CRITICAL MINERALS SUSTAINABILITY PROGRAM

Courtesy of NETL REE-CM Website

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PROJECT PORTFOLIO
2020 – 2021

U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

DISCLAIMER

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INTRODUCTION

PROGRAM OVERVIEW

Since 2014, the Department of Energy (DOE), Office of Fossil Energy (FE), and NETL have undertaken a research, development, and demonstration (RD&D) program that has focused on the extraction, separation, recovery, and purification of rare earth elements (REE) and critical minerals (CM) from coal-based resources which include run-of-mine coal, coal refuse (mineral matter that is removed from coal prior to shipment), clay/sandstone over/under-burden materials, ash (coal combustion residuals), aqueous effluents such as acid mine drainage (AMD), and associated solids and precipitates resulting from AMD treatment. Over the past 7 years, DOE-NETL's Program has conducted over 40 projects which have involved the mineral processing and process development expertise of our extramural stakeholders at universities and small businesses, as well as at the Los Alamos, Lawrence Livermore, Idaho, and Pacific Northwest national laboratories, and the intramural field work proposal (FWP) efforts at NETL's Research and Innovation Center (RIC). The projects have bracketed the full spectrum of technology readiness levels from the basic and applied sciences (TRL 1–3) through the design, construction and operation of bench/pilot-scale facilities (TRL 3–5/5–7), and most currently, conceptual design for operation of an engineering-scale prototype facility (TRL 7–8) that, when functional, will produce 1–3 metric tons mixed rare earth oxides (MREO) per day using coal-based resources and potentially alternative feedstock materials.

Since 2014, domestic coal-based resources that are REE-enriched have been identified and locations and quantities available for sustainable commercial use continue to be addressed with assistance from geospatial modeling. Development of advanced fiber optic probes and laser induced breakdown spectroscopy (LIBS) field sensors for in-situ field detection of REE at parts-per-billion (ppb) and parts-per-million (ppm) concentrations continues. Funding opportunities issued by NETL in 2016 directed extramural stakeholder efforts to produce at a minimum of 2 wt% (20,000 ppm) MREO preconcentrates. By 2018, small bench/pilot-scale facilities had been constructed, and currently the DOE-NETL program has demonstrated the technical feasibility of producing small quantities of high purity—approximately 98 wt% (980,000 ppm) and greater—MREO in three domestic first-of-a-kind small bench/pilot-scale facilities.

Research has also focused on optimization and efficiency improvement of conventional REE separation systems to achieve process economic viability as well as development of advanced, transformational REE and CM separation processes. Notably, all conventional and transformational REE and CM separation process designs have undergone rigorous techno-economic analysis (TEA) prior to bench/small-pilot-scale facility construction and operation.

In 2019, RD&D efforts at NETL were additionally directed to co-production of CM, as cobalt (Co), manganese (Mn), lithium (Li), and potentially aluminum (Al), zinc (Zn), germanium (Ge), and gallium (Ga) from domestic, coal-based, REE-containing feedstock materials. Currently, state-of-the-art conventional separation process concepts are being assessed for near-future production of 1–3 metric tons per day of high-purity MREO in engineering-scale prototype facilities.

In 2021, DOE-NETL's REE-CM program is initiating basinal coalition efforts to address realization of the full economic potential value of U.S. natural resources for producing REE, CM, and high-value, nonfuel, carbon-based products, and to holistically assess not only upstream mining of resources and physical separation (e.g., beneficiation), but also midstream processing, separation, recovery, and purification of critical and high-value materials, and ultimately on-shore downstream manufacturing that incorporates these materials into commodity and/or national defense intermediate or end products.

BACKGROUND

Rare earth elements (Figure 1) are essential materials in a broad range of technologies significant to national security, energy, medical, and consumer products (Figure 2). REE occur throughout the earth's crust, commonly at low concentrations. They are not found in an isolated form readily available for extraction, but are distributed throughout a variety of minerals, and are also found in coal and coal by-products. REE-bearing mineral deposits are relatively rich in either light rare earth elements (LREE) or heavy rare earth elements (HREE), with LREE being more abundant. The environmental footprint created by conventional REE processing techniques has long been a key consideration in determining where these elements are mined and subsequently produced.

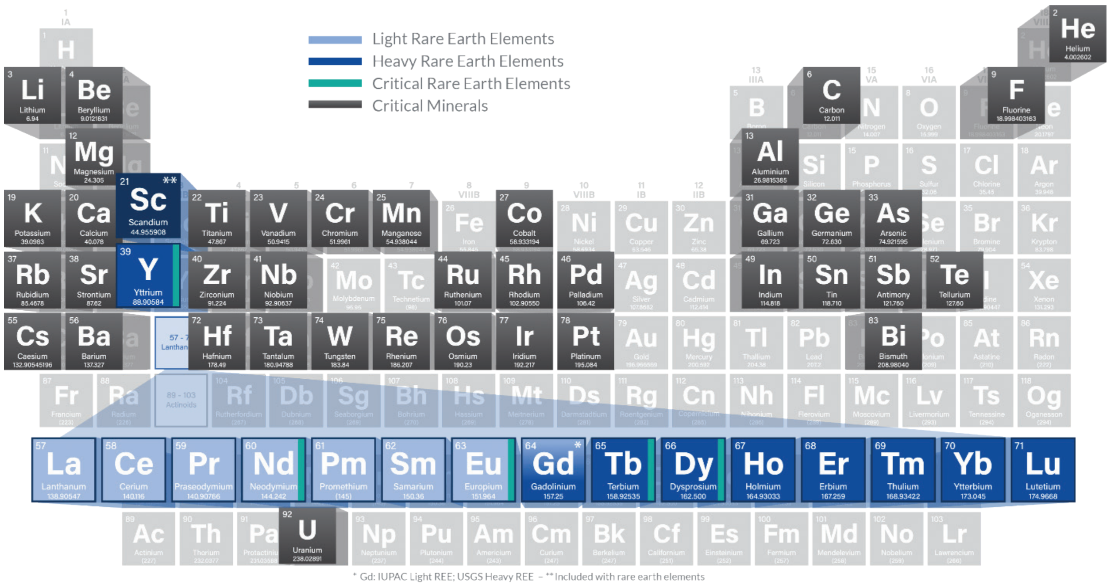


Figure 1. Rare earth elements (including scandium and yttrium) and additional critical minerals.

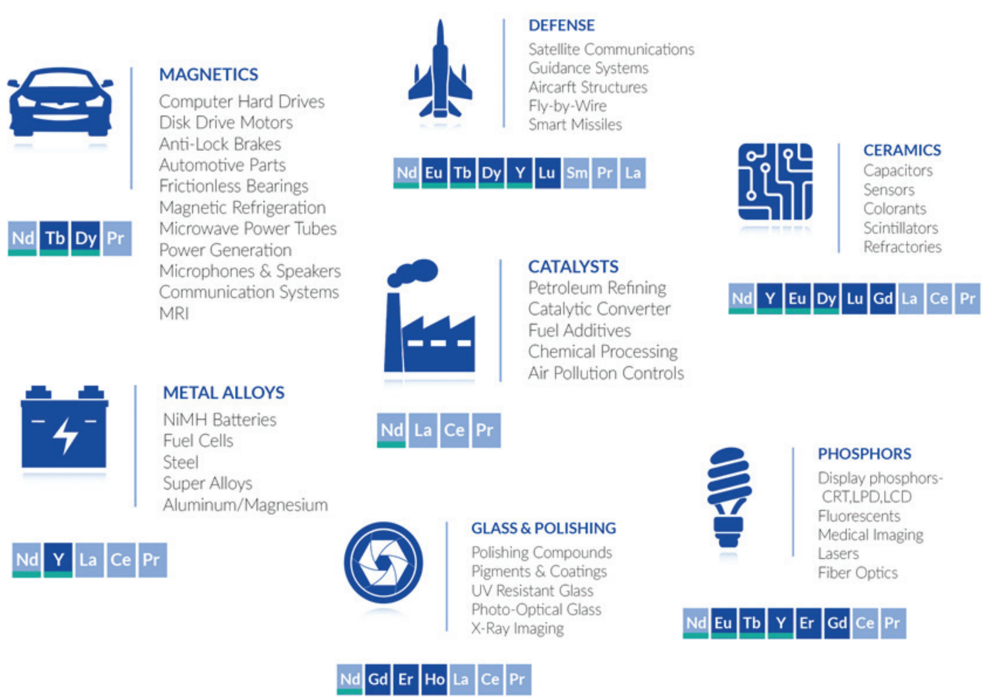


Figure 2. Rare earth element applications.

In contrast to the 1980s, when the United States produced more rare earth elements (REE)[1] than any other country in the world (Figure 3), the nation currently imports 80% of its REE directly from China, with portions of the remainder indirectly sourced from China through other countries. Similarly, the United States imports more than half of its annual consumption for thirty-one of the thirty-five critical minerals (CM)[2], and has no domestic production for fourteen CM and is therefore dependent on imports to supply demand for them [1].

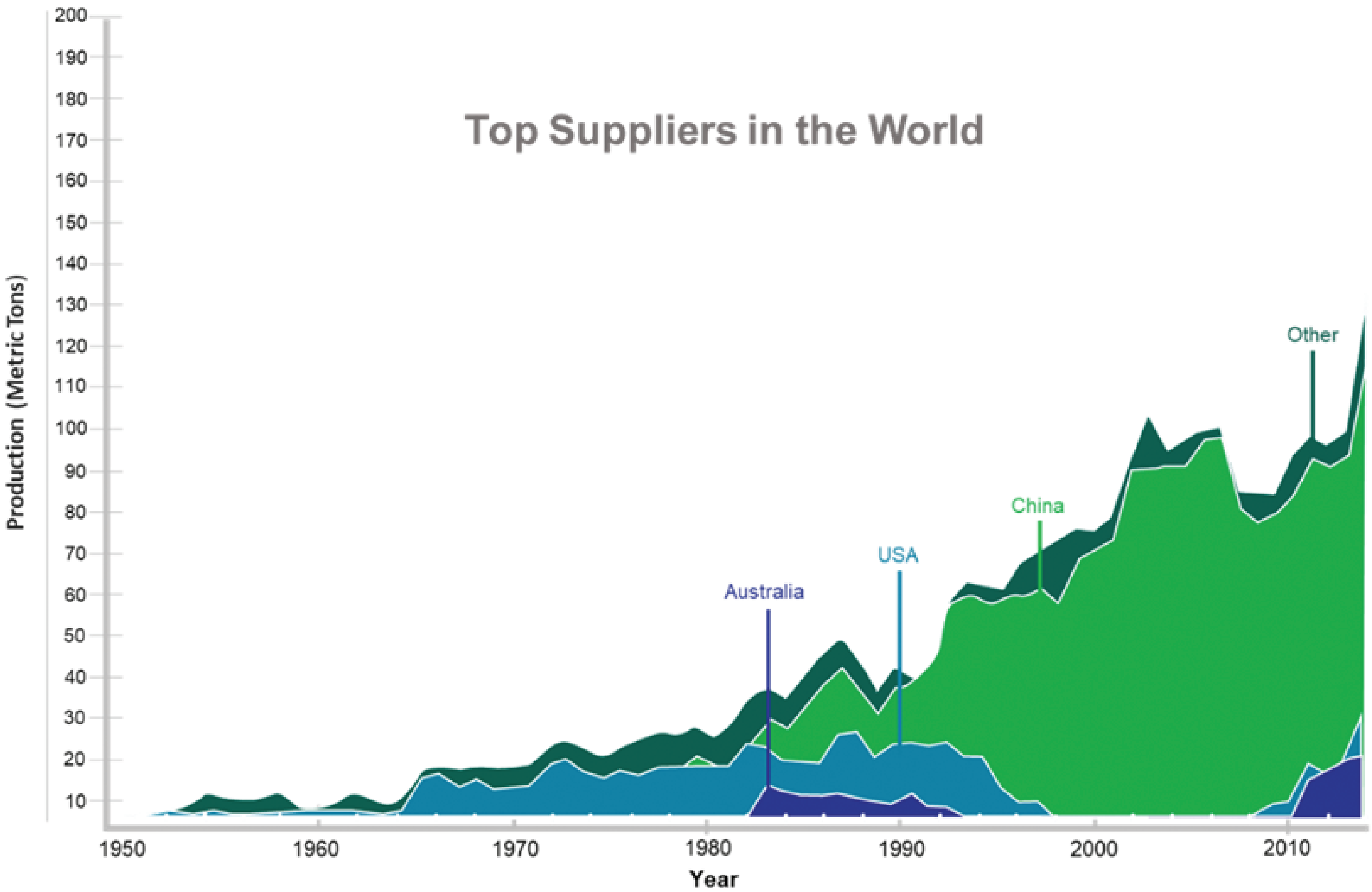


Figure 3. Major international rare earth suppliers.

