

Report on Rare Earth Elements from Coal and Coal Byproducts

Report to Congress January 2017

> United States Department of Energy Washington, DC 20585

Message from the Secretary

I am pleased to submit the enclosed report, *Rare Earth Elements from Coal and Coal Byproducts*. This report outlines the 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.

This report was prepared by the Department of Energy, Office of Fossil Energy (FE), National Energy Technology Laboratory (NETL) in response to an Explanatory Statement introduced in the House of Representatives in connection with the Consolidated Appropriations Act, 2014 (Public Law 113-76 (Jan. 17, 2014).¹ The assessment and analysis effort was led by FE/NETL and conducted in collaboration with industry, academia, and NETL's Office of Research and Development (ORD). In addition, the assessment and analysis was informed by industry, academia, and national laboratory responses to the DOE Request for Information (RFI) for DE-FOA-0001202. The results of this assessment and analysis have been made publicly available through https://edx.netl.doe.gov/ree/. This report is being provided to the following Members of Congress:

- The Honorable Joseph R. Biden, Jr. President of the Senate
- The Honorable Paul Ryan
 Speaker of the House of Representatives
- The Honorable Thad Cochran Chairman, Committee on Appropriations
- The Honorable Harold Rogers Chairman, Committee on Appropriations
- The Honorable Barbara Mikulski Vice Chairman, Committee on Appropriations
- The Honorable Nita Lowey Ranking Member, Committee on Appropriations
- The Honorable Mike Simpson Chairman, Subcommittee on Energy and Water Development

¹ Explanatory Statement Introduced by Mr. Rogers of Kentucky, Chairman of the House Committee on Appropriations Regarding the House Amendment to the Senate Amendment on H.R. 3547, Consolidated Appropriations Act, 2014, 160 Cong Rec H 475 at H 877 (January 15, 2014).

- The Honorable Marcy Kaptur Ranking Member, Subcommittee on Energy and Water Development
 - The Honorable Lamar Alexander Chairman, Subcommittee on Energy and Water Development
 - The Honorable Dianne Feinstein Ranking Member, Subcommittee on Energy and Water Development

If you need additional information, please contact me or Christopher King, Acting Assistant Secretary, Office of Congressional and Intergovernmental Affairs, at (202) 586-5450.

Sincerely,

Ernest J. Moniz

Enclosure

Executive Summary

In response to an Explanatory Statement introduced in the House of Representatives in connection with the Consolidated Appropriations Act, 2014 (Public Law 113-76 (Jan. 17, 2014), the Department of Energy, National Energy Technology Laboratory (DOE/NETL), has performed 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. Consistent with the Explanatory Statement, this report presents the results of DOE/NETL's assessment and analysis, to the Committees on Appropriations of the House of Representatives and the Senate.

As suggested in the explanatory statement to the FY 2014 appropriations bill, DOE's Office of Fossil Energy (FE) explored the potential of coal and coal byproducts as viable sources of Rare Earth Elements (REE). A series of activities to assess REE resources associated with major coal basins in the U.S. were conducted. Over 1800 samples, representing approximately 30,000 individual REE analyses, were taken from various sources. Through both literature surveys and testing samples from U.S. mining operations, a preliminary reserve base has been established in two key coal-producing regions in the U.S. While the global REE market demand is expected to remain on the order of 100,000 tonnes per year, these two regions alone in the U.S. have potential reserves in the millions of tonnes.

Data have been generated by university mineral processing laboratories regarding the potential for commercial mineral separation processes to produce REE concentrates from these materials. Based on these results, preliminary economic analyses are underway, indicating the need for cost improvements. These results suggest that the key to unlocking this potential reserve base for economic U.S. REE production from coal and coal byproducts is the improvement of separation technologies. In turn, research and development in this area can provide this expansion in the U.S. REE reserve base.

The pathway toward economic recovery of REEs, from coal and coal byproducts, requires:

- 1. Continue identification of domestic sources of coal and coal byproducts with the highest known concentration of REEs.
- 2. Conduct research to better understand the form and structure of REEs in coal and coal byproducts. This will support the design of alternative separation technologies.
- Design, development, and testing of alternative separation technologies to recover mixed REEs from coal and coal byproducts for downstream processing and purification of individual elements by REE refineries.



Report on Rare Earth Elements from Coal and Coal Byproducts

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I. LEGISLATIVE REPORT LANGUAGE

This report responds to an Explanatory Statement Introduced by Mr. Rogers of Kentucky, Chairman of the House Committee on Appropriations in connection with the Consolidated Appropriations Act, 2014. The Explanatory Statement provides:

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.

In accordance with the Explanatory Statement, this Report discusses the relevant assessment and analysis of REEs in coal and coal byproducts performed by DOE/FE and NETL. DOE has drawn on a number of U.S. government, industry, academic, and research organization sources, and has included relevant information from respondents to an NETL Request for Information.

II. ASSESSMENT AND ANALYSIS

Overview

While comprising just 17 elements of the periodic table, the group known as rare earth elements (REEs) provides significant value to our national security, energy independence, environmental future, and economic growth. Currently greater than 90 percent of the world's REE production capacity is controlled by China (DiLallo, 2014).

The World Trade Organization's recent report regarding China's actions related to the price and supply of certain REEs (World Trade Organization, 2014) and the creation of the U.S. DOE's Critical Materials Institute funded in part by

- The REE value chain comprises many recovery and processing steps to produce high purity rare earth oxides that are subsequently offered for sale in the global marketplace.
- Few sources of REEs are in commercial operation today although approximately 25 new REE production projects are currently at different stages of pre-production development.

DOE's Office of Energy Efficiency and Renewable Energy provide evidence of the need for a new REE supply chain. As the pursuit of current and developing technologies in military, energy, and medical fields continues to expand, so does the need for a reliable and affordable domestic supply of REEs (Blunt, 2014). By 2022, however, China's market share of REE production is anticipated to fall from 95% to 46% with around 25 new REE production projects under development, including 2 in the U.S. (Visiongain, 2012).

A recent analysis of the economic importance of the REE industry in the U.S. (American Chemistry Council, 2014) indicated that:

- Intermediate products (magnets, catalysts, metallurgical additives, polishing powders, glass additives, ceramics, and batteries) delivered \$39.2 billion in revenue.
- Intermediate products created 101,800 jobs generating \$6.1 billion in payroll.
- End-market products/technologies (health care, hybrid electric vehicles, lighting, communication systems, audio equipment, defense technologies, optics, oil refining, and wind power) delivered \$259.6 billion in revenue.
- End-market products/technologies created 433,500 jobs generating \$27.3 billion in payroll.

Current Market

Introduction

REEs are found throughout the earth's crust but most often occur in low concentrations. They are not found in isolated form but in a variety of minerals where, in most cases, they exist in concentrations too small for economical extraction. The REEs (as shown in Figure 1) are: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). The rare earths are also often considered to include the metals scandium (Sc) and yttrium (Y).

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Actir	nides	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Figure 1. Periodic Table Depicting Heavy and Light REEs

Value Chain

The REE value chain shown in Figure 2 is process-intense. The REE value chain begins with exploration and mining. Once the ore has been mined, it is typically crushed and milled into a finer concentrate, which is further processed to separate REE-bearing minerals (such as bastnaesite). The next phase in the value chain is separation and purification of REE-bearing minerals into their pure oxide form, rare earth oxide. Rare earth oxides can be standalone products; however, market demand dictates their conversion into metals. Rare earth metals are very soft and have specific chemical properties and end uses; they can be processed into alloys by mixing two or more elements in order to create harder and stronger final products for additional end uses.

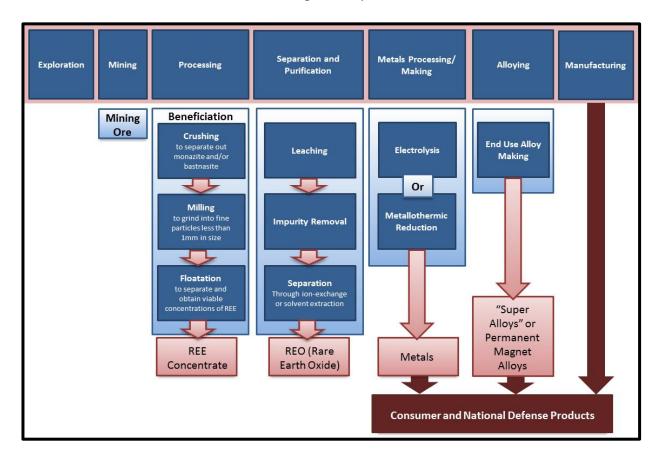


Figure 2. REE Value Chain

Supply

The market for REE has been increasing since they were first mined in the mid-1900s. Historically, the U.S. has had a large market share, being the largest producer of REEs from the 1960s to the 1980s. China began production in the 1980s and by 1988 secured the position of the world's leading REE producer. In 2011, global production of REEs was approximately 132,000 metric tons (MT)—95 percent of which was supplied by China (Visiongain, 2012).

Within the U.S., Molycorp actively mined rare earths at its Mountain Pass, California, site from the 1960s to the 1980s. During that time, the company was the world's major producer of REEs due to the mine's higher-grade deposits and low production costs combined with a rapid increase in global demand for REEs. Following a more recent restart by a new corporation formed in 2010, the Mountain Pass operation was again idled in 2015 due to bankruptcy.

China has the world's largest known rare earth deposit—the Bayan Obo deposit—holding over 48 million MT of REEs. China has controlled the global market throughout the majority of the last 30 years (Visiongain, 2012) (Blakely, Cooter, Khaitan, Sincer, & Williams, 2012).

