From NETL's Office of Research & Development

Research news

January 2015, Issue 4

FEATURE STORY:

Flowing Free: Promoting Chemical Looping Combustion

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NETL | the ENERGY lab
NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

Research news

January 2015, Issue 4

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Research News is a monthly publication from the National Energy Technology Laboratory's Office of Research and Development. We focus on the exciting research done at NETL by our scientists and collaborators.

Research News welcomes your comments, questions, and suggestions. Call us at **541-967-5966**.

Integrating Safety in Research:
Safety Always in ORD!

"Safety First" is much more than just a slogan in NETL's Office of Research and Development (ORD). Safety is one of the initial considerations in the conceptual stage of a research project, but it also remains a strong and constant presence throughout system design, research execution, and system and research modifications. Safety considerations continue to be present for project decommissioning, dismantling, and final dispensation.

ORD management is deeply committed to fostering a culture of safety, and does so primarily through a two-pronged approach: professional engineering services for research system design, maintenance, and management of change to experimental systems; and a Safety Analysis and Review System (SARS) for operations. The ORD Conduct of Research Operations process provides the roadmap to integrate and synchronize these two primary processes through which safety considerations are embedded and integrated into both experimental system design and research operations.

Beginning very early in the project conception stage, a multidisciplinary team of design engineers and safety professionals is assembled to determine engineering design requirements and conduct preliminary hazard identification. Experimental system design is completed and installed in full compliance with all applicable local, state, federal, and agency requirements. On-going engineering services are provided to support research projects to ensure the safety of our employees, facilities, neighbors, and the environment.

Safe operations are fostered through the implementation of the NETL Research and Development SARS Procedure; assuring employees meet project-specific training requirements; conducting root cause analyses, and formulating recommendations based upon lessons learned. Anytime an unplanned event occurs, it is viewed as an educational experience and an opportunity for improvement. A thorough root cause analysis is conducted promptly, and any approved recommendations made to ORD management are swiftly implemented into our standard research practices.

Safety always!

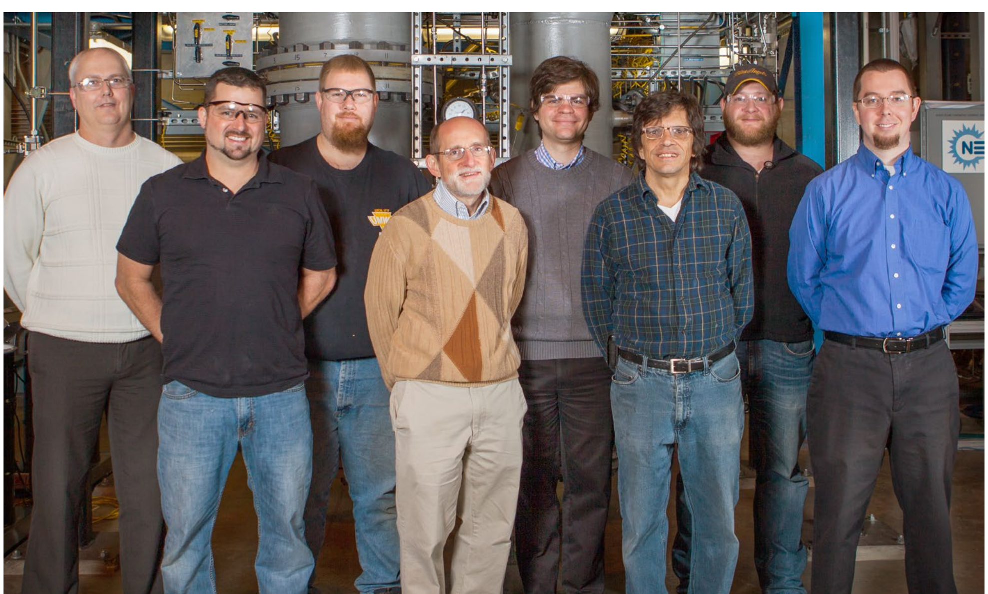
Mara Dean, Director
Crosscutting Research Support Division

Cover image
NETL's chemical looping reactor in Morgantown, WV

Flowing Free: Promoting Chemical Looping Combustion

NETL's chemical looping reactor in Morgantown, WV.