[1]Rare Earth Elements: Lanthanum, cerium, praseodymium, neodymium, (promethium), samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, and which additionally include scandium and yttrium.

[2]Critical Minerals: Aluminum (bauxite), antimony, arsenic, barite, beryllium, bismuth, cesium, chromium, cobalt, fluorspar, gallium, germanium, graphite (natural), hafnium, helium, indium, lithium, magnesium, manganese, niobium, platinum group metals, potash, the rare earth elements group, rhenium, rubidium, scandium, strontium, tantalum, tellurium, tin, titanium, tungsten, uranium, vanadium, and zirconium. Critical minerals are nonfuel minerals or materials that are essential to our modern economy and national security and that have a supply chain vulnerable to disruption.

PROGRAM MISSION, OBJECTIVES AND GOALS

The mission of the DOE-NETL program between 2014 and 2020 was the development of an economically competitive and sustainable domestic supply of REE to assist in maintaining our nation's economic growth and national security. In 2020, the program's mission was expanded to include CM [2].

The objectives of the DOE-NETL 2014-2020 ***Feasibility of Recovering Rare Earth Elements*** program were to:

- Recover REE from coal and coal by-product streams, such as run-of-mine coal, coal refuse, clay/sandstone over/under-burden materials, power generation ash, and aqueous effluents as acid mine drainage (AMD).
- Advance existing and/or develop new, second-generation or transformational extraction and separation technologies to improve process system economics and reduce the environmental impact of the coal-based REE value chain (Figure 4).

The goals of the program were to (1) validate the technical as well as economic feasibility of recovering REE from coal-based materials, and (2) accelerate the design, construction and near-term operation of a domestic engineering-scale prototype facility in an environmentally benign manner, producing 1-3 metric tons/day of mixed rare earth oxides or salts (MREO/MRES) from coal-based resources at purities of a minimum of 75 wt%.

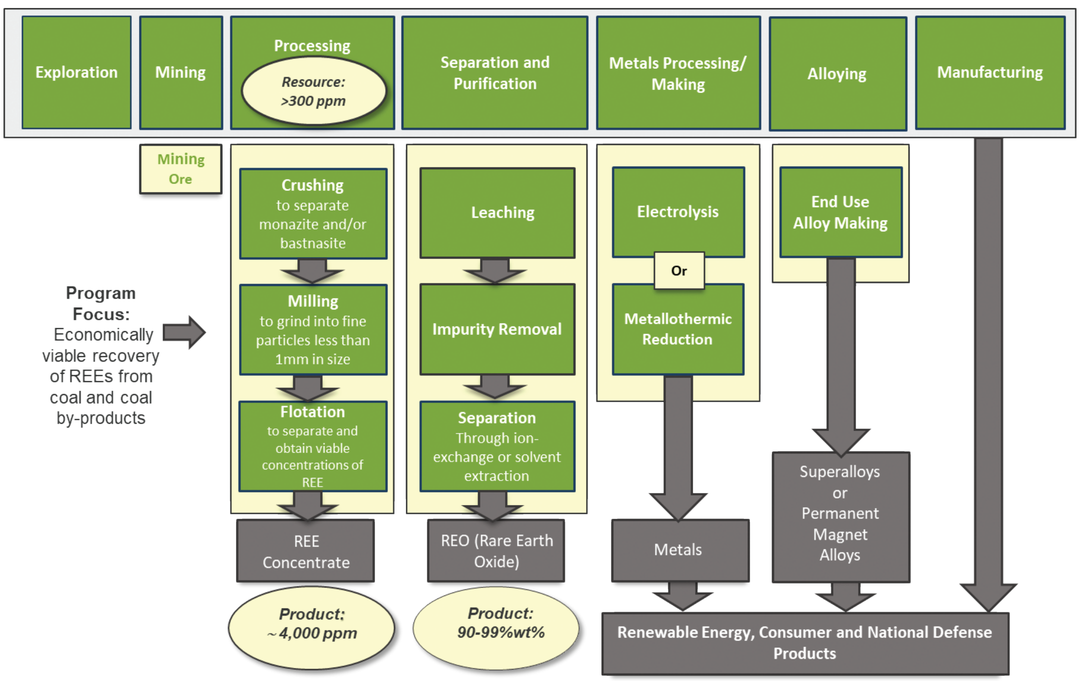


Figure 4. Rare earth value chain.

KEY TECHNOLOGY AREAS

From 2014-2020, the ***Feasibility of Recovering Rare Earth Elements*** program consisted of three key technology areas. These included (Figure 5):

- **Enabling Technologies:** Develop DOE-NETL's technology knowledge basis through resource identification, field sampling and characterization, techno-economic analysis development, and field and/or process sensor development.
- **Separations Technologies:** Address the viability of utilizing commercially available extraction and separation equipment and/or systems that have been developed for alternate technologies, and demonstrate their capability (i.e., technology transfer) for the extraction and separation of REE from coal-based materials. In parallel, develop new/novel embryonic/transformational REE extraction and separation concepts.
- **Process Systems:** Design/construct/operate bench-scale and/or pilot-scale systems to validate the capability of producing REE from coal-based resources.

PROGRAM DIRECTION

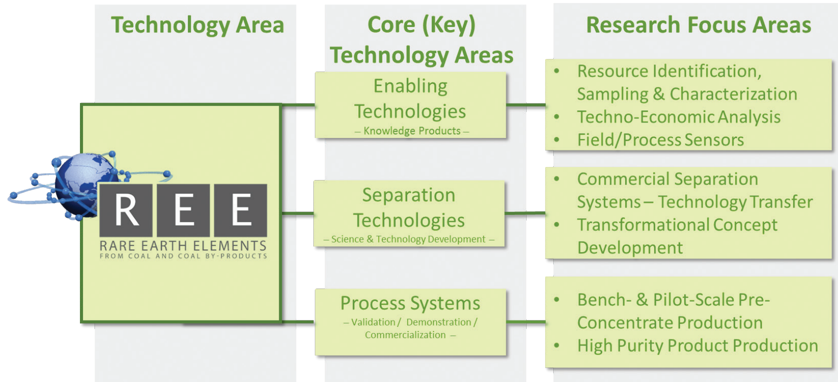


Figure 5. Program structure.

Transitioning the production of these dual-use materials and their associated supply chains back to the United States is a strategic priority, as evidenced by recent and proposed U.S. legislation, as well as by several recent executive orders [1,2]. Consequently, RD&D efforts to create new domestic sources of REE have been accelerated with the goal of making our domestic supply chains more resilient.

In order to comply with Executive Order 13817 [2], DOE's program expanded its technology development effort in 2019 to include the recovery of CM from coal-based resources. As a result, DOE's program in 2020 was renamed as the ***Critical Minerals Sustainability Program***, required existing domestic small pilot-scale facilities to co-produce CM in addition to producing REE.

Building on the accomplishments achieved between 2014 and 2020 in DOE-NETL's ***Feasibility of Recovering Rare Earth Elements*** program, and aligning the program to further support Executive Order 13817, the following five focus areas were identified for conduct in DOE-NETL's ***Critical Minerals Sustainability Program***:

- **Characterization Technology Development:** Technology development and validation for environmentally sustainable exploration and production of CM and REE from various sources. This includes the economic recovery of CM and REE through identification (including physical and chemical properties), mineral assays, prediction and assessment of resources and volumes of CM and REE from various feedstocks.
- **Sustainable Mining Technology Development:** Novel technology development and validation for sustainable conventional and unconventional mining to enable the recovery of CM and REE from sources that are not currently used for recovery, or that could be recoverable through the use of more sustainable practices.
- **Concentration and Processing Technology Development:** Advanced environmentally friendly and economically feasible technology development for beneficiation, concentration and processing of CM and REE. This includes development of models to be used as virtual test platforms to optimize process separation designs.
- **Individual Separation and Reduction to Metals Technology Development:** Environmentally friendly and economic technology development of individually separated high purity (ISHP) rare earth oxides/salts (REO/RES) and ultimately rare earth metals (REM) and CM. High purity elements will be critical for use in manufactured products.
- **Techno-Economic Analysis:** Evaluation of the international CM and REE markets and assessment of the economics of commercial production.

RD&D efforts will continue to enable the sustainable recovery of CM including REE throughout the supply chain. Understanding the basinal deposit relationships of these CM and REE from carbon ore,[3] other ores, mining by-products, abandoned mines and other valuable sources will enable projects to address resources holistically. Advanced technologies developed throughout the supply chain and co-production business models will continue to improve the economics of future projects. The program will strive to develop and test in engineering-scale prototype facilities the technologies that industry will need to establish a domestic supply chain to help fuel our nation's economic growth, transition to clean energy technologies, secure our energy independence by reducing our reliance on foreign sources, and increase our national security.

REFERENCES

1. Executive Order 13953, Addressing the Threat to the Domestic Supply Chain from Reliance on Critical Minerals from Foreign Adversaries and Supporting the Domestic Mining and Processing Industries, September 30, 2020.
2. Executive Order 13817, A Federal Strategy to Ensure Secure and Reliable Supplies of Critical Minerals, December 20, 2017. List of Critical Minerals posted in Federal Register/Vol. 83, No. 97/Friday, May 18, 2018/Notices.

[3]Carbon Ore: Coal, coal by-products, and coal waste streams such as acid mine drainage (AMD) and fly ash.

DESIGNS FOR PRODUCTION OF 1-3 METRIC TONNES PER DAY MIXED RARE EARTH OXIDES (>75 WT%)

Production of Mixed Rare Earth Oxides from Coal-Based Resources

Performer	**Various**
Award Number	Various
Project Duration	10/01/2020 – 12/30/2020 (Concepts)
Total Project Value	Up to $150,000 each
Technology Area	Process Systems – Engineering-Scale Prototype Facility

Thirteen projects were selected to receive an approximate total of $1.95 million in federal funding to develop conceptual designs using commercially viable technologies that will extract rare earth elements (REE) from U.S. coal and coal by-product sources. Each contract received up to $150,000 in DOE funding.

The conceptual designs included system configurations, equipment features, performance characteristics, and associated costs for systems that produce at least 1–3 metric tons per day of mixed rare earth oxides (MREO) or rare earth salts (MRES), and in some designs, other critical minerals (CM).

DOE's ***Critical Minerals Sustainability Program*** has demonstrated the technical feasibility of extracting these materials from coal-based resources. The program has moved from bench/pilot scale to engineering-scale prototype materials processing to address scale-up challenges for future opportunities.

