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Research news

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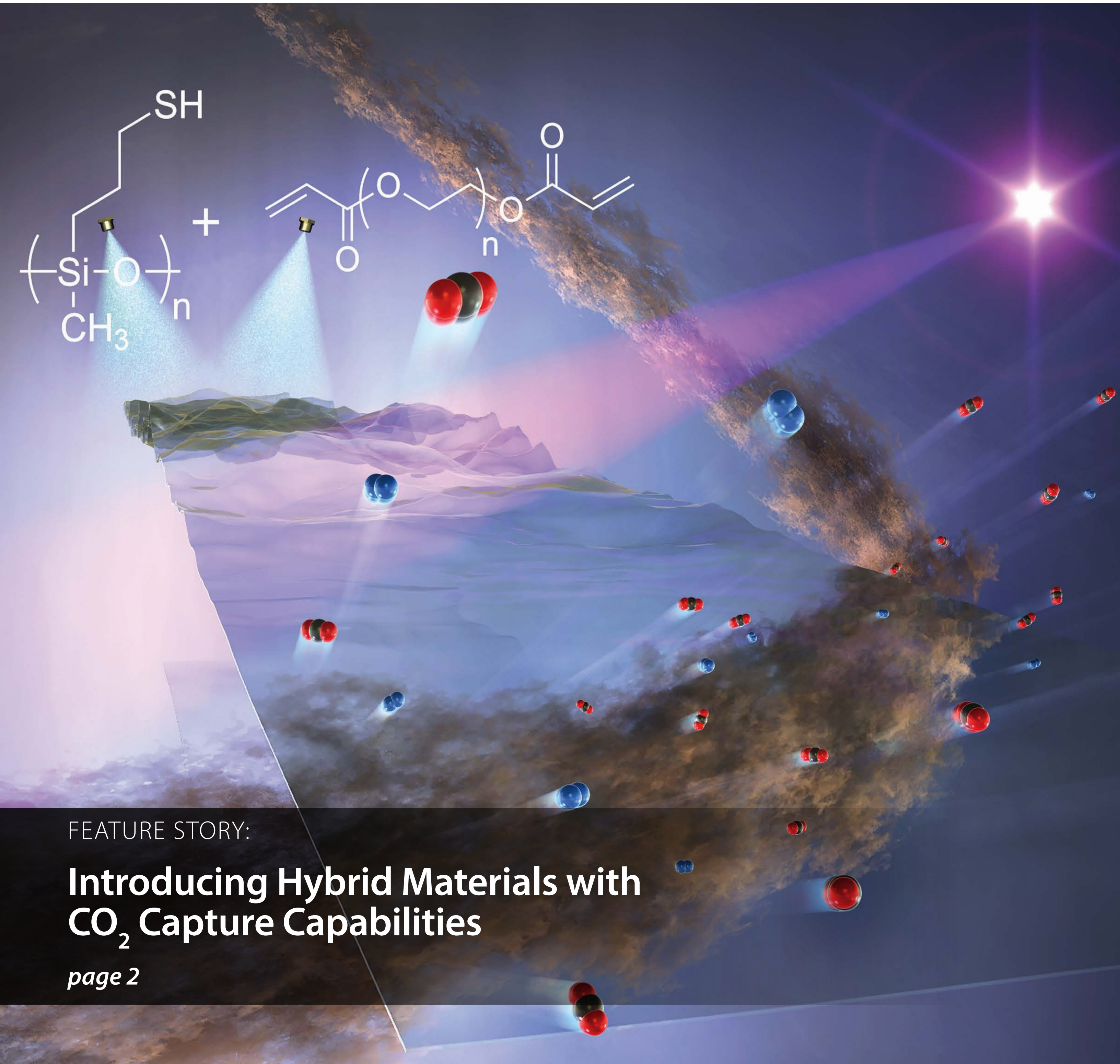

FEATURE STORY:

Introducing Hybrid Materials with CO_2 Capture Capabilities

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the ENERGY lab
NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

Research news
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INTRODUCING HYBRID MATERIALS WITH CO_2 CAPTURE CAPABILITIES

If you ever had a cavity filled, the dentist may have used a little blue light to solidify or cure the new filling. A similar curing process inspired NETL researchers to develop new film-forming materials that may someday lower the cost of mitigating carbon dioxide (CO_2) emissions or even aid in adult human stem cell transplants.