Researchers are enabling power generation with a simple way to control carbon dioxide (CO_2) by combusting fossil fuel in nearly pure oxygen rather than air. The process, called chemical looping combustion (CLC), operates at conditions similar to those present in today's power plants. For that reason, energy systems built using conventional construction materials and techniques can accommodate CLC, which decreases capital costs. Another benefit of CLC is that the combustion in one part of a CLC reactor (the "fuel reactor") produces highly concentrated CO_2 and water. That CO_2 can be purified, compressed, and sent for storage or reuse. Doing so makes a separate—and expensive—CO_2-separation process unnecessary.



NETL's Chemical Looping Reactor Team. From left to right: Douglas Straub, Richard Eddy (URS), David Reese (URS), Dr. George Richards, Justin Weber, James Spenik (REM Engineering), David Vukmanic (URS), and Stephen Carpenter (URS).

As part of NETL's Advanced Combustion Program, researchers at NETL are investigating and advancing CLC technologies. CLC was also the subject of a 4-year research effort at NETL (called the Industrial Carbon Management Initiative), funded through the American Recovery and Reinvestment Act.

During CLC, a solid material—an "oxygen carrier"— supplies the oxygen needed to burn fuel in a fuel reactor. The oxygen carrier (now depleted of oxygen) then travels to the air reactor, where contact with air renews its oxygen content. The carrier can then return to the fuel reactor and start the process over again. The exhaust gases from this process consist of CO_2 and water vapor. Condensing the water and isolating the CO_2 is straightforward, unlike removing CO_2 from the gas mixtures that

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conventional coal-fired plants emit. "With other carbon capture concepts, it takes more parasitic energy to run the process," says Justin Weber, an engineer with NETL. "The whole point of chemical looping is that we avoid those problems by using an oxygen carrier to transfer the oxygen to the fuel reactor." CLC will also work in natural-gas-fired plants, which (like coal-fired plants) produce CO_2.

The research "cuts across a lot of different disciplines," says Doug Straub, the Technical Lead for NETL's Industrial Carbon Management Initiative. "It involves mathematical modelers, chemists, chemical engineers, mechanical engineers, and electrical engineers" from NETL. Graduate student interns, including several Mickey Leland Fellows, have also contributed to the project.

NETL has invented improved oxygen carriers for the CLC process, including one based on hematite (see **Grounded in Science**). "We are one of the few groups that has manufactured a new carrier, patented it, and proved performance at pilot scale," says **Dr. Geo Richards**, NETL's Energy Systems Dynamics focus area lead. But NETL researchers aren't just concerned with studying oxygen carriers. They're also interested in advancing CLC technology toward commercialization. "We're … developing modeling tools that you could use to scale the technology up," says Straub. Using NETL's chemical looping reactor, researchers have assessed how oxygen carriers perform in a realistic setting, developed sensors that reveal how evenly carriers circulate, validated the accuracy of CLC computer models, and verified that the CLC process is viable (see **Facilities** sidebar–right).

And, as Dr. Richards points out, "we are providing the public with information about things like how the solids move around and how we model them, so other researchers can use the information to further this technology."

Contact: Geo Richards

Energy Systems Innovation Laboratory

Advances in CLC technologies get a jumpstart in NETL's Energy Systems Innovation Laboratory. There, a chemical looping reactor can circulate 1,000 pounds of oxygen carrier each hour, at temperatures up to 1,000 degrees Celsius. The lab also houses a cold-flow replica of the reactor, which lets researchers directly observe the flow of solids through an identical process. Other instruments in the Lab help researchers evaluate oxygen carriers' durability and reactivity.

