situ REE reserve base (relative to interpolation and mapping efforts of in situ REE reserves). Furthermore, future drilling efforts may involve developing borehole patterns to locate smaller targets (or hot spots) within a particular coal seam, not just the presence and quality of coal reserves. It is important to note that although hot spots may very likely be identified through additional surface drilling efforts, the access and extraction of these identified locations with high concentrations of REEs may not become available for years or decades depending upon the coal industry's access or economic ability to extract coal at specific locations using current extraction technologies.

Surface Prospecting—Conventional prospecting, which typically occurs in natural settings, involves the extraction of materials from natural settings and is conducted over broad spatial areas. However, surface prospecting for REEs will need to occur within confined industrial complexes, active and abandoned. An industrial complex as it relates to the lifecycle of coal is defined as: surface solid waste disposal sites (associated with coal refuse and power plant ash); process plants (coal cleaning and power generation); slurry ponds and impoundments (associated with both cleaning and burning of coal); as well as abandoned mine complexes.

Figure 48 shows the vast number of coal preparation facilities and coal-fired electric units currently present in the United States. Such that there are approximately 475 power plant and 313 coal cleaning facilities operating or idled. In addition, of the 313 coal cleaning facilities, 143 are mine-mouth facilities, in which the mine and coal cleaning operations are encompassed within one industrial facility. These types of facilities offer the best opportunities for surface exploration of REEs from a single coal seam.

It is important to note that each of these facilities identified in Figure 48 generates significant amounts of coal-related wastes that potentially contain REEs and are currently being disposed of (on the surface) in a regulated manner, abandoned or legacy sites are not depicted in this figure. The waste materials generated from a coal cleaning facility are generally disposed of in close proximity to the plant. Although the same can be said for the power generation facilities, there is a haul back option that is sometimes associated with power plants. Such that, the power generation company will contractually require the coal company to haul back wastes (for disposal) in the empty coal train, subsequent to coal deliveries.

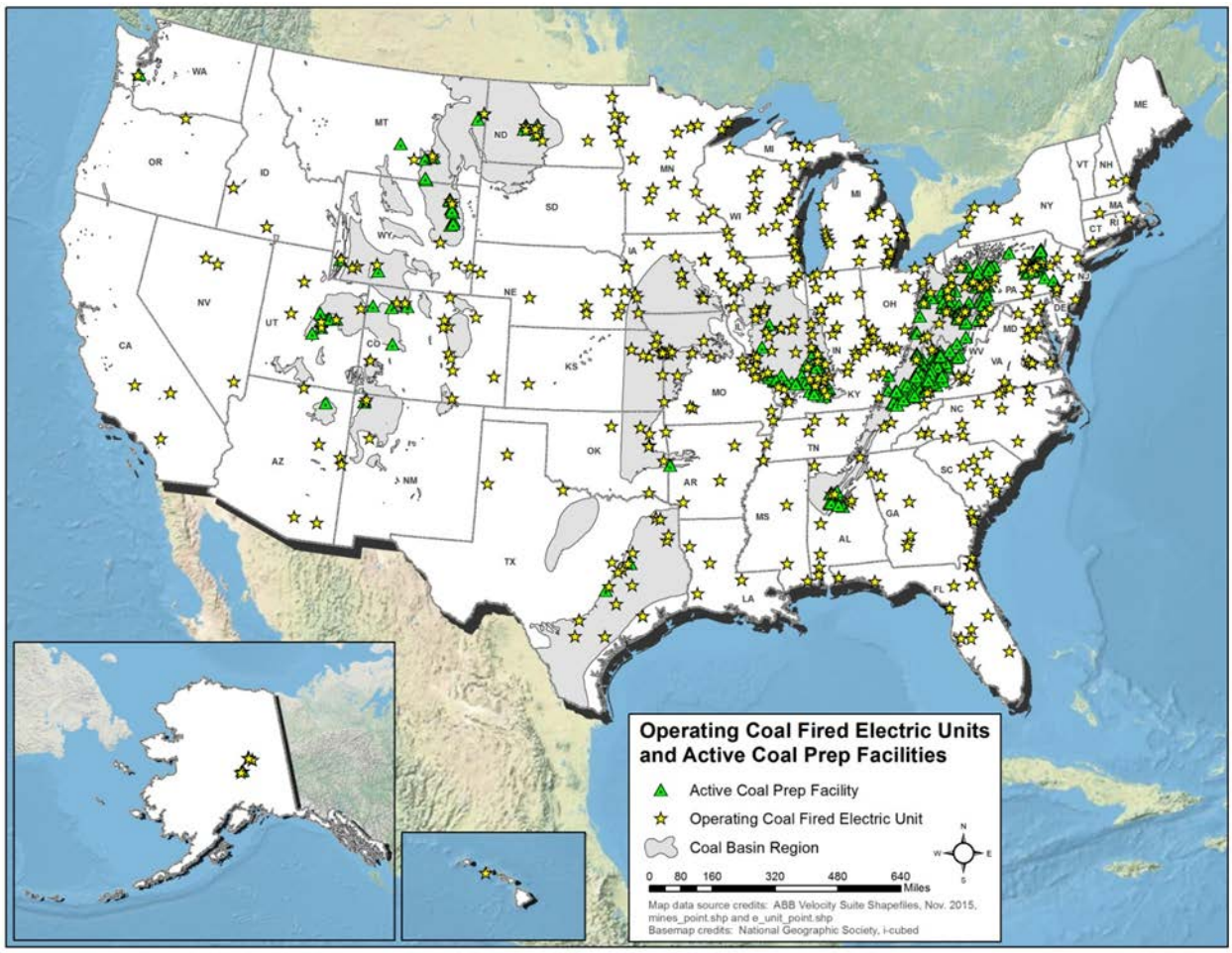


Figure 48. Locations of Coal Waste Generation Facilities in the United States

Furthermore, it is assumed on the basis of the USGS drilling data (of remaining U.S. coal reserves), that "hot spots" or areas of high REE concentrations also existed in those coal reserves that have already been extracted over the past two centuries. Figures 49 and 50 show two examples of major U.S. commercial coal seams that are nearly depleted of recoverable reserves and that the bulk of the remaining coal is either thin and a significant challenge relative to economic extraction or presents environmental challenges relative to surface conditions (water bodies, interstate highways, homes, etc.).

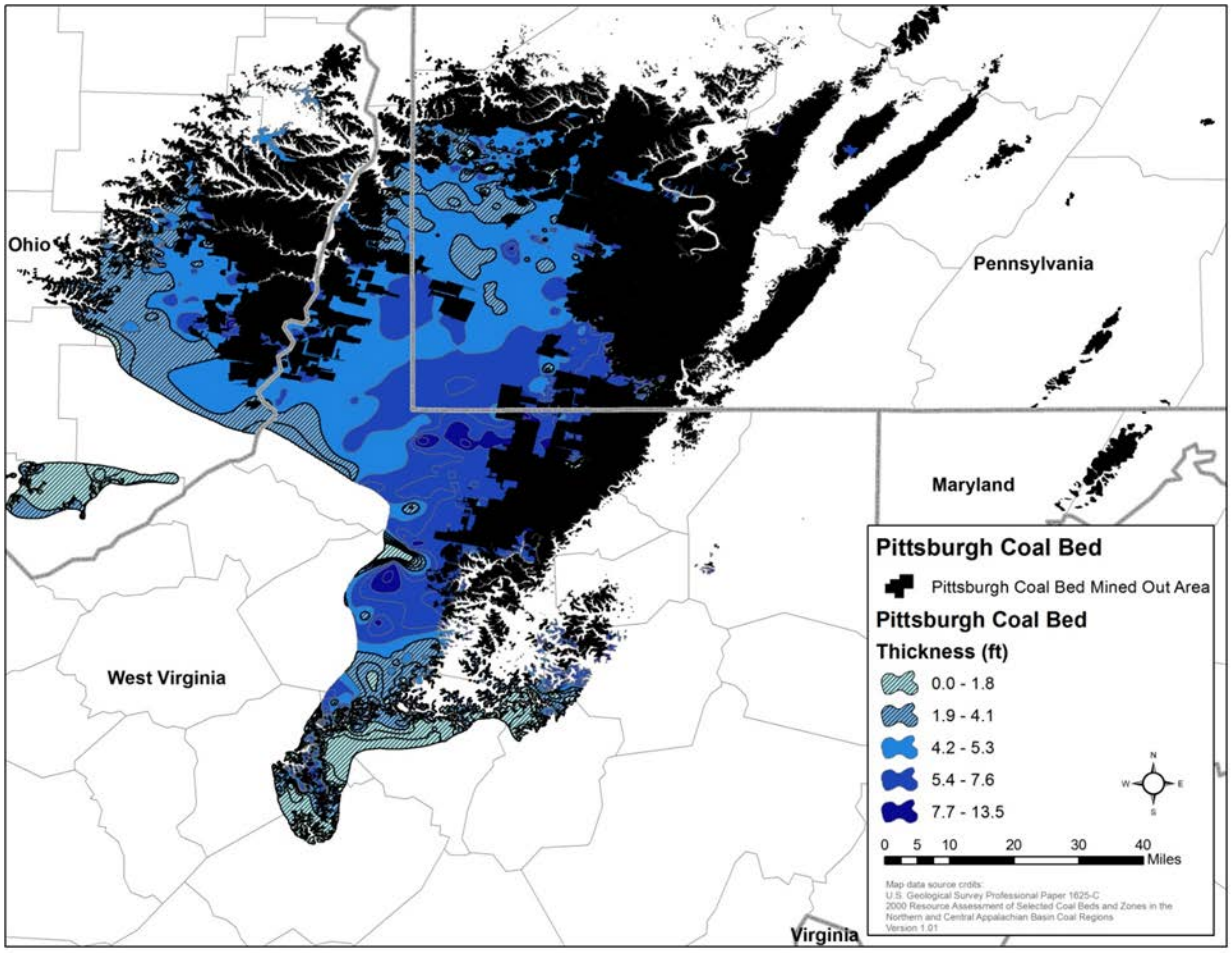


Figure 49. Remaining Reserves in the Pittsburgh Coal Seam

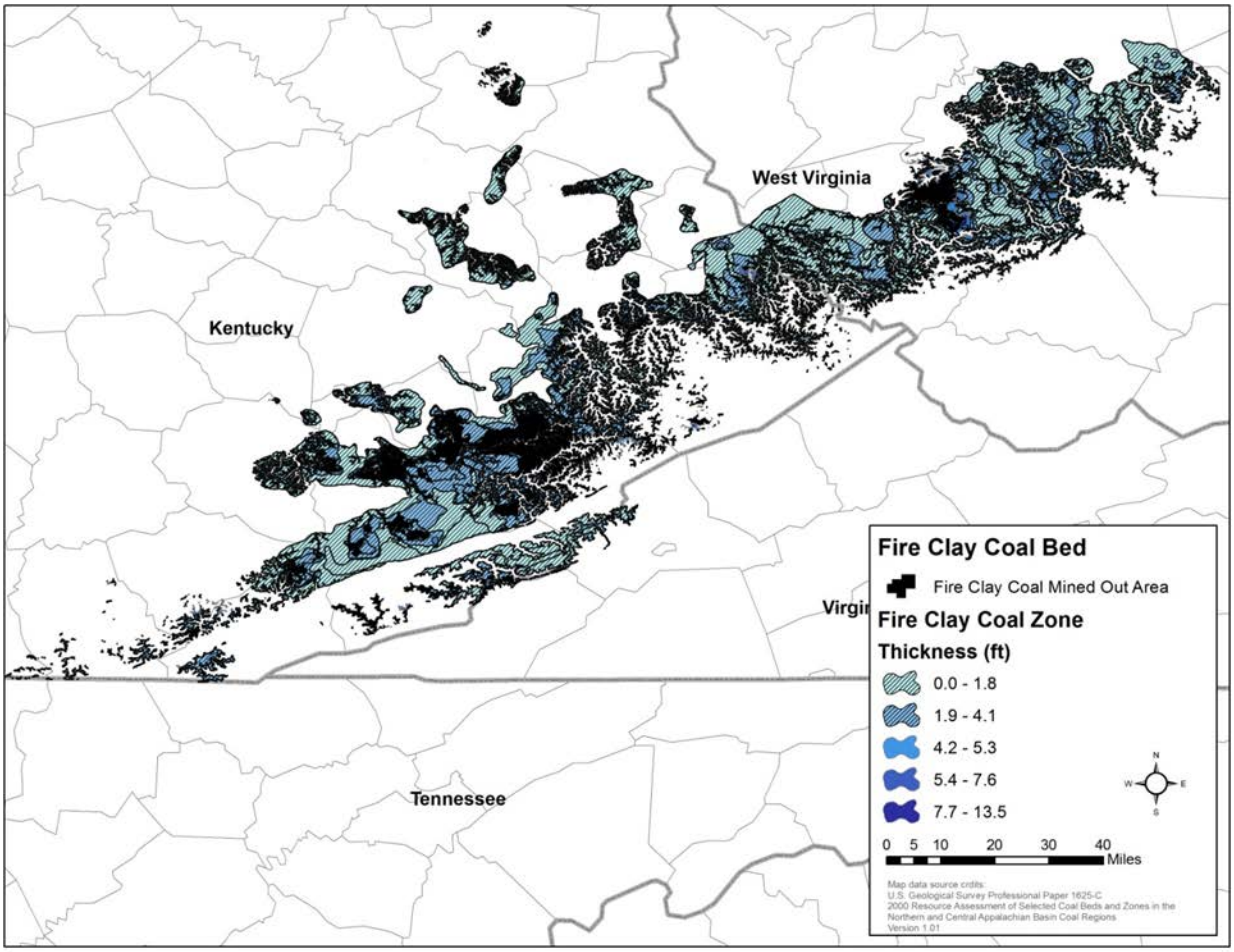


Figure 50. Remaining Coal Reserves in the Fire Clay Coal Seam

Relocated REEs currently reside in the numerous, and typically, massive surface waste disposal sites located throughout the United States.

The surface exploration opportunities depicted in Figure 48 has three sub-categories; ash piles, refuse piles, and processing plants (refuse cleaning and power generation). It is important to note that it is very feasible that if half or more of the U.S. coal reserves (in lower 48 states) has already been extracted from mineable coal seams (during the past 2 centuries), then it is likely that half or more of the nation's available REEs from coal and coal-related materials are presently scattered throughout the United States in distinct and confined industrial complexes (regulated and abandoned).

Furthermore, over 1 billion tons of coal is burned each year in the U.S., resulting in the generation of significant amounts of potential REE containing waste materials being disposed of on the surface on an annual basis. For example, coal combustion waste materials, alone, constitutes the nation's second largest waste stream after municipal waste (ref. 4-10). The annual surface deposition of coal refuse is considered to be of similar magnitude as that of coal ash. For example, in Pennsylvania alone, the total amount of coal refuse is unknown. However, based on the known amounts located on abandon mine lands (only) and estimates associated with historical mining operations, the amount of coal refuse (disposed of on the surface) is anticipated to range between 200 million and 8 billion cubic yards, with 2 billion cubic yards being the consensus. This estimate does not include those refuse materials currently being disposed of by the existing coal industry in a regulated manner associated the 1997 Surface Mining Control and Reclamation Act (SMCRA)(ref. 4-11). In Pennsylvania alone, there are more than 5,000 abandoned, unreclaimed mining areas covering approximately 184,000 acres. The coal refuse piles (Figure 51) associated with abandoned mines cover an aggregated area of 8,500 acres of surface land. Although Pennsylvania is only one coal-producing State, it is considered very likely that other coal-producing States (e.g., WV, KY, VA, OH, etc.), particularly in Appalachian coal basins (see Figure 48), have a similar magnitude of materials (piles), which again, may contain elevated or concentrated amounts of REEs.

Figure 51. Legacy Refuse Site in Western PA Encompassing Hundreds of Acres

4.3.2 Insight—Prospecting or Exploration Challenges

The primary challenges relative to conventional surface drilling practices are typically, obtaining access to surface land for drilling activities (access road, pad, right-of-ways, reclamation of drill site, etc.) and the funding to do so. An alternative to conventional vertical drilling, would be to employ directional drilling technology, such that the number of well pads would be reduced (or perhaps piggy-backed with the gas industry) and the resulting horizontal coal seam sample would be able to provide significantly more detailed lateral coal seam data than the point sampling typical of vertical drilling activities. It is feasible that directional drilling of surface waste sites Piles) may also be possible with modifications (e.g., hole casing). It is also important note the USGS COALQUAL data was approximately a decade old when LTI began its first review of these data regarding REEs.

Consequently, it possible, if not likely, that some of these targeted "hot spots" (albeit the accuracy of the interpolations is questionable) may have already been extracted, processed and disposed of.

There are varying field scenarios in which waste sites have been constructed, such as, the building of benched piles, valley fill, and slurry impoundments/ponds. Consideration on how a particularly waste site is to be sampled, such as drilling and/or excavation is needed. The field geometry and volume of materials located on these waste sites can vary significantly. How many samples are to be gathered from a unit area or volume and the spacing of the sample location should be known prior to field sampling. Furthermore, if there is to be a statistical element to the sampling scheme, it needs to be identified prior to sample collection.

4.3.3 Further Insight—Lifecycle of REEs

It is considered important to consider the lifecycle of REE recovery and processing and re-disposal at an early stage of research, particularly those aspects of analysis and separation. It will be of paramount importance as to what the final chemical constituency of waste products will be subsequent to removal of REEs and other valuable (and toxic) elements.

The future identification and location of in situ REEs, their subsequent recovery from in-situ coal reserves begins with conventional coal extraction methods (longwall, room-and-pillar). If a known area or block of un-mined coal were identified, this raw material can be segregated for future, specialized processing, and recovery.

The recovery of REEs from surface piles however, presents a different challenge, such that these materials (piles/disposal sites) will need to be totally or partially re-mined and re-disposed at existing or new disposal sites. There will be environmental issues to address and possibly additional research needs to address the second deposition of materials in an environmentally and socially beneficial manner.

Some options relative to the environmental and social benefits of re-mining ash or refuse piles (for REE recovery) would include making use of the pozzolanic properties (silica) of fly ash and combining with calcium (lime or scrubber ash) to generate a cementious-like material that requires about 30 days to set and 90 days to cure and is chemically resistant to leaching if maintained in an alkaline environment (https://en.wikipedia.org/wiki/Fly_ash). Enormous volumes of this cement-like material could be injected into the

massive underground voids of the depleted underground mines, which currently exist located throughout the various U.S. coal basins. Research leading to such disposal practices would lead to the elimination of environmental concerns associated with such surface disposal practices and regulations and would result in making significant surface space area, now occupied by waste materials, available for beneficial local development. Furthermore, research is needed to determine if refuse materials could be added to the cementious mix as an aggregate. It should be noted that past NETL research had only touched upon concepts such as this before program direction had changed (ref. 4-12 and 4-13).

4.3.4 Insight—Sources of REEs

In the case of un-mined coal, it will be possible in the future to track and control extracted portions of any coal seam (with high REE concentrations) that has had specific boundaries identified from drilling and good quality interpolation data. Identifying waste materials generated from a specific coal seam within surface waste disposal sites (constructed piles) is feasible, but would require significant time, cost, and effort to review past industrial and regulatory records (paper and electronic). It is also feasible to identify where within an underground mine the surface waste materials originated and a specific location within a constructed waste pile. But again, the required records review would be extremely burdensome and time consuming. Although feasible, it is considered unlikely that such an approach to locate REEs within surface waste disposal site would be successful (beyond a few isolated cases) due to coal blending which has occurred over the past several decades.

Surface drilling, vertical and horizontal, is considered an optimal approach to sampling constructed waste disposal sites. In such a drilling approach, all materials are subject to inquiry. Furthermore, drilling would allow samples to be gathered on tight spacing (e.g., every 10 feet), although analyses could be on those samples collected at 50 feet intervals. If additional data is needed, then samples collected at a closer spacing can also be analyzed. This approach will allow for a 3-D mapping REE concentrations of the waste pile and the actual source (coal seam) of REEs becomes irrelevant.

5 MINERALOGY AND PROCESSING

5.1 REE-BEARING KEY MINERALS

Bastnaesite, monazite, and xenotime are three common minerals shown to have high total mass fractions of rare earths compared to other chemical elements. The amount of REE present in each of these three routinely exceeds 60 percent of the total mass. Although many REE-bearing minerals exist, total rare earth element concentrations reported vary widely from mineral to mineral (ref. 5-1 and 5-2). These two web sites provide access to comprehensive listings by individual REE. Table 10 below is taken from a British Geological Survey (ref. 5-3) publication about some of the minerals which have been studied. Information about individual REE-bearing minerals can show significant variations depending upon the source of the data. The amount of a particular REE also varies from. The work performed within this project relied on prior observations that REEs in coal were found predominantly in monazite and xenotime.

Table 10. Typical List of REE-Bearing Minerals and Typical REO Content

Mineral	Formula	Approximate REO %
Aeschynite-(Ce)	$(Ce,Ca,Fe,Th)(Ti,Nb)_2(O,OH)_6$.	32
Allanite-(Ce)	$(Ce,Ca,Y)_2(Al,Fe^{3+})_3(SiO_4)_3OH$.	38
Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$	19
Bastnäsite-(Ce)	$(Ce,La)(CO_3)F$	75
Brannerite	$(U,Ca,Y,Ce)(Ti,Fe)_2O_6$	9
Britholite-(Ce)	$(Ce,Ca)_5(SiO_4,PO_4)_3(OH,F)$	32
Eudialyte	$Na_4(Ca,Ce)_2(Fe^{2+},Mn,Y)$ $ZrSi_8O_{22}(OH,Cl)_2(?)$.	9
Euxenite-(Y)	$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$	24
Fergusonite-(Ce)	$(Ce,La,Nd)NbO_4$	53
Gadolinite-(Ce)	$(Ce,La,Nd,Y)_2Fe^{2+}Be_2Si_2O_{10}$.	60
Kainosite-(Y)	$Ca_2(Y,Ce)_2Si_4O_{12}CO_3.H_2O$.	38
Loparite	$(Ce,La,Na,Ca,Sr)(Ti,Nb)O_3$	30
Monazite-(Ce)	$(Ce,La,Nd,Th)PO_4$	65
Parisite-(Ce)	$Ca(Ce,La)_2(CO_3)_3F_2$.	61
Xenotime	YPO_4.	61
Yttrocerite	$(Ca,Ce,Y,La)F_3.nH_2O$.	53
Huanghoite-(Ce)	$BaCe(CO_3)_2F$.	39
Cebaite-(Ce)	$Ba_3Ce_2(CO_3)_5F_2$.	32
Florencite-(Ce)	$CeAl_3(PO_4)_2(OH)_6$.	32
Synchysite-(Ce)	$Ca(Ce,LA)(CO_3)_2F$.	51
Samarskite-(Y)	$(Y,Ce,U,Fe^{3+})_3(Nb,Ta,Ti)_5O_{16}$.	24
Knopite	$(CaTi,Ce_2)O_3$	na

Although data from an individual site may be available that provides a compositional breakdown as to the structure of a particular mineral (and the relative amounts of any individual REEs present), that information does not appear to be comprehensive. In addition, compositions of minerals found in one deposit may not be similar to those found in another given the nature of the geological processes by which REEs are concentrated at particular locations. From an economic standpoint, laboratory characterizations and plot-scale tests are essential to develop processing schemes that can successfully recover enough of the original rare earth elements to justify continued development of the mine site and of any unique processing scheme.

The rare earth phosphates (here considered as lanthanides +Y), exist in nature as the phases monazite and xenotime; monazite preferentially incorporates the larger, light rare earth elements (LREEs, here La-Gd) whereas xenotime tends to incorporate the smaller, heavy rare earth elements (HREEs).

Figure 52 shows the typical crystalline structure of the mineral Monazite. It is comprised of a PO4-tetrahedra (BLUE, P = Phosphorus, RED,O = Oxygen) and an AO9-polyhedra (A = La, Ce, Pr, Nd, Pm, Sm, Eu, Gd). The rare earth oxide (REO) content of monazite is approximately 70 weight percent (weight %) and the distribution has a better intermediate REE content than bastnaesite (ref. 5-4).

