From NETL's Office of Research & Development

Research news

November/December 2015, Issue 14

FEATURE STORY:

Rare Earth Element "Tracers" Can Help Protect the Environment

page 3

the ENERGY lab
NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

Research news
Nov./Dec. 2015, Issue 14

Contents

Newsletter Will End Production

The year 2016 will bring a transformation to NETL's organization, which will better integrate the organization's in-house and extramural research. To reflect this change, *Research News* is ending production with this issue to give way to new publications covering all of NETL's research portfolio. We are excitedly anticipating these new publications! In looking back on the articles featured in Research News, we realize again the breadth and impact of NETL research on important energy-related issues. We will bring about a better future! Here are examples of how NETL is making a difference.

- Future production of massive hydrate resources requires understanding the behavior of these ice-locked natural gas compounds; and solving air and water impacts of large-scale natural production.
- Future energy technologies include chemical looping combustion, which uses metal oxide particles to carry oxygen to the combustor, but requires separation of ash from the particles, and high-performing solid oxide fuel cells. Both will produce more energy with less fuel and make it easier to capture the CO_2 resulting from energy production.
- Tomorrow's power plants will also depend on metal alloys that withstand higher temperatures and pressures and operate in harsher environments.
- Capturing CO_2 from power plants may be done with membranes fabricated using novel techniques. And CO_2 can be converted to useful products with catalysts. With models to explain how CO_2 interacts with other fluids, and tools to quantify the risks of injecting and maintaining CO_2 in geological formations, it can also be permanently stored deep beneath the earth's surface.
- Our skills are also valuable to other problems of national interest; multi-phase flow modeling assists with cleanup of historic nuclear sites.
- Hints to solving any problem lie in existing data as well as new, and tools like the Energy Data eXchange preserve vast amounts of widely-dispersed energy-related data, making them available to researchers now and into the future.

NETL research has made great strides in these and many other areas. We hope you have enjoyed reading *Research News*. Stay linked to the NETL website to be informed of our latest research and accomplishments.

The Editors.

Cover image

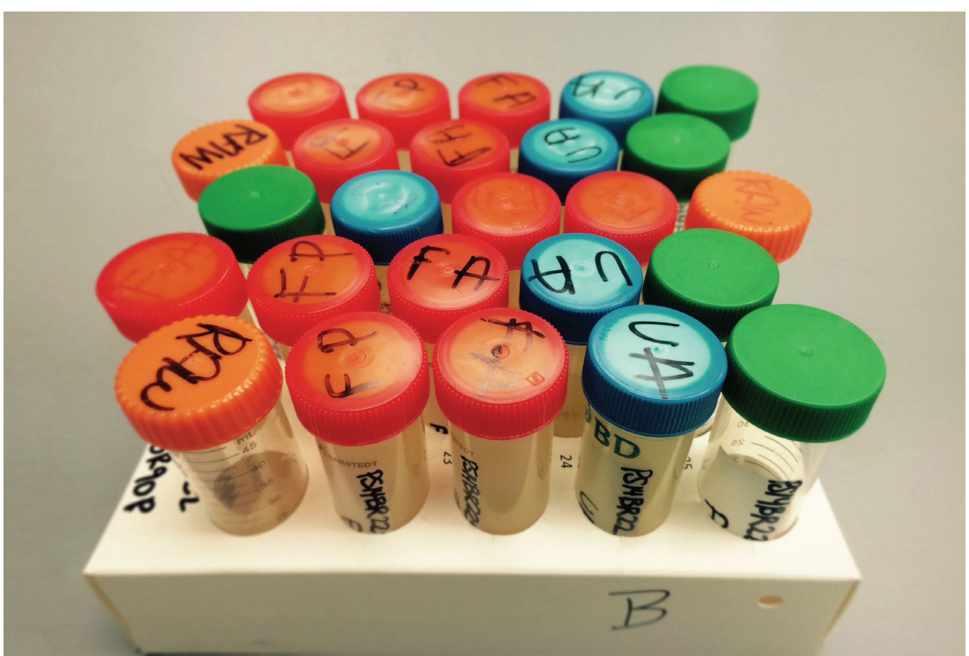
Artist's rendering of shale hydraulic fracturing operations.

RARE EARTH ELEMENT "TRACERS" CAN HELP PROTECT THE ENVIRONMENT

Oxides of rare-earth elements. Clockwise from top center: praseodymium, cerium, lanthanum, neodymium, samarium, and gadolinium.

Rare earth elements (REEs), a set of 17 chemical elements found in the Earth's crust, have become common ingredients in everything from cell phone batteries to color televisions. However, NETL experts believe REEs might also be able to help prevent environmental damage by providing warnings when natural gas and oil development efforts could cause well water contamination and methane seepage.