DOE's National Energy Technology Laboratory managed conduct of the thirteen conceptual design projects that were carried out by the following recipients:

- Battelle Memorial Institute (Columbus, OH)
- BioCarbon Technologies LLC (Missoula, MT)
- Concurrent Technologies Corporation (Johnstown, PA)
- Energy Fuels Resources (Lakewood, CO)
- MATERIA USA LLC (Inwood, NY)
- MP Mine Operations LLC (Mountain Pass, CA)
- Tetra Tech, Inc. (Pittsburgh, PA) Project 1
- Tetra Tech, Inc. (Pittsburgh, PA) Project 2
- Texas Mineral Resources Corp (Sierra Blanca, TX)
- University of North Dakota (Grand Forks, ND)
- UPSHOTS, LLC (Forsyth, GA)
- West Virginia University Research Corporation (Morgantown, WV)
- Winner Water Services Inc. (Sharon, PA)

The conceptual design projects included a potential option for conduct of a follow-on feasibility (pre-FEED) study. This study supported an Association for the Advancement of Cost Engineering Class 4 cost estimate on conceptual facilities that are capable of producing 1–3 metric tons per day of a minimum of 75 wt% mixed rare earth oxides or salts (MREO/MRES), and if feasible, additional CM.

Rare earth elements: essential dual-use materials.

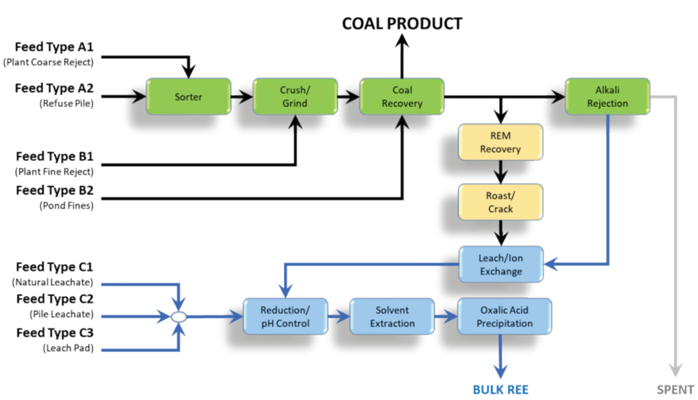
CONVENTIONAL RARE EARTH ELEMENT SEPARATION SYSTEMS

Pilot-Scale Testing of an Integrated Circuit for the Extraction of Rare Earth Minerals and Elements from Coal and Coal By-products Using Advanced Separation Technologies

Performer	**University of Kentucky Research Foundation**
Award Number	FE0027035
Project Duration	03/01/2016 – 06/30/2020
Total Project Value	$ 8,820,009
Collaborator	Alliance Resources; Blackhawk Mining; Minerals Refining Company; Mineral Separation Technologies; Virginia Polytechnic Institute and State University; West Virginia University
Technology Area	Process Systems – Small Pilot-Scale Facility

In Phase 1 of this project, the University of Kentucky (UK) identified two bituminous coal-related feedstocks qualified as having ample supply with high rare earth element (REE) content (above 300 parts per million) and developed a preliminary design for a modular small pilot plant to recover REE from those feedstocks. In laboratory experiments, UK achieved greater than 80 wt% concentration of rare earths in the mixed rare earth concentrate while recovering greater than 75% of the rare earths from the incoming feedstock. In Phase 2, the University utilized its ¼-ton per hour pilot-scale plant for the extraction of REE from Central Appalachian and Illinois Basin bituminous coal preparation plant refuse materials.

The system integrated both physical and chemical (ion exchange and solvent extraction) separation processes that are commercially available and environmentally acceptable. The innovative enabling technology utilized in the system included an advanced froth flotation process and a novel hydrophobic-hydrophilic separation process. At the end of Phase 2, the team produced 0.5 kg mixed rare earth oxides (MREO) with a 98 wt% purity in the pilot-scale test. The project was expected to develop critical technology, conditions, and data necessary to design, construct, and operate a state-of-the-art processing facility for the production of REE from various coal and coal by-product streams.



Schematic process diagram and panoramic view of the pilot-scale plant.

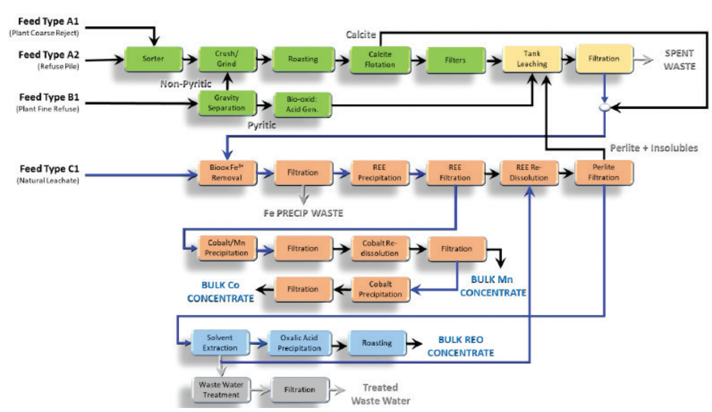
Demonstration of Scaled-Production of Rare Earth Oxides and Critical Materials from U.S. Coal-Based Sources

Performer	University of Kentucky
Award Number	FE0031827
Project Duration	10/01/2019 – 03/31/2022
Total Project Value	$ 6,250,000
Collaborator	Alliance Resource Partners; Blackhawk Mining; University of Utah
Technology Area	Process Systems – Small Pilot-Scale Facility

University of Kentucky is extending the activities of the existing rare earth elements (REE) small pilot-scale plant to integrate and test new technologies and circuits to significantly reduce the cost of producing mixed rare earth oxides (MREO), cobalt, and manganese. Concentrate production will be increased from between 10 and 100 grams/day to about 200 grams/day. To significantly reduce the primary cost of producing the concentrates, naturally occurring coal pyrite is being recovered and used in bioreactors to produce the acid needed for leaching. To assess the technical and economic potential of extracting REE from coal waste, a ¼-ton per hour modular small pilot plant was designed, constructed, and tested as part of an ongoing project funded by DOE. Although the small plant was successful in recovering REE and producing MREO having a purity level greater than 90 wt%, several economic barriers were encountered that required more detailed evaluations and modification of the process circuitry. A reduction in the chemical costs per kilogram of REO recovered is needed for the process to be economically viable for a typical coal source.

This project consists of a team of researchers from the University of Kentucky, University of Utah, and Virginia Tech. Alliance Coal is the host and provider of operational support for the pilot plant as well as the necessary quantity of qualified feedstock. Kentucky River Properties is collecting and transporting several tons of qualified feedstock to the pilot plant location.

Mineral Separation Technologies provided a dual X-ray transmission sorter for separation of the feedstock into materials that contain potentially high concentrations of REE. The information garnered from simultaneous assessment of process cost will guide process development and circuit design to enhance performance success and the potential for commercialization. At the end of the project, a pathway will be established for the production of high-purity MREO (greater than 90 wt%) and other critical material (greater than 50 wt%) concentrates from bituminous coal resources in an environmentally friendly manner at a production rate of around 200 grams daily.



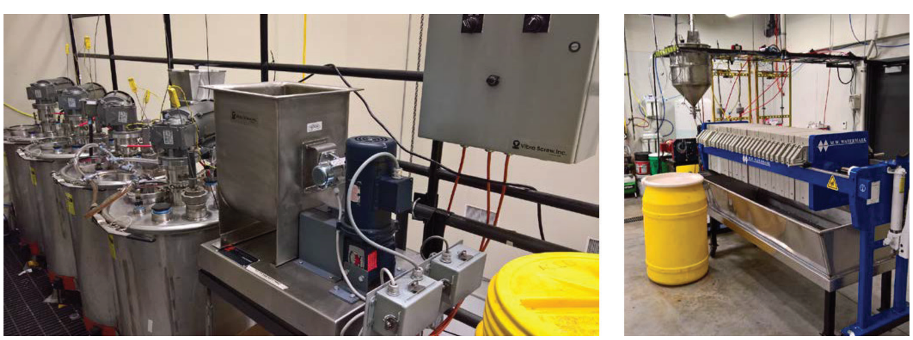
Integrated process flowsheet showing the addition of innovative technologies implemented to enhance the economic extraction of REE, Sc, Co and Mn from pre-combustion, bituminous coal-based sources.

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

Performer	**University of North Dakota Energy and Environmental Research Center (UNDEERC)**
Award Number	FE0027006
Project Duration	03/01/2016 – 12/31/2019
Total Project Value	$ 4,474,347
Collaborator	Barr Engineering, Great Northern Properties, Great River Energy, Lignite Research Program of the North Dakota Industrial Commission, Microbeam Technologies, Minnkota Power Cooperative, MLJ Consulting, North American Coal Corporation, North Dakota University System, Pacific Northwest National Laboratory, University of North Dakota
Technology Area	Process Systems – Bench-Scale Facility

In Phase 1 of this project, the University of North Dakota (UND) project team identified locations in North Dakota with coal-related feedstocks having exceptionally high rare earth element (REE) content and developed a simple, highly effective, and low-cost method to concentrate the REE in the lignite feedstocks using a novel technology that takes advantage of the unique properties of lignite. In laboratory experiments, UND achieved production of a greater than 2 wt% MREO concentrate while recovering up to 35% of the rare earths from the incoming feedstock. In Phase 2, the University partnered with Microbeam Technologies, Barr Engineering, Pacific Northwest National Laboratory (PNNL), and MLJ Consulting to investigate the feasibility of recovering REE from North Dakota lignite and lignite-related feedstocks. The team scaled the technology to 10-20 kilograms per hour feedstock throughput and evaluated the economics for a commercial-scale, rare earth-concentrating facility in North Dakota.

The project also developed a commercialization plan and market assessment. The recovery of REE from lignite and related materials could lead to a significant new industry for maintaining existing and creating new jobs and create new opportunities for marketable use of North Dakota lignite coal. Multiple high-value by-products that could further enhance the lignite industry will also result from the process. There is potential to significantly or completely offset current imported REE and REE-containing products by providing a reliable domestic resource and novel low-cost technology. The ultimate significance of this research is the development of a high-performance, environmentally benign, and economically viable technology for REE production from an unconventional resource that will reduce dependence on foreign supplies and strengthen the economic and national security of the United States.



Semi-continuous bench-scale system.

Rare Earth Element Extraction and Concentration at Pilot-Scale from North Dakota Coal-Related Feedstocks

Performer	University of North Dakota Energy and Environmental Research Center (UNDEERC)
Award Number	FE0031835
Project Duration	10/01/2019 – 03/31/2022
Total Project Value	$ 6,508,555
Collaborator	Barr Engineering; BNI Energy; Critical Materials Institute; Great River Energy; Microbeam Technologies; Minnkota Power; MLJ Consulting; North American Coal Corporation; North Dakota Geological Survey; North Dakota Industrial Commission; Rare Earth Salts
Technology Area	Process Systems – Small Pilot-Scale Facility

The University of North Dakota Energy and Environmental Research Center (UNDEERC) is demonstrating at small pilot scale a high performance, economically viable and environmentally benign technology to recover rare earth elements (REE) from North Dakota (ND) lignite coal feedstocks. To achieve this goal, UNDEERC is:

- Designing and constructing a small pilot-scale system for continuous REE extraction from ND coal feedstocks capable of using a minimum 0.5 tons per hour feed rate of physically beneficiated lignite coal.
- Obtaining approximately 300 tons of ND lignite, containing greater than 300 ppm REE to provide adequate material for shakedown and continuous testing in the small pilot-scale demonstration facility.
- Conducting initial parametric testing of a sample of the ND lignite at bench-scale to cost-effectively identify optimal operating conditions and aid in the design of the small pilot-scale system.
- Commissioning the small pilot facility using selected high-REE-containing coals from various regions in ND.
- Conducting continuous small pilot-scale testing under optimal conditions for REE extraction and concentration using at least 100 tons of ND lignite that contains greater than 300 ppm REE.
- Confirming compatibility of REE concentrate generated during small pilot-scale testing with commercial-scale REE refining.
- Using results from the small pilot-scale testing to conduct a techno-economic analysis (TEA) and preliminary front end engineering design (pre-FEED) study on a potential commercial facility where an economic feasibility study and workforce assessment will be performed.
- Working with industry partners to develop a technology roadmap and commercial deployment plan.