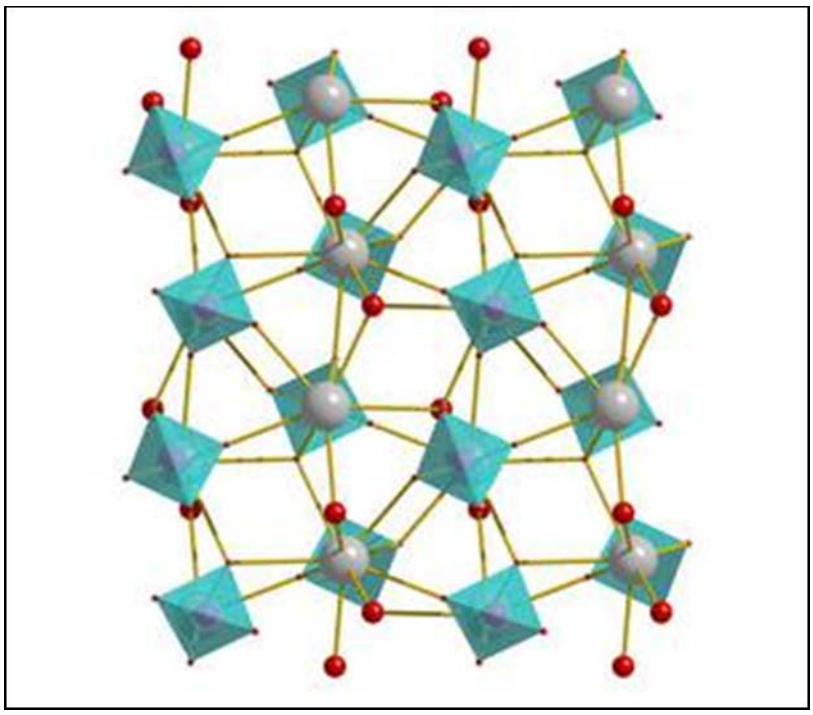


Figure 52. Crystalline Structure of Monazite

An empirical concentration relationship can be developed from individual concentration data from a number of crystals. Table 11 lists both average compositional data and other key physical properties of monazite. Based on averaged values, an approximate empirical formula for a typical monazite crystal can be stated as: $Ce_{0.5}La_{0.25}Nd_{0.2}Th_{0.05}$ (PO_4). The total amount of thorium in different monazite deposits varies from ≈0.0 percent upward (monazite as often been identified as a potential commercial source of thorium and some black sand placer deposits can contain monazite with thorium and uranium in the percent or higher range—that is 10,000 ppm or more).

Table 11. Composition and Physical Properties of Monazite

Monazite (Ce) Composition Molecular Weight = 240.21 Hardness = 5-5.5 Mohs (Apatite-Knife Blade), Specific Gravity = 5.15 g/cc		
Lanthanum	14.46% La	16.95% La_2O_3
Cerium	29.17 % Ce	34.16 % Ce_2O_3
Thorium*	4.83 % Th	5.50 % ThO_2
Phosphorus	12.89 % P	29.55 % P_2O_5
Neodymium	12.01 % Nd	14.01 % Nd_2O_3
Oxygen	26.64 % O	
*trace amounts of radioactive elements	100 %*	100.17 % = Total Oxide

Xenotime is essentially an yttrium phosphate, (YPO_4) but usually contains erbium and in some cases cerium, various other rare earths, silicon and thorium. An empirical formula has been developed that captures the presence of small amounts of other REEs: $(Y_{0.77}Dy_{0.07}Er_{0.05}Yb_{0.03}Gd_{0.02}Ca_{0.01})(P_{1.01}Si_{0.01})O_4$. Figure 53 provides a model for Yttrium Orthophosphate which is the main component of xenotime.

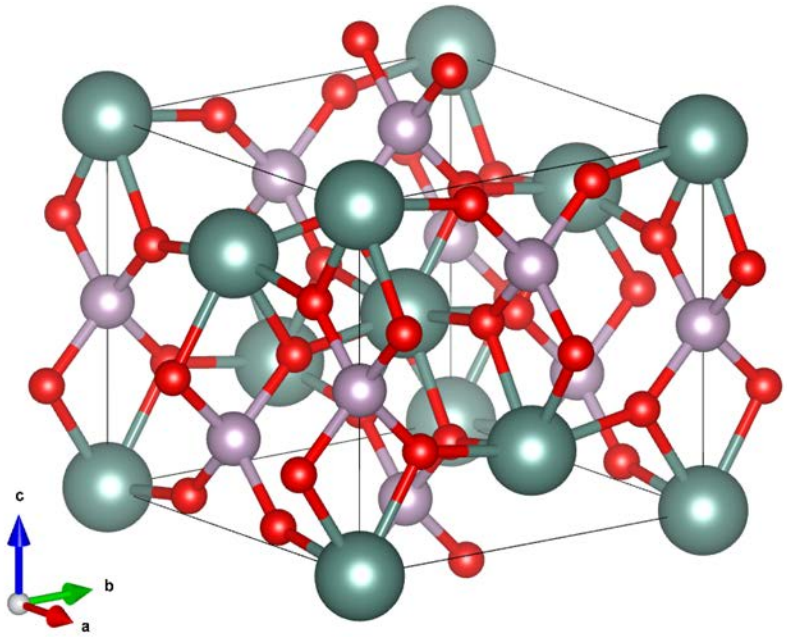


Figure 53. - Crystalline Structure of Yttrium Orthophosphate

Xenotime is infusible, insoluble in acids and, with difficulty, soluble in molten microcosmic salt. It is distinguished from zircon by its cleavage and inferior hardness. Table 12 presents compositional data along with selected physical properties. Xenotime has a slightly lower specific gravity and is somewhat softer than is monazite. Both of these minerals present challenges when attempting to extract rare earth elements (ref. 5-5).

Bastnaesite is another mineral with a high percentage of the total mass coming from rare earth elements (ref. 5-6). It is more complex that monazite and has the following empirical formula: $Ce(CO_3)F$. The mineral occurs in several forms, one with lanthanum as the main REE (as La-Ce), another with cerium as the main REE (Ce-La) and as a Ce-Y combination. Small amounts of other light REEs often substitute for either lanthanum or cerium in the crystal structure shown in Figure 54. In the crystal structure of bastnaesite-(Ce) depicted below, atoms of cerium appear as white spheres.

Table 12. Composition and Physical Properties of Xenotime

Xenotime Composition Molecular Weight = 183.88, Hardness = 4-5 Mohs, Specific Gravity = 4.4 – 5.1g/cc		
Yttrium	48.35% Y	61.4% Y_2O_3
Phosphorus	16.84% P	38.6% P_2O_5
Oxygen	34.8% O	
*trace amounts of other REEs and radioactive elements	100%*	100% = Total Oxide

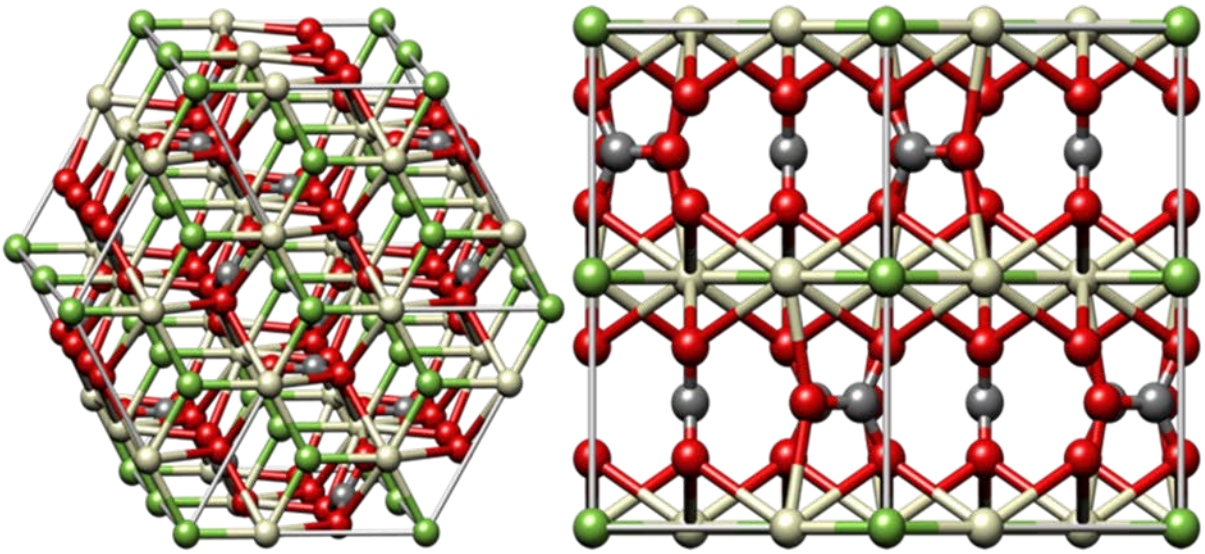


Figure 54. Crystal Structure of Bastnaesite-(Ce)

Color code: Carbon, C: blue-gray, Fluorine, F: green; Cerium, Ce: white, Oxygen, O: red

Individual rare earth elements are similar to each other in some ways—making them difficult to separate from each other—but different in equally important, ways. Properties of individual rare earth elements bond in a similar manner but the pure elements differ

amongst each other in a number of ways. First, the relative abundance varies as even-numbered REEs occur in greater abundance than their odd-numbered neighbors (Oddo-Harkins effect) see Figure 55.

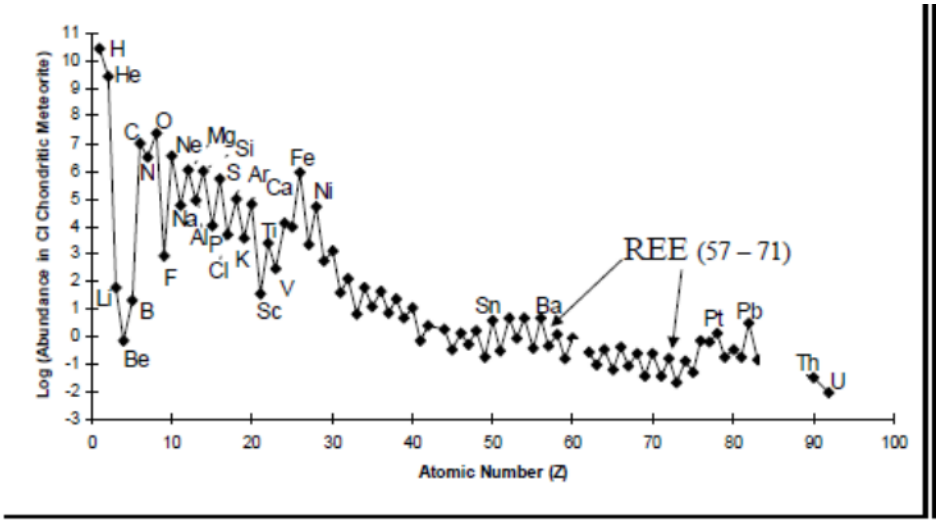


Figure 55. Oddo-Harkins Effect

Table 13. Composition and Physical Properties of Bastnaesite

Bastnaesite (Ce) Composition Molecular Weight = 219.12 Hardness = 4-5 Mohs (Fluorite-Apatite), Specific Gravity = 4.97 g/cc		
Cerium	63.94 % Ce	74.90 % Ce_2O_3
Carbon	5.48 % C	20.08 % CO_2
Oxygen	21.90 % O	
Fluorine	8.67% F	8.67 % F
-	-% F	-3.65 % -O=F_2
*trace amounts of radioactive elements	100%*	100% = Total Oxide

This effect applies to more than rare earth elements but it can make observations of trends difficult when looking a plots of a number of samples. One means of smoothing out the variations is a form of normalization. Data sets representing elemental abundances in various crustal samples (both terrestrial and from the sea floor) can be used where each elemental value is divided into the concentration values in the samples of interest. Similarly, abundances of each rare earth element, our area of concern, found in chondrites (a stony, non-metallic meteorite containing small mineral granules [chondrules]) can be used as the divisor. An example is given below (ref. 5-7). Two sets of data, one for lava from Mt. Kilauea and the other from a chondrite are listed in order of the mass numbers of the rare earth elements in columns two and three of Table 14. The ratio is presented in the fourth column. When plotted the saw-toothed nature—also apparent in Figure 55—normally seen is smoothed (Figure 56).

Table 14. Comparison of REE in Kilauea Lava with Chrondite Abundances

Comparison of REE in a Kilauea lava with Chondrite abundances
(data in ppm)

REE	Chondrite	Kilauea	Kilauea/Chondrite
La	0.31	9.05	29.19
Ce	0.808	22.4	27.72
Pr	0.122	3.09	25.33
Nd	0.600	15.6	26.00
Sm	0.195	4.02	20.61
Eu	0.0735	1.40	19.04
Gd	0.259	4.36	16.83
Tb	0.0474	0.72	15.19
Dy	0.322	3.93	12.20
Ho	0.0718	0.77	10.72
Er	0.210	1.91	9.095
Yb	0.209	1.58	7.55
Lu	0.0322	0.22	6.83

Divide sample by chondritic abundance

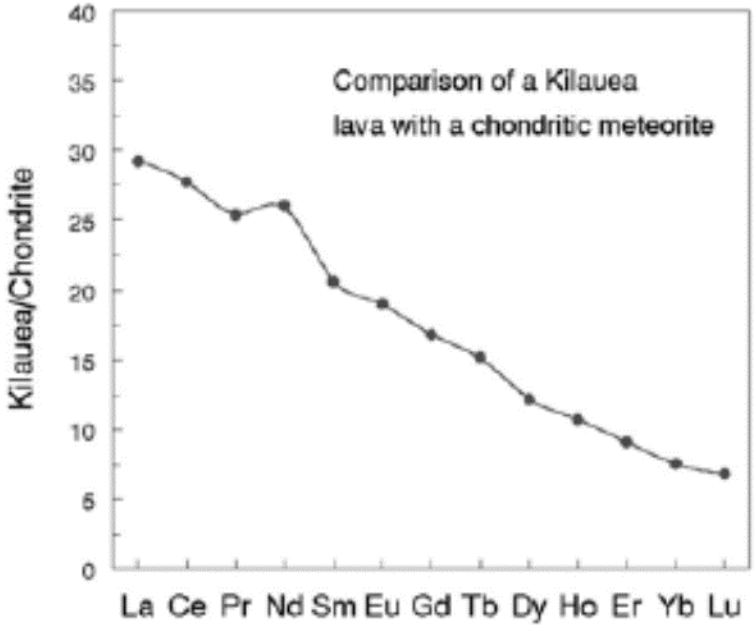


Figure 56. Comparison of Kilauea Lava with Chondritic Meteorite

A similar calculation was performed for a number of fly ash samples collected and analyzed in this study (Figure 57). The data plotted includes a line representing a typical concentration profile for the REE deposit at the Mountain Pass mine (ref. 5-8).

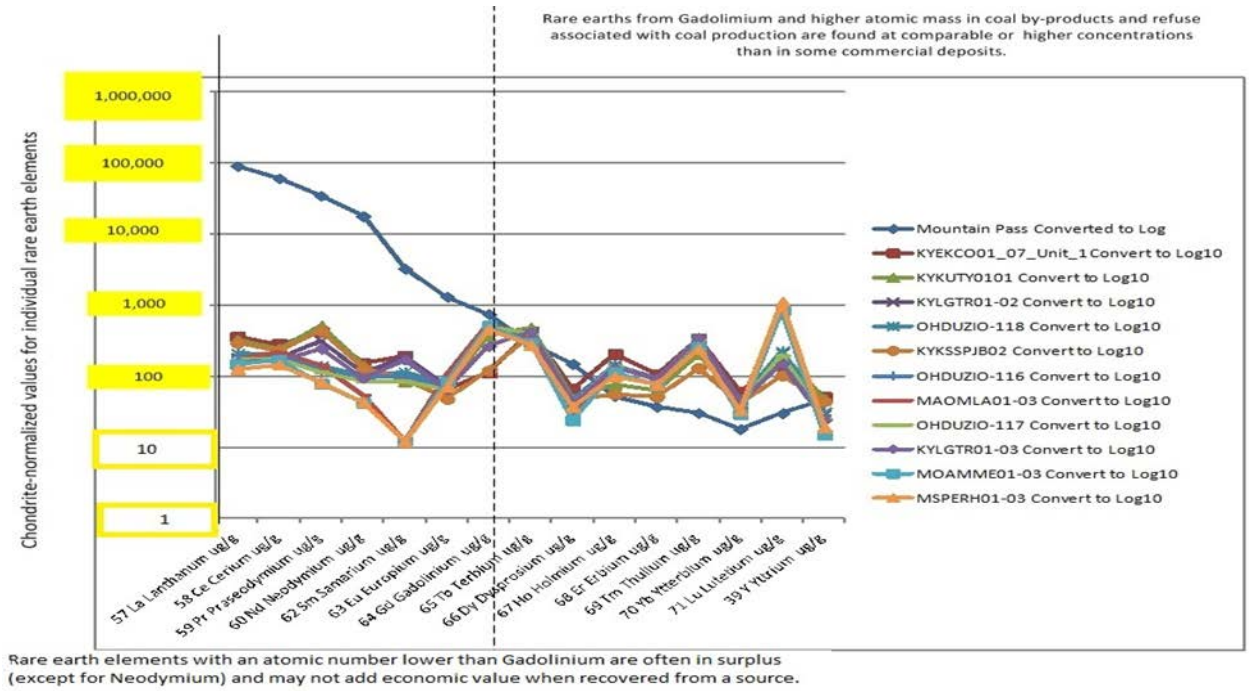


Figure 57. Chondrite Normalized Values for Individual REEs from Fly Ash Samples

Source: LTI

5.1.1 Impact of Mineral Form on Processing

ATOMIC STRUCTURE OF RARE EARTH ELEMENTS

In addition, the relative amount of each successive REE decreases with an increase in atomic mass number. Loose correlations have been observed between estimated elemental abundances in the universe and in samples from the Earth's crust and the nuclear binding energy curve. Roughly speaking, the relative stability of various atomic isotopes has exerted a strong influence on the relative abundance of elements. (ref. 5-9). The saw-tooth alternation between relative abundance and scarcity of adjacent atomic numbers in the elemental abundance curve follows a similar pattern to energy levels in the nuclear binding energy curve. This alternation is caused by the higher relative binding energy (corresponding to relative stability) of even atomic numbers compared to odd atomic numbers. (ref. 5-10).

The figure below (Figure 58) shows the ionic radii of the rare earth elements (based on the normal valence state of +3) and how the radius of each successive element decreases as electrons are added to inner orbitals. The two outliers are for Eu which can react with a +2

valence and cerium which can also bond with a +4 valence. Due to the atomic structure, REEs can substitute for one another in crystal structures (hence the "typical" empirical formulas noted earlier).

The atomic size or ionic radii of tri positive lanthanide ions show a steady and gradual decrease with the increase in atomic number from La to Lu. Although they show some irregularities, the ionic radii decrease steadily from La to Lu. This gradual decrease in the size with increasing atomic number is called the lanthanide contraction. (ref. 5-11 and 5-12)

CAUSE OF LANTHANIDE CONTRACTION

An examination of the lanthanide contraction will yield insights regarding REE separation which will be discussed in the next section. The major cause for lanthanide contraction is due to the inappropriate shielding of the 4f electrons due to the improper shape of the f-orbitals. As the atomic number increases in the lanthanide series, for every proton in the nucleus the extra electron goes to fill the 4f-orbitals.

The 4f-electrons constitute inner shells and are rather ineffective in screening the nuclear charge. Thus, there is a gradual increase in the effective nuclear charge experienced by the outer electrons. So the attraction of the nucleus for the electrons in the outermost shell increases as the atomic number increases and the electron cloud shrinks.

This results in gradual decrease in the size of lanthanides with increasing atomic number. The decrease in size is not regular throughout the lanthanides. A rapid decrease is seen only in the first six elements compared to the rest of the elements.

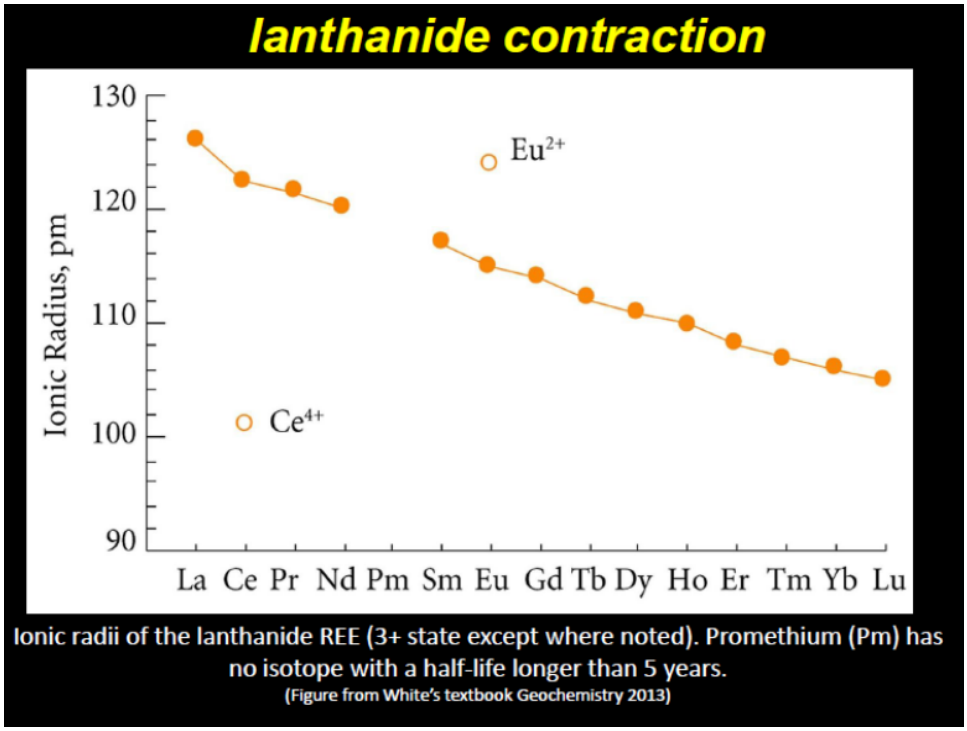


Figure 58. Ionic Radii of the REEs

Two Consequences of Lanthanide Contraction

- **Difficulty in the separation of lanthanides**—As there is small change in the ionic radii of lanthanides so their chemical properties are similar. This makes the separation of elements in the pure state difficult. This contraction makes the slight difference in size so the properties like solubility, complex formation, hydration, etc., shows some differences and it is possible to separate them by ion exchange methods.

- **Effect on the basic strength of hydroxides**—As the size of lanthanides decreases from La to Lu, the covalent character of the hydroxides increases and hence their basic strength decreases. Thus, La(OH)3 is more basic and Lu(OH)3 is least basic.

Differences in abundances of individual rare earth elements in the upper continental crust of the Earth represent the superposition of two effects, one nuclear (as described above) and one geochemical. First, the REEs with even atomic numbers (58Ce, 60Nd) have greater cosmic and terrestrial abundances than the adjacent rare earth elements with odd atomic numbers (57La, 59Pr). Second, the lighter rare earth elements are more incompatible

(because they have larger ionic radii) and therefore more strongly concentrated in the continental crust than the heavier rare earth elements.

All the elements of the lanthanide series resemble each other very closely due to the presence of the same number of electrons in the outermost and the penultimate shells. Although Lanthanum is a d-block element it is included in the lanthanides series as it resembles them.

Some general characteristics are given below:

- *Oxidation States:* Lanthanides show variable oxidation states. The most stable oxidation state of Lanthanides is +3. They also show +2 and +4 oxidation states due to the presence of either half-filled or completely filled or empty 4f sub shell.
- *Color:* Many of lanthanide metals are silver white. The lanthanide ions with +3 oxidation state are colored both in solid state and in aqueous solution. The color of a cation depends on the number of unpaired f electrons.
- *Magnetic Properties:* The lanthanide ions other than f0 and f14 type are paramagnetic in nature due to unpaired electrons in f-orbitals.
- *Melting and Boiling Point:* They have fairly high melting point but there is no definite trend in the melting and boiling point of lanthanides.
- *Density:* They have high density ranging between 6.77 to 9.74 g cm-3. Its increases with increasing atomic number.
- *Ionization Enthalpies:* They have low ionization enthalpy.
- *Complex Formation:* They don't have much tendency to form complexes because of low charge density. The order of complex formation can be best represented as Ln4+ > Ln3+ > Ln2+.
- *Reactivity:* All the lanthanides show the same electronic configuration and the +3 oxidation states, they show similarity in the reactivity which is greater than the transition elements. This is due to shielding of the unpaired electrons of the inner 4f-orbital by the outer 5s, 5p, and 5d orbital's. Due to the small change in the size of the ions, they show great similarity in their chemical properties. The first few members are quite reactive. A few properties are given below.

- All lanthanides react rapidly upon exposure to air.
- They dissolve in hot water and react with acid, liberating hydrogen.
- They act as a strong reducing agent because of the strong electro positive nature
- They form the nitrides and hydrides after reacting with nitrogen and hydrogen respectively.
- They also react with non-metals like halogens, sulfur, phosphorus, carbon and silicon and form their corresponding compounds.