The U.S. Department of Energy (DOE) calls REEs "technology metals" because of their unique magnetic, phosphorescent, and catalytic properties that allow them to play a critical role in a myriad of essential world-wide products. For example, they can be used in renewable energy technologies like electric vehicle batteries, wind turbines, lighting, and films for solar cells. These REEs are also found in geologic formations like the Marcellus Shale. As a result, their migrations when horizontal drilling and hydraulic fracturing occur could make them valuable indicators, or "tracers," of when action is necessary to keep potentially harmful chemicals from seeping into water supplies or being dispersed through the disposal of fracturing wastewater.



Samples of "produced waters" from hydraulic fracturing.

According to **Alexandra Hakala**, a geochemist who leads NETL's Analytical Biogeochemistry team, the laboratory's research has characterized REEs in Marcellus Shale outcrops and core samples. She described the work as a "solid first step" toward determining whether the REEs can be effective geochemical tracers. If so, they could be useful in detecting potential underground fluid migration associated with shale gas operations, as well as indicating the presence of contaminants in the waters that return to the surface after hydraulic fracturing (known as produced waters). The work supports DOE's strategic goals of advancing energy security and environmental quality.

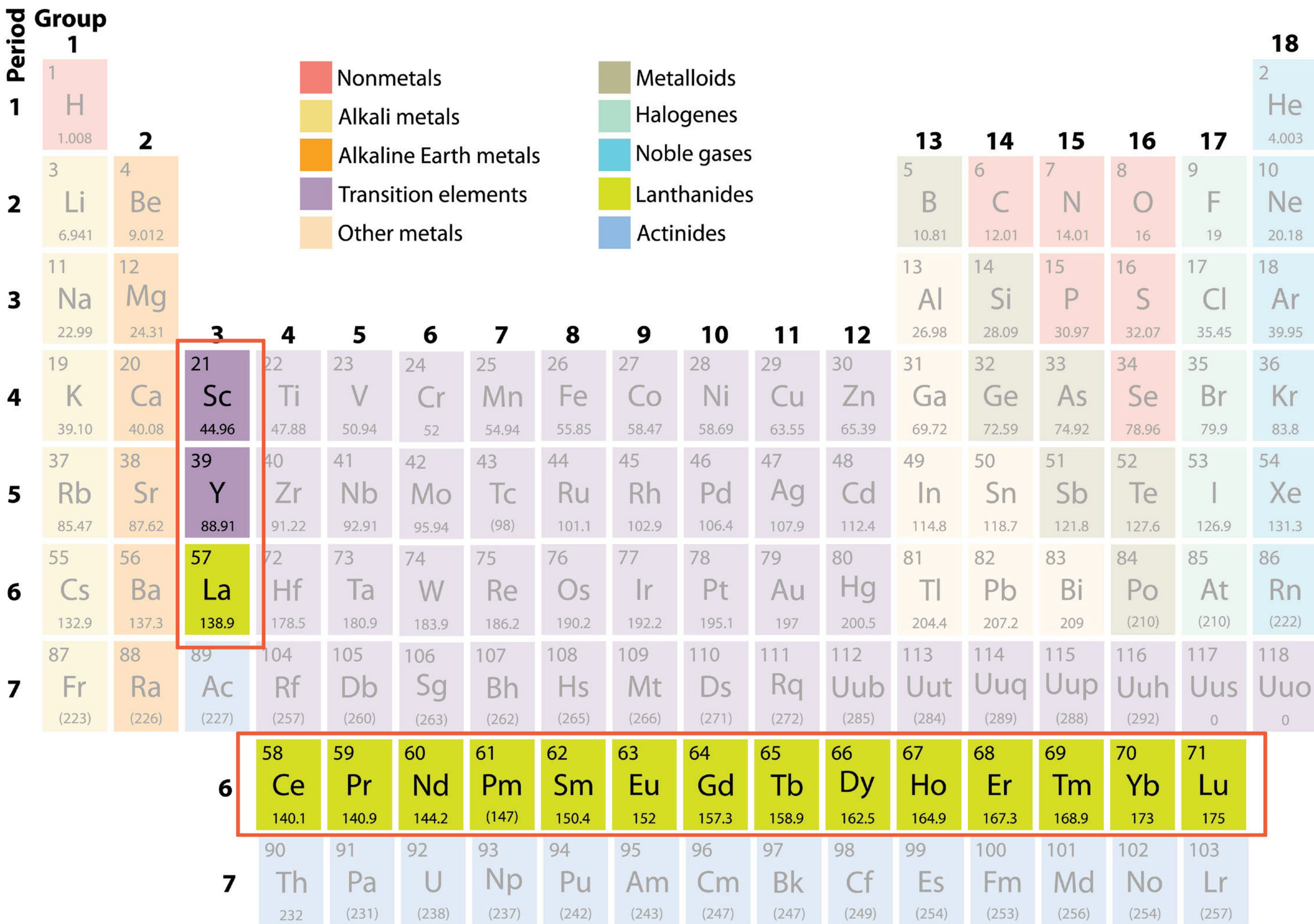
Hakala said more research is needed to confirm the tracer theories related to REEs, including the role of water-rock-cement reactions, which are being investigated by NETL researcher **Circe Verba** and colleagues at Oregon State University.