UNDEERC's efforts will provide information on availability of the proposed feedstock; information on environmental impacts; process flow diagram(s); product yield and concentration; and estimated system costs.

Coarse (left) and fines (right) coal piles extracted from Freedom Mine.

Recovery of Rare Earth Elements from Coal Mine Drainage

Performer	**West Virginia University Research Corporation**
Award Number	FE0026927
Project Duration	03/01/2016 – 12/31/2019
Total Project Value	$ 4,340,789
Collaborator	Rockwell Automation; Tetra Tech, Inc.; Virginia Polytechnic Institute and State University
Technology Area	Process Systems – Bench-Scale Facility

In this project, West Virginia University (WVU) and its partners developed a cost-effective and environmentally benign process to recover rare earth elements (REE) from solid residues (sludge) generated during treatment of acid coal mine drainage (AMD). This project took advantage of autogenous processes that occur in coal mines and associated tailings which liberate, then concentrate, REE.

Phase 1 findings showed elevated concentrations of REE, particularly in low-pH AMD, and nearly all precipitating with more plentiful transition metals in the AMD sludge. REE extraction using hydrometallurgical methods produced a concentrate with 4.6 wt% total REE (TREE) content. A techno-economic analysis also found that REE extraction from AMD sludge is economically attractive with a refining facility projected to generate positive cash flow within five years. WVU's bench-scale facility was commissioned in July 2018.

Also, in Phase 1, AMD treatment residues were identified as a domestic source of REE feedstock. In Phase 2, recoveries from precipitates were generally in the range of 30-60% with heavy REE (HREE) consistently showing a significantly higher recovery than light REE (LREE). In some cases, the recovery of HREE approached 70% through solvent extraction.

An economically attractive extraction and refining process was identified with the potential to generate significant income for operators of AMD treatment sites and to assist in mitigating the U.S. manufacturing industry's reliance on foreign REE supplies. Estimates based on the volume of AMD generated in Pennsylvania and West Virginia indicate that the AMD sludges represent 610 to 2,700 tons of REE per year. Moreover, a survey of 154 AMD treatment facilities reported 225 tons of sludge (dry weight basis) in surface storage, with an inherent REE value of $122 million.

The Rare Earth Extraction Facility used during Phase 2.

Development and Testing of an Integrated Acid Mine Drainage (AMD) Treatment and Rare Earth/Critical Mineral Plant

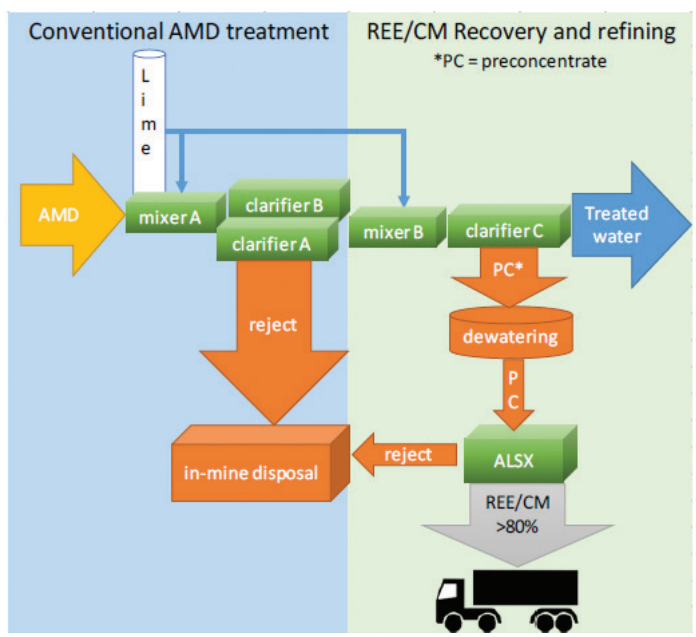
Performer	**West Virginia University Research Corporation (WVURC)**
Award Number	FE0031834
Project Duration	10/01/2019 – 06/30/2022
Total Project Value	$ 6,886,791
Collaborator	Rockwell Automation; Virginia Polytechnic Institute and State University
Technology Area	Process Systems – Small Pilot-Scale Facility

The primary objectives of this project are to design, construct, and test a small pilot-scale continuous, integrated process for simultaneously and efficiently treating up to 1,000 gpm of acid mine drainage (AMD) while producing an enriched REE/CM (Rare Earth Elements/ Critical Minerals) concentrate. WVURC—in conjunction with partners West Virginia Department of Environmental Protection and Rockwell Automation, Inc.—are carrying out these objectives in two developmental stages. The first stage is focused on the engineering design, construction, and assembly of a small pilot-scale process to be used in the project. To support these development efforts, WVURC is constructing a small-scale, fully continuous test unit to emulate the performance of the upstream concentrator. This test unit allows for rapid optimization of various operational variables and limits the need for extensive testing at the larger scale facility.

During the second stage of this project, the integrated small pilot- scale plant will be operated on a continuous basis to validate process performance and refine process cost estimates. During both stages, additional efforts will focus on critical support tasks including technical and environmental systems analysis.

WVURC has identified that AMD produced from sulfur contained in coal and other ore bodies is an attractive source of REE and CM since it relies on natural processes to create a concentrate that is easily extracted from the feedstock.

WVURC has also demonstrated that this process is environmentally beneficial since it would incentivize treatment of AMD. If successful, this plant will generate about 1,000 tons per year of REE and CM oxides with an estimated contained value of $237/kg.



Schematic flowsheet for AMD REE.
Conventional AMD treatment is shaded blue.
REE-CM recovery and concentration is shaded green.

High Yield and Economical Production of Rare Earth Elements from Coal Ash

Performer	**Physical Sciences, Inc.**
Award Number	FE0027167
Project Duration	03/01/2016 – 10/31/2021
Total Project Value	$ 9,999,968
Collaborator	University of Kentucky Center for Applied Energy Research; Winner Water Services
Technology Area	Process Systems – Small Pilot-Scale Facility

In Phase 1, Physical Sciences, Inc. (PSI) and the University of Kentucky's Center for Applied Energy Research (UK CAER) undertook a comprehensive research effort to investigate the REE content including yttrium and scandium (REYSc) of coal-fired power plant ashes. PSI also conducted feasibility and techno-economic analyses (TEA) for recovery of REYSc from the coal ashes and developed the design of a small pilot-scale facility to economically produce salable REYSc-rich concentrates and commercially viable co-products from coal ash feedstock using environmentally safe and high-yield physical and chemical enrichment and recovery processes.

In Phase 2, PSI, Winner Water Services (WWS), and UK CAER constructed both a micro-pilot facility located at PSI (Andover, Massachusetts), and a small pilot facility located at WWS (Sharon, Pennsylvania) for chemical processing. The small pilot plant is operating at the scale of approximately 0.4-1 tonne per day (tpd) ash throughput for physical processing and about 0.5 tpd for chemical processing. The plant produced at least 50 grams (g) of dry REYSc nitrates containing more than 10 wt% REYSc, and targeting 500 g of dry REYSc nitrate concentrate containing more than 20 wt% Sc. The ash material used in this effort is from the Dale power plant in Ford, KY. The ash feedstock contains at least 300 parts per million (ppm) of REYSc content and has the potential to yield greater than 500 ppm of REYSc content. The data obtained from the small pilot-scale plant operations will be used to enhance and validate the TEA analysis that was completed for both the physical and chemical processing plants at a scale of 600 tpd in Phase 1, and will be used to design a commercial-scale plant (hundreds of tpd throughput) with a projected return on investment of less than seven years. Demonstration of PSI's technology to recover REYSc from coal ash will enable utilization of coal mining/coal combustion wastes in environmentally benign ways to produce REE of strategic importance for the United States while generating jobs and economic growth in economically-depressed regions of this country.

PSI-WWS small pilot-scale facility.

TRANSFORMATIONAL RARE EARTH ELEMENT SEPARATION

Recovery of High Purity Rare Earth Elements (REE) from Coal Ash via a Novel Electrowinning Process

Performer	**Battelle Memorial Institute**
Award Number	FE0031529
Project Duration	11/16/2017 – 02/29/2020
Total Project Value	$ 874,940
Collaborator	Rare Earth Salts
Technology Area	Separation Technologies

Battelle Memorial Institute's (BMI's) project demonstrated favorable results that showed potential toward developing an environmentally benign and economically sustainable process for generating rare earth element (REE) products from domestic coal ash sources, marking a step forward in enabling a domestic supply of these critical materials. As part of an NETL-funded cooperative agreement, BMI and Rare Earth Salts (RES) worked together to advance the development and validation of BMI's acid digestion process, along with RES's novel electrowinning separation and purification process. Acid digestion is a method of making metals easier to separate by first dissolving coal ash into solution by adding acids and heating it until the metals break away from the other undesired materials. Electrowinning is a process in which metal ions present in solution are separated using a direct current. BMI successfully scaled up its acid digestion process to increase the concentration of mixed REE materials and provide enough material for testing in RES's facility. In solution with the REE were zinc and aluminum.

Aluminum was easily removed whereas the high quantity of zinc presented a challenge in the separation and purification process. To overcome this challenge, BMI selected a new extractant composition selective for zinc over the REE prior to traditional solvent extraction steps as a pretreatment to remove zinc. With the zinc interference minimized, RES's electrowinning process can recover a concentrated rare earth oxide (REO) product. BMI and RES delivered a sample of lanthanum oxide with a purity of approximately 90 wt% to NETL, successfully meeting the objectives of the project and the goals of NETL's ***Feasibility of Recovering Rare Earth Elements*** program. A purity of 90 wt% or greater REO renders the material suitable for further processing into a pure metal form for subsequent incorporation into commodity or national defense products. A subsequent techno-economic analysis (TEA) indicated the economics of the process show promise and the technologies investigated merit further investigation and improvement.

Solvent extraction upgrading of coal ash pregnant leach solutions.

Low Temperature Plasma Treatment for Enhanced Recovery of Highly Valued Critical Rare Earth Elements from Coal-Based Resources

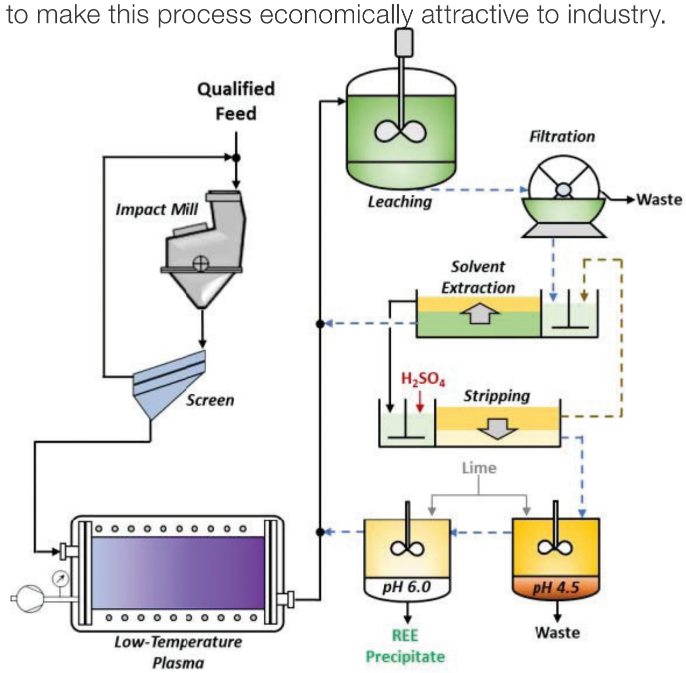
Performer	**University of Kentucky Research Foundation**
Award Number	FE0031525
Project Duration	11/16/2017 – 08/31/2019
Total Project Value	$ 404,969
Collaborator	Virginia Polytechnic Institute and State University
Technology Area	Separation Technologies

As the world continues its transition to a highly tech-driven economy, NETL supports innovative techniques to develop a reliable and sustainable domestic supply of rare earth elements (REE), which are vital materials for modern technologies. To that end, the University of Kentucky (UK) and subcontractor Virginia Tech (VT) addressed the potential for a novel unconventional separations process to produce REE.