STRUCTURAL INFORMATION RELEVANT TO OCCURRENCES OF REEs IN COAL DEPOSITS

Another mineral processing consideration would be partitioning in a given deposit. Zielinski (ref. 5-13) reported on the results of a study of a coal formation in Wyoming (one of a series of studies) examining elemental partitioning between a tonstein, surrounding coal bodies, and the intermediate, interfacial zone above and below the tonstein. (A tonstein is a compact, kaolinite-rich mud-stone, which developed as a kaolinitic palaeosol, and is frequently found as thin bands within coal seams or resting directly above the coal. Some tonsteins are laterally extensive and are believed to be the product of weathered volcaniclastic ash.) His work focused on the processes that might cause REEs to be enriched in one or more layers in a coal deposit while being somewhat depleted in the tonstein, thought to be the source of all (or most) of the rare earth elements. Tonsteins of pyroclastic origin typically have undergone a process that causes the ash to become kaolinite through the mobility of numerous elements. The work studied mobilities of a large number of different elements, but his conclusions that address the fate of REEs can be summarized as trace elements that are considered relatively immobile during low-temperature alteration (including REE and Y) were apparently leached by the low-Eh, low-pH organic-rich pore fluids of the coal-forming deposit. The researchers found that REEs were enriched in the layers close to the tonstein and depleted in the tonstein itself. In addition, the levels of REEs some distance removed from the tonstein are not enriched in the REEs.

In order to fully evaluate the amount of REEs that are potentially recoverable (reserves, not resources), it is necessary to understand how REEs are distributed within a deposit; information is needed for all three dimensions. Figure 59 depicts the distribution of rare

earth elements in a particular core sample taken through each of several locations in eastern Kentucky.

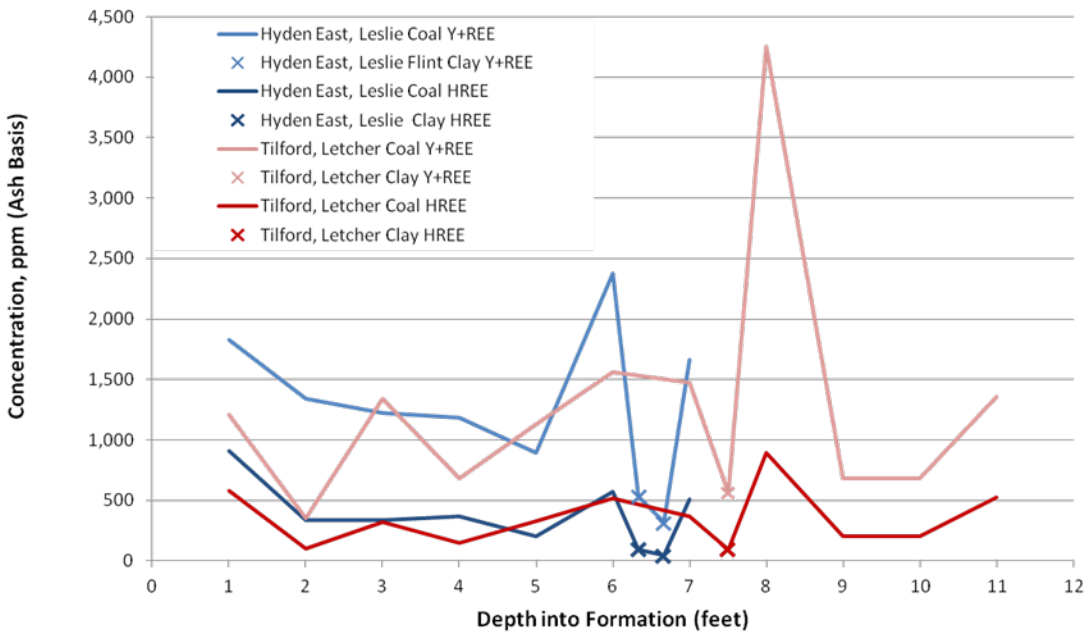


Figure 59. Measured REE Concentration in Each Foot of Core at Two Locations within the Fire Clay Coal Seam

The data are presented on an ash-only basis in the paper from which this is taken. The Fire Clay coal features a prominent tonstein—the fire clay—between 6 and 8 feet deep within the coal seam (the vertical height of the tonstein varies across the extent of the Fire Clay deposit). One can see that, on an ash-only basis, the coal just above (5-6 foot depth) and just below (8-9 foot depth) contains a higher concentration of rare earth elements.

Figure 60 highlighted REE variability from a bench analysis (ref. 5-14). Note that the REE content on the coal benches just above and below the partings are higher than they are in other parts of the coal deposit which is consistent with the work of Zielinski. These values in the Figure are presented on a whole coal basis and are derived from the reported lanthanum measurements (only La and Y were reported in this study). If one converted values to an ash-only basis, for the top three coal benches (to a depth of one foot) and for the two partings immediately below that layer, the value for the REEs in the coal would be ≈4,500 ppm (ash-only) and for the partings ≈2,800 ppm (ash-only).

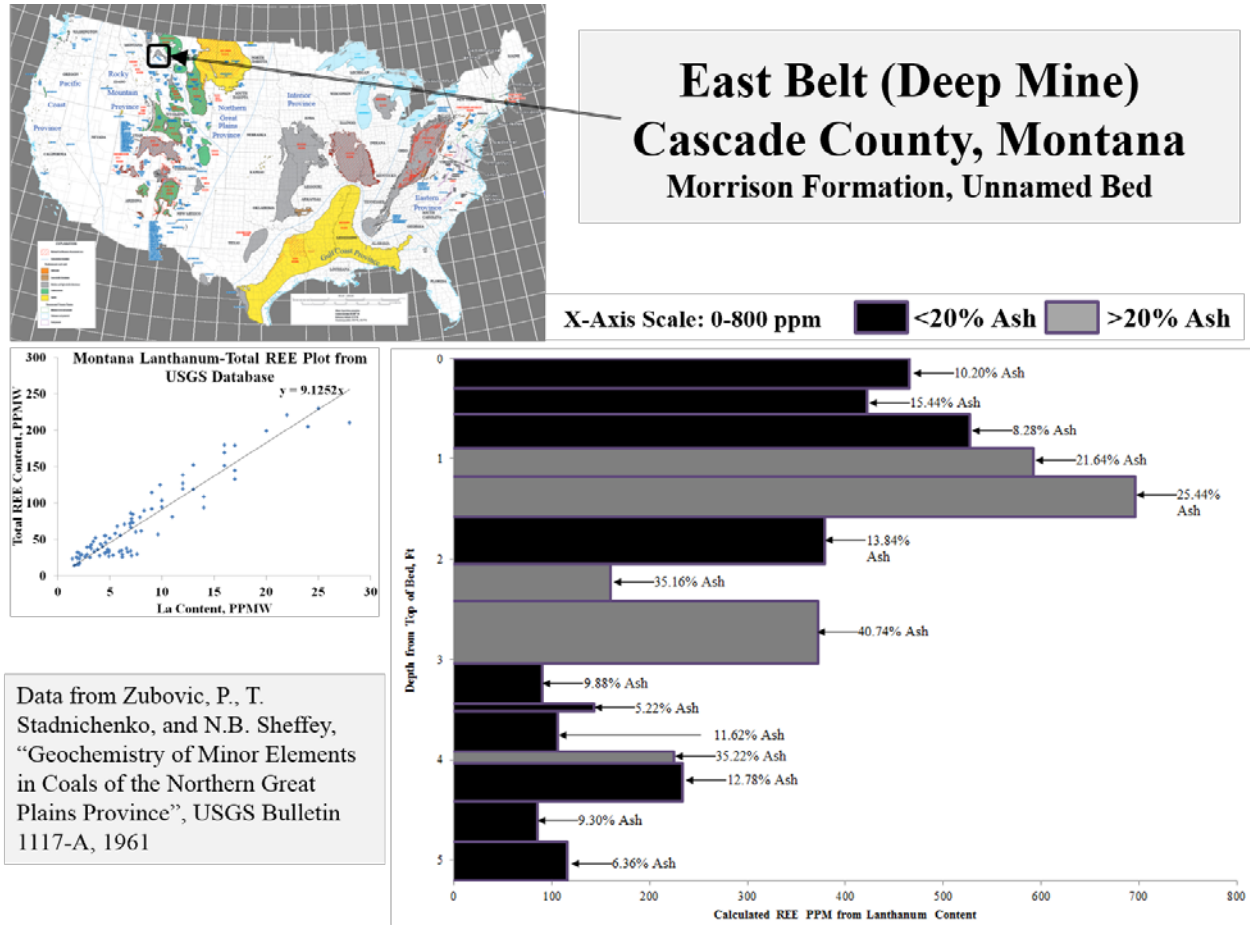


Figure 60. REE Variability in Bench Analysis

The fact that REE occurrences in coal bodies are heterogeneous is no surprise. Mining practices typically involve development of a mining plan to extract resources effectively and profitably. Mining plans are written to: document geological knowledge to instill confidence that the operator can manage variations in structure and quality; allow the operator to maximize resource recovery; optimize waste removal; enable production planning to achieve product blend requirements; and generally support design, permitting and operational aspects of a project.

Mining plans also provide input into REE processing schemes. These schemes routinely start with physical separation similar to other mining projects. However, the rather unique mineralogy of most deposits leads to custom processing schemes (extraction) for each

project. The technologies available for concentrating and extracting REEs will be discussed in the next section of this report.

5.2 OVERVIEW OF REE PROCESSING

Current processing technologies for REEs can be highly complex but they all start with standard mineral preparation practices including crushing, grinding, and flotation.

Bastnasite and monazite are the most common REE sources. Lateritic-ion adsorption clays are rich in REEs, but their occurrence is primarily limited to China. Figure 61 below provides a comparison of processing steps employed to obtain REEs from bastnasite, monazite, and lateritic ion-adsorption clay. This figure shows similar processing steps employed in the preparation of coal with highlighted locations where potential processing steps may be inserted to obtain REEs from selected coal preparation plants which is discussed in later sections of this report.

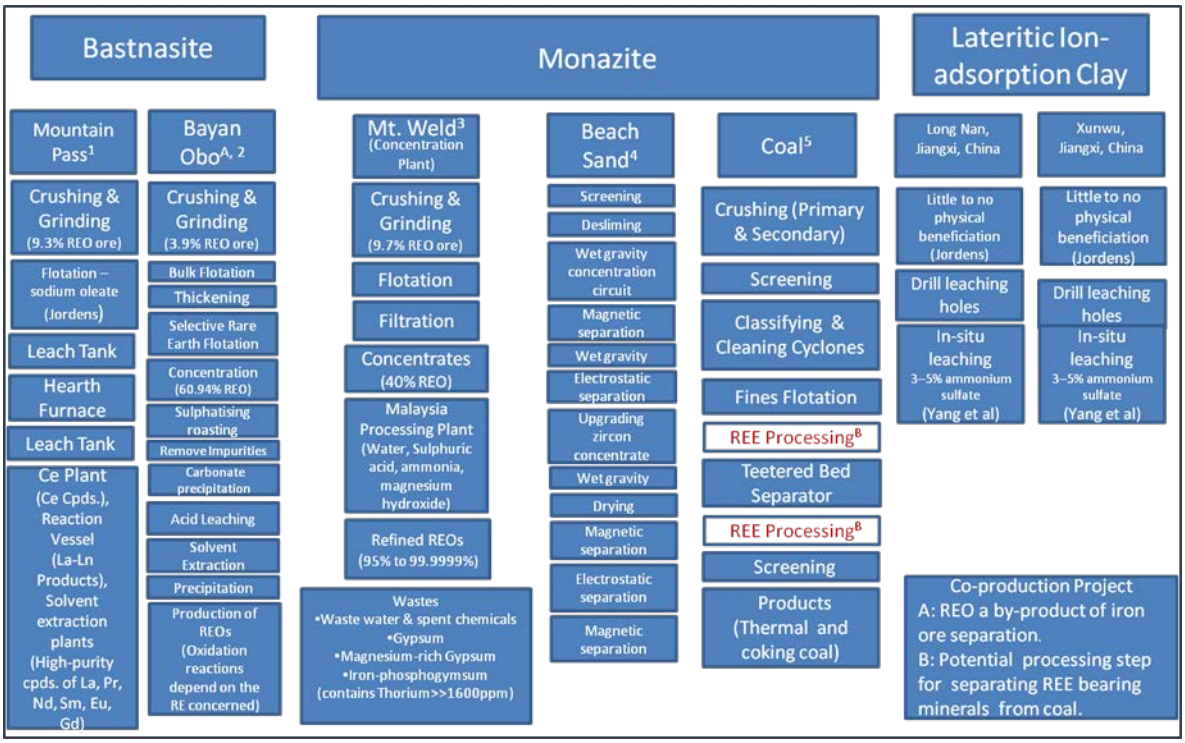


Figure 61. Summary of Processing Schemes by Major REE Bearing Mineral Form and by Project

Various processing technologies are employed for REE separation and extraction from REE rich ore deposits or byproduct materials from processing of non-REE ores. Table 15 below identifies processing technologies utilized for Mountain Pass and Mt. Weld identified in Figure 62 along with other REE projects. Process reagents for these technologies are included in the last column of the table.

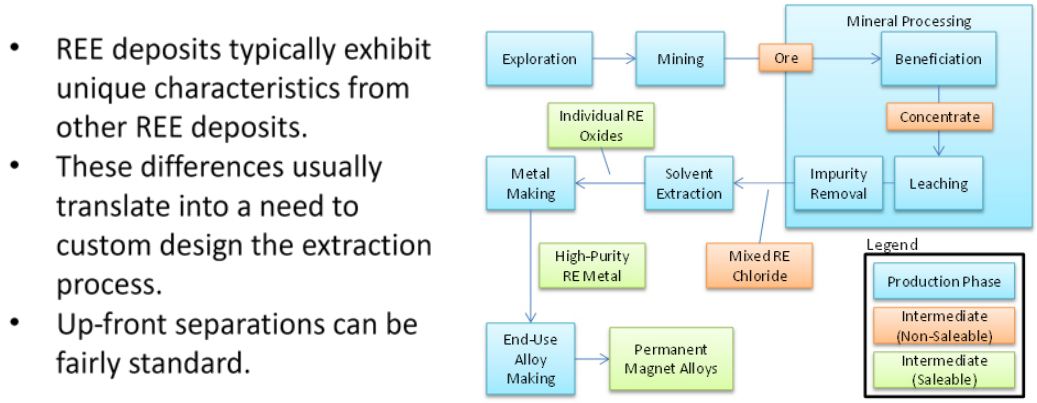


Figure 62. Processing to Concentrate and Extract REEs

Table 15. REE Processing Steps and Reagents

Project (Location)/Mineralogy	Process Technologies	Primary Processing Reagent(s) (Extractants)
Bayan Obo (Baotou, China)/bastnaesite, monazite	Roasting; flotation; leaching; neutralization; solvent extraction (SX), and precipitation	Hydroxamic acids,H2SO4; H2O; HEHEHP (P507-acidic organophosphorus); alternates: ammonium chloride (NH_4Cl), NaOH, and HCl.
Bear Lodge (Northeast Wyoming)/ancylite and bastnasite	Gravity separation; acid leaching	Hydrochloric acid, oxalic acid; nitric acid/proprietary pechnology (chloride solution; oxalate reagents)
Bokan Mountain (Alaska)/Thalenite, bastnaesite, xenotime, and monazite	X-ray and magnetic separation, acid leaching, solid phase extraction (SPE) per Preliminary Economic Assessment (PEA), Molecular Recognition Technology (MRT) per Nature article**	Nitric acid (HNO_3)/acetic acid, sulfuric acid, nitric acid, calcium oxide, and ammonia. Tailored REE binding compounds (IBC Advanced Technologies), metal-selective ligands
Kutessay II (Kyrgyzstan)/mine ore concentrate	Solvent extraction (SX)	Nitric acid; C7-C9 based fatty acids

Kvanefjeld (Greenland)/phospho-silicate minerals (steenstrupine)	froth flotation; leaching	H2SO4
Mountain Pass (California)/carbonatite-hosted bastnasite	calcination; flotation; leaching; solvent extraction (SX); reduction; precipitation; Sorb-X	Fatty acids; sodium oleate; HCL leach; HCl solution with 10% D2EHPA (Phosphoric acid) in kerosene. Zinc amalgam; H2SO4; ammonium and sodium hydrogen sulfide; Sorbx-100 (cerium-based)
Mt. Weld and LAMP (Australia and Malaysia)/monazite	Flotation; leaching; calcination; purification; solvent extractions (SX); precipitation	H_2SO_4 leach; H_2O leach; ammonia magnesium hydroxide, NH_3 Mg(OH)2
Nechalacho (Northwest Territories, Canada)/allanite (3.6%), monazite (1.5%), synchysite (0.9%), columbite (0.9%), fergusonite (0.6%), bastnasite (0.4%), and zircon (11.0%)	Flotation; Gravity separation; Pre-leach; Calcination; Leaching; Precipitation	HCl; NaOH; H_2O; H_2SO_4
Rhone-Poulenc/monazite	Solvent extraction (SX); digestion; dissolution;	NaOH; HCl, HNO_3, carboxylic acids, organophosphorous acids, neutral organophosphorous compounds, and quaternary amines
Round Top Mountain (Hudspeth County, Texas)/rhyolite, yttrofluorite, yttrocerite	Heap leaching, Solvent extraction (SX), continuous ion chromatography (CIC)	Sulfuric acid (H_2SO_4), activated carbon based media
Steenkampskraal (ZAF, Africa)/monazite (main REE bearing mineral), bastnasite, xenotime, apatite, yttrofluorite and gadolinite	Magnetic separation, acid leaching, solvent extraction, alkali reduction	Sulphuric acid, hydrochloric acid, hydrated lime, sodium hydroxide, sodium sulphate
Strange Lake B (Newfoundland, Canada)/peralkaline granite: hypersolvus and subsolvus granites – Na-K feldspar, quartz, albite, arfvedsonite, aegirine, fluorite; mineralized material – elpidite, gittinsite and zircon; fluorcarbonate minerals, monazite and polylithionite	Flotation, acid bake; leaching, precipitation	Barium Chloride (BaCl2); NaOH; oxalic acid [C2O2(OH)2]; sulfuric acid, HCl, organic extractant (not identified)

*http://tmrcorp.com/

** Lim, Xiaozhi, "Degrees of Separation," Nature, Vol 520, April 23, 2015. Pp. 426-427, http://www.nature.com/news/chemistry-degrees-of-separation-1.17359

*** Rare Element Resources website: (Bear Lodge Project) http://www.rareelementresources.com/company#.V_eyjU2a06Q

**** National Instrument 43-101 Independent Technical Report on the Results of a Feasibility Study for the Steenkampskraal Rare Earth Element Project http://www.gwmg.ca/sites/default/files/VMD1445%20Steenkampskraal%20Project%2020%20June%20%20FINAL%20GWMG.pdf

As shown in Table 15 above, different reagents are used to process the ores. This is due in part to differences in the overall ore characteristics and processing steps. The flotation process of monazite minerals is different from that of bastnasite due to the different mineralogy of the deposits. Monazite gangue minerals can include ilmenite, rutile, quartz, and zircon and typically require slightly different flotation reagents than bastnasite ores to achieve a reasonable separation. Numerous investigations have been carried out pursuing a flotation scheme for selectively separating bastnasite and monazite, including a report on the flotation separation of bastnasite and monazite using N-hydroxylphthalimade as collector. Phthalic acid in a weakly acidic slurry was used as a selective collector to produce a bastnasite concentrate of 98 percent purity, but with only 38 percent recovery. Other collectors have been also recommended, namely Hydroxy-naphthlylhydroxamic acid and N-hydroxyl ph-thalicimide. Depressants also play an important role in the flotation of rare earth minerals.

A variety of information was located and reviewed for recent advances and the current state of extraction and separation techniques. These include bioleaching, dielectrophoresis (DEP) separation, flotation, gravity separation, hybrid separation, leaching, liquid-liquid phase extraction, magnetic separation, molecular recognition technology (MRT), solid phase extraction, solid-liquid phase extraction, solvent exchange, and solvent extraction. The processing technologies employed for REE bearing ores are discussed in the following paragraphs.

Acid Bake

After concentrating REE bearing minerals, rare earth elements have to be extracted from the concentrate. Several procedures for decomposition of REE bearing minerals are available. The major part includes thermal treatment of the ore in the presence of acidic or caustic reagents. Depending on the composition of the ore concentrate an appropriate method is identified.

Acid baking with sulfuric acid is a very common process. The powdered ore is mixed with concentrated sulfuric acid and baked at temperatures between 200 and 400 °C for several hours. The resulting cake is leached with water to dissolve REE as sulfates. Optimal reaction conditions and reagent use have to be matched specifically with each tested ore. There are different factors influencing the reaction, e.g., the presence of iron oxide leading to an increased consumption of acid. At roasting temperatures above 300 °C the recovery of REE

decreases in most cases, while Th leaching is also reduced. Since thorium is generally an undesired leaching product, roasting temperature will be a trade-off between REE recovery and Th leaching.

Acid baking is a standard process since it is applicable for many of the common rare earth minerals such as monazite, bastnaesite, xenotime, apatite, or aeschynite.

Bioleaching

Bioleaching uses microbiological processes naturally performed by bacteria to remove rare earth ions. The cost of this process is remarkably low, and recovery rates can be as high as 90 percent. The process is often dismissed as it is much slower than other refinement methods (approximately 30 days in comparison to about ten hours for other methods), but bioleaching already accounts for 20 percent of copper on the market and can be sped up through additional research to find optimum operational temperatures of different bacterial species ("What is bioleaching?" 2011). Due to the complexity of the rare earth refinement process, research into integrating bioleaching with other common methods of purification could make this solution more viable (for example, unwanted minerals could first be removed using in-situ leaching, shortening the time needed for the bioleaching stage)

Dielectrophoresis (DEP)

DEP has the advantage of operating at lower voltages and is widely used for separating particles by microfluidic manipulation. REE separation by DEP is an environmentally friendly technique as it does not require additional reagents or processing.

Flotation

Froth flotation is commonly applied to the beneficiation of rare earth ores due to the fact that it is possible to process a wide range of fine particle sizes and the process can be tailored to the unique mineralogy of a given deposit.

Choices for depressants are invariably influenced by the composition of the ore deposit and the major gangue minerals present in the flotation feed. There are several depressants that have been thoroughly investigated in the established rare earth flotation processes. Sodium carbonate is used extensively in bastnäsite flotation to control the supply of carbonate anions which affect both the pH of flotation and the surface properties of bastnäsite and related gangue minerals (CO_3 is a potential-determining ion for these

minerals).It also showed that the addition of sodium carbonate preferentially increased the magnitude of the negative surface charge on both calcite and barite while leaving bastnäsite unaffected. However, other research has shown that with elevated sodium carbonate additions (mM) the surface charge of both calcite and barite are positive at pH 9 while bastnäsite has a negative surface charge. This effect helps the negatively charged lignin sulfonate molecule to achieve its depressant effects by adsorbing onto the positively charged surfaces of barite, allowing fatty acid molecules to adsorb in greater quantities to the surface of the bastnäsite mineral.

The flotation process of monazite minerals is different to that of bastnäsite due to the different mineralogy of the deposits, as well as the lack of research sources dealing with the same deposit (unlike the Bayan Obo and Mountain Pass processes). Monazite gangue minerals can include ilmenite, rutile, quartz, and zircon and typically require slightly different flotation reagents than bastnäsite ores to achieve a reasonable separation.

Monazite behaves in a similar manner to bastnäsite in terms of collectors used (fatty acids and hydroxamates) as the monazite surface will contain many of the same rare earth cations present on the bastnäsite. The adsorption mechanism of both fatty acids and hydroxamates onto a monazite mineral surface is believed to be chemical in nature, similar to bastnäsite minerals, and the increased bastnäsite selectivity of these collectors with increasing temperature applies similarly to monazite flotation.

Two of the typical monazite gangue minerals, zircon and rutile, require a depressant in order for selective flotation to be possible. Common depressants used for this purpose include sodium silicate (also used in bastnäsite flotation), sodium sulfide and sodium oxalate. The depressing action of both sodium sulfide and sodium oxalate has been proposed to be in part due to a selective activation of monazite. The available literature on sodium sulfide and sodium oxalate employs reagent nomenclature (gangue activators referred to as depressants) that is not in accordance with generally accepted flotation terminology. To ensure their work is accurately represented, the original authors' terminology will be used when describing these two reagents.