She explained that understanding trace metal geochemistry in shales is important because of the expanding global development of unconventional oil and gas reserves through horizontal drilling and hydraulic fracturing.

"Characterizing and managing the risk of fresh water contamination by solid and liquid wastes associated with these developments begins with a good understanding of the geochemistry of compounds in host shales like Marcellus," she said. "Stimulation of shales during fracturing will modify pathways of water-rock reactions that release natural tracers. That's why these analyses can serve as a starting point for further investigation into understanding how the reservoir changes during hydraulic fracturing, and ways to monitor solid waste disposal."

NETL and research partners from Carnegie Mellon University documented the research in a research paper titled "Rare Earth Element Geochemistry of Outcrop and Core Samples from the Marcellus Shale." Published in June of 2015, the article has already been accessed more than 2800 times.

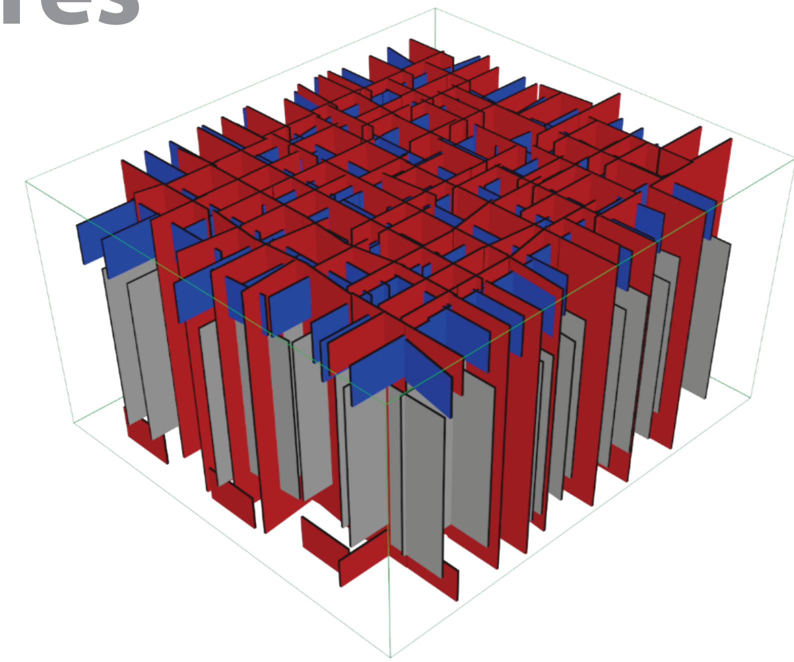
Contact: Alexandra Hakala



Rare earth elements in the periodic table. See "Fundamental Facts" on page 9 for more information on REEs.

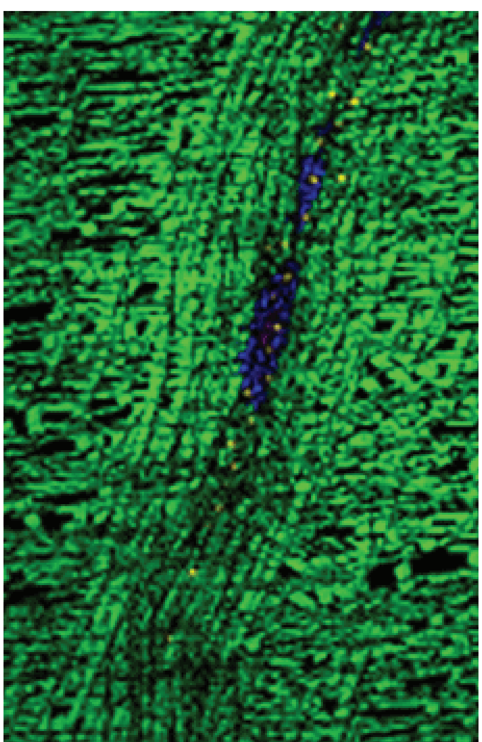
Tools to Imagine Fluid Flow in Rock Fractures

Traditional reservoir simulators are designed to represent flow through highly permeable, intact rock, such as sandstone, where fractures offer minimal additional permeability. NETL researchers recognized the need for a flow simulator for reservoirs where most of the flow occurs through fractures rather than through intact rock. Working in collaboration with researchers from West Virginia University, they developed and tested several software tools that generate fracture network models and simulate gas flow in naturally-fractured reservoirs.