Demand

In 2013 global annual demand for REEs was approximately 125,000 MT, with the United States consuming approximately 18,100 MT. Specific end uses of REEs include developing technologies in the communications, electronics, and military weapons markets. Examples are shown in Tables 1a and 1b.

r	Table 1a.	End	Uses for Light REEs	

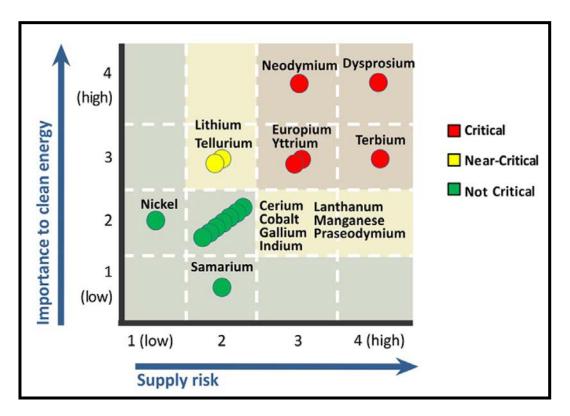
Light Rare Earths	Major End-Use
Scandium	TVs, fluorescent and energy-saving lamps
Lanthanum	hybrid engines, metal alloys
Cerium	catalysts, metal alloys
Praseodymium	Magnets
Neodymium	catalysts, hard drives in laptops, headphones, hybrid engines
Promethium	watches, pacemakers
Samarium	Magnets
Europium	red color for television, computer screens

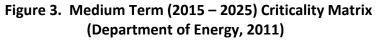
Table 1b. End Uses for Heavy REEs

Heavy Rare Earths	Major End-Use				
Terbium phosphors, permanent magnets					
Dysprosium permanent magnets, hybrid engines					
Erbium	phosphors				
Yttrium	red color, fluorescent lamps, ceramics, metal alloy agent				
Holmium	glass coloring, lasers				
Thulium	medical x-ray units				
Lutetium	petroleum catalysts				
Ytterbium	lasers, steel alloys				
Gadolinium	magnets				

Supply/Demand Balance

The supply/demand relationships for individual REEs, among other topics, were presented in a paper by a group at the Massachusetts Institute of Technology in 2012 (Alonso, et al., 2012). Several cases—from a business-as-usual scenario to a revolutionary demand scenario—were developed that tracked the technology forecasts in the International Energy Agency's Blue Map Greenhouse Gas scenario that would drive demand for individual REEs, including all five REEs identified by DOE as critical, as shown in Figure 3 (Department of Energy, 2011). The study indicated that the supply of these critical REEs would likely be subject to shortages between now and 2035 under all five of the identified scenarios, which include increased use of wind energy, electric vehicles, etc.





Projected Market

Future Supply

In 2011, there were over 400 REE production projects in various stages of implementation worldwide. More recently, market conditions have resulted in many of these projects being cancelled or put on hold. Pending successful project development, some projects could be in production by 2022, including two in the U.S. Should these projects result in additional REE production, some supply and price stabilization may result.

A number of other projects focusing on co-production of REEs and other valuable minerals are being pursued (for example, the Eco Ridge mine and Nechalacho projects, both in Canada). The average REE concentration is low (0.15 and 1.3 percent, respectively) in these two projects, but the coproduction opportunities and the composition of the REEs—favoring REEs in high demand for the foreseeable future—support continued development. Co-production, as would occur if coal, alumina, and other minor constituents having commercial value were produced, is often cited as a far more secure path toward developing sources of REEs (Streetwise Reports, 2013).

- Global market forecasts suggest some REE supply and price stabilization, with the majority of LREEs being in ample supply and HREEs (high-value) remaining in limited supply.
- Many new projects focused on diversifying supply are in various stages of implementation, but new efforts to purify and refine REEs are limited.
- Domestic and international activities have been initiated to address supply concerns and reduce the environmental impact of current processing operations.

Global production of LREEs is expected to increase from 122,000 MT in 2011 to 346,000 MT in 2022, and production

of HREEs is expected to grow from 13,000 MT in 2012 to 46,000 MT in 2022. A supply surplus of many LREEs and a shortage of HREEs are expected. HREEs accounted for 9.8 percent of total REE production in 2011 (Visiongain, 2012).

Adequate supply is only a part of the solution to any REE supply shortfall. Additional processing, refining, and manufacturing capacity is necessary to meet growing demand (Humphries, 2013).

Future Demand

Multiple research and industry sources have projected that global demand for REEs will increase over the next 10 years, with an ample supply of LREEs but a limited supply of HREEs being available (Visiongain, 2012) (Kingsnorth, 2011) (Hatch, Gareth P). Demand is expected to be driven by growth in the technology and clean energy markets. In particular, growth in green technologies such as wind turbines, which use permanent magnets, is expected to push REE consumption higher (Visiongain, 2012).

Individual REEs have variable supply and demand profiles and are found in varying proportions at mining sites. Heavy REEs, in particular, are found in smaller quantities, are more difficult to extract, and require more intensive processing for purification. As a result, they are more expensive from a value-chain perspective.

Additional Activities Addressing Supply

Nations are investing in REE research, developing REE deposits, and evaluating facilities to extract REEs from native ore. Organizations formed to explore solutions to increase supply and reduce demand include: (1) DOE's Critical Materials Institute, (2) the Rare Earth Technology Alliance, an initiative of the American Chemistry Council (3) Australia's Commonwealth Scientific and Industrial Research Organization, (4) Japan and Vietnam's joint Rare Earth Research and Technology Transfer Centre, (5) the Canadian Rare Earth Elements Network, and (6) the European Rare Earths Competency Network.

Opportunities and Challenges Associated with Producing REEs from Domestic Coal and Coal Byproduct Streams

Coal and coal byproducts are a potential source of REEs, particularly HREEs. While the concentration of total REEs in coal and coal byproducts is generally much lower relative to deposits

that currently serve as commercial supply sources of REEs, the concentration of HREEs may be comparable to that found in current commercial sources and can be greater than that found in major sources of LREEs. However, the challenges associated with extraction from such feedstocks are significant.

The mineralogy and distribution of the REEs in coal and coal byproducts will pose challenges for any recovery and separation concept, including those involving physical, chemical, and other more novel separation technologies. Limited data developed during this study were used to identify promising paths that can be applied to different source streams within the coal value chain to concentrate the REEs.

Numerous scientific investigations have identified coal as containing potentially significant quantities of REEs. Both coal processing refuse and ash residues have received attention for the economic value of the REEs they might contain (Coal Ash: A Resource for Rare Earth and Strategic Elements, 2013). Thus, the potential opportunities for recovering REEs from coal and coal

- The strong global interest in developing an additional REE supply creates an investment opportunity for commercial firms seeking REEs recovered from coal and coal byproducts to find competitive entry points into the REE global value chain.
- REEs present in coal-based materials currently being mined for coal production represent potential savings when compared to production of virgin ore in a mine dedicated solely to REE recovery.
- The core challenges with REE recovery from coal and coal byproducts center on the large volume of material that must be processed to recover REEs.

byproducts are twofold: REEs are present in materials that are already being produced. Certain coal

and coal byproducts have elevated concentrations of HREEs—which are lowest in supply, rank high in criticality and price, and are projected to increase in demand—making them potentially attractive targets for REE recovery despite their low composite REE concentrations. The REEs found in coal often exhibit a compositional distribution of those REEs that would command a higher basket price than would be found for more conventional and well-recognized ore bodies. Basket price can be used as a rough tool to compare the compositional distribution of REE-bearing ores based on the current relative value of each element or oxide as a pure—nearly 100 percent pure—commodity.

DOE/NETL performed an assessment of the amounts of REEs that are likely to be found in coal deposits and the mineral matter—particularly the clays—associated with these deposits. The initial resource estimates indicate that 6 million MT of REEs could potentially be produced from recoverable coal reserves in select western state coal basins in Montana, Wyoming, Colorado, Utah, New Mexico, and Arizona. Similar estimates indicate that 4.9 million MT are potentially available from among the coal deposits found in Pennsylvania, West Virginia, Kentucky, and Virginia. These estimates represent total resources, with REE contents in associated mineral matter over a cutoff grade of 500 parts per million, and are based on estimates of recoverable coal reserves in these regions found elsewhere (Administration U. E., 2012). The actual amounts that could be recovered would be a function of mining practices and the economics of recovery from operations actively producing, processing, and utilizing newly mined coal. However, given (as previously cited on page 7 of this report) the forecast REE demand in the hundreds of thousands of tonnes per year, this technically recoverable resource of over 10 million tonnes in two of the U.S. coal-producing regions is substantial. In addition, there is potential additional tonnage in coal ash and coal mine refuse/reject.

Further, the REEs are typically associated with clays (small particles of clay trapped in the organic phase or larger partings and roof or floor material rich in clay minerals). These materials can be sources of both alumina (as the clay mineral can be described as hydrous aluminosilicates) and other valuable trace metals.

As a result, opportunities to recover REEs from coal and coal byproducts appear possible, but require more information and technology development to create pathways toward both improved economics and environmental footprint. New processing systems must incorporate steps to recover, separate, and/or refine REEs without generating additional unwanted products or negative environmental impacts. These advances may also facilitate recovery of REEs from large volumes of fly and bottom ash as well as other spent and low-concentration sources. Moreover, the co-production of REEs with other useful materials available in coal and coal-byproduct sources offers the potential to further enhance the economic viability of REE recovery from coal and coal byproducts.

Figure 4 provides a conceptual schematic of the coal value chain as it relates to opportunities to recover REEs. The concentrations of REEs stemming from the production, processing, and utilization processes shown in the figure below vary greatly depending on specific source.

Data generated to date through this project suggest that the most significant opportunities are associated with mining byproducts (pit cleanings and water resources), as well as preparation

refuse. In Figure 4, these categories are shown in the "production" and "processing" portions of the diagram, respectively.