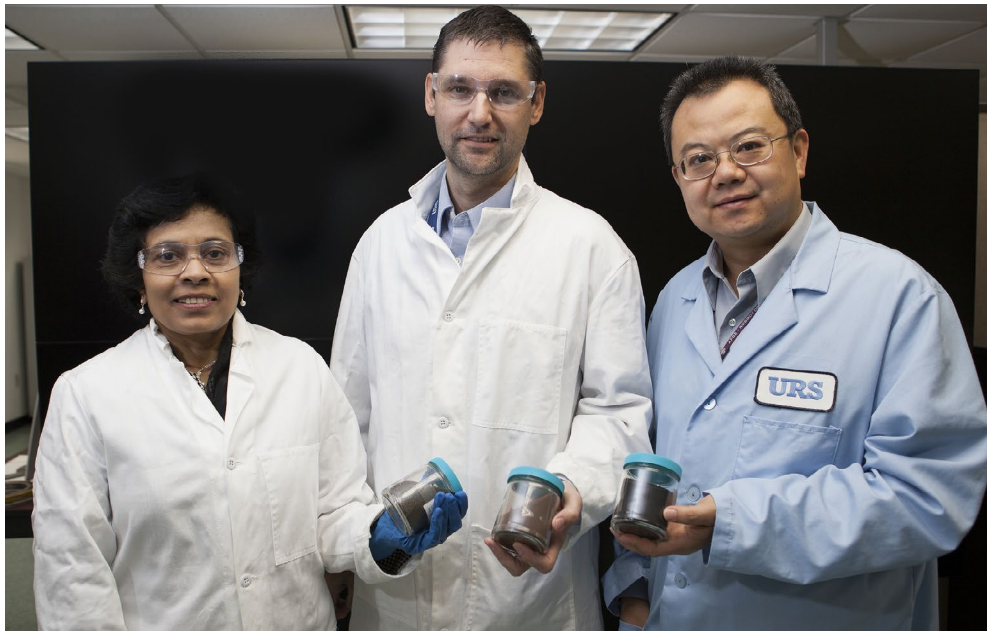
CLC is just one technology researchers are exploring in the Energy Systems Innovation Lab. The Lab also includes facilities for investigating the performance of solid oxide fuel cells, as well as hybrid energy systems that combine solid oxide fuel cells with turbines to dramatically raise the efficiency of a gasification-based power plant.

Senators Joe Manchin (D-WV) and Sheldon Whitehouse (D-RI) visited the Lab on October 22, 2014. Senator Manchin said it was "a pleasure" to show Senator Whitehouse the "innovative energy facilities in West Virginia," and Tweeted that NETL is conducting "the latest research in future coal technologies." The equipment in the lab—and the dedication of the experts there—will help make tomorrow's Fossil Energy-based power cleaner and cheaper.

Contact: Geo Richards

Dr. Geo Richards (left) talks with Senators Joe Manchin (D-WV, far right) and Sheldon Whitehouse (D-RI, second from right) about the Energy Systems Innovation Lab.

Grounded in Science:
NETL Invents Improved Oxygen Carriers



Drs. Ranjani Siriwardane, Duane Miller, and Hanjing Tian (L–R) pose with the oxygen carriers they developed and tested.

One of the keys to the successful deployment of chemical looping technologies is the development of affordable, high performance oxygen carriers. One potential solution is the naturally-occurring iron oxide, hematite. "Hematite is pretty cheap," says Doug Straub, Technical Coordinator for NETL's Chemical Looping Combustion (CLC) projects and the just-completed Industrial Carbon Management Initiative (ICMI). "You just dig it out of the ground and run it through a screen." That affordability makes hematite attractive as an oxygen-carrier material, but high performance at the conditions imposed by the chemical looping process is also important. NETL researchers are investigating how to enhance hematite-based oxygen carriers so they can stand up to high reactor temperatures. Oxygen carriers also need to be resilient in the face of frequent impacts with reactor walls, with each other, and (in coal-burning reactors) with coal particles. Researchers are also improving oxygen carriers so that they more completely combust the fuel.

Their work has paid off. **Dr. Ranjani Siriwardane** (who leads the CLC oxygen carrier research) and **Dr. Duane Miller** (a chemical engineer at NETL) have invented an oxygen carrier that pairs magnesium oxide with hematite. During a pilot-scale run through NETL's fluidized bed reactor last year, their carrier showed better performance than carriers that contained just natural hematite.

Oxygen carriers are similar in texture to sand. NETL researchers Drs. Ranjani Siriwardane and Duane Miller invented the oxygen carrier pictured here, which blends magnesium oxide and hematite.

What's next? In the words of Dr. Siriwardane, "this is a big scale-up problem," and that scale-up can be difficult. The quantities of carriers used at the laboratory scale are small, and techniques for preparing them are easier to control. But, as Dr. Siriwardane explains, "some of the techniques we use for lab-scale preparations are not practical for large-scale preparations, where different techniques and equipment are used. Finding the proper production techniques for our carriers that still deliver the required performance is a big challenge." However NETL researchers are clearly up to the challenge: when Drs. Siriwardane and Miller applied for the patent for their magnesium-oxide-and-hematite carrier, they had about 100 grams of material, just enough for a lab-scale run. Since then, they have worked with NexTech Materials, a commercial materials vendor, to prepare a 400-pound batch of the carrier for the pilot-scale test.