Sodium sulfide has been reported to have both an activating and depressing effect on zircon, dependent on dosage. For small additions (10 mg/L) it was shown that sodium sulfide activated zircon, pyrochlore and monazite minerals. However, as the dosage increased (up to 37.5 mg/L) pyrochlore and zircon were depressed, with the monazite

flotation unchanged. Sodium sulfide depression of zircon has been explained by the adsorption of SH and S2 ions to the mineral surface, and the subsequent unavailability of the metal cations on the mineral surface, reducing the potential sites for collector adsorption. The activation of monazite was explained by the large oxidizing power of rare earth cations on the monazite surface which oxidize the SH ions and allow fatty acid collector molecules to adsorb onto the monazite surface. An alternative explanation, for the flotation response of this mineral system in the presence of sodium sulfide is the selective desorption of sodium oleate from zircon and pyrochlore surfaces, with an accompanying incomplete desorption from monazite surfaces. Sodium oxalate has been discussed as both a depressant and activator of monazite flotation, but the prevalent opinion appears to be that sodium oxalate activates monazite when combined with a sulfonate collector. Other important depressants of monazite are starches, which have been used with a variety of collectors including: sulfonates, cationic amines, phosphoric acid esters and a unique collector emulsion (different from the patented collector emulsionused for bastnäsite flotation) of a fatty acid, an emulsifier, a phosphonic acid derivative and optional oil/amine additions. Most of these collector systems have not been extensively applied in industrial settings due to the lack of any significant monazite deposits (on the scale of Mountain Pass or Bayan Obo) that require the use of flotation as a separation method.

Apart from monazite and bastnäsite, there is very little research available on the flotation of rare earth minerals such as xenotime and even less for some of the newer complex ore deposits such as Mount Weld in Australia. The surface characteristics of xenotime have been studied., with the reviewed literature values of the point of zero charge (the point at which the concentration of positively charged ionic species is equal to the concentration of negatively charged ionic species on the mineral surface) for this mineral exhibiting a wide range of values, similar to the point of zero charge (PZC) results obtained for bastnäsite and monazite. This work also confirmed the variation in chemical composition of both monazite and xenotime minerals from surface to bulk, and concluded that this is a likely cause for the wide variation in reported values for the PZC and IEP values of these minerals.

Another study of monazite and xenotime mineral flotation, with a sodium oleate collector, concluded that sodium fluoride additions altered the bubble attachment times as a function of temperature. With sodium fluoride additions in excess of the concentration needed for surface precipitation, bubble attachment times decreased with increasing temperature, but

with insufficient sodium fluoride additions, bubble attachment times were actually shown to increase. This finding illustrates the importance of determining the optimum concentration of flotation reagents, in addition to the correct type of reagents, for the recovery of a rare earth mineral.

Another novel rare earth flotation process involved completely depressing monazite and an unspecified yttrium-bearing mineral using phosphoric acid at acidic pH, and an organic depressant to achieve a separation through reverse flotation. The naturally hydrophobic gangue (albite, chlorites and aegirine) floated without the need for collector addition.

Disregarding Bayan Obo and Mountain Pass, the published literature on flotation as a means of REE concentration is limited.

A flotation scheme was developed to selectively remove monazite from a rare earth bulk concentrate (Baiyunebo mine) comprised of 60.7 percent rare earth oxides, 75 percent as bastnasite and 25 percent as monazite. Potassium alum effectively depressed the monazite at pH 5 while allowing bastnasite flotation with benzoic acid as the collector. This technique recovered 85 percent of the bastnasite in a concentrate that assayed at 69.5 percent rare earths and 97 percent bastnasite.

Gravity Separation

Gravity separation performed with a centrifugal gravity concentrator is commonly used for fine particle sizes. The Knelson concentrator has an inclined bowl with collecting ridges to collect heavy (specific gravity >4) value minerals. This concentrator is most effective in processing ores containing <1 percent high specific gravity (SG) minerals due to its ability to rapidly accumulate high SG minerals. The Falcon Ultra-Fine (UF) Concentrator is designed for very fine particle processing. This design relies on bowl geometry to retain high specific gravity material without the use of fluidizing water. The concentrator must be stopped at intervals to periodically recover the separated materials.

Hybrid Separation

A hybrid separation method combines high-gradient magnetic separation (HGMS) and centrifugation. The set-up involves a wire filter inserted in a centrifuge with the centrifuge being placed inside of a magnet. Magnetic particles attach to the magnetized filter and the centrifugation process cleans/removes the separated particles to clean the filter. The

process is operated on a continuous basis as opposed to batch-wise versions which would not be as efficient. As compared to conventional HGMS, the hybrid method avoids dead times. Separation efficiency is up to 99.9 percent.

Leaching

Leaching is a method which utilizes acid to dissolve elements into a solution. Two of the more common acids are hydrochloric and sulfuric.

Liquid-Liquid Phase Extraction (LLE)

Liquid-liquid extraction typically isolates an organic product from inorganic substances. The organic product is soluble in an organic solvent while the inorganic substances are soluble in water. Organic solvents used for extraction need to meet basic criteria such as (1) readily dissolve the substance to be extracted, (2) not react with the target substance to be extracted, (3) should not react with or be miscible with water since it is typically the second solvent, and (4) have a low boiling point to enable easy removal from the product. If the solvent dissolves a small amount of water, it must be removed to avoid product contamination. An early industrial-scale separation exploited the differing solubilities of the complex niobium and tantalum fluorides, dipotassium oxypentafluoroniobate monohydrate (K2 [NbOF5] H_2O) and dipotassium heptafluorotantalate (K2 [TaF7]) in water. Newer processes use the liquid extraction of the fluorides from aqueous solution by organic solvents like cyclohexane. Complex niobium and tantalum fluorides are extracted separately from the organic solvent with water and precipitated by the addition of potassium fluoride to produce a potassium fluoride complex.

Magnetic Separation (MS)

Magnetic separation is commonly used to separate minerals. Ferromagnetic mineral particles quickly align with the magnetic field lines while the paramagnetic mineral particles align more slowly. Diamagnetic mineral particles are repelled along the magnetic field lines. The effectiveness of magnetic separation of various sized particles is dependent on the dominant effect of one of three main forces on the particle (gravitational, magnetic and fluid drag). A series of wet high intensity magnetic separation (WHIMS) steps are typically used in conjunction with gravity pre-concentration steps to concentrate valuable RE minerals.

Molecular Recognition Technology (MRT)

MRT utilizes what's called a ligand. Ligands are altered molecules that attract another molecule and only that one. For example, if dysprosium is to be recovered, a specific ligand is developed to attract the dysprosium molecule. To implement the process, the ligand coatings are placed on a "bead" and placed in a column. REE leach solution is run through the column, and each element has what they call a selection factor. The target element is attracted to the ligand coat and is firmly attached. Some elements need to be run through more than one column to achieve the desired recovery which is typically 99 percent at 99 percent purity. Columns are tailored for specific elements to ensure separation and ease of processing.

Solid Phase Extraction (SPE)

Solid Phase Extraction (SPE) is a newly developed method of rare earth refinement, which, unlike solvent exchange, takes place with the minerals always in solid state. This solution utilizes a new filter technology produced by Intellimet LLC, in which mined materials are sorted by atomic densities and particle size, and the resulting piles are then purified according to their content, greatly increasing the process's overall efficiency. SPE columns have both the fast equilibration kinetics of SX, and the operating advantages of solid ion exchange columns. REE purification columns with SPE resins are capable of capturing REE ions from solution in seconds. The enhanced kinetics also effect rapid equilibrations of different REE ions, thus enabling separation and purification in minutes. With SPE, a pregnant leach solution is directly processed through two-stage SPE columns to produce subclasses of Ce/LA, Pr/Nd, Sm/Eu/Gd, Y, and heavy REE. The separation is carried out in four pairs of columns wherein a lead column in each pair makes a bulk separation from the purified leach solution while and amplifier column further separates the rare earths eluted from the lead column into subclass fractions. The process for screening ligands and amplifier column eluants is included. Combination of the fractions eluted from the amplifier columns into the five target subclasses is also part of the processing. SPE achieves significant enrichments in relatively few processing steps as compared to conventional technologies. SPE, with relatively few stages, could be carried out at the mine site to (1) provided more enriched and thus higher value products to be sent to a processing facility; and (2) mitigate the need for an expensive bulk oxalic acid precipitation of all the REE. Rapid extraction kinetics allows the SPE process to operate in relatively small SPE columns

for a given throughput. Application of SPE technology may enable the potential production of intermediate enriched products at the minesite.

SPE has recently undergone testing with UCore that supported this as a very viable technology to be utilized in the near future. This solution can yield results within a relatively short time frame (≈10 years), as the technology is already developed but not yet implemented. The precursor to SPE is solvent state extraction. The advantages to using this method are greater recovery rates and less waste (Acevedo 2002).

Solid-Liquid Phase Extraction

Solid-liquid phase extraction allows soluble components to be removed from solids using a solvent. After implementation of this process, the solid carrier phase will still contain some of the transition component (soluble component). Some of the solvent will most likely be adsorptively bonded to the solid carrier phase. Achievement of the fastest and most complete solid extraction possible is accomplished with the solvent having access to large exchange surfaces and short diffusion paths. Therefore, pulverizing the solid to be extracted is a critical variable. Mixing the extraction material and solvent is also important. After completion of the operation, the solvent and the dissolved transition component are removed and regenerated. Evaporation or distillation is used to regenerate the solvent. Upon evaporation of the solvent, a concentrated extract solution is left behind as the product. The last step involves condensation of the solvent for reuse.

Solvent Exchange

The solvent exchange method is based on a solid polymer film forming at the interface between an aqueous solution and a solution of a water-insoluble polymer upon their contact. Formation of a polymer film on the aqueous surface depends on spreading of the polymer solution on the aqueous surface and subsequent phase separation of the water-insoluble polymer. Spreading of the polymer solution is mainly dictated by physical properties of the organic solvent. For favorable spreading of the polymer solution over the aqueous surface, the solvent is required to have a low interfacial tension with both water and air. Phase separation of the polymer film is a result of mass transfer between the organic solvent and water (solvent exchange) leading to decrease in the solubility of the polymer in the solvent. Conventional separation of REEs from an aqueous solution, containing around 10 valuable elements, is carried out by solvent extraction (SX). This

separation process produces individual REOs of various purities or a composite of different elements sold for further separation.

SOLVENT EXTRACTION (SX)

Solvent extraction is a method employed to separate a substance from one or more others by using a solvent. The basis for the method relies on variations in the solubility of different compounds in different substances. Solvents for the process are chosen based on their ability to not mix with the compound in which the substance of interest is currently dissolved. The chosen solvent also needs to not dissolve any unwanted substances in the original mixture. After mixing and allowing the liquid to stand, separation will occur between the two liquids. Multiple stages with different solvents may be necessary for some procedures.

5.2.1 Process-Specific Data on Reagents Used in Creating Concentrates and for REE Extraction

Solvent extraction is an important technology utilized for REE processing and Table 16 below identifies the commercial names of these reagents along with additional comments.

Table 16. REE Solvent Extraction Reagents

Commercial Extractant (Reagent/System)	Comments/Additional Details
P507 and P204; CYANEX® 272, CYANEX® 302, and CYANEX® 301; P507-iso-octanol (ROH)-REs	CYANEX® 272- Phosphinic acid; CYANEX® 301-Dithiophosphorous acid; CYANEX® 302-Monothiophosphorous acid; P204-(D2EHPA-phosphoric acid); P507-(HEHEHP-phosphonic acid) modified with ROH is superior (improves stripping ratio and heightens selectivity) to other systems in separating HREEs.
P507 and naphthenic acid (HA)	Widely applied in China. Provides for production of individual RE purities up to 99.99%.
TOPS 99, PC 88A; CYANEX® 272, CYANEX® 302, CYANEX® 921, CYANEX® 923; ALAMINE® 336, ALIQUAT™ 336	SX of rare-earths (Sm(III), Gd(III), Dy(III) and Y(III)); Mixtures of extractants showed no significant effect on the separation factors of rare-earths as compared to individual extractants. (Kim et al, 2012); [ALIQUAT™ 336- Quaternary amine CYANEX® 272- Phosphinic acid; CYANEX® 302-Monothiophosphorous acid; CYANEX® 921-Phosphine oxide; PC88A-Phosphonic acid]
CA 12 and CYANEX® 272	SX of high purity yttrium oxide (Wang et al, 2011)[CYANEX® 272- Phosphonic acid]
CYANEX® 572	A highly stable phosphorus based chelating extractant that is designed to improve SX performance relative to traditional phosphonic acid extractants. It has been specially formulated ofr the extraction and purification or REEs. It has an extraction strength profile which allows efficient extraction of the HREEs while allowing the back extraction / stripping operation to utilized lower strip acid concentrations.
Adogen 464	Quaternary amine
CA 12	Sec-octylphenoxy acetic acid
CA 100	Sec-nonylphenoxy acetic acid
DBBP	Phosphorous ester
HNO3	Nitric acid
LIX 54	*β*-diketone
N1923	Primary amine
Primeme JMT	Primary amine
P229	Phosphinic acid
TBP	Phosphorous ester
TOPO	Phosphine oxide
Versatic 10	Versatic acid
Versatic 911	Versatic acid

Processing of REE bearing ores at commercial projects and selected projects in the development stage is discussed in the following paragraphs. The largest commercial REE processing operation in the world is the Bayan Obo plant located in China. Currently, there are no operating commercial REE projects located in the United States. Molycorp Inc. in Mountain Pass Rare Earth Mine in California was idled in 2015. Mount Weld is a recent major commercial REE project with ore mining in Australia and subsequent REE concentrate processing in Malaysia.

The Bayan Obo rare earth deposit is actually a very large iron ore deposit with a relatively small quantity of rare earth minerals present amongst the iron mineralization. Major steps involved with processing bastnaesite (at Bayan Obo) are crushing, grinding, bulk flotation, thickening, selective rare-earth flotation, concentration of REOs, sulfatizing, roasting, removal of impurities, carbonate precipitation, acid leaching, SX, precipitation, and production of REOs. Bastnaesite is the primary REE bearing mineral processed at Bayan Obo with smaller quantities of monazite. Numerous processing schemes have been described for this deposit; the common elements for many of these flowsheets involve a non-selective flotation of rare-earths and similar gangue minerals from the iron-bearing minerals followed by a more selective flotation step to beneficiate the REO concentrate. The non-selective flotation step can be completed using a fatty acid, but this poses problems downstream. This is because the fatty acid, a portion of which will chemically adsorb to the surface of gangue minerals, must be removed from adsorption sites, to be replaced by a more selective collector such as hydroxamic acid to facilitate the selective flotation of the REO.

At Bayan Obo, sodium silicate is used to depress iron-bearing and silicate minerals, which are not present in the Mountain Pass ore. Hydroxamic acid and sodium silicate were identified as the two most important reagents for successful flotation of the Bayan Obo ores; the sodium silicate addition was large enough (25 kg/t) to depress the flotation of all minerals, and then a small amount of hydroxamic acid was added to selectively float only the rare earth minerals. This very large requirement for sodium silicate showed that a combination of sodium silicate and either alum or carboxymethyl cellulose (CMC) reduced the dosage required to achieve an efficient depression of gangue minerals in Chinese rare earth flotation. Sodium metaphosphate has been shown to be an effective depressant of calcite gangue at slightly alkaline pH and in the presence of a hydroxamic acid collector. Sodium hexafluorosilicate has also been used at Bayan Obo to depress fluorite, calcite and

barite minerals as well as to act as an activator for rare earth. It was shown that the popular H205collector does not require the addition of sodium hexafluorosilicate to achieve an effective beneficiation of rare earth oxide minerals at Bayan Obo, which is significant as sodium hexafluorosilicate is an environmental pollutant as well as a hazard for plant workers.

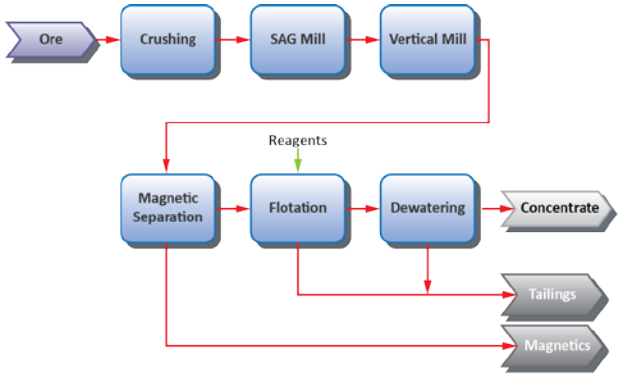
Bastnaesite processing at the Mountain Pass mine includes crushing, grinding, flotation, leaching with hydrochloric acid, multiple hearth furnaces, leaching with hydrochloric acid, and use of various solvents tailored for extraction of specific REEs compounds. The commercial bastnaesite deposit is processed by flotation using a mixture of tall oil and lignin sulfonate at elevated temperature to selectively float bastnaesite from calcite and barite. At Mountain Pass, lignin sulfonate is added as a depressant to suppress the calcite and barite gangue minerals, however it also affects bastnäsite to a certain degree. Research also noted that the selective nature of lignin sulfonate is not affected by the elevated temperatures at which flotation takes place in the Mountain Pass plant. Sodium fluoride and sodium hexafluorosilicate have also been used by different researchers as generic depressants for barite and calcite gangue in the Mountain Pass system.

The other major rare earth deposit that is actively being developed is in Mount Weld in Australia where the complex mineralogy of the deposit is distinct from currently operating rare earth mines. Some of the rare earth minerals comprising the Mount Weld ore body include: monazite, cheralite, cerianite, florencite, and small quantities of rhabdophane. Goethite, apatite, crandalite, dolomite, cryptomelane and jacobsite are present as gangue. Two flotation schemes have been proposed for this ore body. The first describes a blended collector emulsion (separate from previously mentioned collector emulsions) of fatty acid, with an emulsifier such as a secondary amino modified sulfonated fatty acid and an oil as froth stabilizer, with sodium sulfide, sodium silicate and a starch as depressants. This work also mentions the possibility of utilizing an amine collector, provided suitable depressants could be developed, as being advantageous due to the ease with which an amine could be removed from mineral surfaces after flotation. The second method employs a fatty acid collector with sodium sulfide, starch and sodium silicate as the depressants. As the Mount Weld deposit has only recently been brought to full-scale production, there is currently no available data to determine which flotation scheme has been adopted and how it is performing. A comparison between these two reagent schemes shows that the primary path

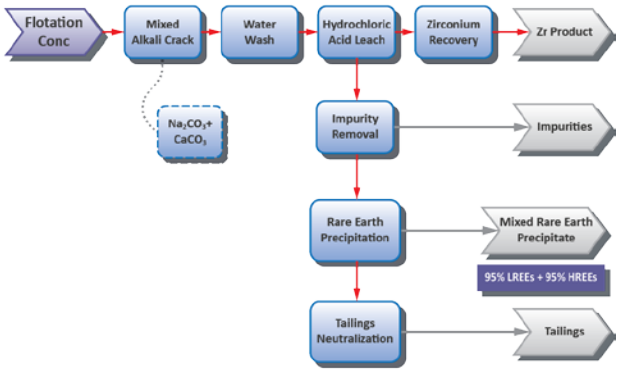
of innovation for new flotation processes for rare earth ores has thus far involved developing new collectors, whilst depressant schemes remain relatively untouched.

The process design represented in the flowsheets in Figure 63 below is optimized to produce site-specific ores as a bulk rare-earth concentrate consisting of the various rare-earth minerals. These flowsheets are provided based on the study for the concentrator and the hydrometallurgical plant in Avalon Rare Metals' Nechalacho project. Chemical reagents to be used for the flotation step have not been identified by Avalon per the most recent Nechalacho Rare Earth Elements project news release, dated October 8, 2014. (http://avalonadvancedmaterials.com/news_media/display/index.php?id=12049)

The flotation step for the Nechalacho project is designed to produce a mixed rare earth mineral concentrate. The hydrometallurgical plant will extract all the rare earth elements from the mineral concentrate to produce a mixed rare earth oxide concentrate. Final refining to separate individual rare earth oxides from the mixed rare earth oxide concentrate will be performed by Solvay (the global leader in rare earth refining) at their facility in France.



Summary Flowsheet for the Concentrator portion of Avalon Rare Metals' Nechalacho project. (Avalon, 2013)



Mixed Alkali Hydrometallurgical Summary Process Flowsheet for Avalon Rare Metals' Nechalacho project. (Avalon, 2013)

Figure 63. Avalon Metals Coproduction Processes

ROUND TOP MOUNTAIN

Heap Leaching Process

Texas Rare Earth holds state leases to explore and develop a 950-acre rare earth minerals deposit in the almost mile-high Round Top Mountain, located eight miles northwest of Sierra Blanca. Texas Rare Earth officials decided to scale down its start-up plan from producing 3,000 tons a year to almost 400 tons a year, so the company could get into production as smoothly and at the lowest cost possible. Seven rare earth minerals would be sold, while other minerals that are mined would be warehoused until the market develops further.

The Round Top Project mine will most likely be an open pit mine. Mined material will be crushed and stacked for a heap leach process using sulfuric acid to extract minerals. Sulfuric acid is the most common of the industrial acids. The pregnant solution will involve a multi-stage cleaning process to remove primary dissolved elements and produce a mixed rare earth carbonate. Hydrochloric acid will be utilized to re-solubilize the mixed rare earth carbonate to feed a solvent extraction phase with subsequent precipitation of various REE minerals. Heap leaching and subsequent separation process are expected to yield recoveries of 80 percent for yttrium, 76 percent for dysprosium, 65 percent for ytterbium, and 65 percent for lutetium.

A recent development for Round Top involves using continuous ion chromatography (CIC) to remove a majority of the lanthanum and cerium from pregnant leach solution. This is a K-Technologies procedure and is employed to remove low value REEs to reduce subsequent processing costs. This technology results in production of a "commercially marketable mid/heavy rare earth mixed concentrate." [Texas Rare Earth Resources announcement] After use of this procedure, lanthanum and cerium make up less than 8 percent of total rare earths present in the stream with the more valuable REEs comprising 68 percent of the product stream.

Additional information and details on the Round Top Project are available at the company website [http://tmrcorp.com/] and in the final version of the Preliminary Economic Assessment (PEA).

[Source: http://trer.com/_resources/pdf/TRER_NI43-101_PEA_FINAL_10Jan2014.pdf, "NI 43-101 Preliminary Economic Assessment Found Top Project," Sierra Blanca, Texas,

December 20, 2013]. Steenkampskraal [http://www.gwmg.ca/sites/default/files/VMD1445%20Steenkampskraal%20Project%2020%20June%20%20FINAL%20GWMG.pdf]

The processing plant includes a metallurgical plant and a hydrometallurgical plant. The metallurgical plant is comprised of a crushing plant, a concentrator plant, a dense media separation plant, a low intensity magnetic separation circuit, a wet high intensity magnetic separation unit and a milling circuit. The hydrometallurgical plant is comprised of acid cracking/baking, water leaching, double salt precipitation, solid/liquid separation, impurity extraction, reagent recovery and precipitation circuits producing a mixed REE carbonate product. The radiological risk mitigation for the thorium and uranium removal circuits within the plant is handled by incorporating areas of graded risk, high security areas, boundary walls, remote CCTB monitoring, dust suppression and remote control inspection. Radioactive material will be stored in an underground long term storage vault. Solvent extraction will be employed to process the concentrate.

Cost reduction features of the processing plant include a sulphuric acid production plant and a sodium sulphate regeneration circuit to address reagent cost.

UCORE-Bokan Mountain

Leaching Process

According to the UCORE Preliminary Economic Assessment of the Bokan Mountain Rare Earth Element Project, Near Ketchikan, Alaska, (January 10, 2013, Tetra Tech), the Bokan Mountain Rare Earth Element Project will be a 1,500 t/d underground operation. This project involves the Dotson Zone located on the southeast flank of the Bokan Mountain. This zone contains only minor amounts of uranium and thorium, while being enriched in REEs, as well as in niobium, yttrium, zirconium, hafnium, and tantalum.

The process plant comprises the following major circuits and their nominal process rates:

- Primary crushing (1,500 t/d)
- Secondary crushing (1,500 t/d)
- Screening to remove the minus 1/4" (6.3 mm) fraction
- X-ray mineralized material sorting (1,125 t/d)

- Tertiary crushing (750 t/d)
- Rod mill grinding (750 t/d)
- Magnetic separation (750 t/d)
- Tower mill re-grinding (375 t/d)
- Leaching (375 t/d)
- SPE (9.2 t/d)

The primary crushing facility will be located near the underground portal to minimize the haulage cycle time of the underground trucks. The majority of process equipment items will be located inside the process facility.

The material will be leached in two stages with nitric acid at 90 °C with an 8-hour retention. Nitric acid (HNO3) leaching is expected to result in 92.7 percent TREE + Y recovery. The slurry will then be filtered and washed and the solids sent to the paste backfill plant to be used as cemented backfill for filling mined out areas underground. The pregnant solution will be treated with diffusion dialysis to reclaim the unconsumed nitric acid to the leach circuit.

The pregnant solution will then be treated by SPE, which is a process developed by IntelliMet in conjunction with Ucore. The element separation process involves four progressive steps:

1. Removal of nuisance elements such as iron, uranium, thorium, and zirconium.
2. Segregation of elements first into impure element subclasses. An acetic acid stream is run through four progressive columns, which deplete the rare earths by subclass, and produces five outputs:
    - The first output contains the heavy rare earths terbium, dysprosium and heavier.
    - The second output contains samarium, europium and gadolinium (SEG) and yttrium.
    - The third output contains neodymium and praseodymium (didymium).
    - The final columns produce cerium and lanthanum.