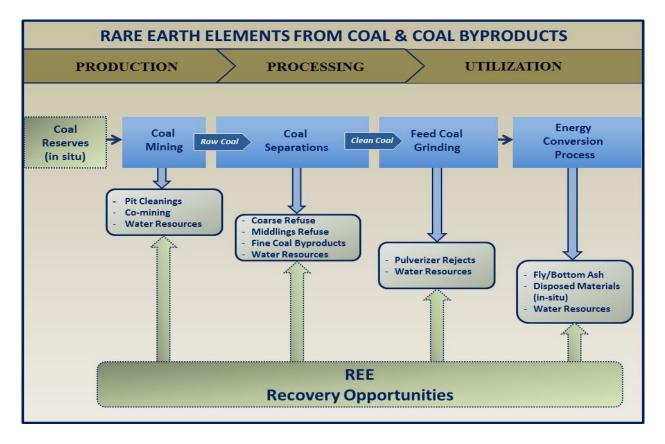


Figure 4. Many opportunities for REE recovery span the coal value chain

Analysis of REEs in Coal and Coal Byproducts

Introduction

The presence of REEs in coal and coal byproducts has been known for many years (Bragg et al., 2014). Additional sampling and analysis within this (DOE's) study were designed to better characterize the presence of REEs in coal resources at active coal mines and preparation plants (the latter comprising the "processing" portion of Figure 4), in aqueous effluents from coal mining and preparation, and in combustion byproducts (the "utilization" portion of Figure 4). Data were also gathered for coal-derived refuse materials such as fine coal refuse, coarse refuse, impounded fly ash and bottom ash, and other related coal refuse.

Coal and coal byproducts are a potential source of REEs, but the concentration of REEs is generally lower than that present in commercial deposits that currently supply REEs.

 Coal and coal byproducts contain HREEs—which are least prevalent, rank high in criticality and price, and are projected to increase in demand.

The complete results of the fieldwork are available at <u>https://edx.netl.doe.gov/ree/</u>. This repository contains

data from a number of contributing organizations. More than 29,000 individual REE elemental concentrations were determined from more than 1,820 grab samples. The samples were taken at 26 coal preparation plants, 18 coal combustion units (including pulverized coal-fired units, fluidized bed units, and industrial stokers), and a number of coal mines. Core samples from state geological surveys in six states are included. In addition, a series of separation tests were run. The most significant results are summarized in the "Analysis of REEs in Coal and Coal Byproducts" and the "Technology Assessment" sections of this report. DOE/NETL has prepared several scientific reports on this topic for public release, including publication of peer-reviewed results.

REE Sampling and Analysis Effort

The study samples were collected from: (1) state geological surveys, (2) companies operating active production and/or processing plants, (3) companies operating a variety of utilization facilities, and (4) companies owning disposal sites (active and inactive). The sampling methodology, which followed ASTM method D6357 (ASTM International) is detailed in Appendix A.

REE Resource Evaluation and Estimation

The resource estimates presented below were derived by statistical analysis of U.S. Geological Survey (USGS) data (1997), (Bragg, et al.), and augmented by data taken during this study. This effort focused on one sub-region in the eastern U.S. and one in the western U.S. A methodology was developed using samples from both eastern and western states to assess REE content, both in the coal-bearing, organic portion of the deposit and in likely REE-bearing minerals associated with the coal. The assumptions made and methodology employed in developing the REE resource estimates are outlined below.

Estimates made during this study indicate that, at a minimum REE concentration of 500 parts per million (ppm) in coal mineral matter, 6 million MT of REEs could be recovered from within the boundaries of the known coal reserves in select western state coal basins in Montana, Wyoming, Colorado, Utah, New Mexico, and Arizona. Similar calculations show that 4.9 million MT are available from within the boundaries of the coal deposits found in Pennsylvania, West Virginia, Kentucky, and Virginia. These estimates are based on total recoverable coal resources (Administration U. E., 2012).

The estimate assumed that essentially all of the REEs are associated with the clay minerals with only minor amounts ion-exchanged into the organic phase. Some of the clays may be finely divided and trapped within the organic portion that is preferentially separated as "clean coal" during the preparation process. Because of the limited distribution and range of samples utilized in the study, the REE estimates are believed to be conservative estimates of the possible REE resources available.

The maps below (Figures 5a, 5b, and 5c) overlay the calculated resources of REEs developed for this study onto an outline of the major coal basins in the U.S. The resource estimates are provided as tons of REEs per block (a "block" being a section one kilometer (km) by one km in surface area and one meter in depth). These maps were developed based on the original USGS data accounting for the full depth of the coal deposit and including associated clay and other mineral matter that are treated as partings or benches and often discarded as refuse. The analysis then produced data on the amount of REEs likely to be found in the full deposit (not just the portion that is predominately coal). The overlay of the REE resource coincides with the general regions from which samples were drawn. These resource maps also made use of other data related to known faults and geologic features known to correlate to REE enrichment as shown on the map. A far greater number of samples from the eastern coal regions were included in the USGS source material. The USGS Coal Quality database originated in the 1970s and was updated most recently in 1998. Some sourcing bias remains; in particular, the number of samples from the Gulf Coast lignite region was small.

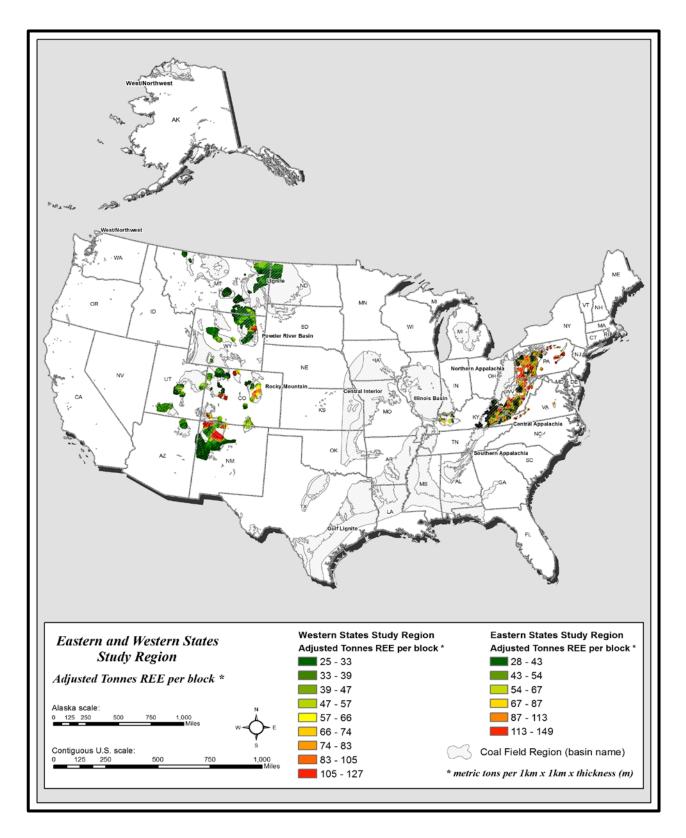


Figure 5a. REEs in U.S. Coal. (a) Map of the continental U.S. (Alaska not analyzed).

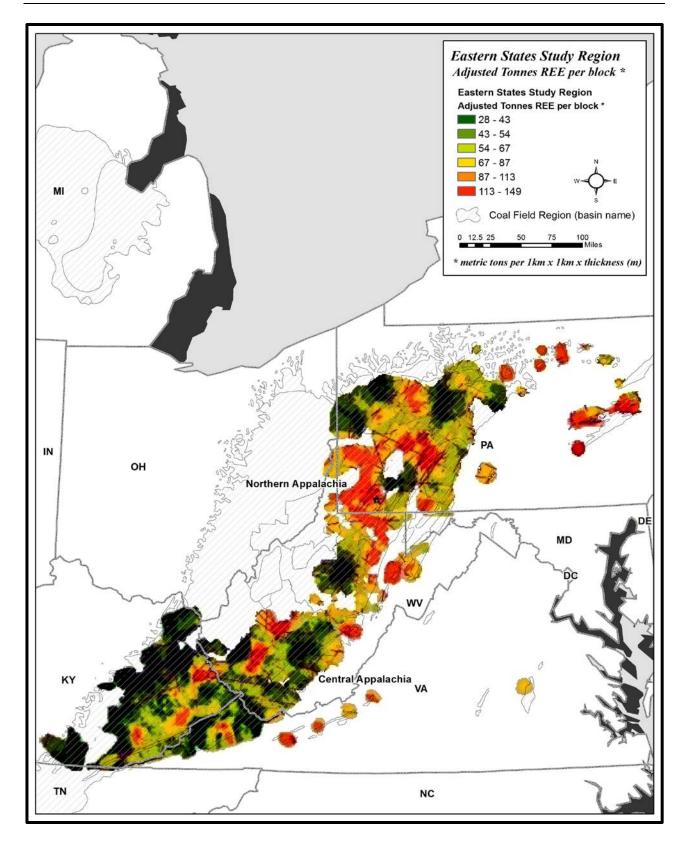


Figure 5b. REEs in U.S. Coal. (b) Map for Appalachian Region.