In addition to the hematite-based carrier, NETL is also exploring alternative carrier materials, with the goal of optimizing carrier performance and affordability for specific chemical looping applications. A second carrier developed by Drs. Siriwardane and **Hanjing Tian** (formerly of NETL but now a West Virginia University faculty member) relies on manmade materials instead of natural hematite. Made of copper oxide, iron oxide, and alumina, it too is ready for pilot-scale testing.

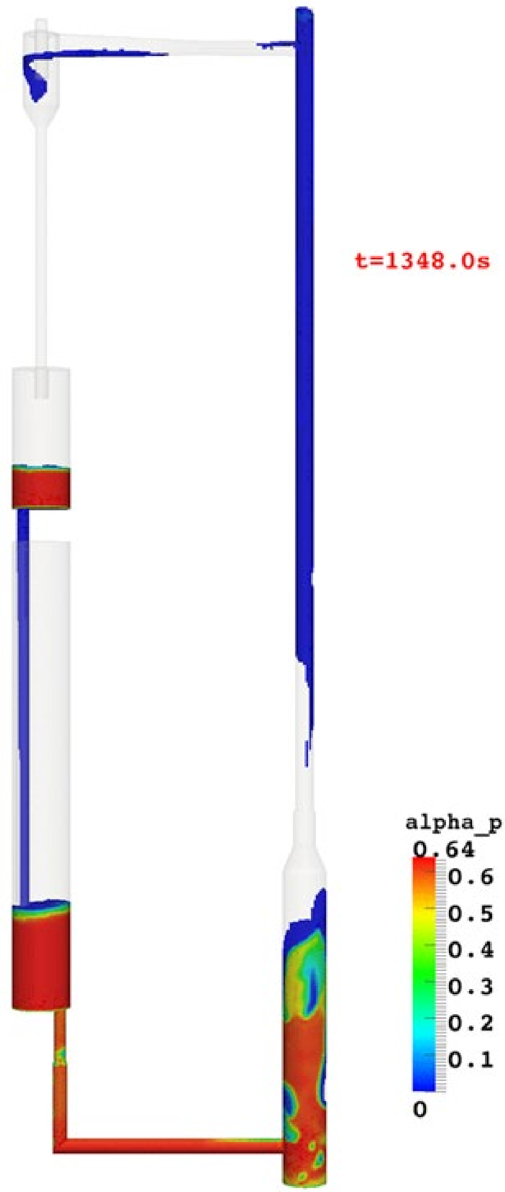
The oxygen carriers that NETL invents to enable CLC could have applications beyond electricity generation. CLC is also useful in industrial steam production, says Dr. Miller, and can be used for the production of hydrogen or syngas from methane. NETL scientists continue research to discover and develop carriers for such real-world applications with the expectation that the energy technologies they enable will one day be very green and very, very affordable.

Contact: Ranjani Siriwardane

Saving Time and Money: Modeling and Simulation Tools Complement CLC Lab Work

Modeling and simulation tools are useful to researchers because, when combined with experimental testing, they provide an opportunity to look at new ideas and predict results without having to perform experiments for every variation, saving time and money. As **Dr. Madhava Syamlal**, the focus area lead for NETL's Carbon Capture Simulation Initiative, explains, modeling and simulation tools help CLC researchers design experimental systems and learn about phenomena they can't measure or observe. The tools' most important purpose, however, is the scale-up of CLC devices. "Gas-solids systems such as CLC are notoriously difficult to scale-up," says Syamlal. "So, our strategy is to validate physics-based models with data from small-scale experiments, and use the models for simulating large-scale devices, to increase our confidence in the scaled-up design."

To investigate the intricate workings of CLC systems, NETL researchers use four computational fluid dynamics (CFD) codes. Two of the CFD codes (Barracuda and Fluent) are commercial products. The others (OpenFOAM and Multiphase Flow with Interphase eXchanges [MFIX]) are open-source codes. The last of these is a direct result of NETL's vision and persistence; not only did NETL researchers develop MFIX, but they continue to cultivate it through upgrades and expansions. "MFIX offers us two distinct advantages," says Syamlal. First, because NETL researchers have access to the entire code—and a thorough knowledge of how MFIX is used—they can "develop models faster and better with MFIX than with other software." Second, the number of simulations that they run and the "number of cores on a high-performance computer" that they use are not limited by the restrictions of commercial licenses. But MFIX isn't valuable solely to NETL. Thousands of scientists and engineers around the world use it. Furthermore, the models and insights developed through MFIX get incorporated into other codes, such as Fluent.