FracGen generates realistic fracture patterns in the matrix rock. The software tool displays different colors to represent fractures of varying widths.

Known as FracGen/NFflow, the software components work together to create predictions that model how compressed reservoir gases flow through discrete irregular fracture networks with thousands of individual fractures in the rock matrix. The software can simulate reservoirs that are multi-layered and have variable thickness, rock porosity, and rock permeability. FracGen and NFflow represent a significant advancement in reservoir simulation by being the first models that readily simulate gas flow and drainage in fractured reservoirs with tens of thousands of fractures. The software directly uses reservoir characteristics such as fracture length, orientation, and size obtained from well logs, outcrop analyses, and other geological data, rather than using simple averaging. NETL has found that its fractured reservoir simulator software is better able to represent realistic reservoir-scale characteristics from the natural fracture network when compared to conventional reservoir simulators.



Information obtained from FracGen is used by NFflow to simulate gas flow and drainage in fractured reservoirs.

Current research projects will further advance the existing suite of reservoir simulation codes and adapt them to sub-surface fracture networks that impact how we recover and use energy resources. An example problem is natural gas production from shale.

The natural gas found in shale formations has become an important part of the United States' energy future due to its abundance and economical availability. Shale, a low permeability rock, normally functions as a trap that locks in gas and oil. Economic production of these fossil fuels requires a process known as hydrofracturing (or fracking). High-pressure fluids are injected to forcefully create fractures in the reservoir rock, so that gas and oil are able to flow from the rock into the well. Understanding the tight natural fractures in rock formations that normally serve as seals and how these fractures change under varying stresses is important to making accurate risk assessments about the impacts of fracking.

FracGen and NFflow are designed to work efficiently on standard desktop computers. The intended users for these programs include small independent resource producers, and academic and governmental researchers. A download of the software is available at Naturally Fractured Natural Gas Reservoir Simulator: FracGen & NFflow. NETL has made the software publicly available to expand the network of active users to assist in identifying and fixing bugs in the current version as well as guiding the most useful development into the future.

Contact: Edward Boyle

Oxygen Carrier's Full Potential **Revealed to Be More than Skin Deep**

In chemical looping combustion (CLC), an oxygen-rich solid (oxygen carrier) provides the oxygen for combustion rather than air (read more about CLC in the January 2015 issue). Now, NETL research is providing a clearer picture of this essential part of the process through mathematical modeling. The oxygen carrier begins the CLC process by giving up its oxygen to combust the fuel (the reduction process); then the spent carrier travels to the air chamber where it is again enriched with oxygen through re-oxidation. The selection of oxygen carrier can greatly affect the ultimate success of a CLC reactor design, as the candidate must be capable of being efficiently reduced and re-oxidized while still being cheaply procured.

"With oxygen carriers, you have two ideals," explained **Ronald Breault**, a research engineer who leads NETL's Reactor and Process Development team. "You can have a material that may be expensive but can be recycled indefinitely, or you can use a less resilient material that is inexpensive enough to continually replace. Realistically, the material will fall somewhere in between."

Breault focused his research on hematite because it is an inexpensive, abundant material that shows great promise as an oxygen carrier. Recent results revealed that the reduction and re-oxidation stages occur differently than previously thought. The model Breault developed showed that the initial release of oxygen was actually the first of two stages in a multi-step reaction. In the first stage, oxygen is quickly consumed in the thin outer shell of the grain of hematite. Oxygen remained in the core of the grain and made its way to the surface during the second stage by a process called oxygen vacancy diffusion, in which a molecule of oxygen travels through space left vacant from a previous oxygen molecule moving up towards the surface.

