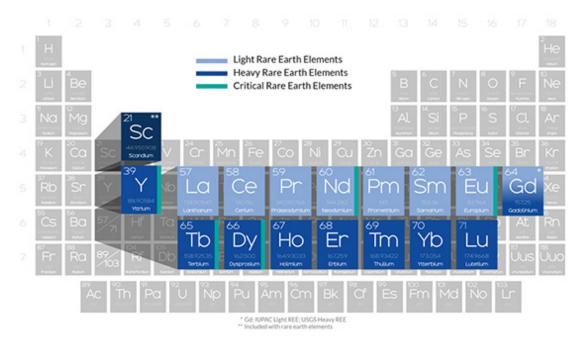


RARE EARTH ELEMENTS



2018 PROJECT PORTFOLIO



the **ENERGY** lab National Energy Technology Laboratory

Disclaimer

This portfolio was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Contents

Introd	Juction5
Rare E	Earth Elements – High Purity REE Production8
	Recovery of Rare Earth Elements from Coal Mining Waste Materials
	Production of Salable Rare Earth Products from Coal and Coal Byproducts in the U.S. Using Advanced Separation Processes
Rare I	Earth Elements – Pilot-Scale Test Facilities10
	High Yield and Economical Production of Rare Earth Elements from Coal Ash10
	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
Rare B	Earth Elements – Bench-Scale Test Facilities12
	Investigation of Rare Earth Element Extraction from North Dakota Coal-Related Feedstocks12
	Recovery of Rare Earth Elements from Coal Mine Drainage13
Rare B	Earth Elements – Transformational Separations Technology Development
	Recovery of High Purity Rare Earth Elements (REEs) from Coal Ash via a Novel Electrowinning Process
	Application of Biosorption for REE Separation from Coal Byproducts15
	Evaluation of Novel Strategies and Processes for Separation of Rare-Earth Elements from Coal- Related Materials
	Rare Earth Elements from Coal and Coal By-Products17
	Concentrating Rare Earth Elements in Acid Mine Drainage Using Coal Combustion Products Through Abandoned Mine Land Reclamation
	Low-Cost Rare-Earth-Element (REE) Recovery from Acid Mine Drainage Sludge19
	Low Temperature Plasma Treatment for Enhanced Recovery of Highly Valued Critical Rare Earth Elements from Coal-Based Resources
	Economic Extraction and Recovery of REEs and Production of Clean Value-Added Products from Low-Rank Coal Fly Ash
	Economic Extraction, Recovery, and Upgrading of Rare Earth Elements from Coal-Based Resources
	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
	Coupled Hydrothermal Extraction and Ligand-Associated Swellable Glass Media Recovery of Rare Earth Elements from Coal Fly Ash24
	At-Source Recovery of Rare Earth Elements from Coal Mine Drainage

Rare Earth Elements – Field Resource Location and Characterization			
University of Kentucky - Rare Earth Element Identification and Characterization of Coal and Coal By-Products Containing High Rare Earth Element Concentrations			
University of North Dakota - Sampling, Characterization and Round Robin Analyses of Domestic U.S. Coal Based Resources Containing High Rare Earth Element (REE) Concentrations			
Tetra Tech, Inc Rare Earth Element Identification and Characterization of Coal and Coal By- Products Containing High Rare Earth Element Concentrations			
Tetra Tech, Inc Rare Earth Element Identification and Characterization of Coal and Coal By- Products Containing High Rare Earth Element Concentrations			
West Virginia University - Rare Earth Element Identification and Characterization of Coal and Coal By-Products Containing High Rare Earth Element Concentrations			
XLight Corporation - Rare Earth Element Identification and Characterization of Coal and Coal By- Products Containing High Rare Earth Element Concentrations			
Rare Earth Elements – Field Sensor Development			
Nondestructive, Bulk Rare Earth Element Measurement System for Coal			
Sensor for Direct, Rapid and Complete Elemental Analysis of Coal			
New Sensing Mechanisms for Rare Earth Detection in Coal and Coal Byproducts			
Evaluation of Laser-Based Analysis of Rare Earth Elements in Coal-Related Materials			
Rare Earth Element Mass Analyzer			
Spectrochemical Detection and Monitoring of Rare Earth Elements During Extraction from Coal/Coal Byproducts			
Rare Earth Elements – Technology Commercialization			
Rare Earth Metal Extraction for Clean Technologies35			
Abbreviations			
Contacts			
Acknowledgments			

Introduction

BACKGROUND

The U.S. Department of Energy (DOE) Office of Fossil Energy conducts programs to ensure the availability of ultraclean (near-zero emissions), abundant, low-cost domestic energy from coal. These efforts are designed to fuel economic prosperity, strengthen energy independence, and enhance environmental quality. As the Office of Fossil Energy's research laboratory, the National Energy Technology Laboratory (NETL) is engaged in research, development, and demonstration (RD&D) activities to create technology and technology-based policy options for public benefit.

As part of its RD&D technology portfolio, NETL has initiated the Rare Earth Elements (REEs) from Coal and Coal By-Products RD&D Program, which focuses on developing REE separation and recovery technologies, addressing the current global REE separations market and process economics, and demonstrating environmentally benign REE separation processing capabilities. The quantities of REEs in our nation's vast coal resources offer the potential to reduce U.S. dependence on foreign sources for these critical materials, and to create new industries in regions **PROGRAM OBJECTIVES**

The overall objectives of NETL's REE program are to demonstrate the techno-economic feasibility and performance of existing commercial or newly developed REE separation technologies. These technologies are focused on separating and recovering REEs from coal and coal by-products containing a minimum of 300 ppm total REEs, and concentrating the REEs to levels greater than or equal to 2 percent by weight, tentatively producing 90 to 99.99 percent high-purity, salable, individual rare earth metal oxides by the year 2020. These objectives will be accomplished through laboratory REE separation projects and demonstration of concept feasibility at bench-scale through pilot-scale facilities and integrated processing systems. Ultimately, these efforts will ready REE separations technology for commercial deployment. Key success factors for this program include co-production of materials and critical elements, successful demonstration of environmentally benign processing, and competitive economics.

KEY TECHNOLOGY AREAS

The REE Program consists of three key technology areas: Enabling Technologies, Separations Technologies, and Process Systems. The figure on page 7 shows how the key technology areas relate to the program efforts.

1. <u>Enabling Technologies</u> include resource identification, sampling, and characterization; techno-economic analysis; and field/process sensor development.

Significant progress in locating field sites and assessing the composition of potential coal and coal by-product materials containing REEs has been made. Efforts continue to focus on identifying the best source of materials to support future commercial REE production. Chemical and physical characterization efforts to determine REE elemental concentrations and phase compositions in coal and coal by-product resources are essential for developing viable REE separation processes.

Techno-economic analyses are being conducted to evaluate the international REE market demand and to assess the economics of commercially producing REEs from conventional separation as well as potentially new and



advanced transformational separation processes. A preliminary high-level REE jobs analysis is being developed that includes an estimation of the economic impacts of constructing and operating a REE separations and processing facility (or facilities) in the United States.

Portable sensors for identifying promising REE coal-based resources in the field, as well as devices for determining REE concentrations in process separation flow streams, are being developed and evaluated. These technologies are tentatively scheduled to be field-tested at bench-scale separations test facilities and validated to commercial-ready status during use in pilot-scale demonstration projects. While significant progress has been made in identifying field site locations and assessing the composition of potential coal and coal by-product REE-containing materials, continued effort is essential to identify the best source of materials to support future commercial REE production. Chemical and physical characterization efforts addressing REE elemental concentrations and phase compositions in the coal and coal by-product resources are essential for developing viable REE separation processes.

2. <u>Separation Technologies</u> include utilization or modification of current commercial physical separation systems (i.e., beneficiation via size, density, froth flotation, magnetic, ultrasound), hydrometallurgy and solvent

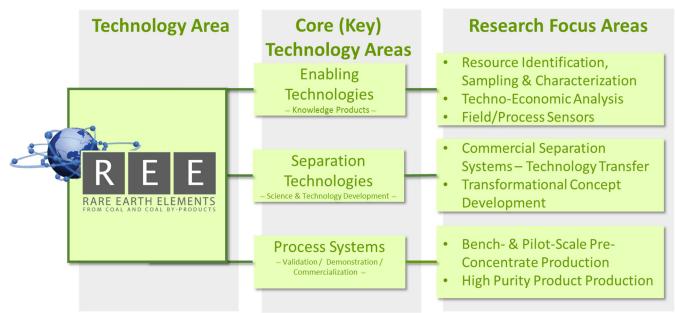
extraction/digestion processes, and pyrometallurgy techniques (i.e., electro-slag refining, acid roasting) to separate and concentrate REEs from coal-based resources such as coal, coal refuse, clay/sandstone over/under-burden materials, aqueous effluents, acid mine drainage sludge, and power generation ash. Advanced or new transformational REE separation concepts such as physical, chemical, electrical and thermal extraction, acid/base leaching, and ion exchange; reactive grinding; photochemical, ultrasonic-assisted, microwave-aided, photophoretic, plasma, and supercritical CO₂ separation; and advanced sorbents and membrane systems are being considered to further enhance REE separation.