Simulations like the one shown here give researchers a better understanding of how chemical looping reactors perform. The example pictured depicts the changing concentrations of solids in different parts of a chemical looping reactor during operation. Different colors indicate different concentrations of solids.

With modeling and simulation tools like MFIX, CLC researchers can compare computational predictions with experimental results, to infer how variations in small-scale physical processes lead to larger-scale behaviors that affect reactor performance. This insight lets researchers propose changes to the system and its operation. For example, "CFD simulations were used to help in the redesign of the chemical looping reactor and to recommend changes to the operation of the unit," says **David Huckaby**, a mechanical engineer and member of the Simulation, Data Analysis, and Visualization Team. These changes included the installation of a secondary cyclone, which reduced the loss of oxygen-carrier material, and the reconfiguration of the fuel-injection system.

Moving forward, Huckaby, Syamlal, and their colleagues plan to combine the knowledge of carrier reactivity gained through NETL's chemical looping research with the coal models in C3M (Carbonaceous Chemistry for Computational Modeling), software developed at NETL for adding complex chemical reactions to CFD codes, to develop models relevant to coal-fueled chemical looping. "NETL has significant expertise in the chemical reaction kinetics of coal gasification," says Syamlal. "That should help us create higher-fidelity models of chemical looping combustors that use coal as the fuel." In addition to coal chemistry, the project will address technical challenges, such as the effective separation of carrier and coal during reactor operation. Crosscutting research like this accelerates the commercialization of CLC technologies to realize the environmental benefits they promise.

Contact: Madhava Syamlal, David Huckaby

NETL Develops Sensors to See Inside Reactors

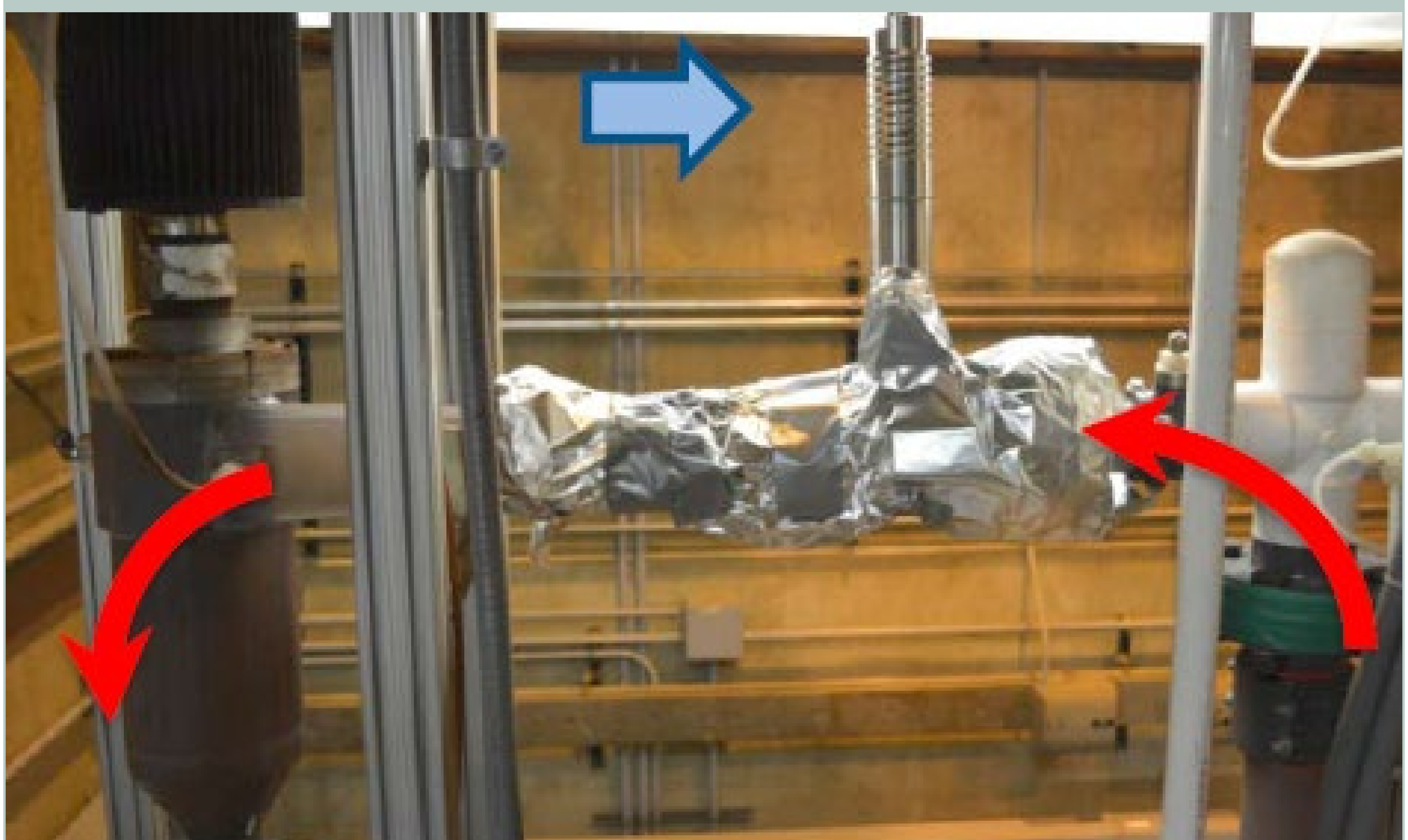
NETL researchers had a problem. They wanted to develop better oxygen carriers for use in chemical looping combustion (CLC), and they wanted to improve how chemical looping reactors were configured. To do so, they needed real-time information about how carriers move through, and perform in, hot- and cold-flow reactors, but the necessary tools weren't on the market. So, they did what inventors do: they invented their own.