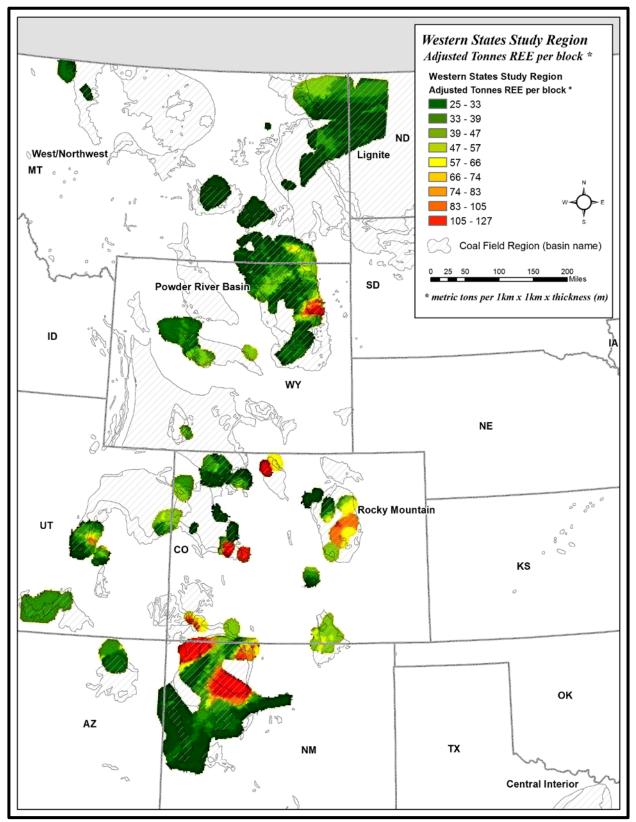


Figure 5c. REEs in U.S. Coal. (c) Map for central and northern Rocky Mountain region.

Data from ten states—six in the west and four in the east—were used to develop this analysis. These data indicate that two coal regions in the U.S. contain significant quantities (10 million MT) of REEs and that some of these deposits might be candidates for REE recovery (particularly those shown in shades of red). Both the northern and central Appalachian basins (Pennsylvania, West Virginia, and Kentucky) show numerous occurrences with higher mass loadings of REEs. Similar data for the western states examined are less common, but the source material used in this analysis included far fewer data points in that part of the country. These states contain approximately 62 percent of the estimated recoverable coal reserves.

REE Extraction Potential: Characterizing Deposits

Coal formations are three-dimensional and the coal quality and concentrations of trace elements (including REEs) will vary within formations by depth and location. For example, the measured compositional characteristics for several bench samples vary across the seam by a factor of three on a whole-sample basis. In addition, well log data were analyzed to explore the correlation between data from the logs and the known presence of REEs. A hand-held device based on X-ray fluorescence was used to screen samples in the field. These techniques and the resulting data can also support assessment of the three-dimensional nature of the REE deposits. The concentration of REEs within a coal seam is not necessarily constant from top to bottom or from one location to another.

REEExtraction Potential: Processing

Approximately 250 coal preparation plants are processing coal in the U.S. Typically, the plants will have a feed stream, two refuse streams, and a clean coal product stream. (In some cases, preparation plants may produce a second product stream with a different set of specifications.)

A series of coal washability tests was conducted in order to better understand REE partitioning potential during coal preparation. Samples covered approximately 10 percent of the preparation facilities in the U.S., chiefly in the northern, central, and southern Appalachian coal basins and in the Illinois basin. Comparable studies were also performed on a limited set of coals from western sources (Alaska, Colorado, North Dakota, Montana, and Texas).

Results have indicated that the REEs found in the clean coal product fraction, from processing coal in a preparation plant (the processing portion of Figure 4), are fully mixed into the organic phase, primarily as fine particles. This suggests that, for the fraction of REEs in raw coal that report to the clean coal product, little can be done to extract these REEs until after combustion. The rare earth concentrations in the lowest-density fractions indicate that: (1) ash-based material remaining finely dispersed within the coal has the strongest affinity for the REEs, and/or (2) the REEs are bound within the organic matrix by adsorption with humic acid components. Data obtained during this study supports the enriched finely dispersed mineral hypothesis, the first of these alternatives.

Figure 6 presents results for one set of analyses for the coarse refuse stream from one coal preparation plant. It shows the total concentrations of REEs for each of the specific gravity fractions

that were used in evaluating the separation of clean coal from mineral matter and the effect of that split on the REE concentration in each fraction. The average concentration of REEs found in the material increases successively from the 1.6 x 1.8 float through the 2.1 x 2.2 float², then remains constant until a significant drop occurs with the 2.9 sink.

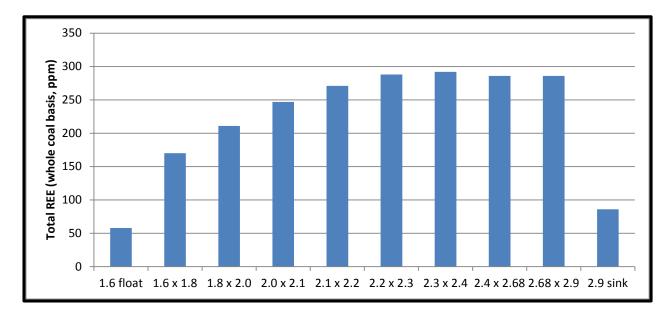


Figure 6. Washability Summary

Additional studies were conducted to determine the mass balance around an operating coal preparation plant. The data in Table 2 represent an actual mass balance around a single preparation plant. The total flow and REE flow numbers are measured values.

Stream	Total Flow (MT/hr.)	Ash (%)	REE Flow (Lb./hr.)
Raw Coal	1889	50.7	867
Clean Coal	882	8.3	261
Coarse Reject	917	87.0	542
Fine Reject	90	56.7	39

The REE data for this plant are typical of many of the plants evaluated in this study, with the bulk of the REE mass found in the coarse reject (which contains approximately 63 percent of the total

² The Float-and-sink analysis uses a series of heavy liquids diminishing (or increasing) in density by accurately controlled stages for the purpose of dividing a sample of crushed coal into gravimetric fractions either equal-settling or equal-floating at each stage. (Mines, 2014)

REEs entering the plant), typical of the various plants studied. For this plant, approximately 30 percent of the REEs are included in the clean coal product, which may be recoverable at the power plant after combustion.

For another portion of this study, a sample of the middlings was subjected to a series of grinding and separation steps to assess the potential of releasing the minerals from the coal hosting the REE minerals. The results are shown in Figure 7, and indicate that the REE-containing materials are fine grained and report to the low-gravity fractions. This conclusion is supported by mineralogical studies that were also performed. As a result, target resource streams can be identified and potential approaches to concentrating, separating, and processing the REEs from coal and coal byproducts can begin to be explored.

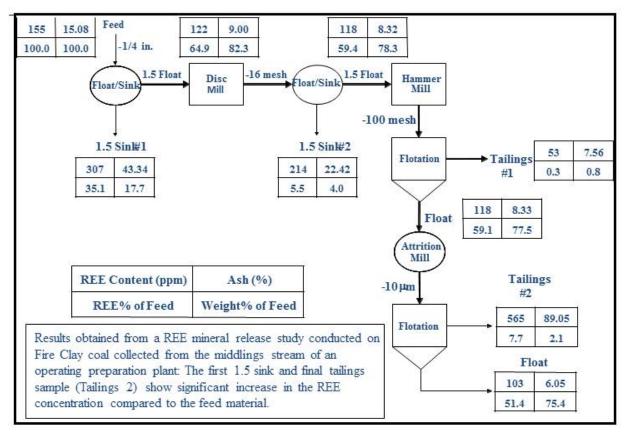


Figure 7. Mineral Release Test, Fire Clay Coal

Figure 8 presents the ratio of LREEs to HREEs for the coal preparation plant samples. LREE to HREE values are shown, from which the HREE proportion as a percentage of total REEs may be calculated. (Thus, a ratio of 5 means that there are 5 parts LREE to 1 part HREE.) These data show that for higher-ash-content samples (samples taken at preparation plants processing coal and additional rock), the LREE/HREE ratio values scatter between 4 and 6. These data also show that for lower-ash samples (less than 20 percent), the ratio varies from 2 to 5 (a ratio of 2 means that one-third of the total REEs are HREEs). These results again suggest that coal preparation processes can be used (or developed) to partition HREES from LREEs.

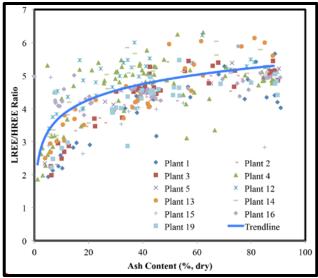


Figure 8. LREE/HREE vs. Coal Ash Content

Other data taken during a study of the performance of 19 preparation plants provides additional evidence of this partitioning. In fact, these data appear to show that cleaning enriches some REEs. Praseodymium is the only REE that is consistently enriched by at least a factor of However, the enrichment seen at the four. finest particle size occurs for all REEs and further supports the observation that the REEs occur in large measure as finely divided material in coal and coal byproducts within preparation plant streams. In addition to profiling the separation behavior as evidenced by the washability studies, bench-scale separation tests were conducted to determine their ability to concentrate the REEs in each particle size

fraction. In general, froth flotation³ was the only process that provided a significant concentration of REEs. The ability to concentrate REEs in a given size fraction will be a direct result of the size of the REE mineral inclusion, and hence, liberation size (the size to which an ore must be crushed or ground to produce separate particles) of the REE values in the host minerals. Results varied across the coals tested by the various participants. Magnetic separation⁴ data, froth flotation results, and riffle table⁵ results did show some concentration of REEs depending upon the particular coal subjected to testing.

The overall results from these studies do not show a single-stage concentration pathway that could produce an REE concentrate suitable for upgrading by use of existing technologies. However, these data do indicate a number of approaches that could potentially lead to significant REE enrichment.

One such promising approach, involving a variant of a so-called rougher circuit (a pre-concentration system using physical separation processing), is presented in the following Technology Assessment section. Many other techniques also appear promising and could benefit from similar exploration.

REE Extraction Potential: Coal Utilization Byproducts

The eighteen power stations in this study included: (1) pulverized coal-fired units (PC units) with wet scrubbers, (2) fluidized bed combustors, and (3) institutional and industrial stoker boilers.