3. <u>Process Systems</u> development, demonstration, and commercialization include validating the performance of bench- and pilot-scale technologies as well as determining the economic feasibility of separating REEs from coal and coal-related resources containing a minimum of 300 ppm REEs and concentrating them to an initial pre-concentrate matrix of greater than or equal to 2 percent by weight, with further integration of additional extraction systems that generate high-purity, salable rare earth compounds (such as oxides and/or metals, carbonates, etc.).

Ultimately, domestic generation of high-purity REEs may lead to the manufacture of REE-containing products in the United States, thus enhancing our national security and stimulating economic growth. Domestic production of REEs will provide secure access for industries involved in defense and national security, energy, medicine, communications, consumer electronics, and others. In addition, an available domestic supply of REEs may lead to commercialization of new and advanced materials and equipment.

Additional information can be found on NETL's Rare Earth Elements web page and Energy Data eXchange database.



Key Technology process map for RD&D focus efforts.

Rare Earth Elements – High Purity REE Production Recovery of Rare Earth Elements from Coal Mining Waste Materials

Technology Partner: Inventure Renewables, Inc. Award Number: FE0030146 Project Duration: 9/1/2017 - 2/28/2019 Total Project Value: \$1,250,000 Key Technology Area: Process Systems Project Partners: K-Technologies, Inc.; Pennsylvania State University; and Texas Minerals Resources Corporation

This Phase 1 project will identify and characterize coal- using CIX/CIC techniques. This project will also related materials, and design and perform a techno- determine the economic viability of mining and economic analysis for a self-contained, modular, and processing REEs associated with Appalachian coal portable continuous ion exchange/continuous ion deposits. If successful, this Phase 1 project may continue chromatography (CIX/CIC) pilot plant capable of into the next stage of development which includes processing and purifying rare earth elements (REEs). installation, field-testing, and evaluation of the REE The process will combine chemical processing with recovery technology. The expected outcomes of the physical beneficiation processes for providing a project are (1) the production of REEs that are salable at concentrated REEs leach liquor stream derived from an output of 10 pounds per day from coal by-products, clay-rich, co-produced coal materials such as those (2) the development of a technology that is versatile and associated with overburden, and clay layers under or modular, (3) the preservation of mining jobs, and (4) a within a coal seam. After concentration, the REEs will be pathway to economic feasibility. separated and purified into their individual elements



Continuous ion exchange pilot system.

Production of Salable Rare Earth Products from Coal and Coal Byproducts in the U.S. Using Advanced Separation Processes

Technology Partner: Marshall Miller & Associates, Inc.

Award Number: FE0029956

Project Duration: 9/1/2017 – 2/28/2019

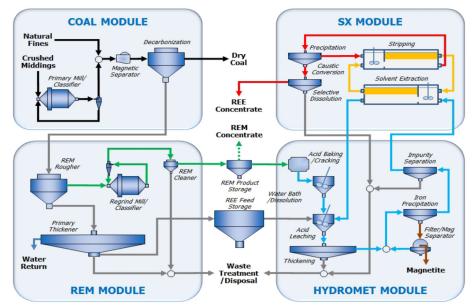
Total Project Value: \$1,250,000

Key Technology Area: Process Systems

Project Partners: Cumberland Mine Services, Minerals Refining Company, Outotec USA, University of Kentucky, Virginia Polytechnic Institute and State University

This Phase 1 project will identify and characterize coalrelated materials and design and perform a technoeconomic analysis for a commercially viable technology to produce salable quantities and purities of rare earth elements (REEs) from coal-based feedstocks. The facility, which will be physically located at an active coal mine in West Virginia, will utilize interchangeable modules that can be easily reconfigured to accommodate changing feedstocks and technology upgrades. The process includes both physical and chemical extraction processes and is expected to produce at least 10 pounds per day of rare earth oxides at purities of 90-99 percent. As part of the feasibility analysis, laboratory testing will be performed, including crushing/grinding, magnetic concentration, flotation release analysis, selective agglomeration, leachability/ion exchangeability, solvent extraction, mechanical dewatering, and solids thickening. Data obtained from the laboratory testing will be used to

design a pilot facility and optimize REE recovery and process costs. Overall, this feasibility study will provide critical insight on the economic parameters and commercial viability of the integrated process system. In addition to the REE products, the facility will also coproduce a salable ultraclean coal by-product that can help to offset the cost of the facility and enhance longterm economic viability. If successful, this Phase 1 project may continue into the next stage of development which includes installation, field-testing, and evaluation of the REE recovery technology. Successful completion of this project is expected to provide a first-generation production facility for recovering rare earth products from coal and coal byproduct streams in a manner that is cost-effective and environmentally acceptable. This outcome will provide a secure domestic feedstock supply of REEs, and will maintain or create additional jobs in coal communities.



Process block diagram for the REE recovery facility.

Rare Earth Elements – Pilot-Scale Test Facilities High Yield and Economical Production of Rare Earth Elements from Coal Ash

Technology Partner: Physical Sciences, Inc. Award Number: FE0027167 Project Duration: 3/1/2016 – 3/31/2020 Total Project Value: \$8,750,166 Key Technology Area: Process Systems Project Partners: University of Kentucky

In this Phase 2 project, the team of Physical Sciences, Inc. (PSI), University of Kentucky/Center for Applied Energy Research, and Winner Water Services will develop and demonstrate a pilot scale plant to economically produce salable rare earth element (REE)rich concentrates including yttrium and scandium (REYSc) and commercially viable co-products from coal ash feedstock using environmentally safe and high-yield physical and chemical enrichment/recovery processes. The pilot plant will operate at the scale of approximately 0.4-1 tons per day (tpd) ash throughput for physical processing and about 0.5 tpd for chemical processing, producing at least 50 grams (g) of dry REYSc nitrates concentrate containing more than 10 percent by weight of REYSc, and targeting 500 g of dry REYSc nitrates concentrate containing more than 20 percent REYSc by weight. The ash feedstock will come from the Dale power plant in Ford, Kentucky, with at least 300 parts per million (ppm) of REYSc content, though more than 500 ppm is anticipated. The data obtained from

the pilot plant operations will be used to enhance and validate the techno-economic analysis that was completed for both the physical and chemical processing plants at a scale of 600 tpd in Phase 1, and use it to design a commercial scale plant (hundreds of tpd throughput) with return on investment in less than seven years. Development and demonstration of modular, transportable pilot-scale physical and chemical plants for REYSc recovery from coal ash, including enhancement and validation of a technoeconomic model of pilot plant operations data, will enable the design of a commercial-scale (approximately hundreds of tpd) REYSc plant. Demonstration of PSI's technology to recover REYSc from coal ash will enable utilization of coal mining/coal combustion waste product in environmentally benign ways to produce REEs of strategic importance for the United States while generating jobs and economic growth in economicallydepressed regions of this country.

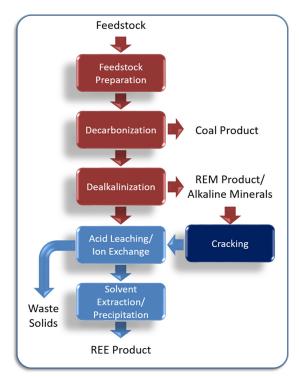
Pilot-Scale Testing of an Integrated Circuit for the Extraction of Rare Earth Minerals and Elements from Coal and Coal By-Products Using Advanced Separation Technologies

Technology Partner: University of Kentucky Award Number: FE0027035 Project Duration: 3/1/2016 – 3/31/2020 Total Project Value: \$8,820,009 Key Technology Area: Process Systems

Project Partners: Alliance Resources, Blackhawk Mining, Minerals Refining Company, Mineral Separation Technologies, Virginia Polytechnic Institute and State University, and West Virginia University

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 mobile pilot plant to recover REEs from those feedstocks. In laboratory experiments, UK achieved greater than 80 percent concentration of rare earths in the mixed rare earth concentrate while recovering greater than 75 percent of the rare earths from the incoming feedstock. In Phase 2, the University will develop and test a one-fourth ton/hour pilot-scale plant for the extraction of REEs from Central Appalachian and Illinois Basin

bituminous coal preparation plant refuse materials. The system integrates 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 includes an advanced froth flotation process and novel hydrophobic-hydrophilic а separation process. The project is 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 REEs from various coal and coal by-product streams.