"We looked around for ways of measuring the carrier circulation rate, and there wasn't really anything that worked at those operating temperatures," said **Doug Straub**, Technical Coordinator for NETL's Chemical Looping Combustion (CLC) projects. NETL's chemical looping reactor can get hot enough to melt steel, so Straub and his colleagues needed a sensor that was—above all—heat-resistant. So **Ben Chorpening**, a mechanical engineer at NETL, teamed up with David Greve (professor of electrical and computer engineering at Carnegie Mellon University), **Tracy Thewlis** (mechanical engineer), and **Jared Charley** (electronics engineer) to develop a sensor that would fit the bill. The result, said Straub, is a sensor that is "kind of like a radar system that uses microwaves instead of radio waves" to track the flow of oxygen carriers through the chemical looping reactor, whether the reactor is operating at high or low temperatures.

"One of the challenges for chemical looping combustion is the measurement of the circulation rate, because that tells us how much oxygen we're transferring to the fuel reactor," explains **Justin Weber**, an NETL mechanical engineer. The microwave flow sensor is also valuable for validating models' predictions of a carrier's performance. The researchers have used the sensor both in NETL's hot-flow chemical looping reactor and its cold-flow replica reactor, with encouraging results.

Researchers have also used an NETL-developed Raman sensor on NETL's hot-flow chemical looping reactor to evaluate the composition of gases coming from the fuel reactor. "Basically," said Weber, "that tells us the performance of the carrier in terms of reacting with the fuel. We want to completely convert the fuel to combustion products—CO_2 and water. We don't want any incomplete combustion, which would produce methane or hydrogen or carbon monoxide." Burning coal will also emit gases such as sulfur and nitrous oxides, all of which are measurable by the NETL Raman sensor. Through innovations like these, NETL researchers will continue to deepen their understanding of—and find ways to improve—the CLC process.

Contact: Doug Straub



Microwave flow sensor installed on a chemical looping reactor. The blue arrow indicates the sensor, and the red arrows denote the direction that the solid material travels as it moves through the chemical looping reactor.

NETL Conducts First-of-Its-Kind Shear Fracture Visualization Test

The aluminum prongs shown here were used to shear a pre-fractured core sample that was analyzed with CT scanners as fluid was injected.

For the first time anywhere, researchers at NETL are able to watch fractures shearing in rock cores at elevated pressures. Utilizing a specially designed holder in NETL's CT Imaging Facility, computed tomography (CT) scans of the core during shearing can show how changes in fracture geometry of the rock lead to changes in its permeability. Shearing occurs when one layer of rock "slips" over another. Existing fractures can shear when local pressures change in a reservoir, such as during the injection of CO_2. "Slippage" events are important to study because little is known about how slippage influences rock characteristics like permeability. Changes in rock permeability can change how CO_2 moves once injected in geologic formations and may determine how much CO_2 can be stored in a given reservoir.