³ Froth flotation is a process in which the minerals floated gather in and on the surface of bubbles of air or gas driven into or generated in the liquid in some convenient manner. (Mines, 2014)

⁴ Magnetic separation is a process in which magnetically susceptible material is extracted from a mixture using a magnetic force.

⁵ A device designed to reduce a sample of coal or ore to half its original size. The box contains about 12 chutes discharging alternately to opposite sides. The width varies according to the largest particle size. The volume reduction is rapid for dry material of suitable fineness.

Though there were variances among different combustors, the summary observation was that the REEs entering the system were not significantly transformed during combustion.

For example, Table 3 summarizes the results of measurements taken around a large PC unit (approximately 1300 megawatts (MW)). The total REEs introduced to the combustion process exit almost entirely to the bottom ash and fly ash in a roughly one-to-eight split, with the larger fraction found in the fly ash.

Location	Feed Coal	Fly Ash	Bottom Ash	Wet Scrubber
Total Ash Flow (MT/hr.)	51.3	46.0	5.28	_
Total REE Flow (Lb./hr.)	47.1	35.9	4.6	No significant mass of REE found in sample

Table 3. Example REE Mass Flows in a Pulverized Coal-Fired Power Station

Table 4 present data for a selection of the samples studied, showing some of the highest REE concentrations found across multiple power plants. These six locations vary greatly in scale and disposal practices. The byproducts are mixed in some cases and not mixed in others. One of the key data needs that must be addressed in evaluating coal byproduct sources is the development of methods to assess REE concentrations throughout large collections of post-use materials. The LREE to HREE ratio in three of the six cases presented indicates that the HREEs comprise more than 33 percent of the total REEs in the sample. Over the past 20 years, U.S. coal-fired power production has generated roughly 54.4 million MT of coal ash per year (American Coal Ash Association, 2012).

	Power plant, Dry ash pond		Ash disposal site at power plant		Fly ash from precipitator hoppers					
Total REEs ppm, (Whole Sample)	1,286	834	761	652	643					
Ratio (LREEs to HREEs)	5.0	2.5	1.7	1.1	1.1					

Table 4. Example Fly Ash/Bottom Ash Concentration Data

The historical inventory of fly ash is accessible and therefore could represent a desirable target because in many cases the source material for power stations consisted largely of coal from a limited number of mines, often within the same coal basin. Current practice often results in power stations burning blends of coal from several sources, which are often preparation plants that process coal from more than one mine (and more than one coal seam).

Finally, older refuse sites and reclaimed abandoned mines may have additional amendments mixed into the refuse that reduce the apparent REE content. Some of these amendments may be easily removed, but no attempt to do so was made in this study.

Technology Assessment

Introduction

The process of recovering REEs involves multiple process steps, some common with current practice in the coal and rare metals industries. The key to successful separation and extraction of any of the REE minerals is to fit the technologies selected to the particular feed material being provided.

- Development and implementation of environmentally benign, highly efficient, and cost competitive separation technologies would be important for the practical and economical recovery of REEs from low-concentration sources.
- The mineralogy of the REEs in coal and coal byproducts will significantly affect the recovery and separation efficiency of particular technologies or processes, including physical, chemical, and other more novel separation technologies.
- Existing and emerging recovery and separation technologies need to be tailored specifically to the recovery of REEs from various low-concentration sources.

The environmental footprint created by conventional REE processing technologies has long been a key consideration in determining where REEs can be mined and where the final products are extracted. Many of the technologies in the REE related R&D pipeline are focused on reducing this environmental footprint. The environmental concerns for conventional processing have elements in common with the needs for recovering REEs from coal and coal byproducts.

Each REE potential coal source and waste byproduct stream will have a slightly different set of environmental challenges because of the heterogeneity of coal and its REE-containing minerals.

Thus, the specifics of how to manage the toxicity of the coal waste materials generated and the chemistry and chemical engineering aspects of the processing streams used for REE concentration may vary from coal source to coal source.

However, several environmental impacts can be identified that will be common to all coal REE projects. These include: (1) the low concentration of REEs in coal and coal byproducts can lead to processing more material, resulting in more energy use; (2) increased production of fine particulate dust from increased grinding and crushing requirements; (3) the potential production of large volumes of liquid and solid wastes; (4) the toxic and caustic nature of chemical reagents required for REE extraction; (5) processing may concentrate unwanted materials, including radionuclides and other hazardous elements (e.g., thorium); and (6) if current refuse piles are considered, their use can lead to issues regarding ownership of environmental burdens of those refuse piles as well as new standards being placed on existing refuse piles.

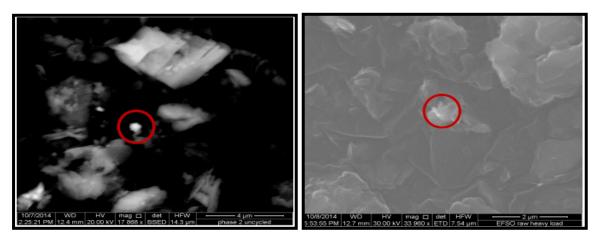
Data collected for this study may suggest means to separate additional trace elements from the basic mineral constituents to produce an REE product stream, a coal byproduct stream, and a secondary refuse stream that can be stored with fewer environmental concerns.

REE Mineralogy

Rare earth elements can be found in many minerals. The chief REE-rich minerals are bastnaesite, monazite, and xenotime (an yttrium-containing phosphate mineral similar to monazite). The separation properties of the mineral forms vary based in part on properties such as chemical formula and density and hardness, and the processes by which they were geologically deposited.

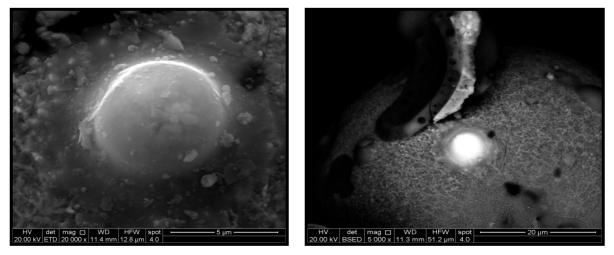
Scanning electron microscopy (SEM) equipped with Energy Dispersive X-ray was used to explore the mineralogical characteristics of coal. Major findings from these analyses are: (1) REEs have been found in mineral form as monazite, bastnaesite, xenotime, and absorbed clay; (2) REE minerals have a particle size below five micrometers; and (3) several researchers have found REE-bearing minerals trapped within fly ash cenospheres (glassy spherical particles). Understanding the REE constituents and their structures could enable industry to pursue the development of innovative concepts to concentrate, separate, and process REEs from coal and coal byproducts.

The SEM images demonstrate the differences that exist between the characteristic distribution of REEs as particles of distinct minerals admixed within the coal, as widely distributed across fine inclusions in associated clays, and often associated with the glassy phase in fly ash particles. The differences between the form and distribution of REEs point to the need for different processing techniques to be keyed to the different forms of occurrence to recover REEs from coal and associated clays.



Figures 9 (a) and (b). Scanning electron microscope images of bastnaesite (a) and monazite (b) particles in the reject generated from the processing of Fireclay seam coal.

The following SEM images depict REE-bearing minerals trapped within cenospheres formed during combustion in a power plant. The distribution of REEs in cenospheres and other glassy phases will most likely vary depending upon both the type of combustion system and the extent of the combustion.



Figures 9 (c) and (d). Cenospheres in fly ash with a monazite particle trapped inside. Secondary and backscatter images of a La, Ce, Nd, Pr, P-rich particle. Chemistry is consistent with monazite. Spherical particle is possibly melted monazite. Note that each image is at a different magnification.

Traditional Rare Earth Processing Technology

Typical REE ores are found below the surface and must have overburden removed prior to reaching the primary REE-containing ore. The REE-bearing minerals are separated from the ores using key technologies including gravity separation, magnetic separation, flotation, and solid phase extraction. The REE-bearing minerals have varying sizes, electrical and magnetic properties, and different specific gravities. Each of these particular characteristics plays a role in choosing the optimal combination of separation techniques. In some cases, the REE-bearing minerals occur with other target minerals and are produced as co-products.

Mining and size reduction for REE recovery share many technologies common to all mineral processing. However, REE processing tends to require more finely sized particles as the starting material for separation techniques such as froth flotation and chemical extraction. Significant research has been focused on developing improved processes, often using molecular modeling to reduce development time and save money. REE plant flow sheets can also include gravity concentration, electrostatic separation, and magnetic separation steps.

The primary source of REEs in China is from the production of iron ore at Bayan Obo, Inner Mongolia, where REEs are produced as a byproduct. Major steps involved with processing bastnaesite at Bayan Obo are crushing, grinding, bulk flotation, thickening, selective REE flotation, concentration of rare earth oxides, sulfatizing, roasting, removal of impurities, carbonate precipitation, acid leaching, scale solvent extraction, and precipitation.

Coal Beneficiation Processes Parallel REE Size Reduction and Separation

Similar size reduction and physical separation techniques are used for both conventional REE processing and coal processing. These include crushing and grinding, sizing, gravity separation, magnetic separation, flotation, and dewatering processing steps. Coal preparation plants produce coal products to different customer specifications, which require different types of equipment. Current commercial coal beneficiation 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. In flotation equipment, surface properties of coal are exploited.

DOE/NETL's data show that the different streams within the coal preparation facilities studied may be handling portions of the original feed coal with different REE content, which may offer an opportunity to develop a recovery process that does not need to deal with large masses of mineral matter containing concentrations of REEs less than the overall average concentration entering the plant.