- This leaves a stream containing calcium with nearly all of the rare earths removed.

3. Separation into purified element subclasses. Each of the four crude oxide products are dissolved in nitric acid to form metal nitrate salts, and are inserted into a series of individual column processes to refine the product. The goal of these steps is to segregate the mixed oxide products into fractions of appropriate content to enter the "element separation hubs."

4. Separation into individual elements. For this step, rare earth element hubs are fed into a ladder of columns to achieve individual element separation. The hubs include the following:

   - Dysprosium/Terbium Splitting Hub
   - Europium Purification Hub
   - Gadolinium/Samarium Splitting Hub
   - Neodymium/Praseodymium Splitting Hub
   - Cerium/Lanthanum Splitting Hub

Greater than 99.9 percent TREE + Y recovery is expected per IntelliMet metallurgical test work results. Additional details for the element separation process steps are in the PEA.

A simplified process flowsheet for the Bokan Mountain Rare Earth Element Project, obtained from the PEA, is shown in Figure 64.

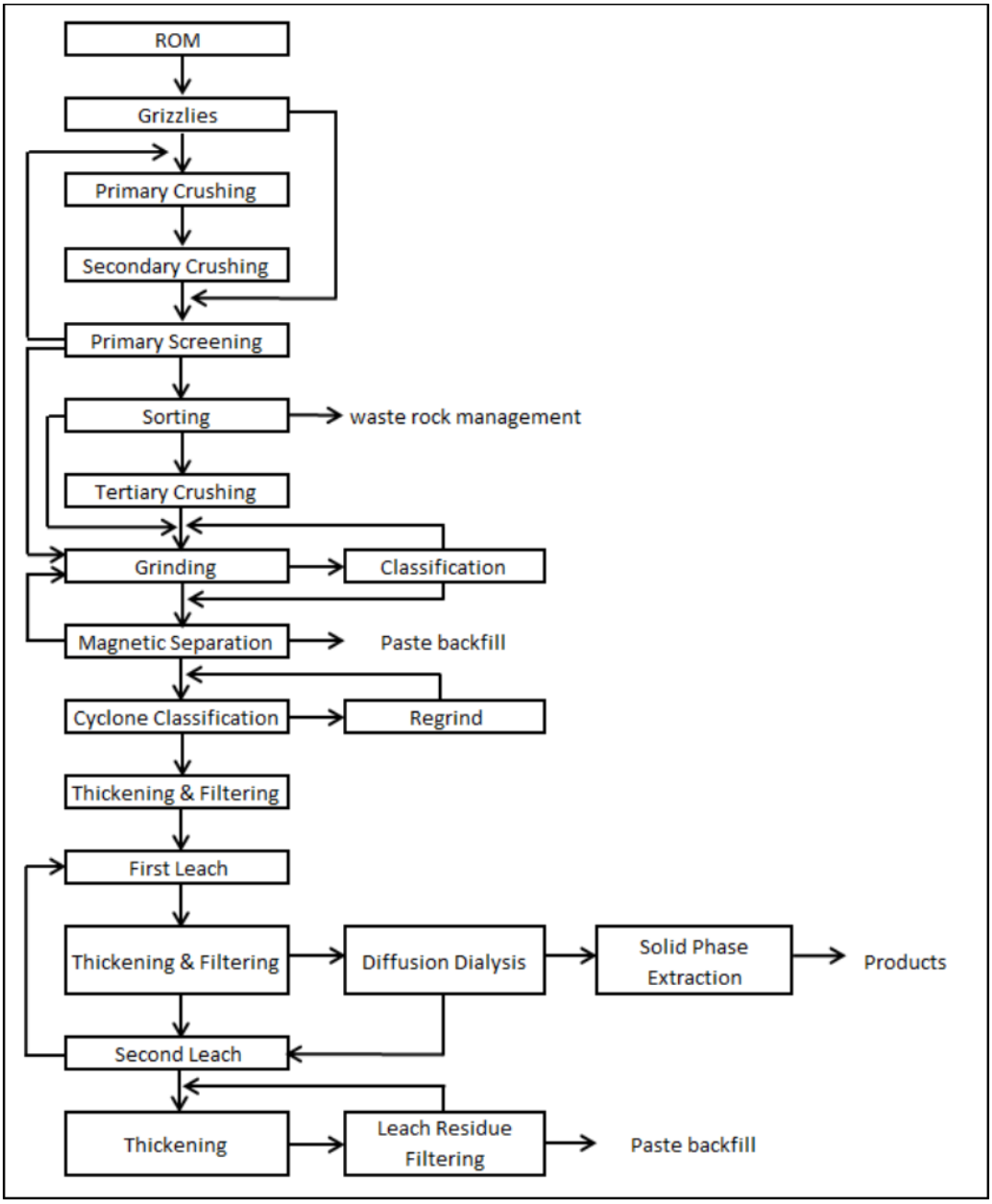


Figure 64. Bokan Mountain Simplified Process Flowsheet

Separation Process

A recent article in Nature, April 23, 2015, indicated that the Bokan project will likely switch to Molecular Recognition Technology (MRT) to separate individual REEs. The following text regarding Bokan is from an article in the April 23, 2015 issue of Nature:

"Some companies are adapting separation methods from other industries. "If they can cut the cost, they will be very competitive," says Lifton. At one deposit in Alaska, for example, Ucore Rare Metals of Bedford, Canada, has turned ore into gram-scale quantities of 99 percent-pure individual rare earth elements, using molecular recognition technology. Developed by the IBC Advanced Technologies in American Fork, Utah, this technique has been used industrially to remove bismuth impurities from copper, and to recover platinum-group metals from scrap catalytic converters.

In the Ucore system, a solution of mixed rare earths passes in sequence through 17 different columns, each loaded with a compound tailored to bind to a specific element. That element can then be extracted in 99 percent-pure form by rinsing the column with dilute acid. Ucore says that the process requires no more than a few repetitions, depending on the desired purity, and so has the potential to be both efficient and environmentally friendly. The company is working with IBC scientists to prove the technology at a pilot plant over the next few months."

Bear Lodge Critical Rare Earth Project

The most recent information on this project is found on an October 2015 factsheet. The Bear Lodge Project is located in northeast Wyoming. Per the factsheet, Bear Lodge has a high concentration of neodymium, dysprosium, europium, terbium, yttrium and praseodymium. These elements are projected to generate 80-85 percent of projected revenues. In October 2014, Rare Element Resources completed a preliminary feasibility study.
[http://www.rareelementresources.com/App_Themes/NI43101PreFeasibilityStudyReport/HTML/files/assets/common/downloads/publication.pdf#.V_e3Fk2a06Q].

The PFS was performed by Roche Engineering, Inc. Project strength includes a high-grade zone that accelerates cash flows and results in a 2.9-year payback period of initial capital. The project has a proprietary technology which features an innovative recovery process to

deliver a more than 99.9 percent pure, cerium-depleted, thorium-free rare earth concentrate.

Geology and mineralization [http://www.rareelementresources.com/bear-lodge-project/geology-and-mineralization#.VipbGCuVDLI]

The rare earth-bearing minerals at Bear Lodge are within carbonatites and are mainly ancylite and rare earth fluorocarbonates of the bastnasite group.

The Bear Lodge Project REE exploration activities focused on three carbonatite-related rare earth resource areas, the Bull Hill, Bull Hill NW, and Whitetail Ridge deposits, and two recently identified exploration target areas, Carbon and Taylor.

Per the PFS, the physical upgrading plant is designed to use a combination of crushing, screening and gravity separation, depending on the ore type being treated, to reduce the physical mass of the ore by reducing gangue and concentrating the rare earth-bearing fines for shipment to the Hydromet plant. The Bull Hill deposit contains varying proportions of weathered high-grade oxide and oxide-carbonate ores. Each of these ore types will have a different mass reduction and upgrade percentage in the Physical Upgrading (PUG) plant. On average, the PUG recovery is expected to be 92.8 percent in years 1-9 and 87.9 percent over the life of mine (LOM). The mineral pre-concentrate produced at the PUG will be transported by covered truck to the Hydromet plant in Upton.

The Hydromet plant is designed to process the pre-concentrate through acid leaching followed by the Company's proprietary recovery technology. This process uses a chloride solution to extract the REE into a liquid, and then uses oxalate reagents to facilitate the selective precipitation of the REE. The benefits of this process are that it achieves a high-purity, near thorium-free, bulk TREO concentrate and has the ability to regenerate and recycle a majority of the water and reagents used in the process. The tailings produced from the processing will be neutralized, dewatered and stored in an engineered, double-lined tailings storage facility.

In years 1-9 of mine life, mined ore will be crushed and screened for direct processing with application of gravity and magnetic separators. The ore will be stage-crushed and screened at a cut-off size of 3 inches. A set of cone and roll crushers will be installed at Upton to reduce the ore from minus 3 inch to 100$ passing—48 mesh mineral pre-concentrate. In years 10-45, the crushing plant will be modified by adding beneficiation units to upgrade

the ore by gravity and magnetic separation. The PUG process produces a mineral concentrate rich in rare earth (RE) minerals. Subsequently, at the hydromet plant the mineral concentrated are leached in hot chloride solution to extract rare earths, thorium, uranium and significant amounts of base metals. The rare earth metals plus thorium are selectively precipitated from the pregnant leach solution (PLS) using oxalic acid while all the base metals, including uranium, remain in the barren PLS. Rare earth oxalate precipitates are dried and roasted to produce a =97 percent pure mixed REO powder.

Bulk REO powder or RE carbonate solids are dissolved in nitric acid to generate a bulk RE nitrate solution containing thorium that serves as feed to the thorium extraction plant. A double hydroxylation process applied to extract thorium selective from RE nitrates. The thorium hydroxide residue is contained and transported to a third-party disposal facility while the pure RE nitrate solution is subjected to a final precipitation process to produce RE hydroxide solids. The RE hydroxide cake is dried and calcined at moderate temperature to produce a marketable +97 percent mixed REO powder.

The barren PLS is a source of significant amounts of reagents (free hydrochloric and oxalic acid), water and base metals. There, a distillation process is applied to recover water and hydrochloric acid at atmospheric pressure. Residual solution from a distillation column is pumped through a chiller to crystalize and recover unreacted oxalic acid.

The metal-rich liquor from the distillation column is neutralized with limerock and small amounts of quicklime to produce a mixed base metal hydroxide cake. The cake is then mixed with the leach residue, dewatered and transported to the double lined tailing storage facility.

The filtrate is passed through a chiller to crystalize calcium as CaCl2 crystals with smaller amounts of NaCl crystals. The final filtrate, with few metal ions, is recycled to the distillation column for water recovery. The metallurgical plant is designed to run without effluent discharge to the environments.

Additional information and flowsheets are available in the PFS.

Alternate Separation Process

A new process was proposed to recover rare earths from nitric acid leaching of apatite without interfering with the normal route for (phosphate) fertilizer production using solvent

extraction with dimethyl heptyl methyl phosphonate CH3P(O)(OC8H17)2 (P350, B). In the present work, the leaching conditions are studied. In selected condition, apatite was dissolved in 20 percent (v/v) nitric acid solution at 60-70 °C while agitating. The most suitable acidity for extraction is 0.4M HNO3. More than 98 percent of rare earths in apatite can be recovered using countercurrent extraction process with six stages when the phase ratio is equal to 0.5. The influences of phase ratio, stage number, acidity and salting-out agent on extractabilities of P350 are studied. The results show that rare earths can be separated with P350 from Ca, P, Fe and other impurities. Mixed rare earth oxides (REO) with a purity of more than 95 percent are capable of a yield over 98 percent.

Environment friendly approaches for rare earth separation have been developed recently. One of these approaches used rare earth carbonates to control the equilibrium acidity during the rare earth loading with 2-ethylhexyl phosphoric acid mono 2-ethylhexyl ester [HEH(EHP)] in a chloride system. This approach is free from environmental pollution because no saponification reagent is introduced. Liao et al introduced a hyperlink extraction technology where a potential process was proposed for clean separation of RE. In conventional RE separation processes, relatively great amounts of acid, base and water are consumed to dissolve raw material and extract REEs.

5.2.2 Critical Areas for Process Improvement

The separation and processing of REE products from concentrated materials are carried out by very few companies, worldwide, and are poorly integrated with the upstream mining operations. Some of them are: AMR Technologies Inc.(Canada), the most important RE downstream joint-operator in China; Inner Mongolia HEFA Rare Earth Science & Technology Development, Gansu Rare Earth Corp., Xinwei Group, Magnequench and Yue Long Non-ferrous Metal (China); Rhodia Electronics and Catalysts (France), that collaborates with similar companies in China, US and Japan; Grace Davison and Santoku America(USA); Shin-Etsu and Anan Kasei (Japan); TreibacherIndustrie AG (Austria); AS Silmet (Estonia). Most of these producers are specialized in magnets and catalysts.

Major deposits scheduled to commence production in the near future, such as the Nechalacho deposit in the Northwest Territories (Canada) and Kvanefjeld (Greenland) will involve minerals and ore compositions that have never been successfully processed and a great deal of industrial and academic research will be required to quickly bridge this knowledge gap. Common minerals have been investigated extensively and there are

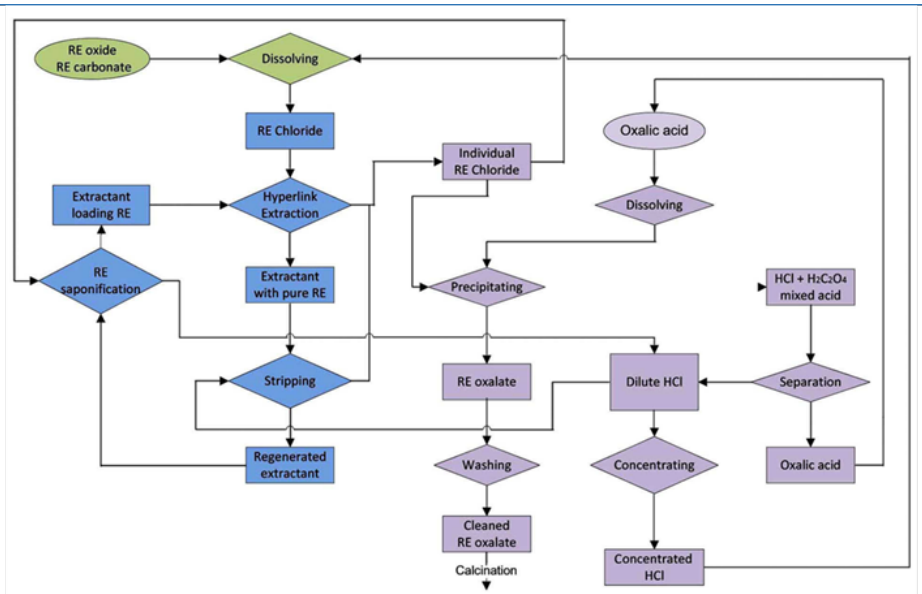
numerous published works on aspects such as interaction with collectors, effects of depressants, and magnetic properties. This type of knowledge base does not exist for many of the REE minerals and is essential for the successful processing of REE bearing minerals.

The hyperlink extraction technology was proposed to reduce the consumption of acid and base during the extraction process by incorporating measures to enable recycling and reuse of the consumables. More specifically, the hyperlink extraction technology incorporated an integral hyperlink process in which the intermediate acid was recycled and reused after being treated as shown in Figure 65 below.

The process makes it feasible to consume no chemicals except for oxalic acid, and has potential to be a promising clean separation technology with a significant reduction on consumables and emissions.

As shown in Figure 66 the hyperlink process shows a significant reduction in the amounts of base, acid, and water needed to process RE oxide.

Kumar et al investigated solid-phase extraction on a mixture containing seven heavy rare-earths (HREs) such as terbium (Tb), dysprosium (Dy), holmium (Ho), yttrium (Y), erbium (Er), ytterbium (Yb), and lutetium (Lu) from phosphoric acid solutions using Tulsion CH-96, a macroporous bifunctional phosphinic acid resin and T-PAR resin, a phosphoric acid resin. The key parameters included time, H_3PO_4 concentration, ratio of volume of aqueous phase to mass of resin, metal concentration, and temperature. The effect of H_3PO_4 concentration from 0.5 to 5M in the aqueous phase containing 25 mg/L of each metal using Tulsion CH-96 indicated that the percent extraction of metals decreases with an increase in acid concentration at any given mass of resin.



- Compared to conventional separation techniques, the Hyperlink process requires less base, acid, and water to process RE oxide
- Oxalic acid is used to co-precipitate yttrium (≥99.999%) with other elements, i.e., Eu, Tb, and Zr.**

Figure 65. Integral Hyperlink Process for REE Separation

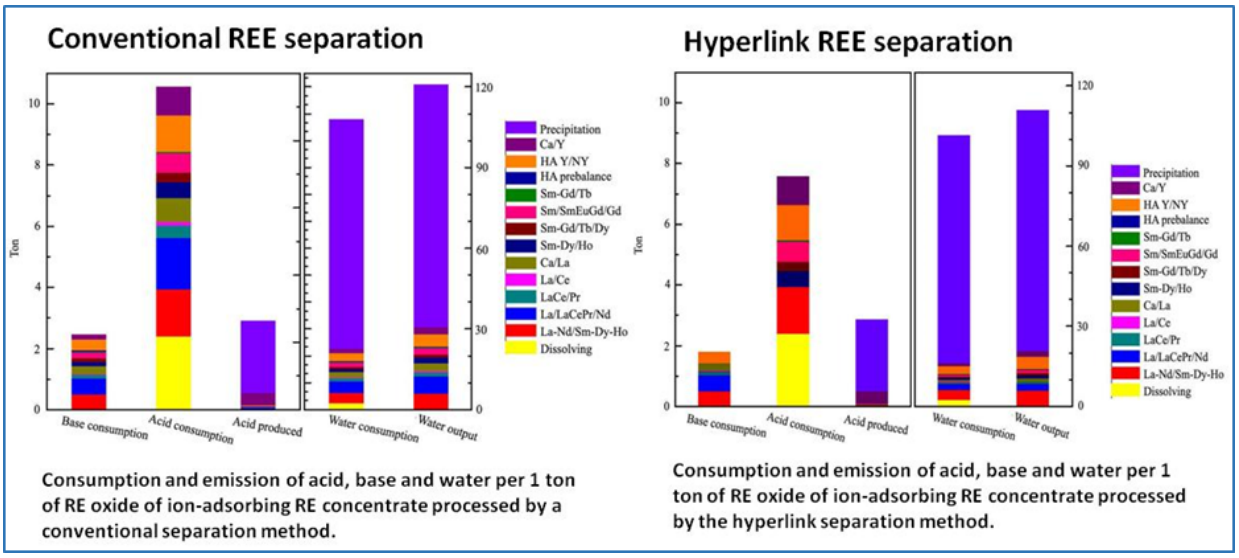


Figure 66. Comparison of Conventional and Hyperlink REE Separation Processes

Recent studies for solvent extraction of lanthanoids (REEs) have consisted of comparisons of the effectiveness of mixtures of chelating extractants such as HTTA, HP, and diphenylsulphoxide. Findings showed that the separation of the REEs with synergistic mixtures was typically a little higher than those obtained using HTTA or HP alone.

The pre-concentration of rare earth elements in Saghand ore are dealt with using a Humphrey spiral using an orthogonal optimization method after scrubbing the sample at 45 percent solid pulp density for 30 minutes. This pulp was diluted and input to the Humphrey spiral for upgrading. Process parameters included feed size, feed solids and feed rate, and Taguchi's L9 (34) orthogonal array (OA) was selected for process optimization. The feed rate and feed size were more significant than the other operational parameters of the process. It was also found that under optimal conditions, the concentrate grade of rare earth elements increased from 2,860 ppm to 6,050 ppm and recovery reached up to 58 percent.

More research has also been recommended to reduce the amount of organic solvents needed during solvent extraction. "Another limitation in traditional solvent extraction is that large volumes of organic solvents are needed, especially when processing dilute solutions, which is not environmentally friendly. Further, the method can be tedious and time-consuming in those cases when many steps are needed to reach a sufficient separation. Another drawback is that the method is difficult to automate and that the liquid phases may form emulsions that at times make it difficult to separate the two phases."

The liquid emulsion membrane (LEM) extraction technique has the potential to offer many attractive features compared to liquid-liquid extraction (LLE). For example, it can reduce the amount of expensive extractant about 10 times. More research is needed to develop the LEM technique before large-scale and widespread application in industry. Some of the areas requiring further study include emulsion stability and osmotic swelling.

Proprietary separations technologies are being developed to reduce REE processing costs. One such separation technology has been developed by Rare Earth Salts, a privately held company claims that its low-cost process could help producers compete with Chinese rare earths pricing. Rare Earth Salts believes that its process is environmentally friendly and will cost below $4 per kilogram. Allen Kruse, CEO of Rare Earth Salts, has said he thinks the technology is "the missing piece to the industry being successful in the Western World once again." Rare Earth Salts claims to have defined a path to near-term production, and has

commenced testing the flows and scalability of its proprietary separations technology. Those tests will facilitate the engineering and construction of a commercial production facility in Southeastern Nebraska, with the plant slated to process 10 tons of rare earths concentrate per month. Rare Earth Salts is seeing support for its process. The company signed a joint development agreement with one of the 10 largest mining companies in the world for the phased development of its plant. The company has reported it is in talks with several juniors from South America, Europe, North America and Australia. Kruse has not divulged much about how the process actually works. The process doesn't produce a hazardous waste stream as all material used in the process is recovered, recycled or removed. In addition, equipment for the process is readily available and has been industrially proven across multiple sectors. It's faster than traditional solvent extraction, and has so far resulted in purities of more than 99.995 percent. The technology is efficient for different types of rare earths concentrates and is not chemically dependent on a set type of concentrate makeup.

Another company with a recent REE separation's patent is Orbite Technologies. As quoted in a press release, the company has been notified that Patent application No. 14/005,885 titled "Processes for Recovering Rare Earth Elements from Aluminum-Bearing Materials" has been found allowable by the United States Patent and Trademark Office ("USPTO"). Per Orbite CEO, Glen Kelly, this patent contains a proprietary technology which enables the selective extraction of valuable components from a variety of feedstocks, such as red mud, fly ash and aluminous clay.

["Orbite Technologies Receives Patent From IP Australia," October 28, 2015, http://investingnews.com/daily/resource-investing/critical-metals-investing/rare-earth-investing/orbite-technologies-receives-patent-from-ip-australia/]

Continued developments to improve processing technologies is a key aspect of projects that are currently active. The following discussion compares process development efforts and the associated cost projections for two major developments in the United States (Bear Lodge and Bokan Mountain). Solvent extraction (SX) technology is widely used to separate REEs from ore to produce REE concentrate. SX is also utilized in the important subsequent step of separating individual REEs from REE concentrate. The SX technology is capable of achieving an efficiency of ≈70–80 percent in producing REE concentrate from ore. The balance of the concentrate (≈30–20 percent) contains impurities which contribute to higher CAPEX and OPEX for processing plants. Impurities removed from processing must be

disposed of and contribute to environmental issues and make permitting of processing plants complex. Ideally, generation of REE concentrate with higher REE composition and reduced impurities would serve to reduce CAPEX and OPEX of REE processing plants.

MRT is an important alternative to solvent extraction based methods of REE concentration and separation. SX is more costly, slower and environmentally invasive than MRT. SX has lower recovery rates and low metal selectivity. This requires many stages for effective separations and requires more expenditure of reagents, time, space, and labor. MRT does not require the use of solvents or pernicious chemicals. Elimination of solvents is supports green chemistry because they often account for the vast majority of mass wasted in chemical syntheses and processes. Many solvents are also toxic, flammable, and/or corrosive. Although they can be recovered in some processes, the recovery systems can require energy-intensive distillation and sometimes cross contamination. For REE processing, MRT design principles are used to design ligands needed for highly selective interactions with the individual rare earth metals. During operation, the tailored ligands remain attached by chemical bonds to silica gel and are used repeatedly without degradation. The MRT process uses minimal energy and relatively low amounts of water. MRT plant size is kept small since metal selectivity is high and reduces the number of stages required to achieve specified purity levels. MRT is highly selective and produces a clean concentrate. Clean is important as it means that the produced concentrate is free of radioactive elements and free of commonly produced elements that interfere with traditional solvent extraction separation such as Aluminum (Al), Iron (Fe), and fluoride.

Additional work was performed to separate individual REEs from the 99 percent+ REE concentrate. On March 2, 2015, (Press release, Mar 2, 2015. Molecular Recognition Technology: Environmentally Friendly, Cost Efficient Separation of Each Individual Rare Earth Element) a press release announced that separation of each individual REE at >99 percent purity with the exception of SM and Gd which had been separated as a pair. On April 28, 2015, (Press release, April 28, 2015. Ucore Updates on the Separation of Individual Rare Earth Elements) another press release announced the successful separation of Sm and Gd from the combined pair at the >99 percent level.