Researchers have long known that curing a liquid polymer called poly(ethylene oxide) in a process known as crosslinking creates a material that can allow one gas to pass through while blocking another, in this case efficiently separating CO_2 from nitrogen, making it an excellent candidate for a gas separation membrane to remove the greenhouse gas from power plant emissions. The current challenge is fabricating the material into films that are only nanometers thick, or as thin as a typical virus and much smaller than a typical bacterium. That is difficult and expensive using conventional means because the chemistry demands a rigorously-maintained oxygen-free atmosphere during fabrication.

NETL researchers have successfully demonstrated a new formulation that could significantly cut the expense of the thin film fabrication and increase the efficiency of the membranes.

Victor Kusuma, on assignment at NETL through the Oak Ridge Institute for Science and Education (ORISE) research program, explained that the new approach exploits a chemical reaction that is less sensitive to oxygen so that thin films can be formed under ambient conditions, which will drive down the fabrication cost of the membranes.

The process, described by an NETL-led team of researchers in an article in the Journal of Polymer Science, uses a principle known as "thiol-ene click photochemistry"— mixing two liquid precursors with specific molecular functionality and then – in a matter of seconds – curing the liquid precursors into solid form using light.

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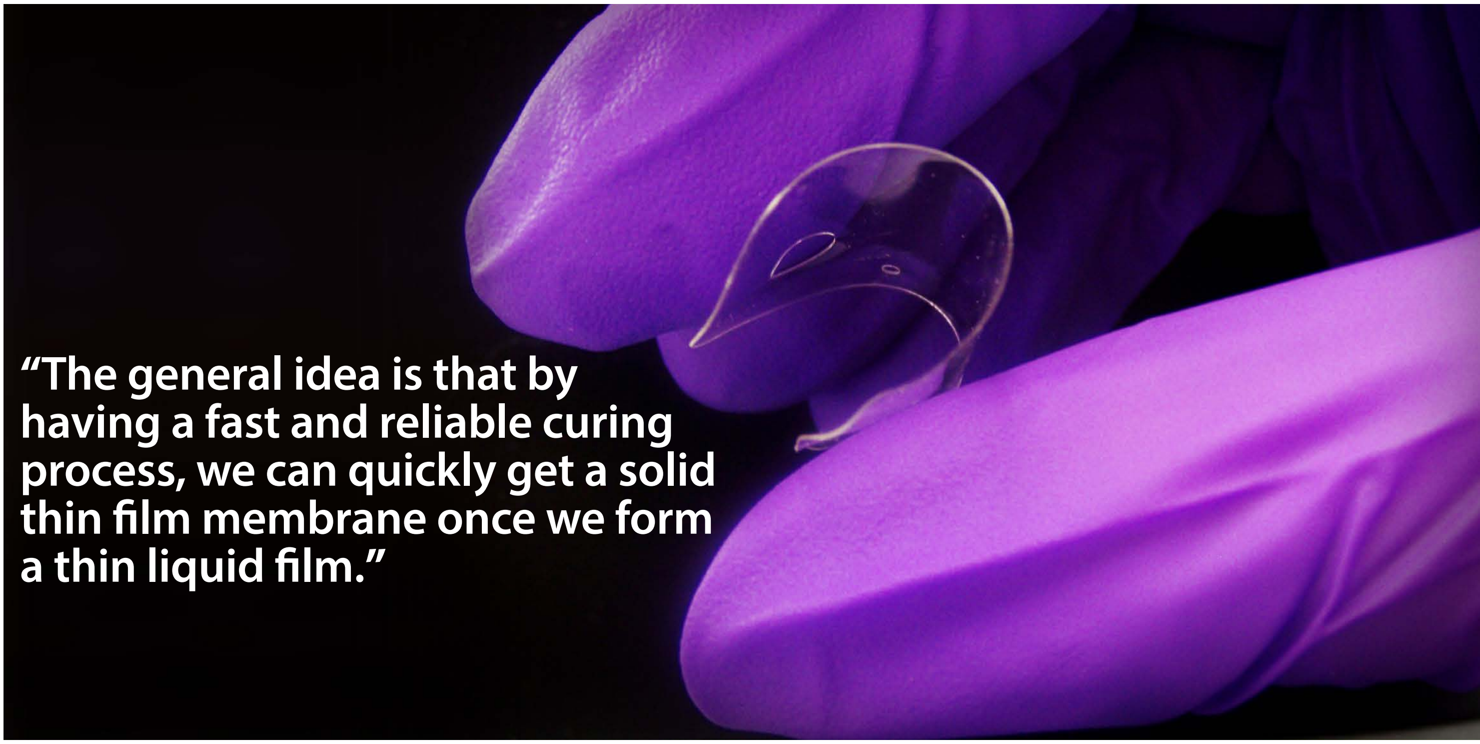
Research News is a monthly publication from the National Energy Technology Laboratory's Office of Research and Development. We focus on the exciting, cutting-edge research done at NETL by our scientists and collaborators to support the DOE Fossil Energy mission.