The University of Kentucky's low-temperature plasma research was shown to be technically viable to extract REE from coal-based resources. Plasma, which is distinct from the liquid, gaseous, and solid states of matter, is formed by striking a gas with enough energy that gas molecules are ionized. During the past century, thermal plasma treatment saw applications in torch welding/cutting, spray coating, metal synthesis, extractive metallurgy, refining metallurgy, hazardous waste destruction and more.

The collaborators researched use of low-temperature plasma to pretreat coal-based materials resourced from West Kentucky No. 13 and Fire Clay mines located within the Commonwealth of Kentucky. Surface area measurements found that plasma treatment provided increased surface area and pore volume which made other processes more effective at recovering REE. This novel technology, integrated with traditional leaching and extraction processes, was demonstrated to effectively recover REE from the coal samples.

Low-temperature plasma treatment was found to provide heavy REE (HREE) leaching performance improvements on the low-density, higher carbon content fractions of the West Kentucky No. 13 coal, and high-temperature oxidation provided exceptionally high REE recovery for all fractions of both the Fire Clay and West Kentucky No. 13 coarse refuse materials. The higher recovery of rare earth elements using this method showed promise. Moving forward, the challenge for UK and VT is refinement and discovering how to make this process economically attractive to industry.



Schematic illustrating the production of greater than 2 wt% REE concentrate with assist of low temperature plasma treatment technique.

Economic Extraction and Recovery of REE and Production of Clean Value-Added Products from Low-Rank Coal Fly Ash

Performer	University of North Dakota Energy and Environmental Research Center (UNDEERC)
Award Number	FE0031490
Project Duration	11/16/2017 – 02/15/2020
Total Project Value	$ 508,812
Collaborator	Pacific Northwest National Laboratory
Technology Area	Separation Technologies

Researchers from the University of North Dakota (UND) and Pacific Northwest National Laboratory (PNNL) identified unique pathways and pretreatments to extract rare earth elements (REE) from low-rank coal (LRC) ash in a more economical and environmentally sustainable manner that can be adjusted to meet variable conditions.

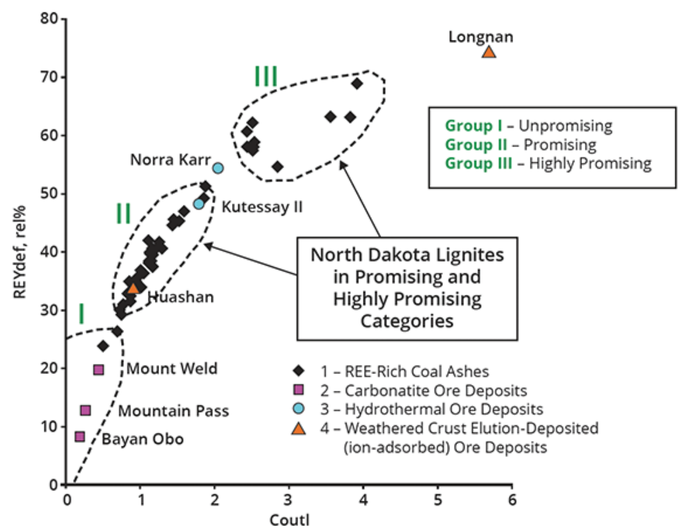
LRCs, such as lignites, are one of the most abundant fossil fuel sources in the world. This project has shown that the ash from LRCs can be a potentially viable source of REE.

The research team conducted an extensive characterization effort to understand the form, associations, and partitioning of the REE along with other relevant elements and minerals in the fly ash samples, as well as the ash chemistry, mineralogy, and morphology. Understanding these intricacies was a vital step in developing the method for extraction and recovery of the contained LCR REE.

Using ash samples collected from a combination of full-scale power generation stations and pilot-scale combustion systems employed at UND, the researchers achieved the goal of producing a mixed REE concentrate greater than 2% by weight, a step forward on the road to securing a financially viable domestic market for these vital materials used in the manufacture of computer components, cell phones, satellites, defense applications, and renewable energy technologies, among others.

The LRC ash-based method developed by UND and PNNL offers an advantage in flexibility. The process can be adjusted to adapt to the differing ash chemical and physical properties characteristic of the LRC ash. This is an important trait considering that all ash materials can be different and require specific extraction processes. This research development means different characteristics in varying ashes can be accommodated in the REE extraction operations.

Furthermore, the researchers determined that if higher levels of REE were in the initial LRC ash, the process can be economically viable even without further optimization so long as additional high-value metals or critical minerals are recovered as well. UND also discovered that a simple water wash pretreatment on the samples can reduce the required amounts of acid for initial REE extraction from lignite ash. Reduced acid use has the bonus of reducing costs and environmental impact while also improving worksite safety.



Classification of coal fly ash (black diamonds) REE distribution in comparison with selected conventional REE deposits.

Seredin, V.V.; Dai, S. Coal Deposits as Potential Alternative Sources for Lanthanides and Yttrium. *International Journal of Coal Geology* 2012, 94, 67-93.

Concentrating Rare Earth Elements in Acid Mine Drainage Using Coal Combustion Products through Abandoned Mine Land Reclamation

Performer	**Ohio State University**
Award Number	FE0031566
Project Duration	12/01/2017 – 04/30/2021
Total Project Value	$ 528,700
Technology Area	Separation Technologies

Innovations by researchers at Ohio State University have shown potential to deliver a supply of strategically and economically vital rare earth elements (REE).

REE are used in everything from green energy applications and personal electronics to defense technology and smart car systems. Important as these elements are, China controls the lion's share of the world market.

The U.S. Department of Energy (DOE) has been tasked with helping secure a domestic REE supply. NETL's research has demonstrated methods by which REE can be extracted from the nation's coal by-products such as acid mine drainage (AMD) and fly ash generated at power generation facilities, with the Ohio State University refining this process even further.

The Ohio State University researchers demonstrated that a conceptual three-stage trap-extract-precipitate (TEP) process can successfully extract REE from coal mine drainage. The TEP process relies on the use of environmentally benign industrial by-products to trap the REE and an organic chelating agent to recover the REE from the mine drainage.

This approach generates lower post-extraction waste and minimizes the associated environmental impacts when compared with other REE extraction techniques. The TEP process retains more than 99% of the REE and produces solids that contain more than 7 wt% (70,000 ppm) total REE.

The team from Ohio State worked closely with several key stakeholders in the region, including those from the public sector. The TEP process demonstrated in Columbus, Ohio, was part of a collaboration between the university, DOE, and state agencies which assisted in preliminary investigations starting in 2017.

As work continues around the country to secure a domestic supply of rare earth elements, the hope is that the efforts of NETL and collaborating organizations can lead to REE production from REE-enriched coal-based resources, which are estimated to be in the hundreds of millions of tons. There are 6,000 recorded abandoned mines in Ohio alone, while 4,000 miles of streams in Appalachia and 5,000-10,000 miles of streams in the western United States have been affected by acid mine drainage which can serve as a foundation for future production of REE.

Bench-scale test facility.

Low-Cost Rare-Earth-Element (REE) Recovery from Acid Mine Drainage Sludge

Performer	**Research Triangle Institute (RTI)**
Award Number	FE0031483
Project Duration	11/20/2017 – 09/19/2019
Total Project Value	$ 500,000
Technology Area	Separation Technologies

The Research Triangle Institute (RTI) explored methods by which REE can be extracted, separated, and recovered from coal-based resources. Zachary Hendren, Ph.D., and his RTI team, including partners Cerahelix and Veolia Water Technologies, tested the efficacy of various approaches to REE recovery and enrichment (with a targeted concentrate goal of 2 wt% mixed REE) from acid mine drainage (AMD) samples using a combination of novel technologies.

This means that of one of the nation's most abundant resources, coal, could provide a potential source of vital REE without the investment required to open a new mine specifically dedicated to their extraction. Already existing coal mines could provide domestic supplies if the extraction methods are refined and desired purities are reached.

Hendren and his team assessed several technologies for REE concentration and recovery. Among them was nanofiltration, in which polymer and ceramic membranes inserted in a tubular structure extract the valuable elements from AMD effluent streams.

Current membrane water treatment technologies are used to remove particulate matter or all dissolved ions. Regarding REE recovery, nanofiltration membranes were designed to allow monovalent ion passage while rejecting multivalent ions. These nanofiltration membranes are similar to those used for enhanced oil recovery.

In RTI's experiments, membranes were used to concentrate desirable elements (e.g., lanthanum and praseodymium, among others) and remove the bulk of the low-value ions (e.g., sodium, potassium, heavy metals, and divalent metal salts) so performance of the final downstream recovery process could be enhanced, achieving maximum recovery of valuable REE.

The assessment of nanofiltration showed that the technology may be more appropriate for REE recovery in non-iron-rich streams. Furthermore, when combined with electrodeposition, membrane nanofiltration showed potential for recovering scandium and cerium, which have applications in aerospace industry components, catalysts in self-cleaning ovens, and other uses.

While the tests did not yield the desired concentrate goal of 2 wt% mixed REE, improved designs of the extraction process, simplified by reducing the volume of the acid, were projected to yield 3.21 wt% concentrate.

Cerahelix ceramic tubular membranes for monovalent/multivalent separation.

Economic Extraction, Recovery, and Upgrading of Rare Earth Elements from Coal-Based Resources

Performer	**University of Utah**
Award Number	FE0031526
Project Duration	11/16/2017 – 12/31/2019
Total Project Value	$ 499,000
Collaborator	Virginia Polytechnic Institute and State University
Technology Area	Separation Technologies

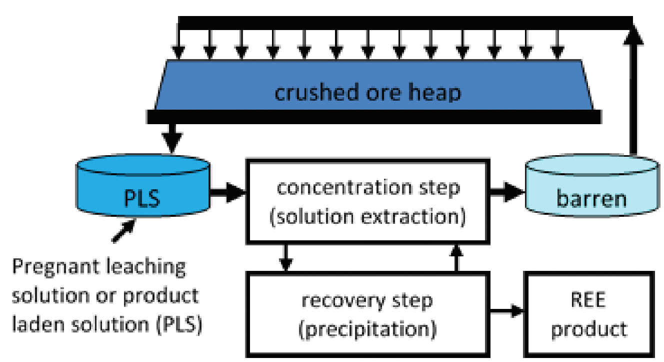
Researchers from the University of Utah and Virginia Tech evaluated a new, low-cost technology to extract and recover an enriched, mixed REE oxide (MREO) product from coal-based resources. The project team successfully obtained six different coal waste samples with REE concentrations that exceeded 300ppm.