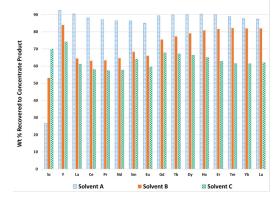
Schematic of the University of Kentucky's process.

Rare Earth Elements – Bench-Scale Test Facilities Investigation of Rare Earth Element Extraction from North Dakota Coal-Related Feedstocks

Technology Partner: University of North Dakota Award Number: FE0027006 Project Duration: 3/1/2016 – 3/31/2019 Total Project Value: \$4,309,347 Key Technology Area: Process Systems Project Partners: Barr Engineering and Pacific Northwest National Laboratory

In Phase 1 of this project, the University of North Dakota (UND) project team identified locations in North Dakota with coal-related feed stocks having exceptionally high rare earth elements (REE) content and developed a simple, highly effective, and low-cost method to concentrate the REEs in the lignite feed stocks using a novel technology that takes advantage of the unique properties of lignite. In laboratory experiments, UND achieved greater than two percent concentration of rare earths in the mixed rare earth concentrate while recovering up to 35 percent of the rare earths from the incoming feedstock. In Phase 2, the University is partnering with Microbeam Technologies, Barr Engineering, Pacific Northwest National Laboratory, and MLJ Consulting to investigate the feasibility of recovering REEs from North Dakota lignite and ligniterelated feedstocks. The team will scale up the technology and demonstrate it at a scale of 10-20 kilograms per hour feedstock throughput and evaluate the economics for a commercial-scale, rare-earthsconcentrating facility in North Dakota. The project also includes development of a commercialization plan and market assessment. The Lignite Research Program of the North Dakota Industrial Commission. North

American Coal Corporation, Great River Energy, Minnkota Power Cooperative, Great Northern Properties, the University of North Dakota, and the North Dakota University System are cost-sharing this project. The recovery of REEs 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 will further enhance the lignite industry will also result from the process. The potential also exists to significantly or completely offset current imported REE and REE products by providing a reliable domestic resource and novel low-cost technology focused on its development. The ultimate significance of this research is development of a high-performance, environmentally benign, and economically viable technology for REE production from an alternative resource that will reduce dependence on foreign supplies and strengthen the economic and national security of the United States. This project will enable transition to pilot scale, and will be a foundation for subsequent larger demonstrations and eventual commercial deployment.



Results of REE extraction from North Dakota lignite using three solvents tested in Phase 1.

Recovery of Rare Earth Elements from Coal Mine Drainage

Technology Partner: West Virginia University Research Corporation

Award Number: FE0026927

Project Duration: 3/1/2016 - 6/30/2019

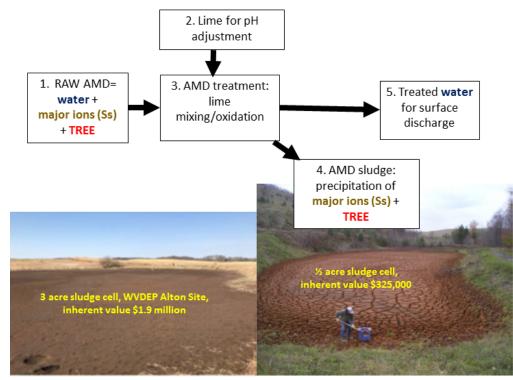
Total Project Value: \$4,339,414

Key Technology Area: Process Systems

Project Partners: Rockwell Automation; Tetra Tech, Inc.; and Virginia Polytechnic Institute and State University

In Phase 2 of the project, West Virginia University and its partners will develop a cost-effective and environmentally benign process to recover rare earth elements (REEs) from solid residues (sludge) generated during treatment of acid coal mine drainage (AMD). This project will take advantage of autogenous processes that occur in coal mines and associated tailings which liberate, then concentrate, REEs. Phase 1 findings showed elevated concentrations of REEs, 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 percent total REE 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. During Phase 2, a

continuously operating bench-scale unit will be constructed and operated, yielding 3 grams per hour of REE concentrate. In Phase 1, AMD treatment residues were identified as a domestic source of REE feedstock. In addition, an economically attractive extraction and refining process was identified with the potential to generate significant income for operators of AMD treatment sites, and relieve the U.S. manufacturing industry's reliance on foreign REE supplies. Estimates based on the volume of AMD generated in Pennsylvania and West Virginia suggest their AMD sludges represent approximately 610 to 2,700 tons of REEs per yearroughly sufficient to supply the 800 tons that the U.S. defense industry needs each year. In addition, a survey of 154 AMD treatment facilities found 225 tons of sludge (dry weight basis) in surface storage, with an inherent REE value of \$122 million.



AMD treatment and sludge storage. TREE: total rare earth elements. Ss: sludge solids. Major ions: Ca, SO₄, Si, Fe, Mg, Mn.

Rare Earth Elements – Transformational Separations Technology Development

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

Technology Partner: Battelle Memorial Institute Award Number: FE0031529 Project Duration: 11/16/2017 – 5/15/2019 Total Project Value: \$874,940 Key Technology Area: Separation Technologies Project Partners: Rare Earth Salts

The objective of this project is to advance development and integration of the novel electrowinning separation and purification process developed by Rare Earth Salts (RES) and Battelle's acid digestion process, and validate that they can generate environmentally benign and economically sustainable rare earth element (REE) products from domestic coal ash sources at purities above 90 percent. An additional objective is to enable domestic REE sources and new outlets for coal products by demonstrating advancements in these purification technologies on coal-based feedstock. These objectives will be accomplished by testing at laboratory scale. Battelle's acid digestion process will be used to upgrade the REE concentrate via solvent extraction, eliminating less-valuable elements such as iron, aluminum, sodium, and calcium, and carefully avoiding enrichment of contaminants such as uranium and thorium. REE

products will then be separated and purified from this upgraded solution using RES's novel electrowinning process—a purification process that can reduce the number of stages and cost of REE purification compared to traditional solvent extraction circuits. The project team will perform a preliminary design of a commercialscale system, using data obtained during lab testing, to generate preliminary capital and operating costs for the process. The outcome of this project will advance Battelle's solvent extraction REE upgrading process, RES's process, and their application to domestic coalderived feedstocks by validating their feasibility in both technical and economical terms. A high-purity (greater than 99 percent) product of separated REE will be generated by the RES process-derived from fly ash extracted with Battelle's acid digestion process from an operating pulverized coal combustion plant.

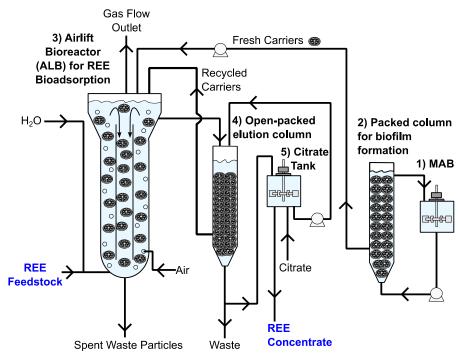


Solvent extraction upgrading of coal ash pregnant leach solution.

Application of Biosorption for REE Separation from Coal Byproducts

Technology Partner: Lawrence Livermore National Laboratory Award Number: FWP-LLNL-18-FEW0239 Project Duration: 3/1/2018 – 2/28/2021 Total Project Value: \$950,000 Key Technology Area: Separation Technologies

The objective of this research is to determine whether biosorption can be used as an inexpensive and costeffective means for rare earth element (REE) recovery from leachate of pre-combustion and post-combustion coal by-products. This project will develop a biofilmbased continuous flow-through system in an airlift bioreactor. This effort will also improve the biofilm stability of *E. coli* 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. This objective will be carried out in parallel with a *Caulobacter* biofilm formation activity in a separate, but related project (TCF-17-13365). A single bacterial platform for the application of airlift bioreactor will be down-selected based on several evaluation criteria, including (1) biofilm density (number of cells per unit area), (2) biofilm forming efficiency (proportion of cells that attach to the surface in a cell population), (3) biofilm stability, (4) REE-binding ligand density (number of REEbinding ligands incorporated per cell), and (5) REE adsorption capacity per unit area of the biofilm. At conclusion, the project is expected to deliver a benchscale demonstration of an airlift bioreactor for REE recovery and demonstrate its technical feasibility with preliminary economic viability analysis and a plan for commercialization.