Research News welcomes your comments, questions, and suggestions.

Cover image
NETL researchers use light to create a CO_2 separation material



"The general idea is that by having a fast and reliable curing process, we can quickly get a solid thin film membrane once we form a thin liquid film," Kusuma said.

Another benefit of this approach is the ability to add functional groups such as siloxanes into the membranes. Siloxanes, polymers consisting of silicon and oxygen atoms, are commonly used in silicone products such as heat-resistant cooking utensils, bathtub sealants, lubricants and medical implants. In the case of gas separation membranes, however, siloxanes confer a huge benefit: improved gas permeability.

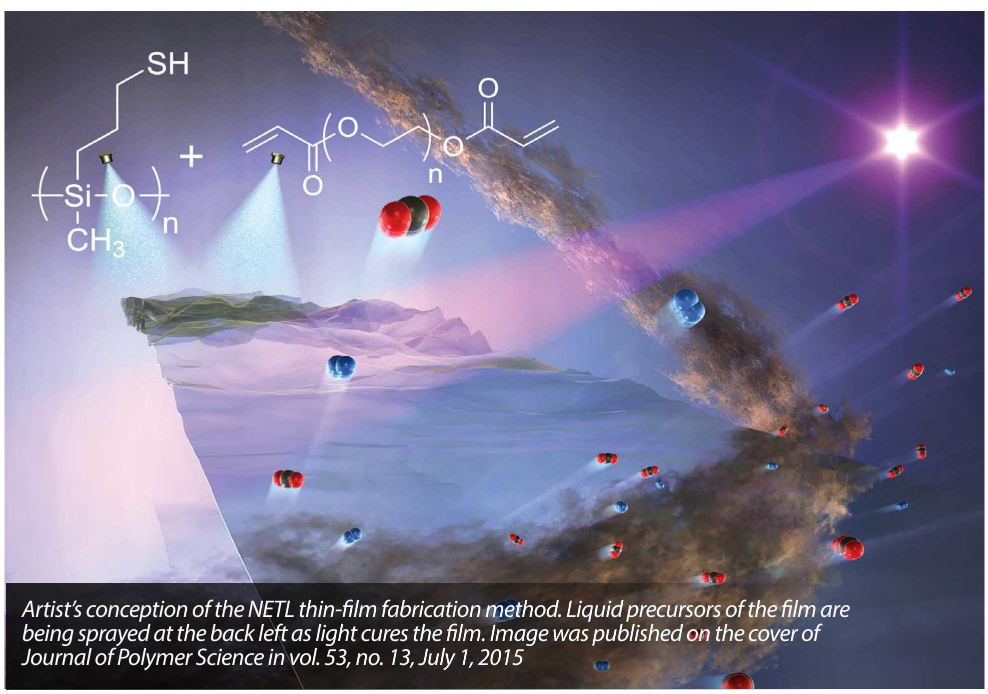
"Siloxanes and ethylene oxide don't really want to mix normally," Kusuma said. "Think oil and water. But, by keeping segments small and pairing them through the thiol-ene click reaction, we are forcing them to mix well and form a film. As a nice bonus, we found we also have control over the proportions of ethylene oxide and siloxanes so we can tune the properties of the membrane, as needed for the application."

NETL tested the new polymer films for CO_2 separation abilities and confirmed that they have better performance than the conventional crosslinked poly(ethylene oxide). The next step is to fabricate a larger high performance gas separation membrane.

David Hopkinson, Kusuma's ORISE mentor and technical leader of the Carbon Capture project (see NETL's In-House Research Program: Carbon Capture, this issue), said that because the process of making the films is relatively simple and the starting materials are commercially available, the cross-linked polymer products could find application in other areas. For example, since the materials are bio-compatible, medical researchers believe that some human adult stem cells are able to retain their potency on these films, so these materials could also find use in cell transplantation.