Comparison of Costs for a Conventional SX REE Project versus a MRT Separation REE Project

Bokan capital cost is estimated at $221.2 million and is separated into direct and indirect capital costs. Direct capital is estimated to be $134.7 million and indirect capital is

estimated at $86.5 million, with an accuracy range of +/-35 percent. The estimate includes provisions for both the mining and mineral process. Infrastructure and project facilities include the process plant, ancillary buildings and accommodations, roadways, material conveyance, tailings and waste management facilities and related site development.

Bokan operating costs for the mine and processing over the LOM is estimated at $636 million which equates to $122.78/t mined. The breakdown of operating costs is shown in Table 17 below.

CAPEX and OPEX for the Bear Lodge and Bokan REE projects are compared in Table 17 below.

Table 17. Comparison of CAPEX and OPEX for the Bear Lodge and Bokan REE Projects

REE Projects	Bear Lodge (Proprietary Technology)	Bokan (MRT Project)	
Processing Facility (PUG)	Capital Costs ($)	Capital Costs ($)	
Mill Building		7,981,333	
Crushing (Bokan: 1500 t/d)		391,196	
Grinding		11,653,969	
Leaching (Bokan: 375 t/d)		32,142,697	
Recovery		6,817,371	
Miscellaneous		3,932,915	
PUG Total Cost	44,800,000	62,919,481	
Hydromet Cost	122,075,000	Na	
Hydromet& tailings storage	147,000,000		
	Bear Lodge Operating Costs (LOM)	Bokan Operating Costs	
	Cost/Ton Ore Processed ($)	Average Unit Cost ($/t mined)	Total LOM Cost ($ million)

Mining	42.98	41.69	216.0
Processing	21.56	54.83	284.0
G&A	19.71 (includes road maintenance)	13.56	70.2
Power		111.78	61.0
Miscellaneous		0.93	4.8
Total Cost		122.78	636.0
Hydromet	212.68 (includes tailings storage)	NA	

The capital costs are based on typical process requirements for process REE-bearing material in crushing, grinding, x-ray and magnetic sorting circuits of an equivalent model for a 1,500 td operation. The estimate includes a hydrometallurgical circuit utilizing nitric acid leaching with a 375 t/d leaching circuit. The total mine operating costs is estimated at $215,700,000 which equates to $41.69/t of material mined or $166.74/t of material leached.

Table 18. Comparison of Some Key Cost Factors for Two Pending U.S.Projects

Attribute	Bear Lodge Proprietary Technology	Bokan	Bokan
Processing Facility (PUG) Operating Cost - Area		Total annual Operating Cost During Full Production ($)	Average Unit Cost ($/t mined)
Process labor		3,709,508	6.87
Process Supplies		12,216,000	22.62

G&A Labor		1,302,075	2.14
G&A Supplies		6,020,775	11.15
Power Supply		6,358,902	11.78
Total Cost	4,470,000	**29,607,332**	**54.83**
Hyrdomet Operating Cost Estimate Summary	Year 1, $/t	Areas of Potential Savings due to MRT	
Reagents	5,000	Reusable and fewer processing stages and higher recovery rates	
Labor Cost	590	Lower due to less equipment and handling of supplies	
Energy Cost	920	Less Equipment	
Thorium Disposal Cost	140	Extracted during Initial Processing by MRT	
Maintenance Supplies	340	Less supplies to maintain	

		less equipment	
Water Treatment Chemicals	10	Reduced due to recycling	
Misc Other processing	20	Lower due to less equipment and lower personnel requirements	
Total	7,020	% lower than another technology would be a gestimate	

Reagents and Supplies for Bokan

The nitric acid and supply types and consumptions are based on the requirements for 375 t/d operations of the leaching circuit. The total costs for reagents and supplies are $12.2 million per year or $101.46t.

Mineral Processing

The REE processing facility to treat 1,500 t/d of mined material was designed based on the results of the metallurgical test programs conducted at Commodas, Hazen and IntelliMet.

The process design includes primary and secondary crushing, screening, DEXRT sorting and magnetic separation circuits, as well and tertiary crushing, a rod mill and a tower mill grinding circuits.

A leaching circuit will produce an upgraded concentrate for further treatment, with the waste sent to the paste backfill plant to be used as cemented backfill for filling mined out areas underground.

A solid phase extraction circuit will separate the bulk REE concentrate into individual REOs as sellable products. For Bokan, the solid phase extraction technique will be molecular recognition technology (MRT) which involves macrocyclic ligands immobilized on a silica or polymer support. (ref. 5-15, 5-16, 5-17)

5.3 OVERVIEW OF COAL AND OTHER WASTE PROCESSING (ADVANCED REE SEPARATION/EXTRACTION TECHNOLOGY)

A coal preparation plant (CPP) is a facility that upgrades coal through a washing process to remove ash and other impurities. The coal can then be crushed into graded sized chunks, and various grades can be stockpiled for subsequent shipping to market. The CPP is also referred to as a coal handling and preparation plant (CHPP), coal handling plant, coal beneficiation plant, prep plant, tipple, or wash plant. Removal of waste materials from coal increases its market value and lowers transportation costs. Coal processing is performed according to the specific coal being cleaned, the coal market, and the mining operation. The United States currently employs 288 coal preparation plants to beneficiate coal according to Coal Age's 2013 Prep Plant Census. Two new coal preparation plants were constructed in the United States during 2013. One of these plants, the Bishop coal preparation plant, is designed to process 600 tons/hour (14,400 tpa). It is a heavy-media plant with primary separation using large-diameter cyclones (>30"). Fine coal is processed by froth flotation and spirals. Other plant features include centrifugal dryers and a programmable logic controller. Figure 67 shows a generic flow sheet for a coal preparation plant.

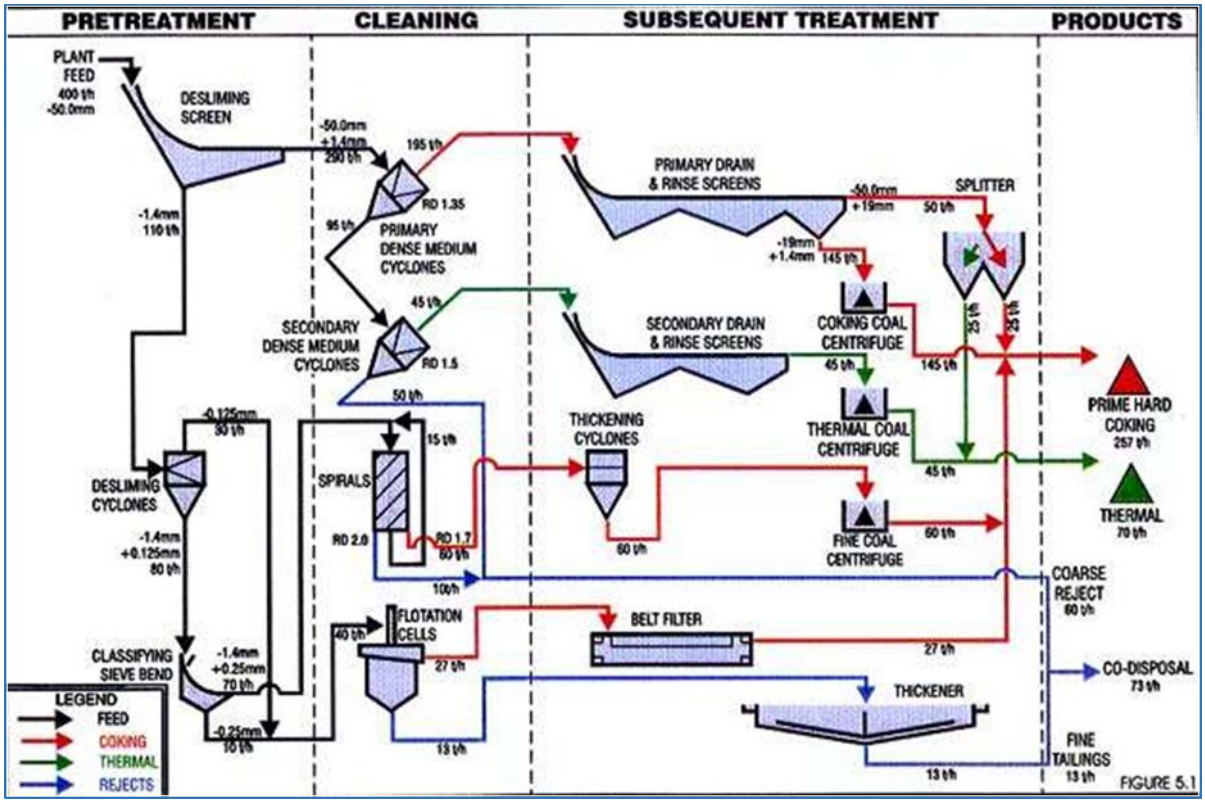


Figure 67. Coal Preparation Plant Flow Sheet
http://www.mine-engineer.com/mining/coal/coalflow.htm

The plant consists of a number of operations including crushing, screening, gravity separations, flotation, dewatering and thickening. Pre-combustion removal of trace elements and minor constituents can be accomplished through coal preparation. Coal cleaning decreases the amount of mineral matter in the cleaned, product coal. The rejected mineral matter is generally higher in minor and trace minerals found in the raw coal although not all trace minerals preferentially concentrate in the refuse streams. Many trace and minor elements are concentrated in and removed from the higher specific-gravity fractions during coal preparation. Data collected from coal preparation plants and from laboratory studies has shown that the majority of trace elements in several commercial coals are associated with mineral matter and not the organic coal matter.

Coal Beneficiation Process Details

Current commercial coal cleaning methods are commonly based on physical separation (density separation) with equipment such as jigs, mineral spirals, concentrating tables, hydrocyclones, and heavy media separators. In the density based processes, coal particles are introduced to a liquid medium in the physical separation equipment. Depending upon the separation equipment, gravity or centrifugal forces separate the organic-rich (float) phase from the mineral-rich (sink) phase. The mineral portion of the coal is approximately 2 to 4 times heavier than the organic portion of the coal.

In flotation equipment, surface properties of coal are exploited. The flotation process takes advantage of surface-property characteristics for fine coal cleaning through addition of water mixed with a collector reagent to increase the hydrophobicity of surfaces. Air bubbles in the flotation device (froth or column flotation) carry the coal particles to the top of the slurry and separate from the hydrophilic mineral particles.

The coal preparation plant flowsheet below in Figure 68 identifies three potential connection locations for an add-on REE processing system.

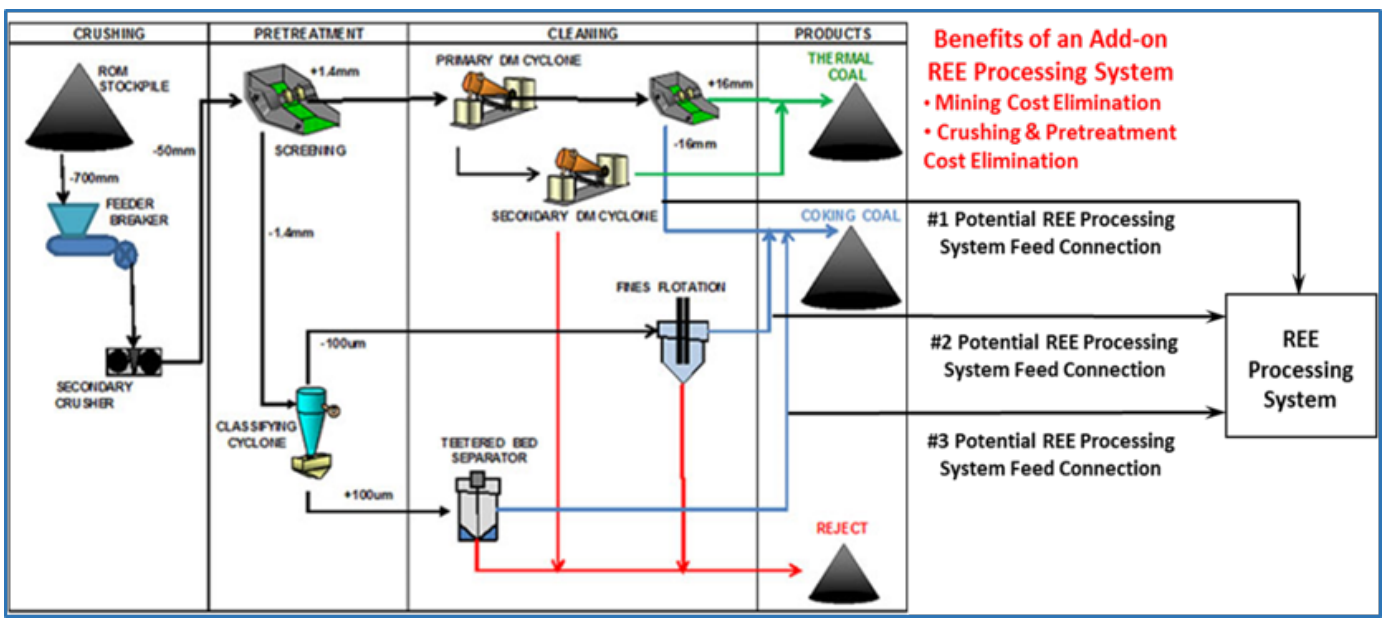


Figure 68. Potential "Clean Coal" REE Process Connections

5.3.1 Process-Specific Data on Reagents Potentially Useful for Creating Concentrates

Collectors, frothers, modifiers, activators, and depressants are flotation reagents utilized for flotation. Consumable reagents are used to increase the stability of mineralized froth, and allow for air dispersion and the formation of bubbles (frothing reagents); increase the natural hydrophobicity of a mineral surface, and increase the separability of the hydrophilic and hydrophobic particles (collectors). The source material being processed may use different combinations of reagents in varying dosages. The optimum dosage for coal flotation depends on the coal hydrophobicity, surface area, degree of surface oxidation, pulp density, and type of flotation machines. Bituminous coals are very hydrophobic as compared to lignite coals. Reagents used in froth flotation for coal are primarily frothers and collectors. The frothers serve to facilitate the production of a stable froth.

The frother chemical reduces the surface tension of water. Methyl isobutyl carbinol (MIBC) is commonly used as a frother for coal flotation. A collector is used to promote contact between coal particles and air bubbles by forming a thin coating over the particles to be floated to make the particle water-repellent. The collector is carefully chosen to be selective in the particles requiring coating while not coating tailing particles and others not desired to be floated. A common collector for coal flotation is fuel oil. The following Table 19 is based on information from Orica, a reagent supplier. It contains a listing of commercially available reagents utilized in the mining industry. Collectors make the mineral surface hydrophobic so the particles will attach to air bubbles on collision and float. Frothers float minerals to the launder while allowing gangue minerals to drain back down into the pulp and out to the tail. The specific reagent(s) applicable to a particular process is dependent on the source material being processed and the intent of separation at the specific step in the process.

Separation of elements with similar characteristics requires multiple processing steps with different reagents. Orica offers a “Mining Chemicals Guide Book” to its customers in order to assist in the selection and use of mineral processing chemicals. In addition to the off-the-shelf chemicals, Orica also offers tailor-made products. Optimization of processing techniques often requires experience and technical assistance from chemical manufacturers who typically have personnel knowledgeable in various types of mineralogy through extraction of specific elements with appropriate processing equipment and

techniques. Extensive laboratory testing and on-site trials may also be necessary to achieve optimum recovery of target elements with appropriate reagents.

Table 19. Reagents Utilized in the Mining Industry

Flotation Reagents (Orica, 2014)				
Collectors	Frothers	Modifiers	Activators	Depressants
Xanthates	MIBC	Lime	Copper Sulphate	SMBS
Dithiophosphates	DSF Specialty Range	Soda Ash	Sodium Hydrosulphide	Sodium Hydrosulphide
Thionocarbamates		Caustic Soda	Sodium Sulphide	Sodium Sulphide
DSP Specialty Range				CMC
Specialty Oxide Reagents				Dextrin, Guar Gum

[http://www.orica.com/Products---Services/Mining-Chemicals/Products/Flotation-Reagents#.UyGyTbSTIxE]

Brief Discussion of Other Waste Resources

A study has recently identified a significant source of REEs in the apatite containing tailings of the Chadormalu iron ore concentrator in Iran.

Apatites are an important mineral for the phosphate industry, and the flotation of this class of mineral is well-established using fatty acid collector systems. Due to the similar chemical nature of common gangue minerals such as calcite and fluorite, fatty acids such as sodium oleate will preferentially adsorb onto these gangue minerals instead of apatite. Apatite from the Kola Peninsula in Russia has been successfully recovered via flotation using a tall oil

collector and sodium silicate as a gangue depressant. After six flotation stages (one rougher, two scavenger and three cleaner stages), the resultant concentrate grade was 94.8 percent apatite with a 94 percent phosphate recovery.

Beach or black sand placer deposits may be the most important candidates for monazite extraction. These deposits are typically concentrated via initial high-capacity gravity separation steps, to take advantage of the high specific gravity (monazite has a specific gravity greater than 5) while the typical gangue minerals in these deposits have specific gravities less than 3.5), followed by additional gravity, magnetic, electrostatic, and occasionally flotation separation steps. Indian Rare Earths has been mining and separating heavy minerals like ilmenite, rutile, zircon, silimanite, garnet and monazite from beach sands.

5.3.2 Alternative Paths to REE Extraction

In Figure 69 below, a detector employs X-ray imaging to separate fine particles of REE bearing minerals. The detectors planned for the Bokan Rare Earth project are shown to the right of the X-ray images. The lower image in the figure shows a schematic of the design of the ore sorter circuit where the higher REE particles are separated from the lower REE particles.

Aside from development of processing technology specific to extracting REEs from the core mineral ore body, as can be seen in the material available for a number of the promising REE ventures, new mining technology is available to further enhance physical separations. The device shown below is commercially available. It is designed to use a powerful, isotope-based, XRF device to identify which particles contain levels of REE that would justify separating them from the other particles so that they can be processed to extract the REEs.

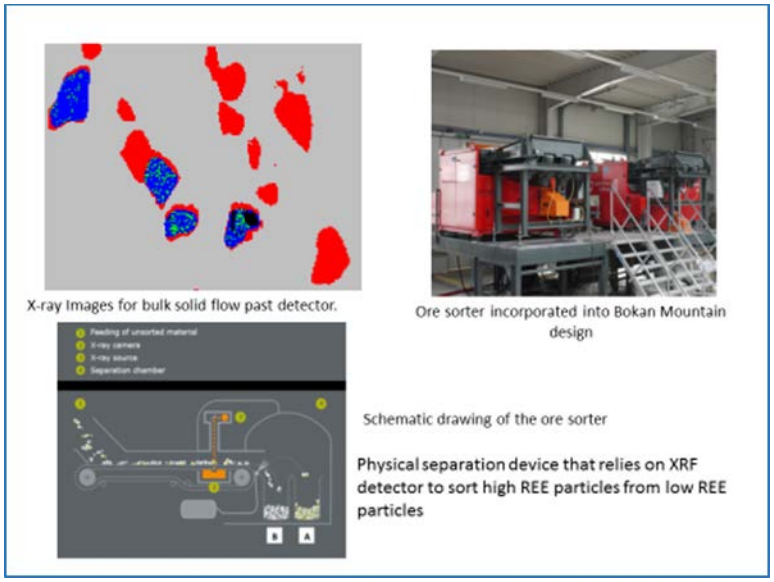


Figure 69. Alternative Paths to REE Separation

Apatite can occur in forms that make it another potential source of REE. Some examples of REE-rich apatite deposits include: Kola and Kovdor in Russia, Palfos in South Africa as well as sedimentary deposits in Jordan and Morocco.

5.3.3 Pathways to Separate Other Rare/Precious Metals or Critical Energy Elements from Coal

Table 20 below identifies several separation technologies applicable to fly ash. Cyclone separation of fly ash has the ability to separate particle sizes down to approximately 10 µm. Fly ash being processed for REEs will need analyzed to determine the size of the REE bearing mineral(s) to determine applicability of this technology. Likewise, if REE bearing mineral(s) are in the 1-3 µm or submicron size range, milling would be required along with and an energy cost processing penalty. However, byproducts with submicron size can be sold for nano-composite use at relatively high prices. Byproducts in the 1-3 µm size range can be used as fillers for polymer and coating applications.

Table 20. Separation Technologies for Fly Ash

Source	Method/Process	Comments
Kashiwakura, 2013	Dissolution	Dilute H_2SO_4 solvent
Separation Technologies LLC, 2008	Electrostatic	Removes unburned carbon
Dong, 2013	Cyclone Separation	Lowest particle size is about 10 µm
Dong, 2013	Milling	1-3 µm or submicron sizes; requires significant energy
Dong, 2013	Screen Mesh	25 µm (500 mesh)
http://www.scientific.net/MSF.70-72.279	Magnetic Separation	
http://www.ecplaza.net/trade-leads-seller/spiral-concentrator--6924348.html	Gravity Separation	Spiral concentrator, BL1500 Concentrator, max capability of slurry is 25m³/h, the capacity is 8≈12 MT per hour.
http://www.kmml.com/php/popup.html Kerala Minerals and Metals Ltd	Magnetic Separation	A Mineral Separation Unit (MS Unit) employs Gravitational, Magnetic and High Tension Electrostatic Techniques for separation of minerals (Ilmenite, Rutile, Leucoxene, Monazite, Silliminite, etc.) from

		sand. Excluding +60 mesh material, monazite is found to be 8 percent of the bulk of black sands.

Separation Technologies LLC has a proprietary separation process (proash.com, 2014) to electrostatically process high carbon fly ash to a 2 percent LOI (Loss on Ignition, or unburned carbon content) product. The advantages of the process include:

- Low power operation, consuming 1-2 kWh for each processed ton
- Production of a high carbon product that can be readily reburned
- Each separator can process up to 40 tons of fly ash per hour
- Dry technology

The electrostatic process may have potential to separate REE bearing minerals from fly ash (may also have potential for fine coal-need further research). The Separation Technologies (ST) LLC website contains an "Applications" page (http://www.stminerals.com/applications) which states in part "the ST technology can be applied to any dry mixture of materials as long as:

- It is composed of discrete particles
- There are differences in surface chemistry among the materials
- The mineral phases are liberated from each other, either naturally, or through grinding

Demonstrated applications of the process included potash (halite), talc (magnesite), limestone (quartz), brucite (quartz), iron oxide (silica), wollasionite (quartz), and carbon (silica). Other potential applications include phosphate, zircon, fluorite which may indicate potential applicability to REE bearing minerals.

The potential application of molecular recognition technology (MRT) to separations involving the recovery of rare earth metals and Li from low-level waste solutions and end-

of-life products has been identified as another topic worth investigation. MRT products are produced by "IBC Advanced Technologies, Inc." and discuss applications on their website: http://www.ibcmrt.com/products/superlig/.

Selected text from the website includes the following: "MRT plants using SuperLig® are used to extract, recover, and/or refine kilogram to multi-ton quantities of purified metals from a variety of primary and secondary feed sources and waste streams. For example, MRT is used worldwide for the refining of precious metals. The greater efficiency of the SuperLig® technology in the refining and recycling of precious metals reduces the need for obtaining new metals by mining and replaces processing steps in conventional metal refining processes that consume excess energy and pollute the environment. The MRT process has a very low carbon footprint since the operations are carried out at ambient temperatures and pressures. Impala Platinum (South Africa), one of the world's largest platinum group metals mining companies, uses MRT to refine its palladium, a critical component in auto catalysts and industrial processes. IBC's SuperLig® products also have the capability to commercially refine and/or recover base, specialty and minor metals including Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Molybdenum (Mo), Rhenium (Re), Uranium (U), rare earths, and others. SuperLig® products are also used to extract impurities, such as Bismuth (Bi), Iron (Fe), Lead (Pb), Antimony (Sb), Cadmium (Cd), Copper (Cu), Nickel (Ni), Scandium (Sc), Fluorine (F) and Chlorine (Cl), from process streams that adversely impact product quality or the environment. SuperLig® products are effective in process waste streams in recovering and/or removing to very low concentration levels (mg/L to µg/L) toxic metals and radionuclides such as Arsenic (As), Cadmium (Cd), Mercury (Hg), Lead (Pb), Thallium (Tl), Caesium (Cs), Strontium (Sr), Radium (Ra) and Technetium (Tc). SuperLig® products have important applications in recycling valuable metals such as Palladium (Pd), Platinum (Pt), Rhodium (Rh), Iridium (Ir), Ruthenium (Ru), Gold (Au), Cobalt (Co), Nickel (Ni), Indium (In), rare earths, Yttrium (Y), Vanadium (V), Rhenium (Re) etc. from spent catalysts, electronic scrap, and a wide range of end-of-life products." MRT has potential to be added to coal preparation plant circuits in order to separate rare earth elements and other metals from tailings or selected in-line streams. This type of application of the technology may enhance the quality of the coal preparation plant products and/or reduce the amount of impurities and metals in the plant tailings.