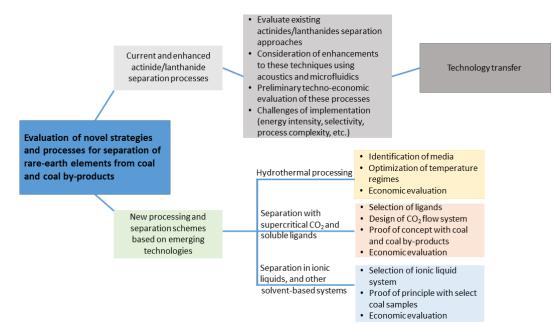
Airlift bioreactor design and process flow diagram. The proposed system consists of a two-stage semicontinuous process including (1) a closed mechanically agitated bioreactor (MAB) used to grow the microbes, (2) an open cylindrical container as a packed column for biofilm formation on carrier disks, (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 Novel Strategies and Processes for Separation of Rare-Earth Elements from Coal-Related Materials

Technology Partner: Los Alamos National Laboratory Award Number: FWP-FE-810-17-FY17 Project Duration: 10/1/2017 – 9/30/2020 Total Project Value: \$1,000,000 Key Technology Area: Separation Technologies

Los Alamos National Laboratory (LANL) has a long history in *f*-element chemistry and separations, as needed to support its core national-security mission. This history has resulted in unique experience in both process innovation and process implementation at a range of scales. Los Alamos will bring this unique expertise in separation of actinides/lanthanides to bear to evaluate new innovative processes in rare earth element (REE) separation from coal and coal byproducts. The Los Alamos effort comprises two complementary tasks. The first task will evaluate current and enhanced actinide/lanthanide separation processes relative to identifying potential processes and strategies for REE separation from coal and coal byproducts. This effort will evaluate existing actinides/ lanthanides separation approaches developed for nuclear materials and their potential application for REEs extraction: included in this will be a consideration of 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 will evaluate the potential of developing new processing and separation schemes based on emerging technologies. The initial phase of the project will screen the following processing approaches: (1) Processing under hydrothermal conditions; this effort builds on previous work that suggests that a better control of lanthanides speciation at elevated temperature can be exploited to perform efficient REEs separation. (2) REE-selective extraction using supercritical carbon dioxide (CO₂) and soluble ligands; this effort builds on initial proof-of-concept studies on supercritical CO₂ that show great promise for simple and effective separation of REE from oxide materials. (3) Separation of REE using ionic liquids, and other solvent-based systems; this effort builds on current effort at LANL to develop actinide/lanthanide separation schemes in ionic liquids.



Schematic representation of the project.

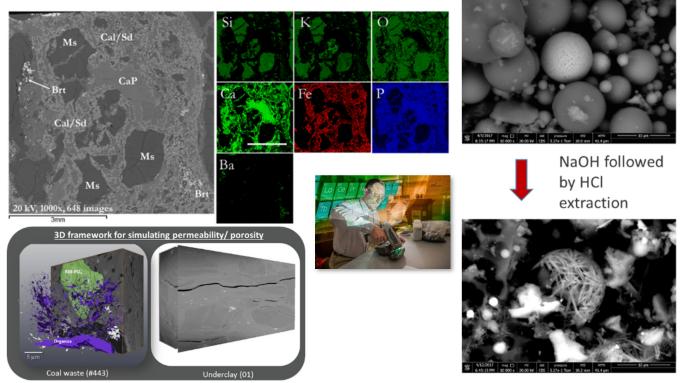
Rare Earth Elements from Coal and Coal By-Products

Technology Partner: National Energy Technology Laboratory – Research and Innovation Center Award Number: FWP-RIC REE FY2016-2020 Project Duration: 10/01/2015 – 3/31/2021 Total Project Value: \$11,868,856

Key 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 (REEs); 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. Past efforts were focused on both the development of novel REE recovery technologies and characterization techniques, and understanding the relative distribution of REEs, their chemical forms, and association with other phases or minerals in the REE source materials. Current work is focused on (1) intelligent prospecting methods to predict high concentrations of coal-related

REE reserves and REE forms which are easily extractable; (2) maturing several promising separation pathways; (3) computational fluid dynamic modeling to enhance separation process development; and (4) techno-economic modeling to understand market opportunities, environmental benefits, and process bottlenecks. Each research area is designed to support the portfolio as a whole and to address key knowledge gaps that are not being investigated by industry. Additional research include areas advanced characterization work in support of separations research, novel and exploratory separations research, and the development of prototype devices for real-time REE quantification in liquids and solids for prospecting and process control of separation processes. Novel separations research will focus on high-risk, highreward recovery technologies and areas of NETL core competencies.



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

Technology Partner: Ohio State University Award Number: FE0031566 Project Duration: 12/1/2017 – 4/30/2019 Total Project Value: \$528,700 Key Technology Area: Separation Technologies

The project research team will develop an integrated process that first uses stabilized flue gas desulfurization material (sFGD) to recover rare earth elements (REEs) from acid mine drainage (AMD) and a sequential extraction procedure to produce a rare earth feedstock with above two percent by weight REE. The objectives are to (1) validate the effectiveness and feasibility of the integrated REE recovery/concentrating process, (2) determine mechanisms controlling the rare earth recovery process, (3) quantify the associated economic and environmental benefits, and (4) evaluate the fullscale application of the process. To achieve these objectives, tasks to be carried out are in four phases. In the first phase, the research team will collaborate with state agencies to carry out field investigations designed to screen and evaluate the seasonal changes of REEs from AMD discharges that have high recovery potential. Next, laboratory-scale tests will be carried out to study the recovery process under a range of percolation

conditions using AMD and sFGDs from selected sources. The associated water quality changes will be monitored. Advanced analytical techniques, including synchrotron based X-ray methods, will be used to identify the mineral forms of retained REEs. In the third phase, a highly selective sequential extraction procedure will be used to concentrate the REEs. In the final phase, techno-economic analysis and life-cycle assessment will be carried out to evaluate the economic and environmental benefits. The rare earth recovery and concentrating process can be integrated with abandoned mine land (AML) reclamation to create an approach that can (1) add economic incentives for AML reclamation, (2) remediate AMD discharge, (3) provide a long-term, high-volume beneficial use for coal combustion by-products, which otherwise needs to be disposed of in a landfill, and (4) eliminate public safety hazards and threats to local environment and ecological systems posed by AMLs.



Bench scale testing setup.

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

Technology Partner: Research Triangle Institute Award Number: FE0031483 Project Duration: 11/20/2017 – 5/19/2019 Total Project Value: \$500,000 Key Technology Area: Separation Technologies Project Partners: Cerahelix and Veolia Water Technologies

This project aims to develop a membrane-based, benchscale system to extract strategic minerals such as rare earth elements (REEs) and other critical minerals from acid mine drainage (AMD) sludge generated as part of coal mining activities in the United States. The effort will use a staged, membrane-based treatment approach to separate, concentrate, and ultimately recover REEs from AMD. Initial work will take water samples from a potential AMD site(s) and characterize them for REE concentration, dissolved metals concentration, and key water-guality characteristics. Each individual process component will be tested with water samples to optimize performance. The work will initially involve proof-of-concept experiments at the bench scale with the aim of varying process parameters such as water chemistry, nanofiltration membrane performance in

monovalent/ multivalent separation, affinity media chemistry, and solvent recovery of REE. From these experiments, separation conditions that can be reasonably transitioned to flow-through systems and larger prototype scales for further techno-economic analysis will be selected so that the economic performance of a continuously fed AMD fluid process for REE recovery can be evaluated. The process has the potential to expand and increase security of our Nation's sources for strategic elements by exploiting a domestic resource such as AMD sludge and reducing U.S. dependence on foreign countries for these critical elements. The process would enable energy-efficient, cost-effective recovery of REEs to a two weight percent REE pre-concentrate. The steps comprising the process are inherently low-cost approaches.