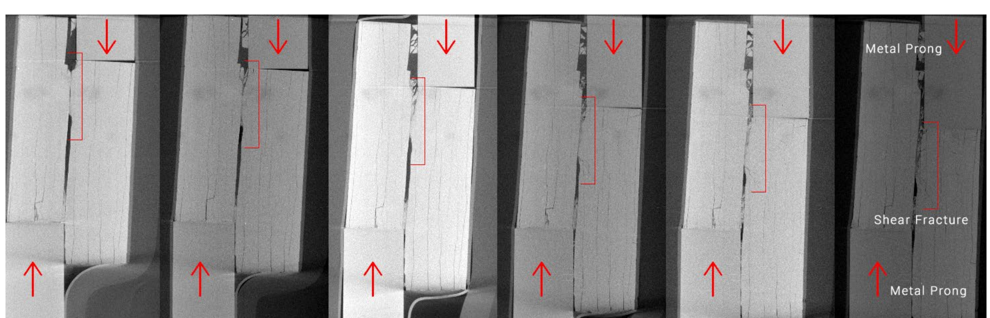
NETL researchers, including **Dr. Dustin Crandall**, want to understand the link between fracture and permeability in geologic formations, so they can more accurately understand and predict the behavior of reservoirs that might be used for the underground storage of CO_2. This project is part of the National Risk Assessment Partnership (NRAP), which uses science to understand the long-term risks of storing CO_2 at different underground sites.

Researchers create shearing in the lab by first manually fracturing the rock core. Then two metal prongs, designed by NETL technician **Bryan Tennant**, are attached to the ends of the core and pushed toward each other, creating the shearing force on the fracture. As shearing begins, fluid is injected through the core sample, and CT scans are made over time. The resulting scans show how the fracture changes as the shearing force alters its geometry. Initial research revealed that fractures can become clogged with sheared material as the rock layers slip over one another, but other tests demonstrate cleaner fracturing. Further testing is needed to provide a clearer understanding.

"These experiments are novel," Dr. Crandall explained. "We are applying pressure on the outside and shearing that fracture while being able to scan in real time." NETL's strong contribution to CO_2 storage research is due both to cutting-edge labs like the CT Imaging Facility, and the ingenuity of its scientists and engineers, to design and create new ways of using those facilities. The core-shearing prongs are an excellent example of that innovative spirit.

Learn more about NETL's CT Imaging Facility here.

Contact: Dustin Crandall



CT scans show a shear fracture as it progresses over time (left to right) in a first-of-its-kind test that allows researchers to study the effects of shear fractures on permeability—a key concern in CO_2 storage.

NETL's In-House Research Program:
Offshore Resources Portfolio

Increasingly, offshore domestic oil and natural gas activities are associated with remote and challenging regions, such as the offshore Gulf of Mexico and the offshore Arctic. Development in these areas poses unique technical and operational challenges, as well as distinct environmental and societal concerns. Domestic resources of natural gas and oil continue to play an increasingly critical role in meeting U.S. energy needs. The Offshore Resources Portfolio seeks to use science-based studies to reduce uncertainty, lower risks, and prevent potential impacts in order to ensure enduring, safe, and appropriate access to domestic energy resources such as those accessed through offshore drilling and production.

ORD researchers have extensive expertise in characterizing engineered natural systems. This expertise is being leveraged for offshore energy research in the following areas:

- Improving understanding of how conventional alloys, advanced alloys, and surface treatments may allow for safe and reliable use of metallic components in extreme wellbore conditions, such as in the presence of seawater, H_2S, and CO_2, and at high pressures and temperatures.
- Developing the science base for the stability of foam cement systems in wellbores at in situ conditions via experiments, computed-tomography scans, models of bubble distribution, and measurements of sound waves traveling through cement.
- Evaluating wellbore integrity along the formation, cement, and casing interfaces to ensure safe and reliable wellbore systems at subsurface conditions by investigating how they corrode, tolerate cyclical stress, and bond to each other.
- Creating higher-accuracy information and predictive tools to understand fluid phase properties, for use in reservoir simulators that quantify the properties of crude oil at high temperatures and pressures—including expanding data on the density and viscosity of hydrocarbon behavior up to 40 kpsi and 400 degrees Fahrenheit.
- Developing an integrated modeling and data system, from subsurface to the shore, for spill prevention—to support informed decision-making regarding offshore activities and spill prevention.
- Developing a low-cost, early-detection system to support safer drilling operations and improve well control during drilling in over-pressured formations.
- Using NETL's Energy Data eXchange to support collaboration for ongoing research and disseminate research results.