5.3.4 Critical Areas for Process Improvement

For coal processing, the National Commission on Energy Policy report identified several broad categories: Recommendations that may lead to these improvements include: (1) development of improved technologies for solid-solid and solid-liquid separations that impact coal productivity and waste reduction; (2) development of new and improved methods for online analysis of coal quality and plant optimization; (3) development of next-generation upgrading systems, including mild conversion processes, that are suitable for improving the quality of western coals in water scarce regions; (4) streamlining of permitting protocols for facilities designed to recover coal and reclaim abandoned refuse and impoundment areas; (5) support for expanding and updating the database of cleanability data for U.S. coal reserves; and (6) support for training and education of a balanced workforce of laborers, technicians, and professionals capable of running sophisticated plant processes. In particular:

TECHNICAL ISSUES

(a) Fine Coal Cleaning:

Run-of-mine coals that are fed to coal preparation plants are typically crushed to liberate rock before washing and to limit the size of particles that enter the plant. Operators prefer to keep particle top size as large as possible (e.g., greater than 50 mm) because fine coal processes are considerably less efficient and substantially more costly. Size reduction improves liberation by reducing the population of intermixed composite particles of coal and rock. Although a systematic assessment has not been performed to date for trace elements, size reduction would also be expected to substantially improve the removal of coal-related pollutants other than just ash and sulfur. Unfortunately, inefficiencies associated with existing fine coal upgrading processes make size reduction for liberation purposes uneconomic in industrial practice where the solid-solid separation processes used to treat fine coal represent the single greatest loss of potentially recoverable coal in a preparation facility. Finding additional products that can be extracted from coal fines can help justify the cost of cleaning fine materials.

(b) Fine Coal Dewatering:

The solid-solid separation processes employed by modern coal preparation plants require large amounts of process water. After cleaning, the unwanted water must be removed from

particle surfaces using mechanical dewatering equipment. Inefficient removal of moisture lowers the heating value, increases transport costs, and creates handling/freezing problems for the cleaned coal. Fines often represent as little as 10 percent of the total run-of-mine feed; however, this size fraction may contain one-third or more of the total moisture in the delivered product. The availability of low-cost mechanical dewatering equipment that can efficiently remove moisture from fine coal is widely considered to be an important need for the U.S. coal preparation industry…The coal preparation industry needs to develop new mechanical solid-liquid separation processes that are substantially more efficient in terms of removing moisture and less expensive to purchase, operate, and maintain.

(c) Dry Coal Processing:

Low-sulfur coal reserves in the western states have become the most important supply of domestic fossil fuel in the United States during the past few decades. Historically, the majority of coal mined in this region was of sufficient quality such that it did not require any coal preparation except for simple crushing and sizing. More recently, however, increased levels of rock dilution have been noted for coals mined in this region, largely because more challenging reserves are being mined and larger mining equipment that is less selective is being used. This trend is pushing some coal producers to consider coal washing for the first time. In addition, new federal and state clean air quality requirements are pressuring utilities and coal companies to use pre-combustion cleaning as a means of reducing SOx and trace element emissions. Dry coal separators, such as pneumatic jigs and air tables, are already finding applications at selected mine and utility sites. Other developing technologies that may be applicable for this purpose include various types of electrostatic and magnetic separators. The development of automated sorters, which use optical, electromagnetic, or x-ray detection to identify and extract rock from coal, also show considerable promise for dry coal concentration. Some energy critical elements are known to be attracted to magnetic separators. There may be an opportunity to develop cost effective processes for their recovery that also improves the quality of residual coal.

(d) Online Analysis and Control:

Tremendous strides have been made in the automation and control of coal preparation plants during the past several decades. The application of online sensors together with programmable logic controllers has allowed modern plants to operate more efficiently and

to improve safety by reducing manpower requirements. On the other hand, the industry continues to struggle with the real-time determination of the quality of coal products. Analyzers are commercially available for real-time analysis of many quality parameters for coal, including ash, sulfur, and moisture, although measurement accuracy is often poor because of sampling and calibration issues. Analyzers cannot be used to determine important data such as particle size distributions and real-time washability. Other parameters may reveal the presence of energy critical elements (such as the rare earth elements).

(e) Water Clarification and Thickening:

Gravity thickeners require large areas and significant capital funds to install. Although these units are typically very effective, there continues to be great interest in finding methods to increase the specific capacity (tons or gallons treated per unit area) of a thickener. Considerable interest is also growing in the application of technologies such as deep-cone thickeners, which can produce a paste of 45 to 55 percent solids as underflow in waste coal applications. Ideally, the paste can be discarded as a stacked pile, thereby avoiding the need for impoundments to handle waste slurry. Alternatively, if the paste is to go forward to another processing step, to recover valuable minerals within the reject stream, reducing the water content can reduce costs for additional processing.

ENVIRONMENTAL ISSUES

Effective environmental controls are essential to the long-term success of any coal mining operation:

(a) Coarse Waste Disposal:

Of the various challenges facing the coal preparation industry, perhaps none are as significant as those which relate to waste handling and disposal. This importance can be attributed to the fact that coal cleaning operations produce large volumes of waste that must be discarded into refuse piles or impoundments. Refuse piles are designed to receive coarse particles of waste rock that can be easily dewatered. This material is relatively easy to handle and can be safely transported by truck or belt haulage systems to the disposal area with little or no potential for environmental damage.

On the other hand, the waste contains solid and liquid components that may present long-term disposal problems depending on the sizes, types, and quantities of minerals present and the conditions under which the wastes are stored (e.g., dry vs. wet, loose vs. compacted). These factors play a key role in establishing the structural integrity

(e.g., slope stability, surface water runoff, sediment containment, and seepage) and chemical nature (e.g., acid generation and metal dissolution) of the wastes. Solid sediments and dissolved ions may be transported by rainwater where they can pollute streams or groundwater. Overall, improved waste characterization, including better methods to define the nature of wastes from coal preparation operations, is considered by many to be a high-priority need for the coal industry.

(b) Slurry Handling and Disposal:

The handling and disposal of fine slurry waste is widely considered to be one of the most difficult challenges facing the coal preparation industry. Fine wastes have historically been discarded into earthen impoundments for permanent disposal.

An impoundment is an engineered structure consisting of a large-volume settling basin formed behind a manmade dam or embankment. The waste, which is difficult to dewater, is normally pumped from the preparation plant thickener to the impoundment as slurry. The slurry contains water, coal fines, silt, clay, and other fine mineral particulates from the processing plant. In most cases, the slurry is retained behind a manmade embankment (earthen dam) constructed from compacted refuse material. The impoundment is designed to have a volume that is sufficiently large to ensure that fine particles settle by gravity before the clear water at the surface is recycled back to the plant for reuse. In some cases, chemical additives may be used to promote settling and control pH.

Several breakthroughs of slurry into old mine workings beneath impoundments have occurred in the recent past. The most notable was the Martin County incident, which released about 309 million gallons of slurry into streams and rivers in late 2000. A number of accidental releases of slurry have also been reported at various plant sites.

Several alternatives to impoundments have been employed by the coal industry in an attempt to avoid any future potential for environmental damage. For example, some mines use new modes of slurry disposal such as slurry cells and underground injection wells. These approaches have raised public concerns about groundwater contamination and well

water quality. To overcome these problems, various types of mechanical solid-liquid separators have been investigated as a means of more fully dewatering the fine solids prior to disposal. Notable examples include paste thickeners and different types of filters (pressure, vacuum, belt press, and plate-and-frame). Unfortunately, these systems have specific problems, such as high costs, large chemical demand, poor performance, high energy consumption, and safety concerns. In the absence of an improved disposal method, continued development of new processes and practices for slurry disposal is critically needed in the coal preparation industry.

(c) Process Water Quality:

The overwhelming majority of cleaning processes used in coal preparation require large amounts of process water. Nearly all of the process water is supplied by thickening units, which settle out ultrafine suspended solids and recycle clarified water back into the plant. A small amount of fresh make-up water from an external source is usually required to satisfy the balance between moisture contents of solids entering and exiting with the plant. The clarification and recycling of process water provides an effective means of reducing fresh water demands and lowing environmental impacts. Deterioration of process water quality is known to reduce sizing efficiency, lower flotation recovery, and increase magnetite losses. Evidence also suggests that dissolved ions adversely impact the performance of dewatering processes.

(d) Permitting of New Facilities:

Regulatory constraints can act as barriers to the introduction of new technologies and practices into the industry potentially limiting innovation within the industry and forestalling development of new technologies aimed at addressing important environmental issues. The additional liability associated with reclamation of abandoned coal waste piles and impoundments may limit any re-mining activity that the industry might otherwise pursue. The application of new coal processing technologies has the potential to provide a financial return on re-mining operations, while simultaneously reducing the waste load in the environment. Technologies from other industries that can be used in re-mining for extraction and processing should be explored.

FUTURE CONSIDERATIONS

Conversion Processes

Coal preparation activities have traditionally been limited to those processes that involve physical separations. These processes include unit operations for particle sizing, concentration of organic matter, and dewatering/disposal of plant products. Conversion processes (for instance carbonization) are by this definition not considered to be part of the coal preparation industry. However, a new generation of coal preparation technology is being developed and commercialized that bridges the gap between traditional coal cleaning and coal conversion processes.

- Locating economical REE Mineral Ore sources
- Obtaining Mining Permits and Time Factor (~10 years for new mine to reach production)*
- REE ore Issues:
  - Beneficiation of large amount of material to obtain target REE mineral(s)
  - A large amount of discarded waste rock (tailings) is generated in hard rock mining
  - REE minerals may contain Th, U which have challenging requirements for handling due to radioactivity
- Monazite Issues:
  - Thorium content of monazite is variable and can be up to 20-30%. Commercial monazite sands typically contain between 6 and 12% thorium oxide. Due to the presence of thorium within monazite, it can be radioactive.
  - Radium and lead present in monazite - require deactivation and lead elimination processes.
  - Solid radioactive waste requires disposal as an "active waste."
  - Thorium hydroxide is a product of the extraction stage – requires conversion to thorium oxalate and storage.
- Complex processing /extraction techniques may require large amounts of consumables

Figure 70. Alternate REE Separation

6 COSTING METHODOLOGY

There were two separate activities that were planned to develop target costs and the necessary level of concentration of the REEs as found in raw input materials (be that coal, coal preparation waste, mine wastes—such as partings, fly ash, and waste water. LTI—with input from NETL and FE—focused on developing flow sheets then costing those flow sheets for both capital costs and operating and maintenance costs.

Booz Allen Hamilton (BAH) was tasked with developing a sufficient knowledge of the REE processing industry to suggest a minimum acceptable concentration for the REEs so that it could be accepted for further processing by conventional players in the REE processing portion of the value chain.

The LTI work is described in some detail in the subsequent section. Additional thoughts on means to improve separations processes will also be presented. A brief summary of the BAH results, taken from a NETL presentation by Timothy Skone of NETL is provided to allow the reader to understand the magnitude of the challenge facing any supplier extracting REEs from a low concentration source.

In addition, an analysis performed on data found in an MIT report about the REE market highlights the importance of the critical REEs listed in the DOE CMS. Aspects of this analysis will also be discussed.

6.1 PRO FORMA STRUCTURE AND RESULTS

In the mid-year 2014 modification, LTI was asked to develop costs for a processing plant that was based conventional gravity-based separations technologies but that could be used to concentration a rare earth element stream from the feed concentration into the plant up to approximately a 2 percent (20,000 ppm) concentrate. At that point in time, facilities existed that would purchase low REE-bearing concentrates and further process them until the product stream could be processed in facilities that processed more typical REE concentrates.

LTI developed flow sheets and equipment costs for two different “rougher” circuits that might yield the desired level of separations to produce a saleable REE concentrate. The first was typical of today’s industry in that it produced a product coal that could be sold into fluidized bed combustion facilities (mineral matter content exceeding 10 percent) and a second stream of REE-rich material. The second was based on the results of a mineral release study performed by the University of Kentucky as part of the subcontract focused on separations test that was described above. This circuit took a middlings stream from within the preparation plant (a stream with a specific gravity intermediate to a clean coal stream—comprised of ≈90 percent coal and less than 10 percent mineral matter—and material with little carbon in it—essentially 100 percent rock) and subjected in to processing to further separate carbonaceous material from rock. Coal preparation plants (as shown in the generic schematic Figure 71 can be drawn from one or more

internal flows at a preparation plant. The limited data that LTI collected from within the two preparation plants that we tested suggest that the best candidate stream varies between the main coarse coal processing loops (for example, the reject from the dense media cyclones compared to that from the spiral separators and may also vary with coal type. These test results lead to development of a second flow sheet for the processing circuit and to development of a second set of equipment costs. It is this second equipment list and the subsequent pro forma financial analysis that will be discussed here.

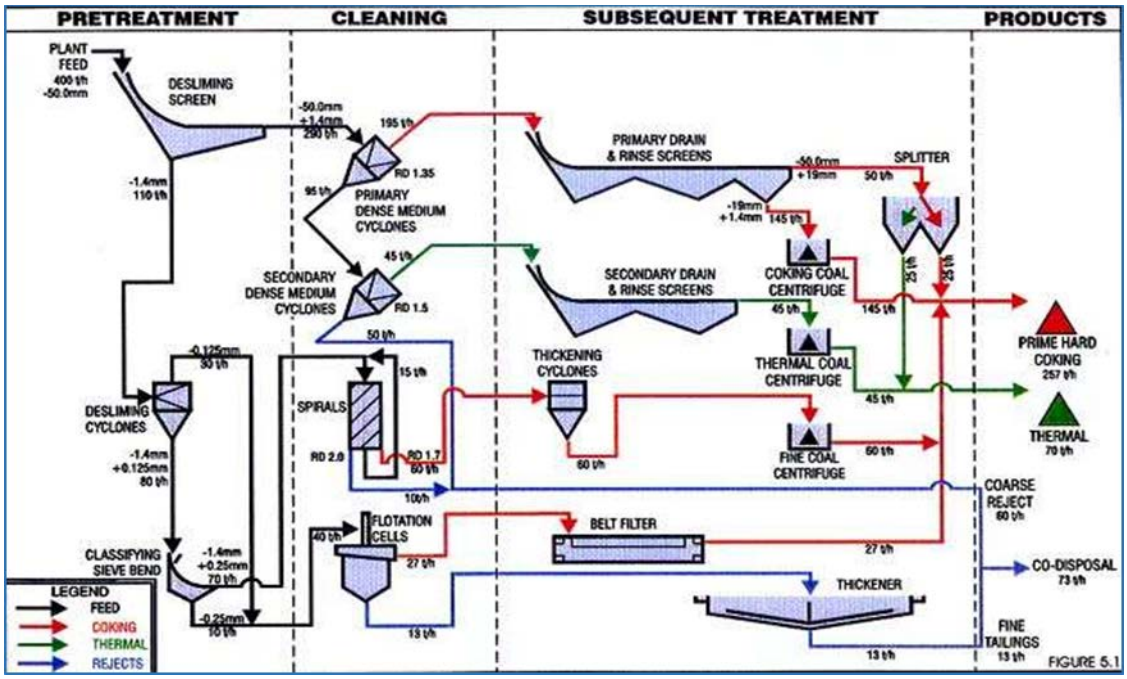


Figure 71. Coal Preparation Plant Schematic

Mineral Release Test

A mineral release study focused on REE concentrations was conducted on Fire Clay coal that had been collected from the middlings stream at an operating preparation plant. Figure 72 presents the data for a series of size reduction steps coupled with float/sink gravity separations. The original feed material had been collected from a coal preparation plant after the initial sizing was done at that facility and screened so that everything passed through a ¼" screen (6.3 mm). It was then subjected to a float/sink separation in a vessel containing a 1.5 specific gravity (S.G.) liquid phase. The sample was split into a 1.5 float

sample and a 1.5 sink sample. Evaluation of the impact of fine grinding then continued on the float fraction. This fraction was ground further in a disc mill to a maximum size of -16 mesh (1 mm). This sample was then subjected to a second float/sink test using a 1.5 S.G. separation. This process of size reduction (using a hammer mill followed by an attrition mill) followed by a gravity based separation was continued until the material had been reduced in size to a 10 micron top size. At that point, the material was separated using a flotation cell. The tailing from that cell had an REE concentration roughly four times that of the feed material.

This test wasn't intended to be a pilot test of a new separation scheme but rather showed that successive rounds of finer-sized particles, when subjected to conventional separations, can result in concentrating the REEs in the mineral matter stream. Neither did it focus on the degree of recovery of the feed REEs which would be an important consideration in process development. But it did suggest that fine grinding offered one approach to concentrating REEs.

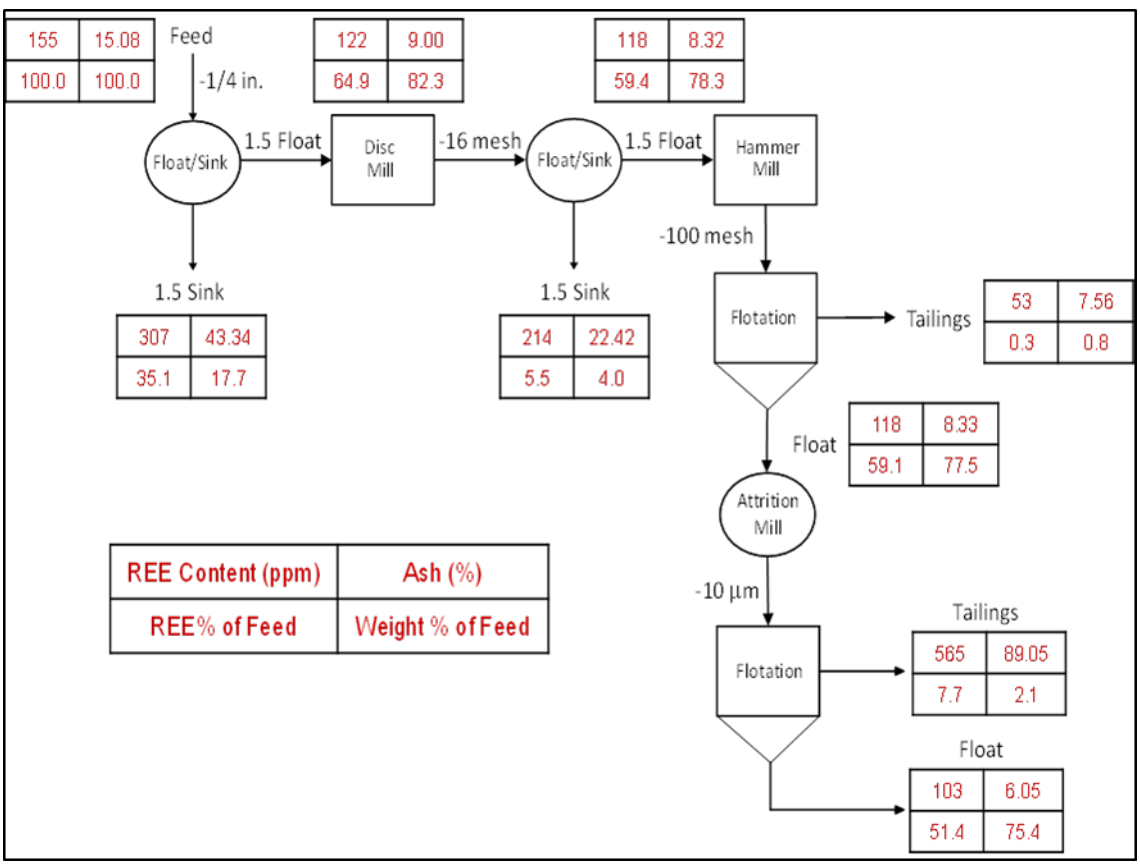


Figure 72. Mineral Release Test Results

Based on these results and other data on the response of REE-bearing particles to respond differently to different flotation reagents suggests that higher levels of differentiation between REEs and other constituents could be achieve. A conceptual flow sheet based on these results was developed and is presented below in Figure 73.

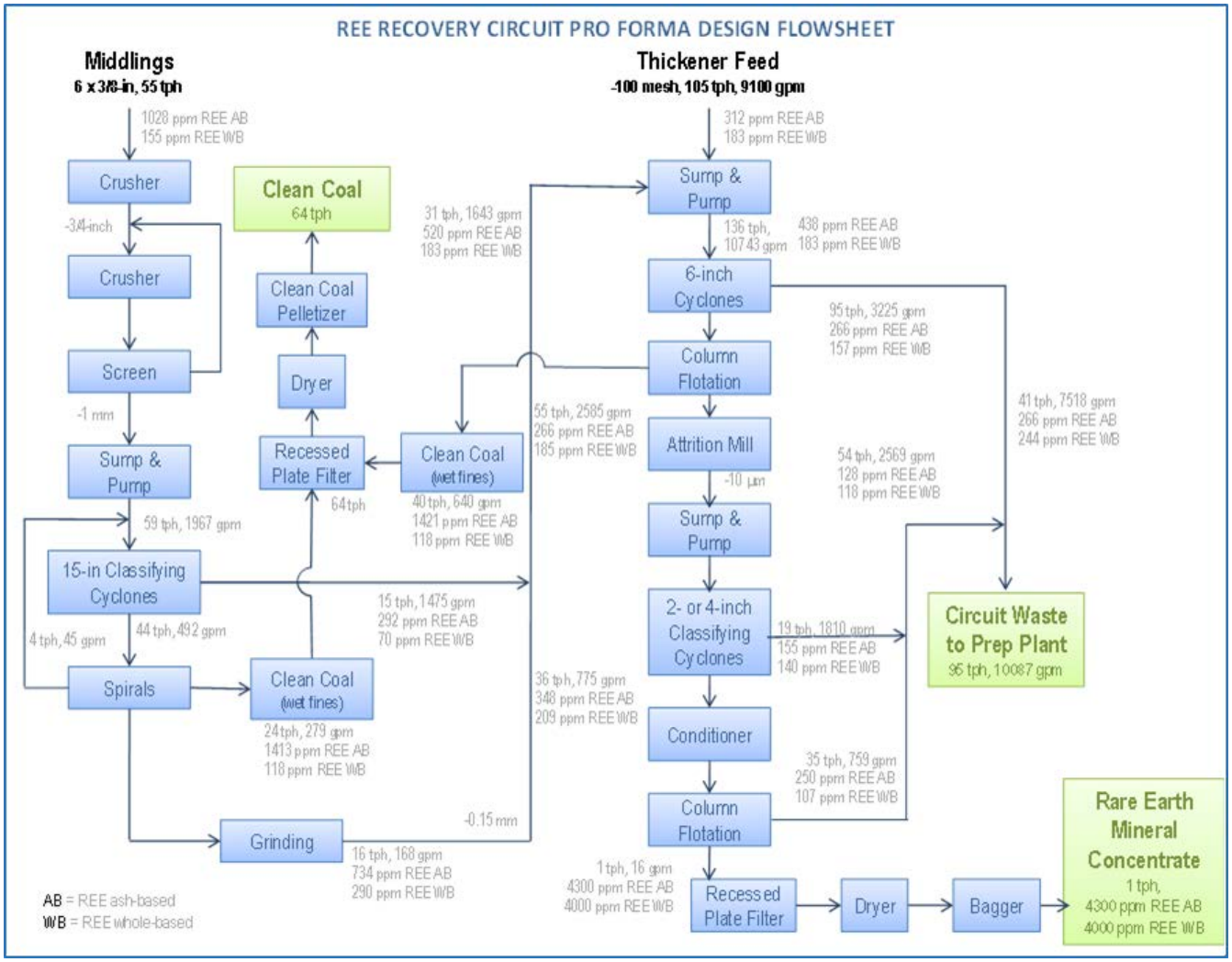


Figure 73. REE Recovery Circuit Pro Forma Design Flowsheet

This flow sheet represents a process that takes a middlings stream and the thickener feed as the source material. The middlings data used represents a coal with exactly the same input REE concentration as that used in the mineral release test. The thickener data are for the same source material. Both of these are waste streams under the economic constraints currently prevalent in the coal industry.

The middlings coal stream is further size reduced and subjected to additional cleaning, first in a spiral which removes some clean coal, and then after a fine grinding stage, mixed with the thickener feed and cleaned via froth flotation. The finely divided clean coal coming from both the spirals and the flotation cells is sent to a pelletizer to create a saleable product.

The rejects from the flotation cell is then very finely ground in attrition mills and sent through classifying cyclones, which separate a waste stream from an REE product stream. The raw REE product stream is further refined via additional column flotation. The waste stream from this step is added to the waste stream generated by the cyclone separators. The product stream goes through a plate filter and is dried. The product is bagged for shipment for extraction of the REEs at another location. Overall, the circuit is based on a total feed of 160 tons per hour of coal refuse; approximately 64 tons per hour of pelletized clean coal are produced and along with approximately 1 ton per hour of a 4,000 ppm REE concentrate. In addition to the clean coal and REE product streams, the waste stream is reduced from the original feed rate of 160 tons per hour to 95 tons per hour (approximately a 40 percent reduction in volume of a material that costs the preparation plant money to dispose of in accordance with current law).