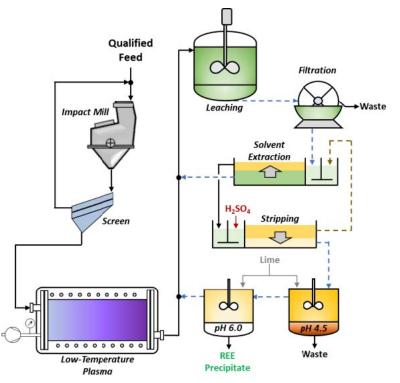


Cerahelix ceramic tubular membranes for monovalent/multivalent separation.

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

Technology Partner: University of Kentucky Award Number: FE0031525 Project Duration: 11/16/2017 – 5/15/2019 Total Project Value: \$404,969 Key Technology Area: Separation Technologies Project Partners: Virginia Polytechnic Institute and State University

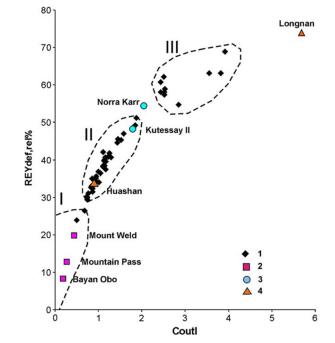
The principal objective of this project is to develop a novel process using low-temperature plasma treatment integrated with hydrometallurgical processes to recover rare earth elements (REEs), especially highly valued REEs (e.g., scandium and critical REEs), from coal and coal by-products. The project will initially evaluate the mineralogy, leachability, and effect of plasma pretreatment for the various segments of selected feedstocks containing greater than 300 parts per million of total REEs on a dry, whole mass basis. A laboratory low-temperature oxygen plasma unit with the ability to control test conditions will be used to optimize the operating parameters of the plasma treatment process (e.g., power, temperature, treatment time, etc.) with respect to feedstock characteristics, such as the exposed surface area, pore size, microstructure, degree of oxidation, etc. After optimizing the process, plasma treatment will be integrated with leaching, solvent extraction, and precipitation processes to produce REE concentrates at improved recovery levels and grades higher than 10 percent total REEs on a dry, whole mass basis. A techno-economic feasibility analysis of implementing plasma treatment into an overall REE recovery system will be conducted. The project, conducted at laboratory scale, has the benefit of providing key information needed to overcome challenges in larger-scale operations and further maturation of the method.



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

Technology Partner: University of North Dakota Award Number: FE0031490 Project Duration: 11/16/2017 – 5/15/2019 Total Project Value: \$508,812 Key Technology Area: Separation Technologies Project Partners: Pacific Northwest National Laboratory

The project's objective is to develop an economically viable and tailorable rare-earth element (REE) extraction and concentration method for low-rank coal fly ash and bottom ash that produces a concentrate containing greater than or equal to two percent by weight total REE. This project will focus on low-rank (lignite and subbituminous) coal combustion/gasification ashes. The ash samples will be collected from industry partner facilities as well as from the existing sample database for North Dakota lignites at the University of North Dakota. The characterization to be performed will fully elucidate the abundance, form, and association of the REEs, both in the feed coals that produced the ash, and in the ashes. Additionally, the chemical composition, mineralogy, and morphology of the ash will be determined. Based on the characterization results, two ash samples will be downselected for laboratory-scale REE extraction and concentration testing. The laboratory-scale testing will involve evaluation of ash pretreatment methods, dilute acid leaching, and solvent extraction testing, which will be followed by REE concentration testing at downselected conditions and materials. The project will also evaluate a novel method of value-added beneficiation of the clean fly ash. Finally, based on the experimental testing, a preliminary technical and economic analysis will be completed to estimate capital and operating expenses and product revenues. The project benefits are the development of a highperformance, environmentally benign, and economically viable technology for REE production from an alternative resource that will limit dependence on foreign supplies and strengthen the economic and national security of the United States.



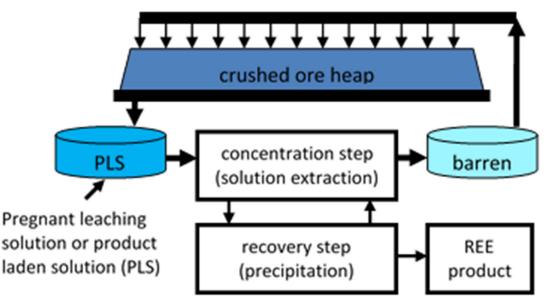
Seredin, V.V.; Dai, S. Coal Deposits as Potential Alternative Sources for Lanthanides and Yttrium. *International Journal of Coal Geology* 2012, 94, 67-93.

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

Technology Partner: University of Utah Award Number: FE0031526 Project Duration: 11/16/2017 – 5/15/2019 Total Project Value: \$499,000 Key Technology Area: Separation Technologies Project Partners: Virginia Polytechnic Institute and State University

The objective of this project is to demonstrate and improve methods that can economically extract, recover, and upgrade the rare earth elements (REEs) contents from coal-based resources using integrated modeling, coal preparation, bio-oxidation, solution conditioning, heap leaching, solvent extraction, and precipitation technologies to cleanly and costeffectively produce rare earth-bearing products with more than 8 percent by weight REE. The project encompasses a range of technologies currently in industrial practice to produce REE products from coalbased sources. Advanced coal processing technology will deliver clean coal for the market as well as REEbearing coarse refuse (non-coal rock) that is the correct size for heap leaching applications. In addition, the technology provides concentrated sulfide minerals (for mid-to-high-sulfur coals) for cleaner coal and enhanced biooxidation to accelerate leaching of REEs from the coarse refuse. The removal of the sulfide minerals cleans the coal, accelerates subsequent REE extraction,

and eliminates the potential for most acid rock drainage. The processing method also utilizes biooxidation to increase ferric ion production to enhance leaching, while also consuming the sulfide mineral and its associated environmental liability. The solution-conditioning processing method removes iron and controls the pH of the leaching solution to mitigate undesirable extraction of thorium, which often occurs below pH 1.5; the heap leaching portion will be modeled and designed to maximize extraction of REEs while minimizing thorium extraction. The solvent extraction portion of the project involves optimizing extraction and stripping for REE recovery in solution that will be precipitated as a final product in the last stage of precipitation processing. This project will provide the technology and data needed to facilitate large-scale implementation that can provide a domestic REE supply that is low in thorium, create revenue and jobs for the coal industry, and mitigate future acid rock drainage issues.



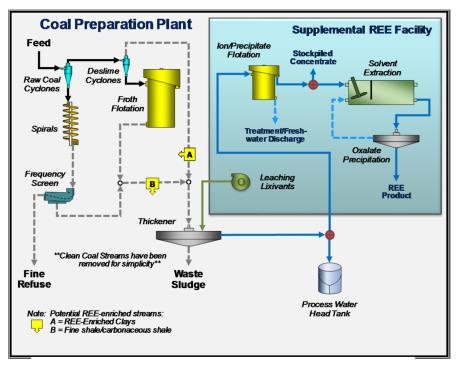
Flow sheet diagram for low-cost extraction, concentration, and recovery of REE product.

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

Technology Partner: Virginia Polytechnic Institute and State University Award Number: FE0031523 Project Duration: 11/16/2017 – 5/15/2019 Total Project Value: \$500,000 Key Technology Area: Separation Technologies

The project will investigate ion-exchange leaching and concentration technologies that can extract and enrich the rare earth elements (REEs) derived from coal resources, specifically clay and shale. Work conducted under this project will include field sample collection, thermodynamic assessments, routine laboratory testing, and engineering analyses. Initial efforts will focus on identifying, collecting, and characterizing at least three distinct feedstock samples that approach or exceed 300 parts per million total REE on a whole sample basis. Next, experimental efforts will focus on two distinct process operations, including (1) ionexchange leaching and (2) ion/precipitate flotation. A limited number of solvent extraction tests will be performed for comparative purposes only. These experimental efforts will be supported by ongoing

thermodynamic assessments, which will provide a fundamental basis for selection and dosing requirements of lixiviant (liquid used for leaching a metal from its ore or mineral). During the final tasks, the results from the experimental program will be used to generate а preliminary system design, and cost/revenue modeling will be used to perform a rigorous techno-economic assessment. The result of project is intended to be a low-cost, this environmentally benign process that can be readily implemented at many of the domestic coal production facilities throughout the coal fields. Successful development of the technology may provide a pathway to commercial extraction of the ion-adsorbed REE reserve in U.S. coal.



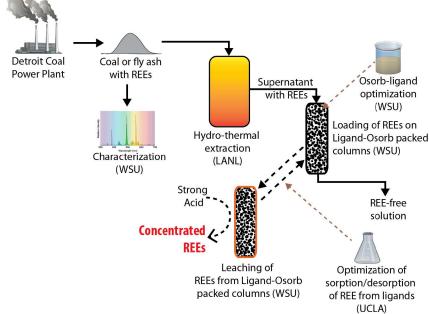
Process flowsheet integrated with existing process circuitry.