In general, the approaches considered in this study included variations on a "rougher"⁶ circuit and recovery of REEs from coal ash streams. A rougher circuit was designed to process a portion of a coal preparation plant's reject material. (A single circuit could be applied to process refuse materials such as pit cleanings, other mining refuse, and coal refuse.) Such a circuit could also be designed to handle coal preparation plant reject material with lower ash compositions.

⁶ A pre-concentration system using physical separation processing to separate out the part of an ore that is not economically desirable but cannot be avoided in mining.

Valuable minerals have been identified in the ash portions of reject materials. These materials typically require disposal and do not undergo further processing. The rougher circuit intercepts this pathway and may be able to size and physically separate the reject material into valuable/marketable products such as REE pre-concentrate and a fuel for cogeneration applications. The performance of the circuit would depend upon the characteristics of the coal refuse being processed and whether the REEs are found to be concentrated predominantly in the organic phase or are present in significant concentrations in the partings and refuse rock associated with a particular mining operation.

A variant on the rougher circuit, focusing on separations from coal refuse generated within a coal preparation facility, is shown in Figure 10. This circuit was intended to depict a potential pathway to concentrate the REEs in a portion of the coarse and fine reject while separating out extraneous rock not part of the REE-rich formation. This study's initial analysis and testing indicate the potential of this circuit to concentrate the REEs in this refuse stream. The technologies, however, have neither been fully integrated nor tested at a significant scale to fully demonstrate feasibility.

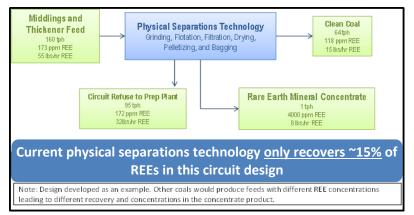


Figure 10. Rougher Circuit

Recovery from Fly Ash and Bottom Ash

A number of developments for recovery of constituents from fly and bottom ash have offered a technological basis for processing coal ash for REE recovery. Investigators have argued their merits and there is a significant amount of literature on the subject (Currie, 2012) (Mayfield & Lewis, Ari). Of late, both Neumann Systems and Physical Sciences Inc. (PSI) have begun developing technologies to recover REEs from coal ash.

Fly ash being processed for REEs will need to be analyzed to determine the size of the REE-bearing mineral(s) to determine the applicability of these and other ash-based technologies. Likewise, if REE-bearing minerals are in the one-to-three micron or submicron size range, milling will be required, with an energy processing cost penalty. However, byproducts of submicron size can be sold for nano-composite use at relatively high prices. Byproducts in the one-to-three micron range can be used as fillers for polymer and coating applications (Dong, Jow, & Lai, 2013).

Several responses to the NETL-issued RFI for Funding Opportunity Announcement (FOA) DE-FOA-0001202 from academic institutions, national laboratories, and industry stakeholders have offered potential technology pathways for the economic and environmentally benign pre-concentration and extraction of REE materials from coal and coal byproducts. The respondents have offered novel technology solutions focused on: (1) addressing current technical challenges, (2) improving upon the current convention, and (3) maturing technologies for the intended application. Specifically, the respondents offered novel technology solutions aligned to the following Key Technologies:

- Process/Production Technologies (Detection, Concentration, Separations, and Advanced Processing)
- Resource Sampling, Analysis, and Characterization (REE Constituents and Concentration, Structures, and Reserves)
- Environmental Management (Coal-byproduct, REE Processing, and Environmental Lifecycle)
- System Integration and Optimization (System Design, Integration Opportunities, and Advanced Manufacturing)

Aqueous Effluents

Mine pool water might represent another potential source to be screened. A limited number of samples collected during this study were wet. No dramatic differences were noted in the coal ash or coal preparation solid refuse sitting in aqueous media (along with other dissolved chemical species) for long periods. No attempt was made to test the water content in ash ponds that had held fly ash, bottom ash, or any other coal refuse for long periods. Recovery of REEs from mine effluents would have the additional potential benefit of offsetting costs of acid mine drainage remediation projects.

Tangential Technology Development

Add-on technologies and novel technologies under development may offer additional pathways for REE extraction from coal and coal byproducts. Significant federal investment is being made to advance the current state of REE separation, extraction, and processing technologies from traditional sources (most notably DOE's Critical Materials Institute, headquartered in Ames, Iowa). Technologies reviewed by DOE/NETL include low-intensity extraction techniques to reduce environmental impacts. Numerous advanced separation and extraction methods were also reviewed. These include advances in technologies not presently used in the coal industry, such as dielectrophoresis separation, leaching, liquid-liquid phase extraction, solid phase extraction, solid-liquid phase extraction, and solvent extraction.

Advanced Sensing, Detection, and Control

Advances in sensing, detection, and control offer opportunities to improve efficient characterization of the REE-containing resources, optimize the economics, and minimize the environmental impact. Technologies supporting this pathway have been reviewed by DOE/NETL.

A number of commercial instruments are available that might contribute to characterizing either REE concentrations or those of other key elements with geologic REE associations. Real-time information about their variances would help operators identify quality differences (for any of a number of potential quality-related parameters) much more efficiently.

For REEs and elements with geologic REE associations the techniques evaluated included X-ray fluorescence, instrumental neutron activation analysis (INAA), inductively coupled atomic emission spectroscopy (ICP-AES), and inductively coupled argon plasma-mass spectrometry (ICAP-MS). Currently, ICP-AES and ICAP-MS are the preferred methods, although INAA might be of use. However, none of these techniques have been specifically designed to measure the small concentrations (less than 1000 ppm total) that might be needed for REE processing.

One means of remote detection of REEs in sedimentary rocks is through the use of geophysical logs from oil and gas exploration, especially spectral gamma ray logs. Recent activity in the oil and gas industry has resulted in significant availability of the logs in Log ASCII format (LAS), which lends itself to conversion of data in commercial log processing software.

The DOE/NETL team has developed a means of using spectral gamma ray thorium measurements as a low-cost way to prospect for elevated REE-content zones logged through coal measures. The method uses cross plots of thorium and total REE content from the USGS database to develop an algorithm to convert thorium content to total rare earth content, as seen in Figures 11 a and b.

Figure 11a shows a thorium-total REEs cross plot for the Utah data in the USGS database. This correlation was then input to the log processing software (in this case, Petra) to develop a rare earth concentration profile over the interval for a well in Duchesne County, Utah, as seen on Track 3 of the log presentation in Figure 11b. Track 1 in the figure includes total gamma ray and caliper measurements, and track 2 shows a delta log R plot, which is an overlay of resistivity and density logs.

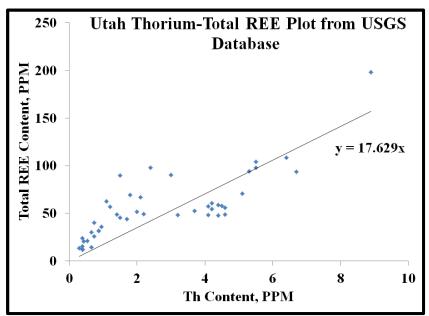


Figure 11a. Thorium-total REEs cross plot

The latter plot can indicate the presence of organics (red shading) in the interval. Several zones with elevated rare earth content are indicated in this example.

Approximately 150 LAS files of this type have been secured from state agencies and data have been generated for subsurface zones in Colorado, North Dakota, Pennsylvania, Utah, and Wyoming. High REE content intervals are being correlated with mud log data, identifying coal zones where available, to identity these zones.

This DOE/NETL-developed technique provides a low cost means of screening coal-bearing geologic formations across multiple states, and is providing results that will inform the procurement of further samples for this project.

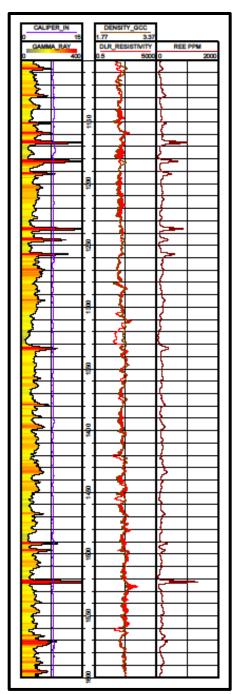


Figure 11b. Rare Earth Concentration Profile

III. ECONOMIC ASSESSMENT

An assessment and analysis of the feasibility of recovering REEs from coal and coal byproduct streams requires knowledge of the economics of REE production from coal-related feedstocks. The results of this activity are financial models of production facilities using currently available technologies. The preliminary analysis presented in this report focuses on selected coal-related feedstocks.

It should be noted that each REE recovery project would have a distinct design and economic outlook. These model operations do not project to be profitable using conventional technologies.

The workflow required to construct a financial model for a mineral processing operation to recover REE values from coal and coal byproducts requires inputs developed via laboratory testing of coal and coal byproduct samples, analysis of REE concentrations for fractions separated from the original samples, mineral processing flowsheet design and simulation, and financial model development. Current financial model development is focused on producing a total REE concentrate from a coal byproduct feedstock and using physical separation and hydrometallurgy to produce a mixed rare earth oxides product. The workflow and information required for developing a financial model are shown in Figure 12.

- The economic returns on recovering REEs from coal and coal byproducts are largely determined by supply and demand in the international market. In order for domestic coal and coal byproducts to competitively supply REEs to the marketplace, commercial techniques need to be tailored to the specific nature of coal-based sources and integrated with new technology.
- Co-producing REEs and other useful materials contained in coal and coalbyproduct sources can enhance the economic viability of REE recovery.
- Economic viability hinges on concentrating and refining marginal (subcommercial) feedstocks. The best nearterm opportunity may be via a combination of advanced physical and chemical separation techniques.
- Long-term opportunities to economically recover REEs from coal and coal byproducts require leveraging the knowledge gained to develop novel recovery approaches. These new processing systems must incorporate steps to recover, separate, and/or refine REEs without generating large volumes of unwanted products.