The subsequent technology evaluation began with selectively separating resources from coal waste, followed by passing bio-oxidized and conditioned solutions over columns of coal (i.e., heap leaching). The REE resulting from this process were concentrated by solvent extraction, a method utilized to separate compounds or metal complexes, and recovered via precipitation, which is the process of producing solids from a solution. The project was undertaken with the goal of achieving a 2–8 wt% MREO product, but far exceeded the goal with the successful production of 36.7 wt% MREO.

Throughout this project, the research team successfully demonstrated several concepts such as the separation technologies to enrich pyrite for bio-oxidation; column leaching with bio-oxidation and extraction of REE; concentration of REE by solvent extraction; and iron removal along with REE recovery by precipitation. These technologies, when combined in an appropriate series, allow for the production success demonstrated in this project. These demonstrations can also pave the way for further extraction and refinement developments.

A very promising techno-economic analysis was also carried out. The experiments and analyses led to the important finding that separating coal refuse using available technologies (e.g., dual-scan X-ray sorting, comminution, and spiral concentration) to concentrate pyrite-rich coal, which can feed a bio-oxidation reactor, decreases acid consumption during heap leaching, thereby improving the economics of the process and making it more attractive for further development.

These accomplishments illustrate the feasibility of not only recovering the economic and strategically vital REE from the nation's coal resources but doing so at low cost, which is a crucial step on the road to commercialization. If lowering the costs of extracting and refining REE in satisfactory quantities and purity can be achieved, it can incentivize further investment by industry. NETL remains committed to lowering these costs by funding and managing select projects with academia and private industry throughout the nation. The work conducted by the University of Utah and Virginia Tech stands as an example.



Schematic for the low cost REE recovery process.

Development of a Cost-Effective Extraction Process for the Recovery of Heavy and Critical Rare Earth Elements from the Clays and Shales Associated with Coal

Performer	**Virginia Polytechnic Institute and State University**
Award Number	FE0031523
Project Duration	11/16/2017 – 12/31/2019
Total Project Value	$ 500,000
Technology Area	Separation Technologies

Researchers at Virginia Tech developed a safe and efficient processing technology that can extract and concentrate rare earth elements (REE) from coal refuse material already found throughout the Appalachian region, namely in shales and clays. The new process opens the door to future commercialization, as it decreases the size and cost of needed systems. The research was recognized by the American Energy Society (AES) via an AES 2020 Energy Award as one of the top energy and technology developments of the year for its game-changing economic potential.

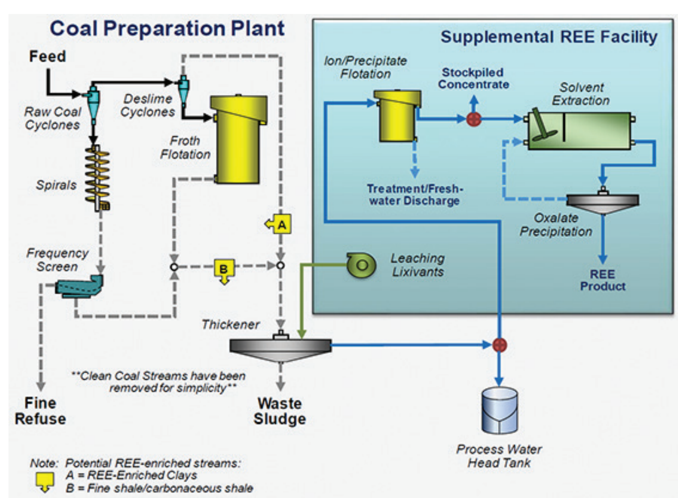
The technologies involved in this process leveraged simple ion-exchange leaching techniques currently used by industry. The Virginia Tech team focused on modified leaching lixiviants, a novel liquid material, instead of acids commonly used to concentrate and extract REE. Lixiviants are liquid media used in hydrometallurgy to selectively extract the desired metal from the ore or mineral. They assist in rapid and complete leaching, in this case extracting valuable REE from coal refuse.

Virginia Tech's experiments focused on several fine coal waste materials sampled from active preparation plants in central and northern Appalachian coal basins. Findings throughout the project discovered or verified that novel leaching lixiviants outperformed industry standards in effectively isolating and concentrating REE-enriched clay materials — often at lower doses.

The project successfully produced a solution containing a final REE concentrate of 15 wt%–18 wt%, exceeding the objective of 2 wt% REE.

Ion flotation demonstrated by Virginia Tech's researchers offers a technical benefit because it can effectively increase REE in the leach solutions prior to solvent extraction. Feeding a solvent extraction unit with a higher concentration of REE would reduce the size and cost of such a system.

The project also presents environmental benefits because modified leaching lixiviants would potentially be less hazardous than strong acids that are generally used to extract REE from solid feedstocks, ensuring safer operating environments for workers and easier storage and disposal of these materials.



Process schematic integrated with existing process circuitry.

Coupled Hydrothermal Extraction and Ligand-Associated Swellable Glass Media Recovery of Rare Earth Elements from Coal Fly Ash

Performer	**Wayne State University**
Award Number	FE0031565
Project Duration	03/15/2018 – 12/31/2019
Total Project Value	$ 518,849
Technology Area	Separation Technologies

Wayne State University (WSU) researchers used a newly developed sorbent and a process previously developed for nuclear applications to produce an economically viable concentration of rare earth elements (REE) from domestic coal fly ash, signaling an important step toward commercialization.

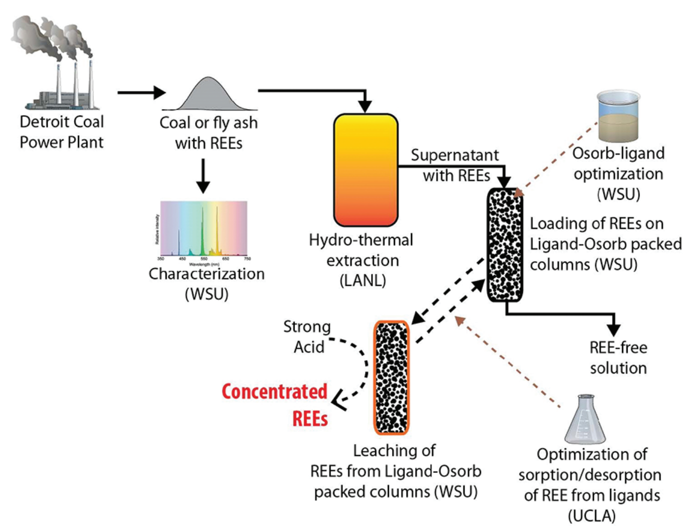
The new sorbent medium developed by WSU researchers, in collaboration with the University of California-Los Angeles (UCLA) and Los Alamos National Laboratory (LANL), successfully concentrated the REE in a coal fly ash sample taken from a coal-fired power plant near Detroit, MI, resulting in a mixed rare earth oxide (MREO) powder of more than 13 wt%.

Using custom-built reactors at LANL, researchers used hydrothermal leaching to extract the REE content from the fly ash. A new sorbent developed at WSU was used in a solid-liquid recovery process, which eliminated the use of potentially hazardous organic solvents. The process combined multiple techniques previously developed to process spent nuclear fuel and other nuclear materials.

The project successfully identified a commercially viable fly ash supply. With Wayne State's hydrothermal process, more than 76% of the REE in the coal fly ash can be extracted, representing a 20% increase over conventional acid-based methods.

The newly developed sorbent medium that was used to concentrate REE also demonstrated a selectivity for middle and heavy REE, and the potential for use in separating individual rare earth elements. With ease and efficient recovery of these elements, consideration for inclusion and use on a larger industrial-scale separations facility may be an opportunity in the future.

An invention disclosure for the sorbent media was filed and a patent application was submitted.



REE extraction process flow schematic.

At-Source Recovery of Rare Earth Elements from Coal Mine Drainage

Performer	**West Virginia University Research Corporation**
Award Number	FE0031524
Project Duration	11/16/2017 – 11/15/2019
Total Project Value	$ 864,258
Collaborator	Virginia Polytechnic Institute and State University
Technology Area	Separation Technologies

NETL has funded and supported multiple projects across the nation to extract REE from coal and coal-related by-products. A notable example is coal acid mine drainage (AMD) and sludge originating from abandoned or operating mines. However, NETL and its partners are making progress refining a method to purify AMD in order to extract the vital REE needed for the U.S. economy to remain competitive on the global market while providing environmental remediation.

This sludge is enriched in REE and contains an average total REE content several times higher than raw, untreated AMD. However, separating the valuable REE can be very expensive.

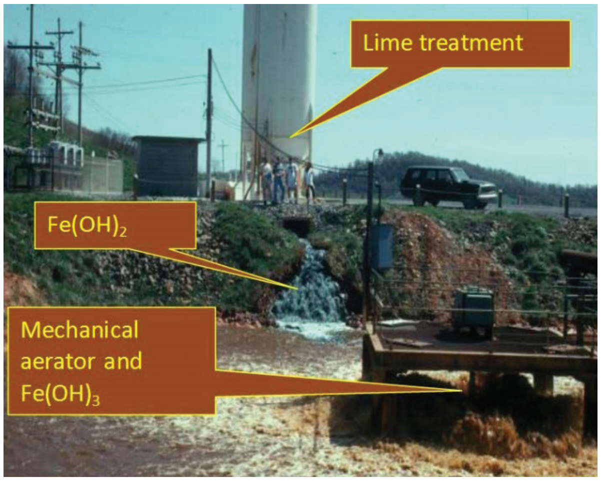
With its dedicated Rare Earth Extraction Facility on campus, researchers at the West Virginia University Research Corporation, aided by its partnership with West Virginia Department of Environmental Protection (WV DEP), may have solved this problem. Researchers evaluated the potential of precipitating (that is, causing solid constituents to be physically separated out) REE upstream of the AMD treatment stage.

The WVU team evaluated extracting REE from acidic AMD and net-alkaline AMD streams using electro-membrane extraction and other methods, and the precipitates (solids) from this concentration method were then further processed. The results showed that although the total REE concentration in raw AMD is significantly lower than AMD sludge, target REE oxide purity levels ranging from 60 wt% to 98 wt% from acidic AMD could be achieved.

An analysis compared the two potential REE production scenarios (i.e., from the AMD sludge and from the upstream, raw AMD). The results showed that the upstream concentrator increases the grade of the REE feedstock, reduces acid demand, and reduces processing costs.

The techniques tested at WVU showed that nearly 100% of the REE in the raw AMD or sludge can be recovered, which is a significant development toward realizing commercialization.

By utilizing the naturally acidic, raw AMD instead of AMD sludge, target REE oxide purities can be recovered while lowering the costs of extracting them—a significant step forward to encourage further investment and to show that a domestic supply of rare earth elements is feasible.



Typical AMD treatment facility showing the lime treatment unit, reduced $Fe(OH)_2$ sludge (blue), the mechanical aerator, and resulting $Fe(OH)_3$ oxidized sludge.