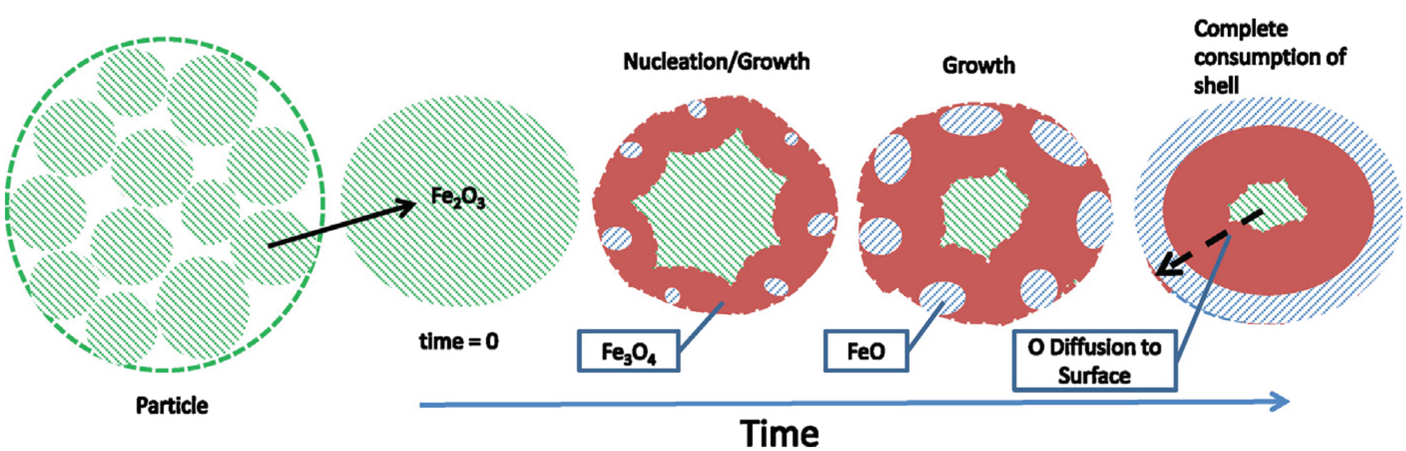
Sample of Hematite. Photo courtesy of Rafael Vila.

In the past, because researchers were not aware of this secondary process, the hematite was being sent back for re-oxidizing well before all of its oxygen had been consumed. This same oxygen vacancy diffusion process occurs in reverse during the re-oxidation phase, so hematite particles were also being returned to the fuel chamber before they were fully oxidized. Because the hematite was not being used to its full potential, more of the oxygen carrier than expected was needed to provide sufficient oxygen to fully combust the fuel, resulting in the design of larger than necessary reactors to accommodate more hematite.

Using this new model to understand the reaction mechanisms of hematite, researchers will be able to design a CLC reactor of appropriate size that allows for the optimal reduction and re-oxidation time for the oxygen carrier. This research has explained phenomena observed by not only NETL researchers, but those studying oxygen carriers around the world as well.

The work also benefitted from DOE's Mickey Leland Energy Fellowship (MLEF) program. MLEF intern Jared Carpenter helped process the data. Results were published in three papers, including one coauthored by Carpenter.

Contact: Ronald Breault



Hematite reduction. Oxygen in the outer shell of a grain of hematite (green) is consumed relatively quickly during reduction, but oxygen diffusion continues to bring oxygen up from the core long after the surface is oxidized.

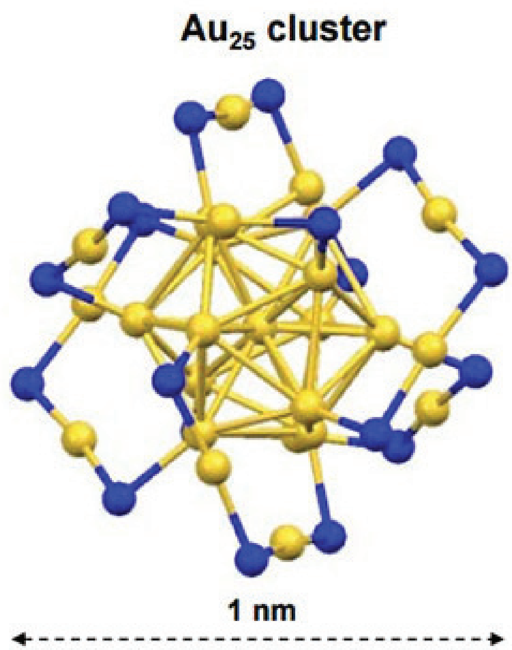
Novel Process Recycles CO_2 Using Gold Nanoparticles and Renewable Energy

A new process has been demonstrated for efficiently converting carbon dioxide (CO_2) to a feedstock for chemicals and fuels. The new findings could lead to developing large scale CO_2 conversion technologies powered by clean, renewable energy resources.

NETL researchers, in collaboration with their academic partners, developed a special form of gold nanoparticle composed of exactly 25 gold atoms to catalyze the CO_2 conversion. This "Au_{25}" catalyst proved to be highly efficient. Just as importantly, researchers were able to power a small CO_2 reactor with inexpensive renewable energy sources, such as solar panels and solar-rechargeable batteries. According to the study's lead researcher, **Douglas Kauffman**, "Demonstrating that renewable energy resources can efficiently power CO_2 conversion is a game changer that will hopefully lead to the development of large-scale systems."