To learn more about the Offshore Resources Portfolio, contact Kelly Rose or see https://edx.netl.doe.gov/offshore.

FUNDAMENTAL FUN

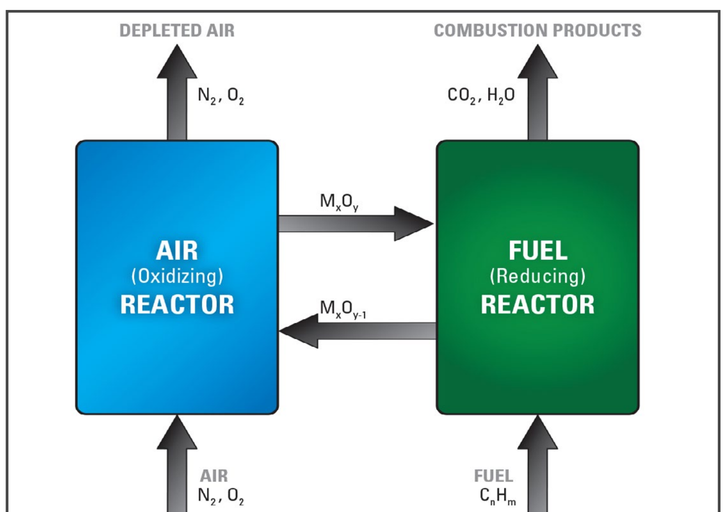
Chemical Looping Combustion

Chemical looping combustion (CLC) uses an oxygen carrier loop to transfer oxygen from the combustion air to the fuel. As shown in the simplified schematic of a two-reactor CLC process, the products of combustion (CO_2 and water) are kept separate from the rest of the flue gases (primarily N_2), simplifying CO_2 capture for eventual storage or use. The "loop" between the two reactors is traveled by the oxygen carrier, usually a solid, metal-based compound (represented as "M_xO_y" in the figure to designate a compound of metal and oxygen molecules). Most oxygen carriers are made of an oxide of copper, nickel, or iron and have the texture of sand.

In the fuel reactor, the oxygen carrier reacts with the fuel at high temperature in a combustion reaction (also known as a reducing reaction). The oxygen carrier is now depleted of oxygen and can be regenerated by exposure to air at high temperature (also known as an oxidizing reaction) in the air reactor. The combustion product from the fuel reactor is a highly concentrated CO_2 and water stream that can be purified, compressed, and sent to storage or for beneficial use. The hot flue gas from the air reactor can be used to produce steam that drives a turbine, generating power.

CLC enables a more simplified approach for CO_2 capture from fossil fuel combustion plants by eliminating the cost and energy penalties associated with a post-combustion CO_2 separation step and operating at temperatures compatible with today's conventional materials.

Contact: Geo Richards



Chemical Looping is so named because of the "loop" made by the oxygen carrier between two reactors: a fuel combustion reactor (in green) and an oxidation reactor for regenerating the oxygen carrier (in blue)

APPLAUSE

Patent Issued

Fisher, James C. (Morgantown, WV); Siriwardane, Ranjani V. (Morgantown, WV); Berry, David A. (Mount Morris, PA); Richards, George A. (Morgantown, WV); Method of CO_2 removal from a gaseous stream at reduced temperature, U.S. patent 8,888,895 B1, issued Nov. 18, 2014.

Award

Two NETL Employees Recognized for their Efforts in STEM Outreach

On November 19, NETL employees **Lilas Soukup**, Public Affairs and Strategic Outreach Division , and **Kirk Gerdes**, Office of Research and Development, were recognized by the Federal Laboratory Consortium (FLC) for their efforts in Educational Outreach, with the 2014 FLC Mid-Atlantic STEM (science, technology, engineering, and math) Award. Ms. Soukup won the award for her efforts with NETL's K-12 Educational Outreach Program and for 21 years of leadership for the Southwestern Pennsylvania Science Bowl. As NETL's Lead Engineer for the Innovative Energy Concepts team, Dr. Gerdes won especially for his leadership in the West Virginia Science Bowl, both in organization and promotion. The FLC award event took place at the Conference Center at the Maritime Institute of Technology and Graduate Studies in Linthicum Heights, Md.

ORD: Science & Engineering To Power Our Future

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Read all about ORD's Accomplishments in the
Office of Research & Development Annual Review

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