NOVEL RARE EARTH ELEMENT SEPARATION & ADVANCED SENSOR DEVELOPMENT

— FIELD WORK PROPOSAL (FWP) PROJECTS —

Rare Earth Elements

Performer	**National Energy Technology Laboratory – Research and Innovation Center (NETL-RIC)**
Award Number	FWP-RIC REE FY2016-2020
Project Duration	10/01/2015 – 03/31/2021
Total Project Value	$ 18,418,681
Technology Area	Enabling Technologies, Separation Technologies, and Process Systems

The National Energy Technology Laboratory (NETL) is conducting a collaborative Field Work Proposal (FWP) focused on developing methods to locate coal-related reserves with high concentrations of rare earth elements (REE); developing and testing technologies to extract and concentrate REE from coal and coal-related products with emphasis on pathways that are environmentally benign; and reducing technology commercialization risk through the use of modeling and analysis for process optimization and scale-up. The FWP builds upon past NETL research successes and is designed to complement extramural research efforts. Research has been focused on both the development of novel REE recovery technologies and characterization techniques as well as understanding the relative distribution of REE, their chemical forms, and association with other phases or minerals in the source materials. Current research efforts are focused on developing methods to predict high concentrations of coal-related REE reserves that contain REE forms that are easily extractable; maturing several promising NETL RIC-developed separation pathways; and conducting techno-economic modeling to understand market opportunities and environmental benefits. Each of RIC's research areas is designed to address key technology areas that are not being investigated by industry. Additional research areas in NETL's FWP project portfolio include advanced characterization work in support of separations research, novel/exploratory separations research, and development of prototype devices for real-time REE quantification in liquids and solids for prospecting and process control of separation processes. Novel separations research is focused on the development of high-risk, high-reward REE recovery technologies and areas of NETL core competencies.

REE extraction and separation process and sorbent development.

Evaluation of Novel Strategies and Processes for Separation of Rare Earth Elements from Coal-Related Materials

Performer	**Los Alamos National Laboratory (LANL)**
Award Number	FWP-FE-810-17-FY17
Project Duration	08/01/2017 – 09/30/2020
Total Project Value	$ 1,000,000
Technology Area	Separation Technologies

Los Alamos National Laboratory (LANL) has a long history in the chemistry and separation of elements (e.g., the lanthanide and actinide groups) as needed to support its core national security mission. This history has resulted in unique expertise in both process innovation and process implementation at a range of scales. LANL used this unique expertise in separation of elements to evaluate innovative processes in rare earth element (REE) separation from coal and coal by-products.

LANL's effort consisted of two complementary tasks. The first task evaluated current and enhanced actinide/lanthanide separation processes relative to identifying potential processes and strategies for REE separation from coal and coal by-products. This task evaluated existing actinides/lanthanides separation approaches developed for nuclear materials and their potential application for REE extraction. Included was a techno- economic evaluation of these processes and challenges related to energy intensity, selectivity, and process complexity in the context of application to separation of lanthanides from coal-related materials.

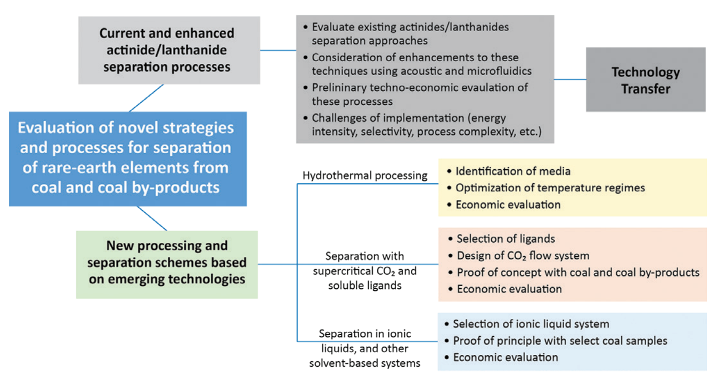
The second task evaluated the potential of developing new processing and separation schemes based on emerging technologies. LANL's project assessed the following processing approaches:

(1) Processing under hydrothermal conditions – an effort that builds on previous work that suggests that better control of lanthanides speciation at elevated temperature can be exploited to perform efficient REE separation.

(2) REE-selective extraction using supercritical carbon dioxide (CO_2) and soluble ligands as an effort that builds on initial proof- of-concept studies on supercritical CO_2 that showed great promise for simple and effective separation of REE from oxide materials.

(3) Separation of REE using ionic liquids and other solvent-based systems as an effort that builds on current efforts at LANL to develop actinide/ lanthanide separation schemes in ionic liquids.

LANL applied its knowledge gained for separating rare earth elements from actinides and achieved favorable results by using ammonium bifluoride to leach rare earths from coal-based materials. LANL found that ammonium bifluoride is an effective leaching agent.

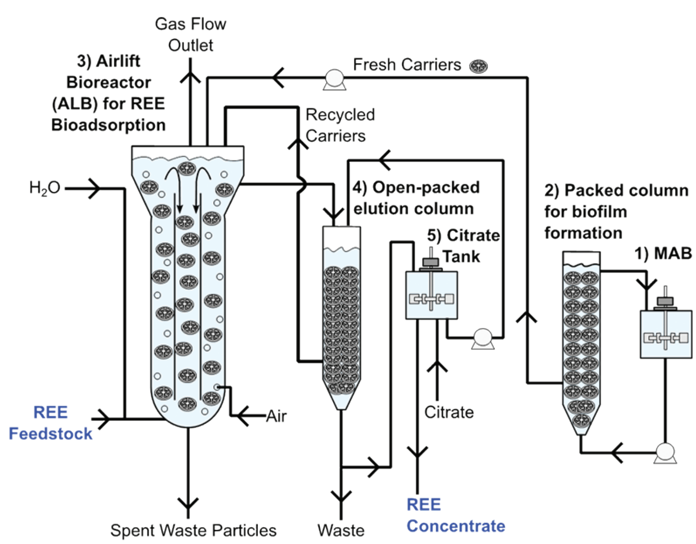


Schematic representation of LANL's FWP project.

Application of Biosorption for REE Separation from Coal Byproducts

Performer	**Lawrence Livermore National Laboratory (LLNL)**
Award Number	FWP-LLNL-18-FEW0239
Project Duration	03/01/2018 – 09/30/2021
Total Project Value	$ 950,000
Collaborator	Duke University; University of Arizona
Technology Area	Separation Technologies

The objective of LLNL's research is to determine whether biosorption can be used as an inexpensive and cost-effective means for rare earth element (REE) recovery from leachates of pre-combustion and post-combustion coal by- products through the development of a biofilm-based continuous flow-through system in an airlift bioreactor. This effort is also focused on improving the E.coli biofilm stability using a bioengineering approach to incorporate surface binding tags. These surface binding peptides are known to improve adhesion and increase biofilm stability under high shear force. A single bacterial platform for application to the airlift bioreactor will be selected based on several evaluation criteria, including biofilm density (number of cells per unit area); biofilm forming efficiency (proportion of cells that attach to the surface in a cell population); biofilm stability; REE-binding ligand density (number of REE- binding ligands incorporated per cell); and REE adsorption capacity per unit area of the biofilm. At the conclusion of LLNL's FWP with NETL, the project is expected to deliver a bench-scale demonstration of an airlift bioreactor for REE recovery and demonstrate its technical feasibility with a preliminary economic viability analysis and a plan for commercialization.



Airlift bioreactor design and process schematic. The proposed system consists of a two-stage semicontinuous process including (1) a closed mechanically agitated bioreactor (MAB) used to grow the microbes, (2) an open cylindrical container as a packed column for biofilm formation on carrier disks, (3) an airlift bioreactor (ALB) for adsorption of REE onto biofilm carrier disks, and (4) an open-packed elution column (EC) with (5) circulating citrate from a citrate tank for REE desorption and recovery.

Evaluation of Laser-Based Analysis of Rare Earth Elements in Coal-Related Materials

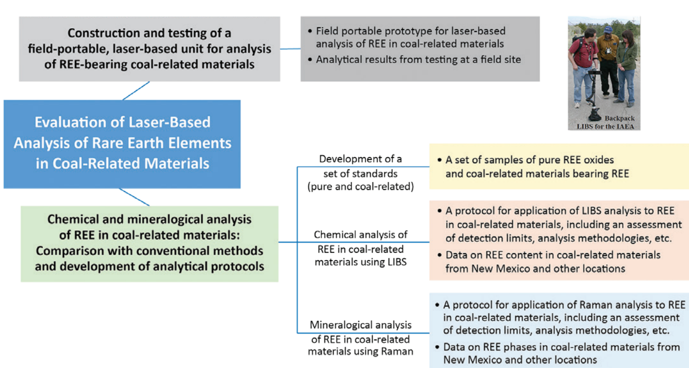
Performer	Los Alamos National Laboratory (LANL)
Award Number	FWP-FE-781-16-FY17
Project Duration	10/25/2017 – 07/31/2021
Total Project Value	$ 1,000,000
Technology Area	Enabling Technologies

The primary objectives of this effort are to (1) develop and test analytical protocols for analyzing the concentration and mineralogy of rare earth elements (REE) in coal-related materials using laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy; (2) develop a field-portable system for LIBS and Raman analysis of REE in coal-related material; and (3) analyze the concentration and mineralogy of REE in a variety of coal-related materials principally from New Mexico coal deposits.

The project consists of two tasks. In the first task, the team was to construct a field-portable prototype unit for LIBS-Raman analysis of REE in coal-related materials; field test and demonstrate the unit at New Mexico field sites; and revise analytical protocols as applicable. Researchers will take advantage of LANL's extensive experience in developing LIBS for quantitative analysis of elements in various matrices and will use this expertise to develop protocols for analysis of REE in coal-related materials. LANL has made recent institutional investments (through laboratory directed research and development) to develop a combined LIBS plus Raman system that can determine both chemistry (LIBS) and physical form (Raman). Researchers will use this new system to explore simultaneous chemical and mineralogical analysis of REE in coal-related materials.

In the second task, the team is developing analytical methods specific to the quantification of REE in various coal-related materials, thereby developing a broader database on REE concentrations and physical forms in a variety of coal-related materials. This step is necessary in the development of protocols for quantitative analysis of REE using LIBS. Interpretation of the data requires determining calibration curves for REE in specific matrices, because the efficiency of plasma generation (a first step in LIBS analysis) can be impacted both by physical form and overall chemistry.

The project successfully developed a method of using fluorobaric acid (HBF4) to digest coal, coal fly ash, and geological samples for REE analysis using inductively coupled plasma mass spectroscopy (ICP-MS). HBF4 preparation and ICP-MS analysis were validated against reference materials and shown to be very accurate. The backpack instrument is in the process of being assembled and the prototype is on track for demonstration in field tests in the summer of 2021.



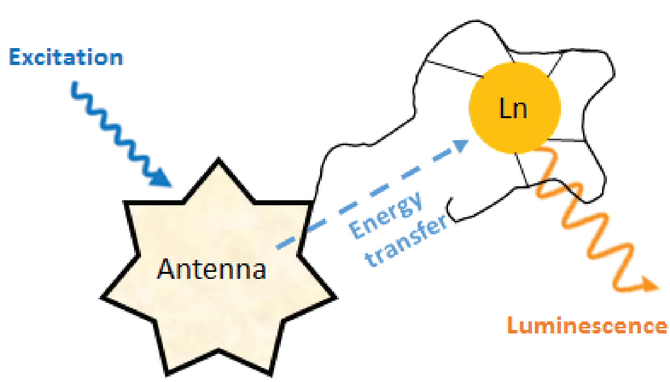
Schematic representation of the project.