Electrochemical conversion of CO_2 is a promising technology that uses electrical energy to convert CO_2 into other high value products. However, most fossil fuel-powered CO_2 conversion processes are currently "carbon positive" (net increase in CO_2 gas) and do not help mitigate CO_2 emissions. The process developed by NETL is a "carbon negative" (net reduction in CO_2 gas) energy cycle, using renewable energy sources to recycle waste CO_2 without generating new CO_2 emissions. The process has the potential to reduce atmospheric CO_2 emissions if implemented on a commercial scale.

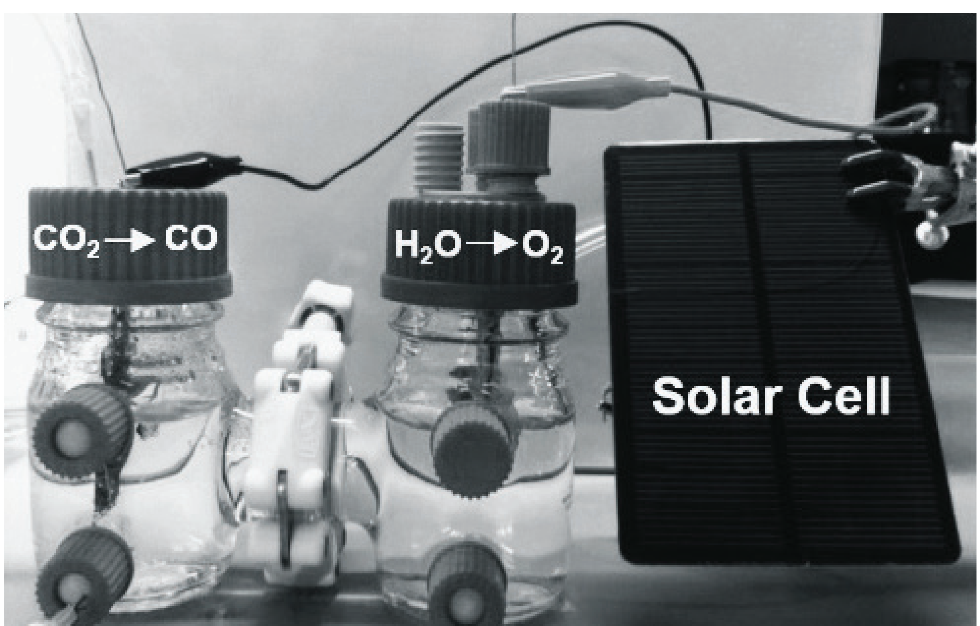
This proof-of-principle study provides some of the initial performance data necessary for assessing scalability and technical viability of electrochemical CO_2 conversion technologies and will serve as a bridge to move the carbon-negative energy cycle out of the lab and into industrially relevant applications. Based on their results, the research team estimates that state-of-the-art renewable energy sources like solar-cells and wind turbines are sufficient to convert metric tonnes of CO_2 per day. The team's future work will focus on designing next generation CO_2 conversion catalysts that produce valuable products and require even less energy.



A model of the structure of the Au_{25} nanoparticle.

This technology as well as a related invention are available for licensing or further cooperative development through NETL's Technology Transfer. You can learn more about the team's work in developing electrochemical catalysts for the conversion of CO_2 by reviewing their recently published article in ACS Applied Materials & Interfaces.

Contact: Douglas Kauffman



NETL researchers designed a study that demonstrated the conversion of CO_2 to carbon monoxide (CO) using renewable energy resources such as a solar panel and rechargeable batteries. The CO produced can serve as a feedstock for the manufacture of high-value chemicals and fuels.

CARBON CAPTURE & COLLABORATION

The Carbon Capture Simulation Initiative (CCSI) is unique. Formed by a vast web of collaborators stretching over eight states, five U.S. Department of Energy laboratories, five esteemed universities, and a number of industry partners, the organization is exceptional in structure and scope. And **David Miller**, the Technical Director of CCSI, is at the heart of this effort.

The initiative launched in 2011 with a deceptively simple sounding objective: accelerate the development and deployment of carbon capture technologies by developing computational modeling tools that will speed scale-up. Physical scale-up is an expensive, laborious, and intensely time-consuming process; most technology takes between 20 and 30 years to make the jump; carbon capture technology, however, is urgently needed as soon as possible.

“I consider the work I do with CCSI as really, really important to mitigating climate change,” Miller affirmed. “The models we’ve been working on have the potential to reduce development time significantly. A reduction of up to 25 or 30 percent is expected.”