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

Technology Partner: Wayne State University (WSU) Award Number: FE0031565 Project Duration: 3/15/2018 – 9/14/2019 Total Project Value: \$518,849 Key Technology Area: Separation Technologies

This project will investigate the use of hydrothermal leaching under alkaline conditions to rapidly dissolve rare earth elements (REEs) from coal ash solids to an aqueous solution; transfer REEs from the solution to an Osorb platform (commercially available swellable organically modified silica) functionalized with the appropriate ligand system; and extract the REEs to an aqueous system that will acidic have high concentrations of the targeted REEs (2-10 percent by weight). The project will examine the potential to couple hydrothermal leaching of coal fly ash with a custom-engineered, ligand-associated medium to provide an organic solvent-free method of extracting and recovering REEs. The fly ash feedstock will be collected from Detroit-area coal-fired power plants, characterized for composition, and subjected to a bench-top batch hydrothermal leaching/dissolution process inside custom-built pressure reactors. Ligands

known to be effective in lanthanide/actinide separation will be evaluated based on a series of criteria, such as selectivity and association to Osorb through hydrophobicity. Batch experiments will then be conducted to establish the best conditions (e.g., pH, eluent, etc.) and best ligand systems for effectively extracting REEs from the alkaline feed solution obtained from the hydrothermal leaching process. Once the Osorb-ligand extraction system is optimized for REE concentration, an aqueous solution adjusted to the appropriate pH will be used to back-extract and concentrate the REEs into a heavily REE-laden solution. This project will result in a solvent-free extraction process that is more environmentally benign than many liquid-liquid extractions that typically incorporate organic solvents. The successful completion of this project will allow for easy expansion to the bench scale and future pilot scale.



REE extraction process flow chart.

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

Technology Partner: West Virginia University Research Corporation Award Number: FE0031524 Project Duration: 11/16/2017 – 5/15/2019 Total Project Value: \$864,258 Key Technology Area: Separation Technologies Project Partners: Virginia Polytechnic Institute and State University

The project objective is to develop a process to extract an enriched, mixed rare earth element (REE) product from acid mine drainage (AMD) at the site of production, upstream of conventional AMD treatment. Two AMD cases— net acid and net alkaline (Cases A and B, respectively)—will be explored. The products will be processed through an acid leaching/solvent extraction (ALSX) plant to compare performance with ongoing ALSX trials using conventional AMD sludge feedstock. The project team will evaluate the benefits of separating REEs from the AMD stream under reducing conditions such that iron and manganese will remain in their reduced (Fe²⁺, Mn²⁺) states. As reduced species, they will bypass the REE extraction process, improving overall process economics. In Case A, the pH is raised to just pH 4, which will precipitate REEs but not Al, Fe²⁺, or

Mn²⁺, metals that would otherwise need to be separated to achieve high REE purities. In Case B, the team will explore the application of an electrochemically stimulated supported liquid membrane strategy to separate REEs from ferrous ion. The project will demonstrate that significant improvements in REE extraction efficiency can be obtained through separation of REEs from aqueous phase AMD, upstream of conventional AMD treatment, by (1) creating an enriched REE feedstock, (2) producing а more consistent feedstock, (3) reducing transportation costs to an REE refinery, (4) reducing acid consumption in the acid leaching step, and (5) reducing the volume of waste produced at the ALSX plant.



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.

Rare Earth Elements – Field Resource Location and Characterization

University of Kentucky - Rare Earth Element Identification and Characterization of Coal and Coal By-Products Containing High Rare Earth Element Concentrations

Technology Partner: University of Kentucky Award Number: FE0026443 Project Duration: 10/1/2016 – 4/30/2018 Total Project Value: \$400,000 Key Technology Area: Enabling Technologies

NETL is partnering with the University of Kentucky to identify, locate, field sample, and chemically analyze U.S. domestic coal and coal by-product solid and/or liquid materials that contain high rare earth element (REE) concentrations (i.e., greater than or equal to 300

parts per million total REEs). This project supports NETL's REE Program by identifying U.S. coal-based resources for developing technologies to separate and recover rare earth elements for use in producing commercial products and national defense equipment.

University of North Dakota - Sampling, Characterization and Round Robin Analyses of Domestic U.S. Coal Based Resources Containing High Rare Earth Element (REE) Concentrations

Technology Partner: University of North Dakota Award Number: FE0029007 Project Duration: 10/1/2017 – 4/30/2019 Total Project Value: \$ 1,499,580 Key Technology Area: Enabling Technologies Project Partners: University of Kentucky

NETL is partnering with the University of North Dakota to collect and analyze samples of primarily lignite based coal; and also, some bituminous coals from Northern, Central, and Southern Appalachia regions, and coalrelated materials (run-of-mine coal; roof rock; overburden clay; shale interlay formations; mine seam underlays; coal preparation refuse; ash from coal combustion, gasification, and liquefaction) that have a minimum concentration of rare earth elements (REE) of 300 parts per million as the material is removed from the ground, with no processing other than drying. This sample analysis for REEs will be done by inductively coupled plasma mass spectroscopy. A round robin analysis study will also be performed to quantify the within-lab and inter-lab variation of the most commonly used methods for analyzing REE content in ores and coal bearing materials. The project will provide a more quantitative indication of the location of coal and coal-related materials that have high REE content for economic recovery.

Tetra Tech, Inc. - Rare Earth Element Identification and Characterization of Coal and Coal By-Products Containing High Rare Earth Element Concentrations

Technology Partner: Tetra Tech, Inc. Award Number: FE0026648 Project Duration: 10/1/2016 – 4/30/2018 Total Project Value: \$373,300 Key Technology Area: Enabling Technologies

NETL is partnering with Tetra Tech, Inc. to identify, locate, field sample, and chemically analyze U.S. domestic coal and coal by-product solid and/or liquid materials that contain high rare earth element (REE) concentrations (i.e., greater than or equal to 300 parts

per million total REEs). This project supports NETL's REE Program by identifying U.S. coal-based resources for developing technologies to separate and recover rare earth elements for use in producing commercial products and national defense equipment.

Tetra Tech, Inc. - Rare Earth Element Identification and Characterization of Coal and Coal By-Products Containing High Rare Earth Element Concentrations

Technology Partner: Tetra Tech, Inc. Award Number: FE0026929 Project Duration: 10/1/2016 – 4/30/2018 Total Project Value: \$376,200 Key Technology Area: Enabling Technologies Project Partners: Nexus Geo LLC and PrepTech

NETL is partnering with Tetra Tech, Inc. to identify, locate, field sample, and chemically analyze U.S. domestic coal and coal by-product solid and/or liquid materials that contain high rare earth element (REE) concentrations (i.e., greater than or equal to 300 parts

per million total REEs). This project supports NETL's REE Program by identifying U.S. coal-based resources for developing technologies to separate and recover rare earth elements for use in producing commercial products and national defense equipment.

West Virginia University - Rare Earth Element Identification and Characterization of Coal and Coal By-Products Containing High Rare Earth Element Concentrations

Technology Partner: West Virginia University Award Number: FE0026444 Project Duration: 10/1/2016 – 4/30/2018 Total Project Value: \$400,000 Key Technology Area: Enabling Technologies

NETL is partnering with West Virginia University to identify, locate, field sample, and chemically analyze U.S. domestic coal and coal by-product solid and/or liquid materials that contain high rare earth element (REE) concentrations (i.e., greater than or equal to 300

parts per million total REEs). This project supports NETL's REE Program by identifying U.S. coal-based resources for developing technologies to separate and recover rare earth elements for use in producing commercial products and national defense equipment.