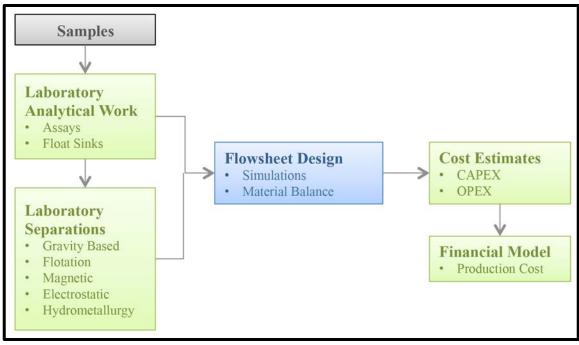


Figure 12. The Inputs and Workflow Required for Financial Modeling of REE Product Recovery from Coal and Coal Byproducts

The economic modeling effort requires:

- 1. Knowledge of the assay (i.e., the REE content) of coal and coal byproducts in the U.S. Sampling and analyses of coal and coal byproducts provide this information.
- 2. The extractability of REEs from these products, which is used in sizing of equipment and material balances required for flowsheet construction. Specialized capabilities with respect to laboratory separations testing have been provided by academic institutions that have mineral processing capabilities.
- 3. Flowsheet design and attendant capital- and operating-cost information associated with flowsheets. The analysis described herein uses currently available technologies for baseline construction. This effort required specialized knowledge and experience associated with the mineral extraction industry in the U.S. and was undertaken using both federal DOE/NETL and contractor resources (including those available from academic institutions).
- 4. Construction of financial models representing the projected economic performance of businesses using the example plants.

Information from DOE/NETL's REE investigation provided REE material balances, industry-related economic studies, technical reports, and feasibility studies, as well as its own engineering experiences within the mineral extraction sector.

As discussed previously, samples from multiple coal fields in the U.S. were analyzed for bulk REE content and potential value shown in screening of samples.

These data were used for mineral processing flowsheet construction, which was produced using federal DOE/NETL mineral processing experience as well as contractor expertise, including that available from academic institutions. The flowsheet output includes material balance and unit capacity data required for financial model development.

The recovery of REEs from an individual coal production operation with relatively low REE concentrations can be expected to produce low tonnages. However, preliminary work under this project showed that some REE concentration is possible using physical separation processing. For these reasons, the first set of financial modeling, as well as the supporting research, was developed around a scenario where pre-concentration systems using physical separation processing, known here as rougher systems, are located at coal preparation plant sites. Multiple rougher systems produce pre-concentrates using physical separation systems, and supply the pre-concentrates to a central hydrometallurgy facility, here called the cleaner system, which further processes the pre-concentrates into a salable high-assay concentrate.

This type of production system, shown in Figures 13 (a) and (b), provides some advantages in minimizing rare earth concentrate production costs:

- 1. Reducing shipping costs to the facility producing the salable REE concentrate by increasing the assay (concentration) of the material to be shipped.
- 2. While physical separations alone may not (given the current state of the technology) produce a salable concentrate, some increase in concentration is possible. Owners and operators of coal production facilities are familiar with current physical separations technologies and required operations practices.
- 3. Vendors of physical separation technologies have an established presence in coal-producing regions.

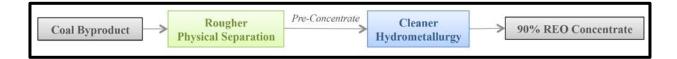


Figure 13 (a). Portions of the REE Extractive Metallurgy Value Chain Covered by the Current Financial Modeling Effort

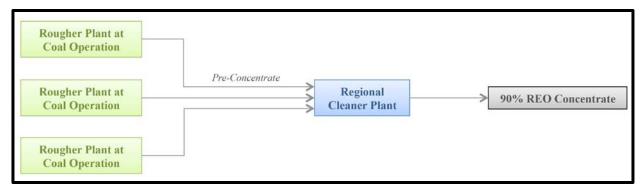


Figure 13 (b). Illustration of Logistics Associated with Current Financial Modeling Effort (REO = rare earth oxides)

The cleaner system uses hydrometallurgy⁷ technology, and the system shown in figures 13 (a) and (b) would take advantage of economies of scale due to being fed pre-concentrate via multiple operations. The cleaner product would then be suitable for use in an existing system to further process and separate individual REEs.

The target assay for the output from the cleaner plant is 90 percent rare earth oxides.

The required output for this effort is a projected production cost for an REE product from coal and coal byproducts. The model used to generate this output is a set of financial statements built around businesses representing the rougher and cleaner operations, including cash flow statements, from which the levered internal rate of return (IRR) is calculated. Costs are input based on a uniform capital structure and debt interest rate, capital and operating cost estimates, and material balance data generated by DOE/NETL. A hurdle rate (required levered IRR) is set at 20 percent (as an example), and the sales price for the REE concentrate product required to achieve the IRR hurdle rate is the resultant production cost.

A value for the rougher REE concentrate product is based on USGS REE ore trading data. The flowsheets found in Figures 13 (a) and (b) are linked financially (rougher plants captive to cleaner plant). While the rougher concentrate has a lower REE assay than might be found in commercially traded REE ore (i.e. <60 wt%), the cleaner plant is a multiple-product operation. Other constituents in the rougher plant (for example alumina) would be of value to the operation. Thus the value of the REE concentrate to the cleaner plant has been set based on an assay/price algorithm developed from USGS data.

Multiple financial model runs have been completed for rougher plant cases where capital cost items have been varied and the REE concentrate and production rate have been fixed based on research results to date. Figure 14 shows required sales prices for high- and low-cost cases

⁷ Hydrometallurgy is a branch of extractive metallurgy that uses aqueous chemistry to extract metals from ores. In the case of the "cleaner" system mentioned in this report, it uses hydrochloric acid to extract the rare earth elements from the rougher product.

resultant from model runs. Also shown is a value to the cleaner plant, which has been calculated from USGS REE ore sales data.

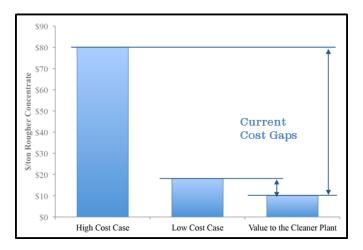


Figure 14. Rougher plant production costs for low-assay REE concentrates from coal compared with a value required as feedstock for the cleaner plant

Similar to the financial treatment undertaken for the rougher plant, a cleaner system flowsheet and financial model are under development based on the same financial parameters and requirements discussed above. Work in this area, as mentioned, includes a multiple-product operation where the aggregate product (other than REE) sales offset the production cost of an REE product.

The volume of economic activity supported by the REE industry in the United States is significant. In 2013 (RETA, 2014) rare earth *intermediate products* delivered \$39.2 billion in revenue (magnets, catalysts, metallurgical additives, polishing powders, glass additives, ceramics, and batteries), created 101,800 jobs, and generated \$6.1 billion in payroll. At the same time, domestic rare earth *end-market products* and technologies delivered \$259.6 billion in revenue (health care, hybrid electric vehicles, lighting, communication systems, audio equipment, defense technologies, optics, oil refining, and wind power), created 433,500 jobs, and generated \$27.3 billion in payroll. It is estimated that "each job in the rare earth industry generates an additional 5.0 jobs elsewhere in the North American economy." (RETA, 2014)

IV. TECHNICAL CHALLENGES TO RECOVERING RARE EARTH ELEMENTS FROM THESE DOMESTIC RESOURCES AND REQUIREMENTS FOR ADDRESSING THEM

The primary key finding from this work is that results have indicated a large potential resource of rare earth elements in the coal measures of two of the coal-producing regions in the U.S. This potential resource is over a magnitude higher than forecast global REE demand, and may expand as other data from other coal basins in the U.S. are added.

The second finding is the challenge presented in the low REE assays in coal and coal byproducts compared with other REE sources. This is also the most significant challenge. An additional challenge is minimizing the environmental impact of any envisioned production operations.

The economic feasibility of REE production from these sources will require improvements in both the understanding of REE occurrences in coal-bearing strata, as well as the technologies required to recover these materials in marketable forms. Establishment of the economic feasibility of recovering REEs, possibly leading to the creation of competitive REE production in U.S. coal-producing regions, requires addressing the challenge of low assays.

While the work reported here suggests a large REE resource, much knowledge remains to be gained in addressing the low assay challenge. Development of the knowledge required to successfully address this challenge requires activities areas outlined below, which are grouped into topics presented in Figure 12:

- Knowledge of REE distribution in U.S. coals and related minerals (samples/laboratory analytical work): Preliminary work has established that there is variability in the REE contents associated with U.S. coal deposits. It is not known why higher REE contents are found associated with some coal deposits, which can lead to improved understanding of the mineral forms present (in turn, this can lead to separation technology improvements). Additional effort by academic and private industry sedimentary geology experts may assist in directing further sampling and assaying work toward deposits with the highest REE contents.
- 2. Knowledge of REE distributions within minerals associated with specific deposits (samples/laboratory analytical work): Work done to date has shown that REEs can be expected to concentrate in specific portions of strata associated with a coal deposit, and can be expected to concentrate in specific portions of the mined product (i.e. specific gravity). This work has provided valuable knowledge of distributions and mineralogy of REEs in coals, and has been largely contributed by U.S. university mineral processing programs. As improved knowledge of the occurrence and distributions of REEs associated with coal deposits is gained through activities highlighted in (1) above, laboratory separations and characterization work can improve the knowledge base of REE occurrences associated with U.S. coals. This information would support development of

processes to extract REEs from U.S. coals. The world-class mineral processing capabilities resident within in the U.S. academic and industrial sectors will provide the skill sets and capabilities required for this activity.