Miller started working with the initiative shortly after he came to the National Energy Technology Laboratory in 2009. Previous to the move, he had been a professor of chemical engineering at the Rose-Hulman Institute of Technology in Indiana, his undergraduate alma mater. But after taking a sabbatical, a year away from his university, to study gasification and computer modeling, he realized it was time for a change.

“That year made me realize that I was more interested in the energy sector,” he said. “I felt like it was time to do something different, and there was this opportunity at NETL.”

Once at NETL, Miller developed the nascent form of what would eventually become CCSI, an unprecedented collaboration between academia, government, and industry with a singular goal.

Miller recalled, “The original idea, the idea that became CCSI, was that we needed to scale-up capture technologies. We needed to scale them up faster than we’ve ever scaled up energy technologies before.”

CCSI employs computer modeling, or the creation of virtual simulations of complex systems, to advance carbon capture technology development and deployment. The type of modeling done by the initiative relies on expertise from multiple scientific disciplines, from statisticians to chemical engineers to material scientists. Through a blend of physics, math, and computer science, the researchers of CCSI create computer simulations to study and predict the behavior of carbon capture technologies that can be incorporated into existing fossil-fueled power plants.

The initiative has been an unprecedented success. In October 2012, only 19 months after its 2011 launch, CCSI was already prepared to release the CCSI Toolset, its initial suite of computational tools—a full year ahead of schedule. Since then, the initiative has released three updated versions, each providing new capabilities to help industry scale up carbon capture and related technologies. But the project is winding down, with its goals expected to be accomplished in early 2016. Miller envisions a subsequent project.

“We’re putting together plans for CCSI2—Carbon Capture Simulation: Industry Impact,” he explained. “We’ve put together the toolset for industry, now we’re going to work with them to effectively implement it.”

Contact: David Miller

Rare Earth Elements

Rare earth elements (REEs) have become a staple for use in high-tech devices found everywhere from your pocket to local hospitals to high-security military complexes. These elements are used in your smart phone and computers. The military uses REEs in night-vision goggles, precision-guided weapons, alloys used in armored vehicles, and communications and GPS equipment. Medical technology uses REEs in magnetic resonance imaging (MRI) and surgical lasers. The energy industry uses them for rechargeable batteries, LEDs, and gas turbine thermal barrier coatings. Other industries use REEs as catalysts in air pollution control devices, parts of illuminated electronic screens, and many other cutting-edge technologies.

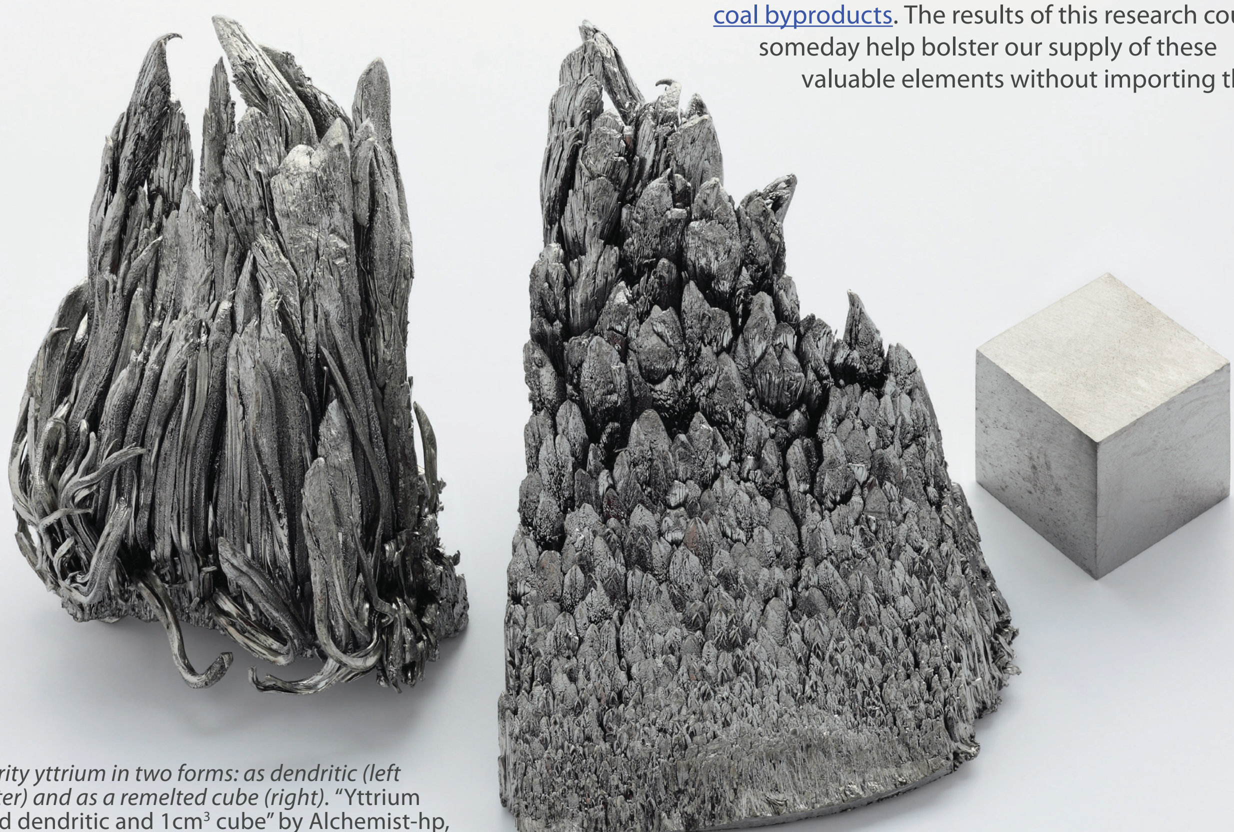
If you check out a periodic table, REEs include the 15 lanthanides plus scandium and yttrium, which tend to occur in ore deposits alongside the lanthanides. These elements are grouped together as REEs because they share chemical properties; they've become invaluable to industry and technology because of their unique magnetic, luminescent, and electrochemical properties.