XLight Corporation - Rare Earth Element Identification and Characterization of Coal and Coal By-Products Containing High Rare Earth Element Concentrations

Technology Partner: XLight Corporation Award Number: FE0026527 Project Duration: 10/1/2016 – 4/30/2018 Total Project Value: \$214,795 Key Technology Area: Enabling Technologies

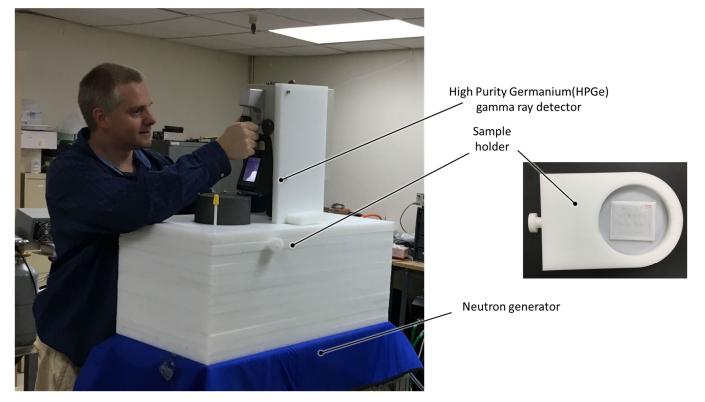
NETL is partnering with West Virginia University to identify, locate, field sample, and chemically analyze U.S. domestic coal and coal by-product solid and/or liquid materials that contain high rare earth element (REE) concentrations (i.e., greater than or equal to 300

parts per million total REEs). This project supports NETL's REE Program by identifying U.S. coal-based resources for developing technologies to separate and recover rare earth elements for use in producing commercial products and national defense equipment.

Rare Earth Elements – Field Sensor Development Nondestructive, Bulk Rare Earth Element Measurement System for Coal

Technology Partner: Adelphi Technology, Inc. Award Number: SC0017943 Project Duration: 6/12/2017 – 3/11/2018 Total Project Value: \$215,851 Key Technology Area: Enabling Technologies

Adelphi Technology will develop a field deployable commercial prototype instrument capable of nondestructively determining the elemental composition of nearly any sample using neutron activation analysis (NAA). Detection and concentration measurement of rare earth elements (REEs) in a sample allows REE reclaim processes to be used cost-effectively by only processing coal containing a sufficiently high concentration of REEs. NAA of an approximately petridish-sized sample using a neutron generator and a highpurity germanium detector will be performed on test samples that are representative of real-world samples, but contain known quantities of REEs. The detection limits for each REE will be determined as a function of neutron flux and sample measurement time for both prompt and delayed NAA under fast and thermal neutron irradiation. Finally, the measurement protocol will be optimized. This project will provide experimental evidence of achievable REE detection limits in a practical real-world system using samples from a mine or burnt-coal processing facility. This research will produce a portable neutron generator capable of accurately measuring the concentration of nearly all elements in a sample, enabling cost-effective REE extraction.



Phase I prototype system (not miniaturized).

Sensor for Direct, Rapid and Complete Elemental Analysis of Coal

Technology Partner: Applied Spectra, Inc. Award Number: SC0017785 Project Duration: 6/12/2017 – 3/11/2018 Total Project Value: \$224,871 Key Technology Area: Enabling Technologies

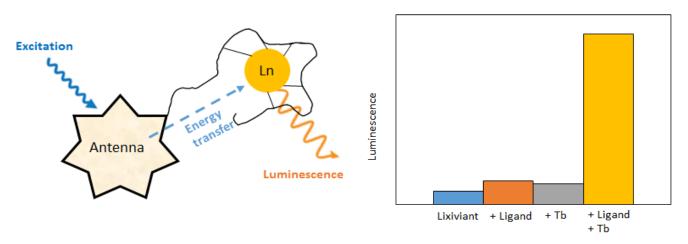
This project will develop and demonstrate laser induced breakdown spectroscopy (LIBS) as an analytical technology for the rapid, direct analysis of rare earth elements (REEs) and concomitants at concentration levels from parts per billion to percent at several stages of the coal value chain (coal, precleaned coal, ash, and non-ash). The configuration of an existing LIBS instrument will be improved for enhanced sensitivity and chemometric data analytics will be implemented for calibration. Simultaneous inductively coupled plasma mass spectrometry will be used to validate LIBS data using National Institute of Standards and Technology reference materials. Finally, a field prototype instrument for automatic REE measurement in the coal value chain will be designed. The developed technology will enable decisions for extracting REE, enhancing the coal value chain. The LIBS system is intended to replace the laborious, slow, and expensive acid digestion processes currently used to analyze coal and its by-products. The expanse (number of elements) and speed of the LIBS vastly exceed those of other available technologies. LIBS also does not require consumables and can be used in the field as an inline or transportable sensor. This instrument will be viable in other markets, including overall mining, environmental remediation, nuclear nonproliferation, forensics, advanced manufacturing, conflict minerals, and other industrial processing applications.

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

Technology Partner: Idaho National Laboratory Award Number: FWP-INL-B000-17-015 Project Duration: 8/31/2017 – 9/30/2020 Total Project Value: \$1,000,000 Key Technology Area: Enabling Technologies

Project Partners: Lawrence Livermore National Laboratory; Rutgers–The State University of New Jersey; and University of California, Davis

The objective of Idaho National Laboratory (INL) in this project is to evaluate novel complexation chemistries for the development of innovative sensing technologies for rare earth elements (REEs). Complexation of lanthanides by peptides, coupled with the unique spectroscopic properties of lanthanides, is the underpinning for luminescent applications of lanthanide binding tags (LBTs), originally invented as biochemical tools for the study of proteins. A peptide sequence specifically designed to bind lanthanides includes amino acids which have chromophore sidechains (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 enrichments may vary by provenance, 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. Specifically, INL will evaluate whether the chemistry of LBTs 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 myriad 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.



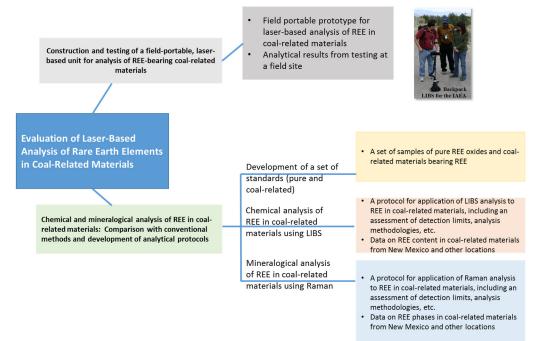
Luminescence is enhanced when a lanthanide binds to a ligand that has an attached antenna chromophore.

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

Technology Partner: Los Alamos National Laboratory Award Number: FWP-FE-781-16-FY17 Project Duration: 10/25/2017 – 10/24/2018 Total Project Value: \$1,000,000 Key Technology Area: Enabling Technologies

The primary objectives of this effort are (1) to develop and test analytical protocols for analyzing the concentration and mineralogy of rare earth elements in coal-related materials using laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy; (2) to develop a field-portable system for LIBS and Raman analysis of rare earth elements (REE) in coal-related material; and (3) to analyze the concentration and mineralogy of REE in a variety of coal-related materials principally from New Mexico coal deposits. The project is divided into two tasks. In task 1 the team will 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; revise analytical protocols as applicable. Researchers will take advantage of the extensive experience of Los Alamos National Laboratory (LANL) in developing LIBS for quantitative analysis of various elements in various matrices, and will use this expertise

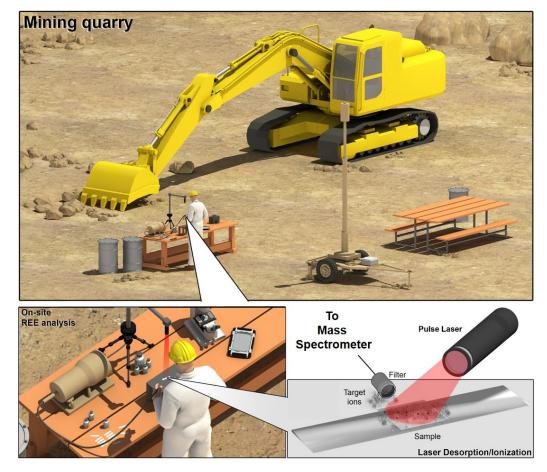
to develop protocols for analysis of REEs in coal-related materials. LANL has made recent institutional investments (through laboratory directed research and development) to develop a combined LIBS plus Raman system that can determine both chemistry (LIBS) and physical form (Raman); researchers will use this new system to explore simultaneous chemical and mineralogical analysis of REE in coal-related materials. In task 2 the team will develop analytical methods specific to the quantification of REE in various coalrelated materials, 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 REEs in specific matrices, because plasma generation efficiency can be impacted both by physical form and overall chemistry.