LTI developed detailed capital and operating costs for this flow sheet. This required development of a business model which led to a number of assumptions that drove the cost recovery calculation and set the cost per unit ton or kilogram of REE concentrate. Note that value of the sale of fine coal pellets was estimated to exceed $5 million dollars; the avoided cost for disposal of the material that had now become clean coal along with the smaller flow of REE concentrate saved the preparation plant operator another $1 million dollars. The calculated cost to recover the REE concentrate was calculated to ≈$400 per ton. The estimated income, savings, and costs are highly dependent upon a number of assumptions. Those are listed in the tables in Appendix 6.

This calculation was performed to illustrate both the impact of the circuit design on cost, to begin to identify research needs that might reduce cost, and to fully compute benefits. This analysis suggests several research needs:

- Conventional physical separations and froth flotation may not offer an opportunity to reduce costs adequately. Alternative approaches such as chemical leaching may be less costly. Clearly, the size issue—how much of the total REE present in any given

particle is at or near the surface and accessible to the leaching agent—may dominate the cost benefit that leaching may provide.

The major assumptions are presented below:

This potential business plan was used to develop the assumptions for this Pro Forma but it is presented as just one of many possible scenarios. In this scenario, we assume two business entities: the preparation plant owner (PrepCo) and the REE Recovery Circuit owner (REECo).

Agreement:

PrepCo agrees to supply REECo with 160 tons per hour (tph)—1.3 million tons per year (tpy) of middlings and thickener feed refuse from the preparation plant. This refuse would otherwise be disposed by PrepCo.

REECo will return the refuse remaining after processing in the REE Recovery Circuit to PrepCo for disposal and PrepCo will become responsible for disposing of the refuse. Because 64 tph of coal fines and 1 tph of REE concentrate is recovered by the REE Recovery Circuit, the amount of refuse disposed by PrepCo will be 95 tph (160 tph less 65 tph).

REECo will own both the coal pellets and the REE concentrate produced by the REE Recovery Circuit.

Potential Business Incentives:

REECo produces REE concentrate for sale to a REE refinery. The cost of this REE concentrate is estimated as $0.46 per kilogram.

In addition, REECo will produce coal fines that can be sold as a coal product. In this example, we have assumed that the fines must be processed into coal pellets to make a marketable product. Total revenue from the sale of coal pellets is estimated at $28.4 million.

PrepCo receives $4.00 per ton of middlings and thickener feed that it provides to REECo. Revenue from these sales is estimated at $5.0 million per year.

In addition, instead of incurring the disposal costs associated with 160 tph of refuse—which are estimated at $3.4 million per year—PrepCo will only incur an estimated $2.2

million per year in disposal costs associated with the 95 tph refuse from the REE Recovery Circuit. The cost savings to PrepCo are therefore estimated at $1.1 million per year (after rounding). These estimated disposal costs for PrepCo include an assumption of $1.00 per ton in chemical costs associated with the thickener feed and $2.00 per ton costs associated with waste disposal of middlings and thickener feed.

REECo and PrepCo will negotiate the price of the middlings and thickener feed supplied to REECo. It is difficult to know how much PrepCo will demand in return for hosting the REE Recovery Circuit. Clearly, PrepCo will have concerns over the possible disruption of their primary business to enable an ancillary source of cash flow via the production of REE concentrate. For the purposes of this potential business plan scenario, we have assumed that $4.00 per ton—when combined with the savings associated with reduced disposal costs—would provide sufficient incentive for PrepCo to provide the refuse feed to REECo.

Note: Costs shown here and in the Pro Forma are pre-tax. For the purposes of this scenario, black lung and abandoned mine reclamation fees are paid by the producer (originating coal mining complex) at the first point of sale.

Table 21. REE Recovery Circuit Pro Forma Summary Results

REE Recovery Circuit Performance	Tons	Kg
Refuse processed by REE recovery circuit (TPY)	1,261,440	1,144,353,139
Total annual concentrate produced by REE recovery circuit	7,822	7,095,600

REE Recovery Circuit Overnight Capital	2014 $
REE Recovery Circuit Total Overnight Cost	$ 47,161,060

REE Recovery Circuit Annual Costs	2014 $
Annual operating costs	$ 22,013,246
Annual capital cost (@20% IRR)	$ 9,684,832
Total Costs	$ 31,698,077

Coal Pelletizer Performance	Tons
Coal fines produced by REE recovery circuit	504,576
Coal pellets produced *	504,576
*12,500 Btu/lb, 0.7% sulfur, 7% ash, 7% moisture	

Coal Preparation Plant Owner Annual Revenue	2014 $
Net Savings to Prep Plant Due to Reduced Waste Disposal	$ 1,103,760
Middlings and thickner feed to REE Circuit (tpy)	1,261,440
Price received for middlings and thickener feed to REE Circuit ($/ton)	$ 4.00
Sale of middlings and thickner feed to REE Recovery Circuit	$ 5,045,760
Total Annual Revenue to Preparation Plant Owner	$ 6,149,520

Net annual revenue requirement - REE concentrate sales	2014 $
REE Recovery Circuit Annual Costs *	$ 31,698,077
Revenue offset from coal pelletizer sales	$ (28,407,629)
Total	$ 3,290,449
* Pre-Tax, 100 percent equity financing	

Cost of REE concentrate (0.4% TREO)	2014 $/Ton	2014 $/Kg
Cost of REE concentrate (0.4% TREO)	$ 421	$ 0.46

Note that value of the sale of fine coal pellets was estimated to exceed $5 million dollars; the avoided cost for disposal of the material that had now become clean coal along with the smaller flow of REE concentrate saved the preparation plant operator another $1 million dollars. The calculated cost to recover the REE concentrate was calculated to be ≈$421 per ton. The BAH analysis was to evaluate whether (and when) the value of the REEs in coal would justify recovery and concentrating of the REEs to the level sufficient to justify further processing. The estimated income, savings, and costs are highly dependent upon a number of assumptions. Those are listed in the tables in Appendix 6.

This calculation was performed to illustrate both the impact of the circuit design on cost, to begin to identify research needs that might reduce cost, and to fully compute benefits.

6.2 FINANCIAL VARIABLES THAT COULD IMPACT OUTCOME

Just as with conventional REE production, the form of the venture (vertically integrated or not), the level of enrichment achieved from the first round of processing, and the waste that are generated and that represent disposal costs are all important considerations. The rougher circuit described above uses existing technology coupled with development of an optimized flotation system to produce a low level concentrate. The process also produces a clean coal stream and reduces wastes that would otherwise need to be processed. The principle financial benefits do not come from the REEs. At the same time, the financial assumptions avoided debt financing and assumed a high internal rate of return.

The nature of the various size reduction steps included a large number of processing units and did not evaluate means to optimize their performance nor to seek out untested technologies that could reduce cost should they be successfully developed for this use. On the other hand, the waste disposal scheme was quite simple; return it to the preparation plant on the assumption that they had an acceptable, environmentally sound means to manage that material. Comparing this to the BAH study discussed below, the financial assumptions in that study are more complex and probably better mirror typical financing for such a facility. Specific items of cash flow would not be comparable

6.3 TECHNICAL ENHANCEMENTS THAT COULD REDUCE COSTS

This calculation was performed to illustrate both the impact of the circuit design on cost, to begin to identify research needs that might reduce cost, and to fully compute benefits. This analysis suggests several research needs:

- First, optimized reagents for use in the flotation step are important. The reagent needs to be able to selectively render the particles highly enriched in REEs hydrophobic while the reject material behaves as a hydrophilic material. Conventional fine grinding often results in particles approximately 1 mm in diameter or less. In the mineral release test described above, the particle size entering the first flotation cell was ≈0.15 mm and down.
- Second, improve performance for size reduction circuits. Attrition mills and sand mills can produce very small particles and can be set up to produce narrow size distributions about a mean size. Assuming that the average size of a monazite or xenotime particle might be on the order of 4 microns, a .15 mm particle (150 microns) from a sample with an average TREE concentration of 4,000 ppm might contain ≈200 REE particles out of a total of 53,000 particles assuming the 0.15 mm particle was comprised of only 4 micron spherical particles. Recent papers discussed the technologies for fine grinding and application issues (ref: Chemical Processing) and explored (ref. 6-1) changing operating conditions to narrow the product size distribution on the initial pass and thereby reduce costs involved in regrinding to attain the desired product size.
- Conventional physical separations and froth flotation may not offer an opportunity to reduce costs adequately. Alternative approaches such as chemical leaching may be less costly. Clearly, the size issue—how much of the total REE present in any given particle is at or near the surface and accessible to the either flotation additives or a leaching agent—may dominate the cost benefit that leaching may provide.

Lastly, a very limited amount of work was done on further splitting the coarse waste stream into a plus 1.8 float, a 1. Sink—plus 2.9 float fraction, and a 2.9 sink. These data show (point to location in Kentucky data) that this approach might separate a heavy fraction which contains less REEs than either lighter fraction but that contains a significant share of heavy elements that may also pose significant environmental risks and demand careful

handling and disposal. There is not enough data in the report to develop specific recommendations but it bears further scrutiny.

6.4 INTERSECTING TECHNICAL COSTING WITH MARKET ISSUES

6.4.1 Booz Allen Hamilton Study

A Booz Allen Hamilton (BAH) study commissioned by NETL sought to evaluate whether REEs from coal, recovered from coal preparation wastes using a process largely dependent on physical separation techniques, could be competitive with other sources of REEs. The Economic Analysis Modeling Approach (ref. 6-2) developed a discounted cash flow analysis (DCFA), referenced to 2014 dollars.

The study team faced a number of challenges in developing a DCF analysis for several reasons:

- There is no "market price" for selling REE concentrates at X percent REEs
- There is no established market for REEs at 100 percent TREO
- Limited information is available on existing and proposed REE operations—most are vertically integrated companies (mine to 99 percent TREO)

The analysis attempted to estimate a selling price for the REE concentrate produced from the REE Rough Circuit (at both the concentration level used in the pro forma analysis and at several other concentrations more typical of commercial practice).

The remainder after performing these calculations is the profit above the WACC that can be used to determine the sales price for the REE concentrate

A series of assumptions were made to reflect both improved technology for creating REE concentrate streams with higher percentages of total REE and about other factors affecting the US demand for REEs. Both the LTI pro forma analysis and the BAH work were intended to provide a basis for developing R&D metrics and to establish the potential benefit that could arise should the research effort increase REE recovery and produce concentrates with far higher levels of total REEs.

6.4.2 MIT Report

An MIT report was published in Environmental Science and Technology in 2012 (ref. 6-3) that explored the interaction between future demand for individual REEs under different scenarios and supply constraints (monopolistic supply conditions, environmentally unsustainable mining practices, and rapid demand growth for some REEs—dysprosium and neodymium in particular). The study included estimates of supply growth based on historical trends and on rapid increases in demand intended to meet environmental goals. The overall intent of the study was to evaluate whether likely supply growth (based on historical rates of growth) would be adequate to meet demand for REEs, particularly for the REEs critical to rapid increases in demand for wind turbines and electric vehicles. Although the overall demand/supply ration for total REEs (all 10) came close to balance for scenario D, the demand/supply ratio was badly out of balance for the Pr, Nd, Dy, Tb, and Y.

Based on the projections in the report, LTI developed tables that projected changes in supply and demand for each of the rare earth elements examined in the study. Only ten REEs were analyzed in the MIT report and those ten are the ones finding some commercial use. LTI grouped these ten into two categories, Ce+La+Pr+Sm+Gd and Nd+Y+Dy+Eu+Tb. The first group contains three of the most common REEs (Ce, La, and Pr). The second group contains one light REE, Nd, and four others finding increasing application. The second group also constitutes the DOE list of critical REEs (CREE) important to expanding use of renewable technologies.

Sets of bar charts were developed matching projected supply and demand for both the CREE group and total REEs (TREE) under two different scenarios, scenario B which projects an annual supply growth rate of 5.3 percent per year and scenario D which projects an annual supply growth rate of 6.0 percent per year. Figure 74 (scenario B) shows the estimated supply and demand values for six years (starting with 2010 and for every five years thereafter through 2035). After 2015, demand is larger than supply. Figure 75 presents the same calculation for scenario D.

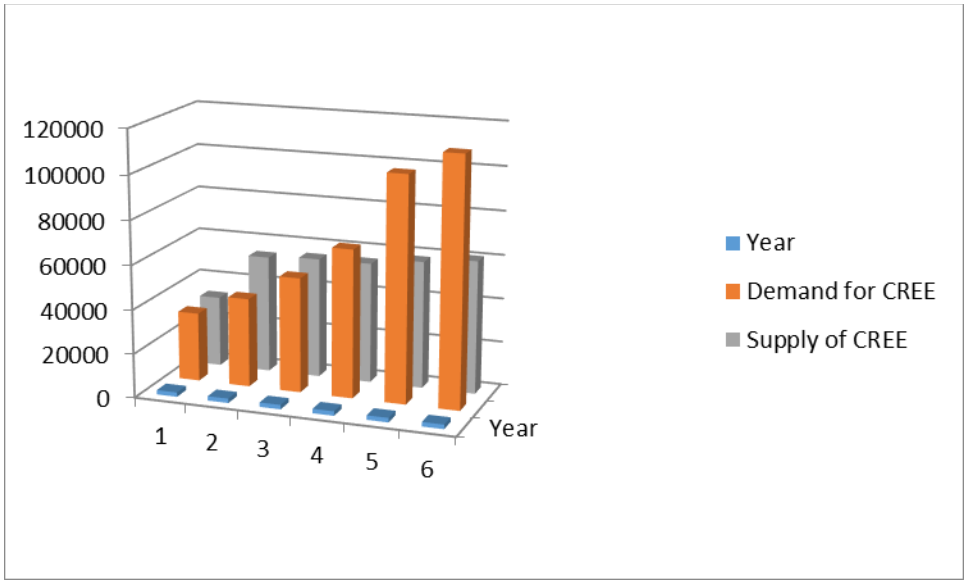


Figure 74. Comparison of Supply and Demand in Scenario B for CREE Group of Elements

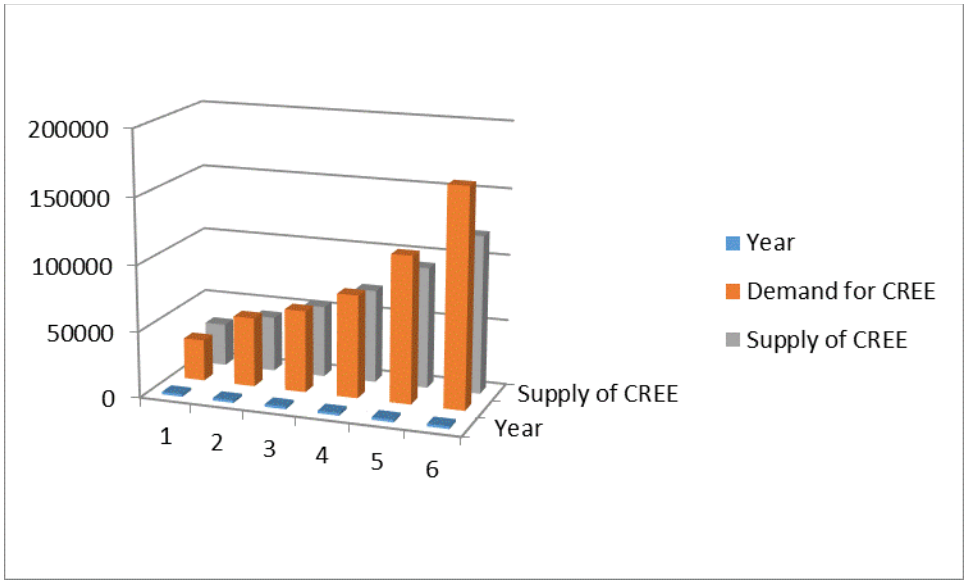


Figure 75. Comparison of Supply and Demand in Scenario D for CREE Group of Elements

By 2020, for both scenarios, the ratio of demand to supply for the CREEs is ≈1 or greater (demand outruns supply). For the TREEs, a similar result is seen. However, most of the demand that might not be satisfied can be attributed to Pr, Nd, Dy, Tb, and Y.

The increase growth rate projected in Scenario D represents a significant increase over long term averages typical of this industry. The authors conclude that: "The applications that will be most negatively affected by constraints in these REEs (i.e., increased costs) will be those dependent upon high performance magnets. Applications such as petroleum refining, which depend on elements whose supply is projected to exceed demand, may be positively affected if primary producers increase overall production to meet the higher demand for specific elements." They also addressed a range of mitigating factors including substitution, recycling, efforts to increase the yield (recovery) of the high-valued REEs, and government intervention in the market.

6.4.3 Insights from Commercial Project PEAs and Joint Ore Reserves Committee (JORC) or National Instrument (NI) Formal Procedures

Ongoing REE projects continue to refine their processing concepts as the project moves forward. Similarly, each project continues to improve their estimates of the quantity and quality of the REE-bearing formation that will be exploited. Typically, preliminary economic evaluations, reports on the exploration plan and the mineral resource reports, and environmental impact assessments follow rigorous procedures laid out in standards that allow financing organizations, governmental bodies holding responsible charge on exploitation of mineral resources, and regulatory agencies to track the development. These reports are generally public documents (ref. 6-4) and follow one of several standards (ref. 6-5) JORC code, which is widely used in the Australasian, the SAMREC code from South Africa (ref. 6-6), and the Canadian code from the Canadian Securities Administrators (ref. 6-7). These standards set minimum standards for public reporting of minerals exploration results, mineral resources and ore reserves. They provide a mandatory system for the classification of minerals exploration results, mineral resources and ore reserves according to the levels of confidence in geological knowledge and technical and economic considerations in public reports. Public reports prepared in accordance with these codes are reports prepared for the purpose of informing investors or potential investors and their advisors.

Adherence to the requirements allows for comparisons between projects and the series of documents produced also tracks the level of development. It also often shows changes, for better or for worse, in the resource and reserve estimates.

Comparison of costs for a Conventional SX REE Project versus a MRT Separation REE Project

Bokan capital cost is estimated at $221.2 million and is separated into direct and indirect capital costs. Direct capital is estimated to be $134.7 million and indirect capital is estimated at $86.5 million, with an accuracy range of +/-35 percent. The estimate includes provisions for both the mining and mineral process. Infrastructure and project facilities include the process plant, ancillary buildings and accommodations, roadways, material conveyance, tailings and waste management facilities and related site development.

Bokan operating costs for the mine and processing over the LOM is estimated at $636 million which equates to $122.78/t mined. The breakdown of Operating costs is shown in Table 22 below.

CAPEX and OPEX for the Bear Lodge and Bokan REE projects are compared in Table 23 below.

Table 22. Comparison of CAPEX for the Bear Lodge and Bokan REE Projects

REE Projects	Bear Lodge (Proprietary Technology)	Bokan (MRT Project)	
Processing Facility (PUG)	Capital Costs ($)	Capital Costs ($)	
Mill Building		7,981,333	
Crushing (Bokan: 1500 t/d)		391,196	
Grinding		11,653,969	

Leaching (Bokan: 375 t/d)		32,142,697	
Recovery		6,817,371	
Miscellaneous		3,932,915	
PUG Total Cost	44,800,000	62,919,481	
Hydromet Cost	122,075,000	Na	
Hydromet and Tailings Storage	147,000,000		
	Bear Lodge Operating Costs (LOM)	Bokan Operating Costs	
	Cost/Ton Ore Processed ($)	Average Unit Cost ($/t mined)	Total LOM Cost ($ million)
Mining	42.98	41.69	216.0
Processing	21.56	54.83	284.0
G&A	19.71 (includes road maintenance)	13.56	70.2
Power		111.78	61.0
Miscellaneous		0.93	4.8
Total Cost		122.78	636.0

Hydromet	212.68 (includes tailings storage)	NA	

Table 23. Comparison of OPEX for the Bear Lodge and Bokan REE Projects

Attribute	Bear Lodge Proprietary Technology	Bokan	Bokan
Processing Facility (PUG) Operating Cost – Area		Total annual Operating Cost During Full Production ($)	Average Unit Cost ($/t mined)
Process labor		3,709,508	6.87
Process Supplies		12,216,000	22.62
G&A Labor		1,302,075	2.14
G&A Supplies		6,020,775	11.15
Power Supply		6,358,902	11.78
Total Cost	4,470,000	**29,607,332**	**54.83**
Hyrdomet Operating Cost Estimate Summary	Year 1, $/t	Areas of Potential Savings due to MRT	

Reagents	5,000	Reusable and fewer processing stages and higher recovery rates	
Labor Cost	590	Lower due to less equipment and handling of supplies	
Energy Cost	920	Less Equipment	
Thorium Disposal Cost	140	Extracted during Initial Processing by MRT	
Maintenance Supplies	340	Less supplies to maintain less equipment	
Water Treatment Chemicals	10	Reduced due to recycling	
Misc Other processing	20	Lower due to less equipment and lower personnel requirements	

Total	7,020	percent lower than another technology would be a guess-estimate	

The capital costs are based on typical process requirements for process REE-bearing material in crushing, grinding, x-ray and magnetic sorting circuits of an equivalent model for a 1,500 td operation. The estimate includes a hydrometallurgical circuit utilizing nitric acid leaching with a 375 t/d leaching circuit. The total mine operating costs is estimated at $215,700,000 which equates to $41.69/t of material mined or $166.74/t of material leached.

Reagents and Supplies for Bokan

The nitric acid and supply types and consumptions are based on the requirements for 375 t/d operations of the leaching circuit. The total costs for reagents and supplies are $12.2 million per year or $101.46t.

Mineral Processing:

The REE processing facility to treat 1,500 t/d of mined material was designed based on the results of the metallurgical test programs conducted at Commodas, Hazen and IntelliMet.

The process design includes primary and secondary crushing, screening, DEXRT sorting and magnetic separation circuits, as well and tertiary crushing, a rod mill and a tower mill grinding circuits.

A leaching circuit will produce an upgraded concentrate for further treatment, with the waste sent to the paste backfill plant to be used as cemented backfill for filling mined out areas underground.

A solid phase extraction circuit will separate the bulk REE concentrate into individual REOs as sellable products. For Bokan, the solid phase extraction technique will be molecular

recognition technology (MRT) which involves macrocyclic ligands immobilized on a silica or polymer support.

7 SUMMARY AND RECOMMENDATIONS

Observations are provided in most of the sections. The summary of findings and observations from the various field sampling programs and analysis efforts (including the work of Tetra Tech) are given in Section 3.6. The main purposes of this study were to (a) gather data and to estimate REEs associated with coal as a national resource; to (b) gather field samples from a full range of coal mining, preparation, waste management, and utilization sites; and to (c) explore the impact of a range of conventional cleaning processes on REE separation and concentration by methods routinely used for physical separation. These purposes did not include assessment of the behavior of coal, mineral matter and associated REEs subjected to advanced separations techniques. Comparisons in Section 3.6 show that there appears to be a difference amongst coal from different basins, that processing can somewhat redistribute the REEs and that HREEs concentrate differently from LREEs (hence the range of values for the LREE/HREE ratio). That point is further supported by the spread in the values for various ratios between one, two or three indicator elements and the total REEs in samples.

The future success of recovering REEs from our nation's coal and coal-related materials relies upon two critical needs: (1) the ability to economically and accurately identify and quantify specific REEs and their geographic locations, whether it be in-situ or re-located or in-process; and secondly, (2) is the critical need to develop an economical and effective process to separate the REEs from their typical mineral matrix. The future REE recovery will not be successful without both critical needs being satisfied. The following discussions will address the first critical need, location of REEs.

Given the changing nature of the coal industry and the large legacy issues that remain, understanding these differences and having improved means to locate higher concentrations of critical REEs wherever they occur are strongly recommended. Improved approaches to prospectivity analyses—both through the use of devices such as the XRF, use of well logs, and additional statistical studies appear to be essential.

Future research should, therefore, be directed toward developing methods for evaluating uncertainties linked to the approaches to mineral prospectivity analysis (cf. Bárdossy and

Fodor, 2004). In the case of mathematical-model-based prospectivity analysis, future research may involve (a) estimating uncertainty linked to exploration criteria and derivative predictor maps, (b) quantifying uncertainty linked to missing and misassigned data, and (c) developing a statistical framework for delineating prospective areas at different confidence levels. In the case of manual prospectivity analysis, more thinking is required in terms of improving the subjective estimation and assignment of probabilities of occurrence of the critical mineralization processes. One way this could be done is by employing probability distributions instead of discrete probability values. Bárdossy and Fodor (2004) provide a comprehensive review of mathematical techniques that can be used for evaluating and handling uncertainty in mineral prospectivity analysis.

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