Rare earth elements aren't actually rare—they are more abundant in the Earth's crust than gold—but they are difficult to separate from their ores. Deposits typically have low concentrations of these metals, frequently making their production uneconomical.

Novel methods for extracting rare earth elements from coal—like this core sample of lignite—and its byproducts could help ensure a stable domestic supply of these sought-after minerals.

In the 1990s, China became the world's largest producer of REE, selling at rates so low that they put mines in other countries out of business. But as demand for REEs in several industries rose, China restricted exports, driving prices up. Manufacturers in the United States and other nations started examining how to cut their use by substituting other materials and designing products that no longer need them. However, REEs remain critical to our economy.

NETL is currently exploring the economical, environmentally benign [separation of REEs from domestic coal and coal byproducts]. The results of this research could someday help bolster our supply of these valuable elements without importing them.



High-purity yttrium in two forms: as dendritic (left and center) and as a remelted cube (right). "Yttrium sublimed dendritic and 1cm^3 cube" by Alchemist-hp, licensed under CC BY-NC-ND 3.0

APPLAUSE

Patents Issued

Method of CO and/or CO_2 Hydrogenation Using Doped Mixed-Metal Oxides, **David A. Berry** (DOE/NETL); **Dushyant Shekhawat** (DOE/NETL); **James Jerry Spivey** (ORISE;LSU); **Mark Smith** (URS); **Daniel J. Haynes** (DOE/NETL); **Victor Abdelsayed** (URS), 9,150,476, issued October 6, 2015.

Creep Resistant High Temperature Martensitic Steel, **Paul D. Jablonski** (DOE/NETL); **Jeffrey Hawk** (DOE/NETL); **Christopher Cowen** (former employee of DOE/NETL), 9,181,597, issued November 10, 2015.

Method of Fabrication of Supported Liquid Membranes, **David Luebke** (former employee of DOE/NETL); **Christina R. Myers** (DOE/NETL)**; Lei Hong** (Global Energy Services), 9,186,854, issued November 17, 2015.

EXTRA! EXTRA!

NETL Collaboration receives 2015 R&D 100 Award

A new, innovative software product has been recognized with a coveted R&D 100 Award. Developed by a team of experts at NETL, West Virginia University (WVU), and Schneider Electric, the virtual reality-based software, known as EYESIM, provides energy industry decision makers with an unprecedented high-tech look inside the operation of power plants, helping to lower costs and increase safety and efficiency.

NETL's **Stephen E. Zitney** explained that the R&D team created the three-dimensional, immersive, virtual reality software technology to give engineers and operators of energy plants a clearer vision of conditions inside plant equipment while in operation so that more-informed efficiency and safety decisions can be made faster and more effectively, saving time and money.

EYESIM is helping the energy industry reduce costs for operations and maintenance, increase environmental performance, and obtain better overall response to plant upsets, malfunctions, rare abnormal situations, and safety-critical events.

The R&D 100 awards, given annually by *R&D Magazine*, are known as the "Oscars of Invention" and celebrate the top technology products of the year.

CONTACT

National Energy Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

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

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

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

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

WEBSITE
www.netl.doe.gov

CUSTOMER SERVICE
1-800-553-7681

For more information about NETL's Office of Research and Development and its programs:
www.netl.doe.gov/research/on-site-research

U.S. DEPARTMENT OF ENERGY | NETL

ORD: Science & Engineering To Power Our Future