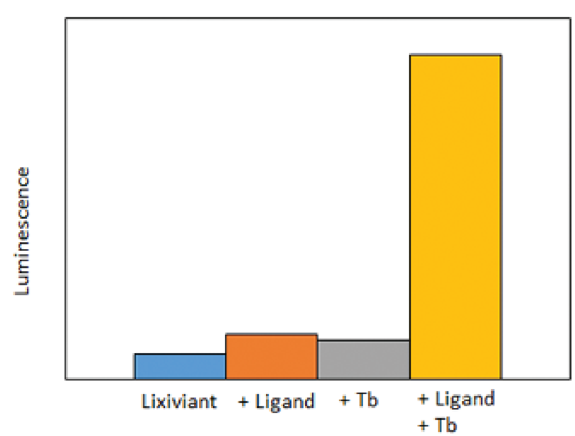
New Sensing Mechanisms for Rare Earth Detection in Coal and Coal Byproducts

Performer	**Idaho National Laboratory (INL)**
Award Number	FWP-INEL-B000-17-015
Project Duration	08/31/2017 – 12/31/2020
Total Project Value	$ 1,000,000
Collaborator	Lawrence Livermore National Laboratory; Rutgers–The State University of New Jersey; University of California, Davis
Technology Area	Enabling Technologies

The objective of INL's project is to evaluate novel complexation chemistries for the development of innovative sensing technologies for rare earth elements (REE). Complexation of lanthanides by peptides, coupled with the unique spectroscopic properties of lanthanides, is the underpinning for luminescent applications of lanthanide binding tags (LBT), originally invented as biochemical tools for the study of proteins. A peptide sequence specifically designed to bind lanthanides includes amino acids which have chromophore side-chains (tyrosine or tryptophan), and upon lanthanide binding the complex exhibits unique luminescence properties, enabling detection and visualization.

In coal and coal by-products, although specific lanthanide enrichment may vary by origin, generally the whole lanthanide series is present. A positive signal generated upon exposure of a sample to the specialized REE ligand would imply that the sample is enriched with REE and is worthy of further examination. INL evaluated whether the chemistry of LBT or other novel chromophore ligands can serve as the foundation for tools enabling rapid screening of REE-containing materials in the field. This work is at the discovery scale, but if successful, it could lead to the development of field-deployable sensors or field test kits for detection of REE in coal or coal by- products. Such sensors could be useful for a myriad of purposes beyond REE detection in coal, such as monitoring of REE content in process streams, detection of upsets during industrial processing, and rapid testing and validation of new extraction or separations techniques. In addition, the modeling and laboratory studies of the REE-ligand associations will contribute to fundamental understanding of the complexation behavior of lanthanides.





Luminescence is enhanced when a lanthanide binds to a ligand that has an attached antenna chromophore.

REDUCTION TO METALS

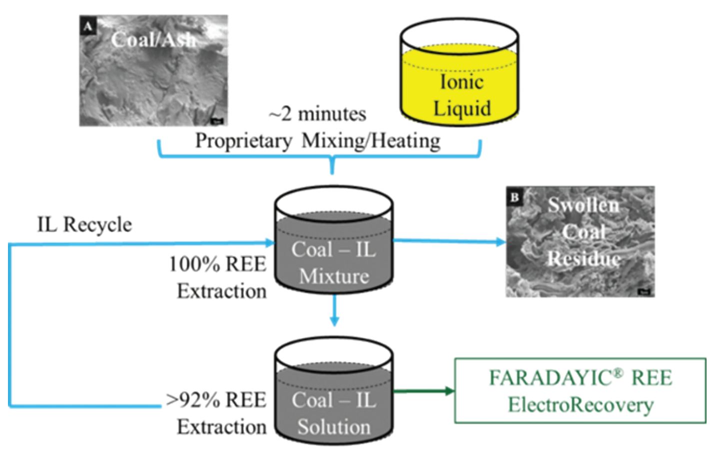
Low Temperature Reduction of Rare Earth Metals Using Ionic Liquids

Performer	**Faraday Technology, Inc.**
Award Number	SC0019794
Project Duration	07/01/2019 – 03/31/2020
Total Project Value	$ 206,500
Collaborator	University of South Alabama, Wyonics LLC
Technology Area	Reduction to Metals

The objective of this Phase 1 SBIR project was to develop a low-temperature reduction method for the production of high-purity rare earth metals (REM) from coal by-product feedstocks. The proposed approach was based on use of novel room-temperature ionic liquid electrolytes and non-steady-state electric fields to facilitate low-temperature electrodeposition applicable to a variety of rare earth elements (REE). This approach offers the benefits of lower energy requirements and a lower-corrosivity electrolyte which enables wider range of cell/system and substrate materials and safer operation over state-of-the-art direct-current electrodeposition conducted with high-temperature molten salt electrolytes.

In Phase 1, the conditions needed for low-temperature deposition of rare earth metals (REM) from rare earth oxides (REO) present in fly ash were explored. Specifically, the following were investigated: (1) the electrolyte formulation needed for electrodeposition reactions, (2) whether a solubilization agent is needed to dissolve metal species in the ionic liquid matrix, (3) the electric field conditions needed to promote high-purity deposition of rare earth metals, and (4) the preferred substrate materials. The results of the experiments conducted in Phase I would be used to design a pilot-scale system that would tentatively be built and validated in Phase 2, if funded.

Faraday Technology Inc., successfully demonstrated the approximate electrolyte composition and the electric field conditions needed to facilitate REE electroreduction for deposition of those REE onto a substrate from simple ionic liquid-based electrolytes. A key finding of this study was that pulse electric fields appear to be necessary for the electroreduction of REE from these simple solutions, since deposition under constant voltage electric fields was not observed under any of the conditions tested in the Phase 1 SBIR project.



REE extraction with sequential REM deposition.

Silicon-Calcium Based Reduction of Rare Earth Oxides

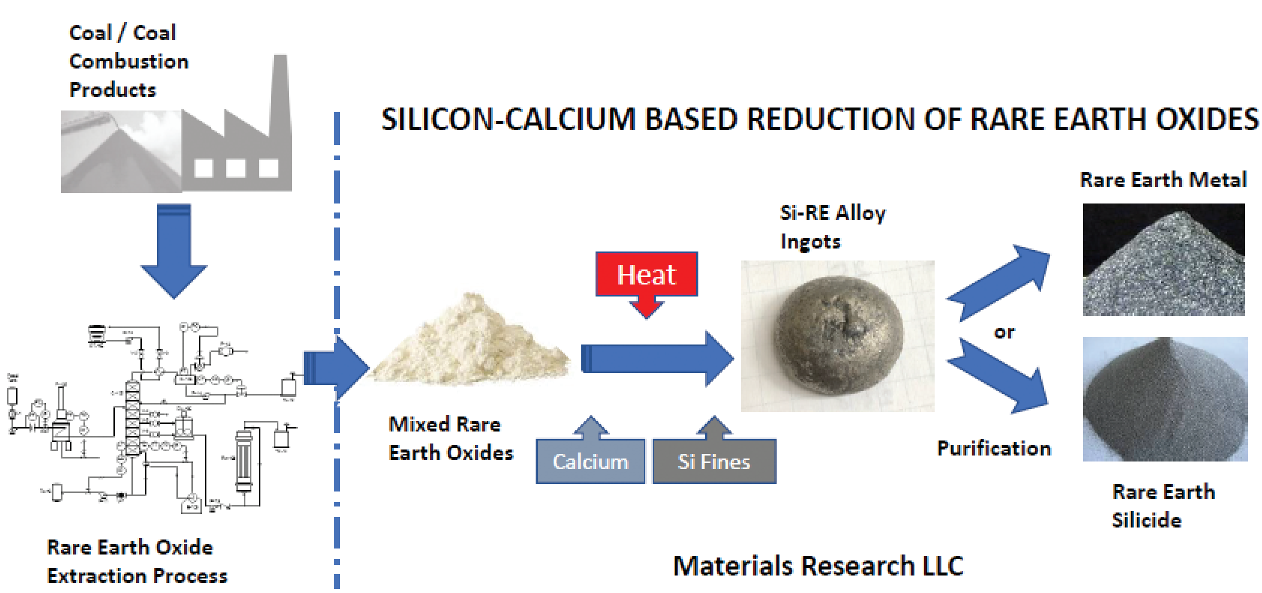
Performer	**Materials Research, LLC**
Award Number	SC0019804
Project Duration	07/01/2019 – 04/30/2020
Total Project Value	$ 199,927
Technology Area	Reduction to Metals

An important fundamental limitation of the conventional metallothermic reduction of rare earth oxides (REO) to produce rare earth metals (REM) is the slow rate of reduction. Adding silicon (Si) powder into a calcio-thermic reaction will improve reduction kinetics and yield, as well as product purity. The main objectives of this Phase 1 SBIR project were to demonstrate that the proposed calcium- silicon reductant system would alleviate limitations of conventional calcio-thermic reduction of REOs, thus producing REM in an efficient and economical way. Starting from commercially purchased oxides of neodymium (Nd_2O_3), samarium (Sm_2O_3) or europium (Eu_2O_3), and holmium (Ho_2O_3) or erbium (Er_2O_3) powders, all constituents of domestic coal, researchers developed a new process to produce high purity Nd, Sm (or Eu) and Ho (Er) metals using a calcium (Ca)-Si reductant system.

The final REM were produced either from condensation of their vapors (Sm or Eu) or the segregation of Nd and Ho (or Er) from Si.

In conclusion, greater than 96 wt% of the RE_2O_3 (RE = Nd, Er, and Sm) was recovered as a single ingot of Si-RE alloy from a molten salt bath. In the case of Eu_2O_3, the Eu recovery yield as Si-Eu alloy was only ≈50% due to the reaction between Eu metal and the halide salt.

This relatively simple protocol, which consists of a single step of heating a mixture of RE_2O_3-Ca-Si and a metal halide salt to 1400 °C, is potentially universal, and can be applied to reduction of all other REO as well as a mixture of REO. This novel approach of REO reduction could potentially provide an economical path to producing the desired REM with high purity and sizeable yield.



Process schematic showing silicon-calcium based reduction of a rare earth metal.

ABBREVIATIONS

AES .... American Energy Society
Al.. aluminum
ALB .... air lift bioreactor
AMD ....acid mine drainage
BMI .... Battelle Memorial Institute
Ca .... calcium
CM ....critical mineral(s)
Co ....cobalt
CO_2 .... carbon dioxide
DOE .... Department of Energy
EC ....elution column
Er .... erbium
Eu...europium
FE..Office of Fossil Energy
FEED .... front end engineering design
FWP .... Field Work Proposal
FY ....fiscal year
Ga .... gallium
Ge ....germanium
Ho ....holmium
HREE ....heavy rare earth element(s)
ICP-MS.............. inductively coupled mass spectroscopy
INL .... Idaho National Laboratory
ISHP..............................individually separated high-purity
LANL.............................Los Alamos National Laboratory
LBT .... lanthanide binding tag
Li .... lithium
LIBS .... laser induced breakdown spectroscopy
LLNL ....Lawrence Livermore National Laboratory
LRC...low rank coal
LREE .... light rare earth element(s)
MAB .... mechanically agitated bioreactor
Mn... manganese
MREO...................................... mixed rare earth oxide(s)
MRES .... mixed rare earth salt(s)
Nd .... neodymium
ND...North Dakota
NETL ....National Energy Technology Laboratory
PNNL ....Pacific Northwest National Laboratory
ppb ....parts per billion
ppm..parts per million
PSI .... Physical Sciences, Inc.
R&D.. research and development
RD&D.......... ...... research, development, and demonstration
REE ....rare earth element(s)
REM ....rare earth metal(s)
REO ....rare earth oxide(s)
RES .... rare earth salt(s), Rare Earth Salts (company)
REYSc.......................... rare earths, yttrium, and scandium
RIC ....Research and Innovation Center
RTI ....Research Triangle Institute
Sa .... samarium
SBIR............................ small business innovative research
Si...silicon
TEA .... techno-economic analysis
TEP ....trap-extract-precipitate
TREE ....total rare earth elements
TRL ....technology readiness level
UCLA ....University of California - Los Angeles
UK.. University of Kentucky
UK CAER..............................University of Kentucky Center for Applied Energy Research
UND ....University of North Dakota
UNDEERC .... University of North Dakota Energy and Environment Research Center
WSU..Wayne State University
WVURC........West Virginia University Research Corporation
WWS.. Winner Water Services
Zn... zinc

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https://edx.netl.doe.gov/ree/

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