- 3. Knowledge of the response of REE-bearing components associated with U.S. coals to industrial separation processes (laboratory analytical work): As has been mentioned, while they could collectively represent a substantial domestic resource, the low REE assays associated with U.S. coal bearing minerals represent a significant challenge in the establishment of economic REE production from these materials. Knowledge of the responses of REE-bearing minerals to physical separation processes is essential for conceptual flowsheet designs (in turn required for economic evaluations). This type of work is also essential for the development of new separations technologies. In addition to broad mineral processing knowledge and the required laboratory equipment, capabilities for mathematical modeling of mineral processing unit operations are required. This set of equipment and capabilities is resident within the U.S. academic and industrial sectors, with university mineral processing programs having contributed the preliminary results that appear in this report. Continued effortby these groups will be required for further work in this area.
- 4. Design of systems specifically for REE recovery from deposits associated with U.S. coals (flowsheet design/cost estimates): Economic analyses of systems for the recovery of REE-bearing concentrates from coal and coal byproducts will require flowsheet designs, from which material balance data, capital costs, and operating costs are extracted for use as inputs for financial modeling of conceptual operations. This activity must also be conducted such that the resulting waste is not objectionable from an environmental standpoint. Preliminary flowsheet design results have been presented here. These results have been developed through DOE/NETL collaboration with academia and industry. Establishment of pathways for commercial REE production would require additional effort by the expertise base available in the U.S. academic and industrial sectors.
- 5. Economic feasibility assessment (financial model): As new results are generated from items 1-4 above, financial models of conceptual production operations could be further developed and refined. This work could describe the economic feasibility of REE production from coal and coal byproducts, for assessments of both existing technologies and the development of new processes. Success in this area would rely on continued engagement by the U.S. stakeholder base (academic and industrial) with specialized knowledge in this area.

In summary, these items represent the work flow that might support investment decisions aimed at turning a mineral reserve into a production business. The primary challenge that has been identified in this work is the low REE assays encountered. Expanded characterization work, improved knowledge that the highest assays can be found, and application of U.S. academic and industrial expertise base can help address this challenge.

V. CONCLUSION

The Department of Energy Office of Fossil Energy (FE) and the National Energy Technology Laboratory (NETL) have conducted an assessment and analysis of the feasibility of economically recovering rare earth elements from coal and coal byproduct streams. Through both literature surveys and testing samples from U.S. mining operations, a preliminary reserve base has been established in two key coal-producing regions in the U.S. While the global REE market demand is expected to remain on the order of 100,000 tonnes per year, these two regions alone in the U.S. have potential reserves in the millions of tonnes.

The key to unlocking this potential reserve base for economic U.S. REE production from coal and coal byproducts is the improvement of separation technologies. REEs tend to concentrate in higher ash content sediments associated with coal seams, and can also be expected to concentrate in byproducts of coal production and coal-based electric generation. University laboratories have conducted separations testing, and while enrichments of REE values were found, continued laboratory work, as well as separations technology development, are needed to improve the economics of REE production. Financial modeling effort will also support potential matching of REE production costs from coal-related feedstocks to market prices for the recovered REE products.

Pursuit of economic recovery of REEs from coal and coal byproducts, would entail:

- 1. Continue identification of domestic sources of coal and coal byproducts with the highest known concentration of REEs.
- 2. Conduct research to better understand the form and structure of REEs in coal and coal byproducts. This will support the design of alternative separation technologies.
- 3. Design, develop, and test alternative separation technologies to recover mixed REEs from coal and coal byproducts for downstream processing and purification of individual elements by REE refineries.

VI. APPENDIX A: DOE/NETL RARE EARTH ELEMENT SAMPLING METHODOLOGY

REE Sampling and Analysis Effort

The study samples were collected from (1) state geological surveys, (2) companies operating active production and/or processing plants, (3) companies operating a variety of utilization facilities, and (4) companies owning disposal sites (active and inactive). The sampling methodology is detailed below.

REE Sampling Program Methodology

Samples were collected with the cooperation of state geological surveys and companies operating active mines, preparation plants, power plants or owning the disposal sites (active and inactive). At times, personnel from regional universities familiar with the coal regions being examined took samples after reaching out to sites selected beforehand as having promise based on previous history, USGS and state geologic survey samples, and use of screening tools such as X-ray fluorescence.

The quantity of material collected and the level of information available to fully document the nature of the samples varied across sources. (How representative is this sample of the process being sampled, or of the long-term production of coal from a particular mine, or of the material held in some sort of waste repository?) For power and coal preparation plants, data gathering was typically supported by operating staff at each facility and the samples were labeled using a standardized approach. The operators provided flow rate data and discussed any operating issues that arose during testing. They often assisted this effort by scheduling runs that would utilize well-characterized feed coals (rather than an ever-changing series of blends). This support allowed the data gathering team to better understand both the value of the data and to document any limitations that arose when testing was conducted on a single feed or a single coal blend.

Samples were shipped for analysis using chain of custody forms which included the sample names. The information developed for each sample was then entered into a database, which contained the relevant information. Identities of the companies contributing samples or access during this exercise are generally protected by non-disclosure agreements and will not be divulged in this report. The samples from state geologic surveys were provided without restriction and may be identified in more detail. For waste sites, the level of interaction and support was less substantial. The specific history of the material held on the site was not always readily available at a sufficient level of detail to characterize the site as a potential source. Active ash ponds were often not in a condition that would permit a comprehensive sampling plan to be defined and representative samples to be collected. In these cases, grab samples were taken to provide preliminary data. Over

1800 samples were obtained and analyzed for this study. ASTM method D6357 was used to determine the amounts of REEs and other trace elements.

ASTM Method D6357

The commercial analytical laboratories selected by NETL for analyses of REEs use two similar sounding but different methods for analysis: ICP-AES and inductively coupled plasma mass spectrometry. These techniques permit simultaneous analysis of a suite of elements from a single sample. Both techniques use plasma generated from an inert gas, usually argon, via a high-powered radio frequency generator. The generator causes the gas to ionize, producing a plasma of electrons and positive argon ions in the argon gas. A fine mist of sample solution is then introduced directly into the plasma via a nebulizer. At the temperatures of the plasma—7,000 to 10,000 degrees Celsius—molecules are converted to their individual elements, which exist as ions in the plasma. These results form part of the publicly-available EDX data set discussed throughout this report.

REE Resource Evaluation and Estimation

The resource estimates presented below are derived by statistical analysis of USGS data (<u>http://energy.er.usgs.gov/products/databases/CoalQual/intro.htm</u>) and augmented by data taken during this study. This initial effort focused on one sub-region in the eastern United States and one in the West. High-value sources were evaluated based on the grade of the source (Bryan, et al, Tetra Tech, 2015).

A methodology was developed, using samples from both eastern and western states, to assess REE contents, both in the coal-bearing, organic portion of the deposit and in likely REE-bearing minerals associated with the coal. The assumptions made and methodology employed in developing the REE resource estimates are outlined below.

The DOE REE resource estimate has been developed for a selected set of eastern and western states. The estimate sought to establish a fundamentally sound resource estimate of the total amount of rare earth elements that could be found within and around the coal deposits in these regions based on statistical methods to infer resources. Key aspects of the methodology are as follows:

- The formation of coal generally occurs in a basin, which is the final resting place for REE enriched sediments from volcanic, intrusive, and detrital sources.
- REE content reported in the coals appears to show a close relationship to aluminum-rich mineral content. REEs associated with coal generally favor partitioning to clay materials. Only small amounts have been described in the literature as likely being fixed by ion exchange into the organic phase. The reported values, therefore, are attributed to the inorganic phase only.

- The analysis used statistical methods to suggest bulk concentration values in the large volumes
 of coal and mineral matter that can be defined by the data points compiled in the USGS
 COALQUAL database. These data include a measure of the total thickness of the core that was
 taken to represent any individual sample point. In this dataset, large partings (>4") were
 removed before the chemical analysis of the elemental composition (including the rare earths)
 was determined.
- A 500 ppm REE cut-off grade emerged as a figure of merit to define a quantity (tons of REEs in situ) that might be recoverable should appropriate technology be available. Any practical attempt to exploit a coal seam to recover REEs—even one currently in production—would require that additional samples be taken to characterize the amount and distribution of REEs in the seam. This requires the creation of a co-mining plan customized to produce the coal, rare earth elements, and any other valuable by-products present (cobalt and platinum group metals, for example).
- Not every "block" of material within the study areas would actually contain material at the 500 ppm cut-off concentration. Some portions of the deposits would exhibit average concentrations below the cutoff concentration and others would exhibit concentrations above that value.
- The cut-off value and the average value apply to the in-situ coal (interspersed with bits of clay) and to clay partings and portions of the roof and floor close to the coal bed, not to the as-mined coal. Coal mining extracts coal with an eye toward the efficiency of extraction. Current mining practices are focused solely on extracting coal, taking as little extraneous material as possible. Some of the variance seen between in-situ estimates and the concentration of REEs actually observed in samples analyzed in this study arise from this difference.

These calculations, as noted earlier, indicate that 6 million metric tons of REEs could be recovered from the known coal reserves in select western state coal basins in Montana, Wyoming, Colorado, Utah, New Mexico, and Arizona. Similar calculations show that 4.9 million metric tons are available from among the coal deposits found in Pennsylvania, West Virginia, Kentucky, and Virginia (Administration U. E., 2012). These amounts would vary slightly depending upon the minimum REE concentration value in any assessed volume of coal plus mineral matter being evaluated as a candidate for recovery. The actual amounts that could be recovered would be a function of mining practices and the economics of recovery from the operations actively producing, processing and utilizing newly mined coal (Administration U. E., 2012). Because of the limited distribution and range of samples utilized in the study, the REE estimates are believed to be conservative estimates of the possible REE resources available.

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