Rare Earth Element Mass Analyzer

Technology Partner: Physical Optics Corporation Award Number: SC0017737 Project Duration: 6/12/2017 – 3/11/2018 Total Project Value: \$225,000 Key Technology Area: Enabling Technologies

This project will develop a compact, universal rare earth element (REE) analysis system. The system will be based on a compact mass spectrometry system developed for atmospheric gas analysis combined with an advanced sample ionization technique that can be used for coal and/or coal by-products in both solid and aqueous forms. A breadboard prototype for REE analysis will be constructed and tested on samples containing REEs. Desorption and ionization techniques will be optimized for coal and/or coal by-products. Samples containing different rare earth species with various concentration levels will be used to demonstrate the feasibility of the system. The design concept for a portable prototype will also be proposed. This technology could allow rapid, on-site characterization to determine any content of rare earth and other elements in a sample. Rare earth elements are crucial in the manufacturing of modern high-technology products, such as cell phones, hybrid automobile engines, high-power lasers, and other high-demand devices. Other than its apparent application in the mining industry, analytic chemistry is extremely important in environmental monitoring and protection, forensic science, chemical warfare, pharmaceutical research and development, as well as in clinical applications. A portable instrument providing real-time analysis of target samples will have a broad impact in many industries requiring field-deployable sensors that provide test results quickly and reliably.

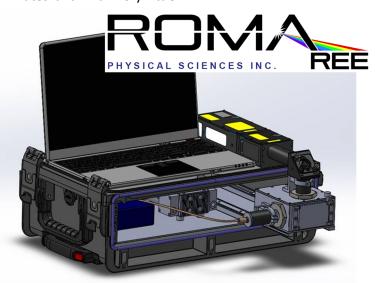


Spectrochemical Detection and Monitoring of Rare Earth Elements During Extraction from Coal/Coal Byproducts

Technology Partner: Physical Sciences, Inc. Award Number: SC0017762 Project Duration: 6/12/2017 – 5/11/2018 Total Project Value: \$224,843 Key Technology Area: Enabling Technologies Project Partners: Calabazas Creek Research, Inc.

The aim of the proposed research is to develop a laserinduced breakdown spectroscopy (LIBS) instrument that pushes the bounds of performance of current portable hardware and LIBS methodologies in order to monitor rare earth element (REE) recovery processes from very high concentration product to very low concentration feedstock. LIBS is a technique that lends itself well to the detection of atomic composition to parts per million levels. The method is applicable to nearly any material make-up or phase, and conducive to the generation of low cost small, portable, and continuous process monitoring systems. Specifically, LIBS is capable of monitoring all of the most important REEs (i.e., yttrium, scandium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, and ytterbium) as well as important matrix elements (e.g., aluminum, calcium, iron, silicon, platinum, titanium, and vanadium). The system will be able to rapidly measure REE content of solid and solution samples within minutes and with very little

sample preparation. This project will optimize an enhanced LIBS methodology via the design, construction, and exercise of a laboratory prototype instrument and quantify the ability of the technique to monitor different REEs, at different points in the REE enrichment process, in different sample morphologies/phases, and for benchtop hardware versus the portable spectroscopic hardware envisioned for an affordable at-line diagnostic instrument. This sensor technology could enable optimized physical and chemical processes with higher efficiencies, increased REE yields, and higher REE concentration final products. Additional applications include: crude oil source fingerprinting by metals analysis, coal/ash content monitoring in slag and combustion particulates, recycling of electronic, magnetic, and nuclear waste, residual metals monitoring in catalytic processes, and process monitoring in the steel, glass, mining, magnet, lighting element and catalytic converter industries.



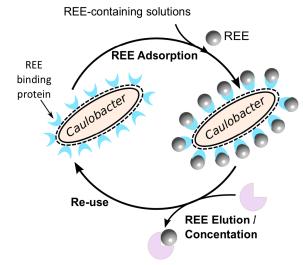
LIBS-based system for rapid measurement of REEs.

Rare Earth Elements – Technology Commercialization Rare Earth Metal Extraction for Clean Technologies

Technology Partner: Lawrence Livermore National Laboratory Award Number: TCF-17-13365 Project Duration: 10/1/2017 – 9/30/2018 Total Project Value: \$300,000 Key Technology Area: Process Systems Project Partners: Duke University

This project will focus on the scale- up and demonstration of an innovative biotechnology that relies on bacterial native systems and enhanced bioengineered features to sequester rare earth elements (REE) from low-grade sources, along with an assessment of its economic viability with feedstock from coal products. Specifically, researchers will (1) demonstrate a cell embedding system that enables an REE extraction process with fast kinetics and high extraction efficiency at the scale needed by industry; and (2) compare REE extraction performance with different feedstocks to better tailor the technology to preferred substrates for improved performance. The team will conduct a techno-economic analysis to evaluate the technology's economic viability. A critical step in scaling up the technology will be developing a continuous flow system using embedded cells, which will allow for complete separation of REE ions from the aqueous solution in a single step. Researchers will test and compare two commonly adopted cell immobilization platforms: cell embedding and cell include attachment. This comparison will REE

adsorption density/ capacity, adsorption/desorption kinetics, and the level of background contamination by the adsorption media. The knowledge gained will help to identify and improve critical factors for REE adsorption and better inform the parameters necessary for future pilot-scale operations. In addition, identifying a preferred feedstock for the technology will help tailor the technology's performance and conduct a more competitive techno-economic analysis. At project end, the team will be able to draw preliminary economic conclusions based on both lab-scale engineering data and relevant market information. The technology is expected to benefit from a competitive cost structure that is at least an order of magnitude less expensive than traditional extraction technologies, while offering a secure source of U.S.-based REE materials. Successful implementation of this technology has the potential to revolutionize waste-toproduct conversions for low-grade REE feedstocks. It will also minimize chemical waste generation by U.S.based mineral extraction companies and mining operations.



Abbreviations

ALSX	acid leaching/solvent extraction
AMD	acid mine drainage
AML	abandoned mine land
Са	calcium
CIX/CIC continuous ior	exchange/continuous ion chromatography
CO ₂	carbon dioxide
DOE	Department of Energy
Fe	iron
FeOH ₂	iron (II) hydroxide
FeOH₃	ferric hydroxide; iron (III) hydroxide
FWP	Field Work Proposal
g	grams
НСІ	hydrochloric acid
HPGehi	gh purity germanium (gamma ray detector)
INL	Idaho National Laboratory
LANL	Los Alamos National Laboratory
LBT	lanthanide binding tag
LIBS	laser induced breakdown spectroscopy
Mg	magnesium
Mn	manganese
NAA	neutron activation analysis
NaOH	sodium hydroxide
NETL	National Energy Technology Laboratory
рН	. potential of hydrogen (measure of acidity)
PLSpregna	nt leaching solution; product laden solution
ppm	parts per million
PSI	Physical Sciences, Inc.
RD&D	.research, development and demonstration
REE	rare earth element
REM	rare earth mineral

REO	rare earth oxide
RES	Rare Earth Salts (company)
REYSc	REE-rich concentrates including yttrium and scandium
sFGD	stabilized flue gas desulfurization material
Si	silicon
SO ₄	sulfate (ion)
Ss	sludge solids
tpd	tons per day
TREE	total rare earth elements
UCLA	University of California, Los Angeles
U.S	United States of America
UK	University of Kentucky
UND	University of North Dakota
WSU	Wayne State University

Contacts

Mary Anne Alvin National Energy Technology Laboratory Technology Manager Rare Earth Elements 412.386.5498 maryanne.alvin@netl.doe.gov

John Wimer National Energy Technology Laboratory Associate Director, Strategic Planning Science & Technology Strategic Plans & Programs 304.285.4124 john.wimer@netl.doe.gov

Regis Conrad Office of Fossil Energy Division Director Advanced Energy Systems 301.903.2827 regis.conrad@hq.doe.gov

Website: http://netl.doe.gov/research/coal/rare-earth-elements

and

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

Acknowledgments

The Rare Earth Elements (REE) Portfolio was developed with the support of many individuals including principal investigators, federal project managers, REE technology manager, supervisors, and National Energy Technology Laboratory site-support contractors.

National Energy Technology Laboratory



www.netl.doe.gov



1450 Queen Avenue SW Albany, OR 97321-2198 541-967-5892

420 L St, Suite 305 Anchorage, AK 99501 907-271-3618

3610 Collins Ferry Rd P.O. Box 880 Morgantown, WV 26507-0880 304-285-4764

626 Cochrans Mill Rd P.O. Box 10940 Pittsburgh, PA 15236-0940 412-386-4687

13131 Dairy Ashford Rd, Suite 225 Sugar Land, TX 77478 281-494-2516

PROGRAM WEBSITE: www.http://netl.doe.gov/research/coal/rare-earth-elements

CUSTOMER SERVICE: 1-800-553-7681