Carnegie Mellon University researchers teamed with NETL on the project.

Contact: Victor Kusuma



Artist's conception of the NETL thin-film fabrication method. Liquid precursors of the film are being sprayed at the back left as light cures the film. Image was published on the cover of Journal of Polymer Science in vol. 53, no. 13, July 1, 2015

Thin Film Deposition Tool Opens Doors in Fossil Energy Research

It's not often than one single facility offers so many benefits to researchers across the length and breadth of a complex laboratory like NETL. The Modular Thin Film Deposition System manufactured by the Kurt J. Lesker Company is just such a facility.

The new depositional tool, known as the Lab 18 Unit, crosscuts many research efforts at NETL and may provide even more refined capabilities for researchers to use in their work to develop devices, sensors, membranes, fuel cell materials, sorbents, and catalysts, among others.

The Lab 18 unit precisely and uniformly applies thin films or layers of a variety of precious metals, metal oxides, and other substances, onto substrate materials. Researchers in the Electrochemical Magnetic Materials (E&MM) Team use the Lab 18 Unit to apply thin films of the team's sensor formulations on transparent substrates and optical fibers that can be tested in the Advanced Sensor Development Laboratory (ASDL), which is used for sensor material and device development activities.

Senior Research Engineer **Tom Brown** described the advantages of the system, "The Lab 18 Unit allows us to apply our thin films under controlled conditions at specific and or uniform thicknesses without the cracking and other imperfections experienced with other application techniques such as sol gel spin and dip coating."

The E&MM Team uses these thin film sensors in the ASDL's novel reactor systems. These reactors can reproduce the high temperatures and low or high pressures and the gas species or harsh environments associated with many of the advanced power generation systems DOE is developing.

The ASDL is also capable of providing representative harsh environments associated with deep and ultra-deep drilling into geological formations for oil and gas production, as well as carbon storage. In these types of environments, sensors manufactured with highly precise thin films can obtain more accurate measurements, which lead to more efficient operations through process monitoring and control.

The Kurt J. Lesker Lab 18 Unit is housed in the Pittsburgh Materials Preparation and Characterization Facility and benefits many researchers at NETL, providing precise application of thin films.

The Lab 18 Unit can apply films in thicknesses from a few nanometers up to a few micrometers. This exacting application allows researchers to create highly sensitive and selective films.

"We can apply multiple thin layers with different formulations to possibly block one or more gas species while letting the specie of interest to diffuse through," Brown explained. "We can also apply different formulations on different parts of the substrate being used."

With so many different areas of research relying on thin films, the benefits realized by adding the Lab 18 Unit to the Pittsburgh Materials Preparation and Characterization Facility will continue to enrich researchers across NETL, opening doors to further fossil fuel research.

Contact: Tom Brown

New Kick Detection System Provides Early Warnings for Safer Drilling

The perception of oil and gas well control has evolved over the last century. In the late 1800s and early1900s, blowouts were held in high esteem, with "gushers" romanticized as a symbol of prosperity. Over time, however, these gushers became associated with the destruction of materials, human and environmental impacts, and a loss of marketable resources, leading to development of well control technologies.

Kicks provide the first indication that a well is becoming unstable. A kick can start as a slow leak from a pressured formation into the wellbore, but the flow increases as the influx of lower density reservoir fluid reduces the hydrostatic pressure exerted by the drilling fluid at the source of the flow. This causes the well to become underbalanced, requiring intervention for the operator to regain control. Failure to regain control usually results in a blowout.

The start of a kick is the optimum time to control the underbalanced condition. Industry has sought solutions to early kick detection and suppression for decades. The method commonly used for kick detection relies on monitoring the drilling mud properties and fluid returns as they come to the surface. However, if the kick is strong there may not be sufficient time to analyze kick-detection parameters before a decision to shut in the well must be made. A complementary method to detect pre-kick trends that offers accurate, direct measurement of key changes in wellbore and formation conditions in a timely manner could be indispensable to industry.

NETL's new kick detection technique holds promise for just this sort of complementary pre-kick detection. The primary goal of this technique is to maximize the amount of time available to the well operator to initiate well control and recovery procedures by detecting pre-kick trends near the bottom of the hole.

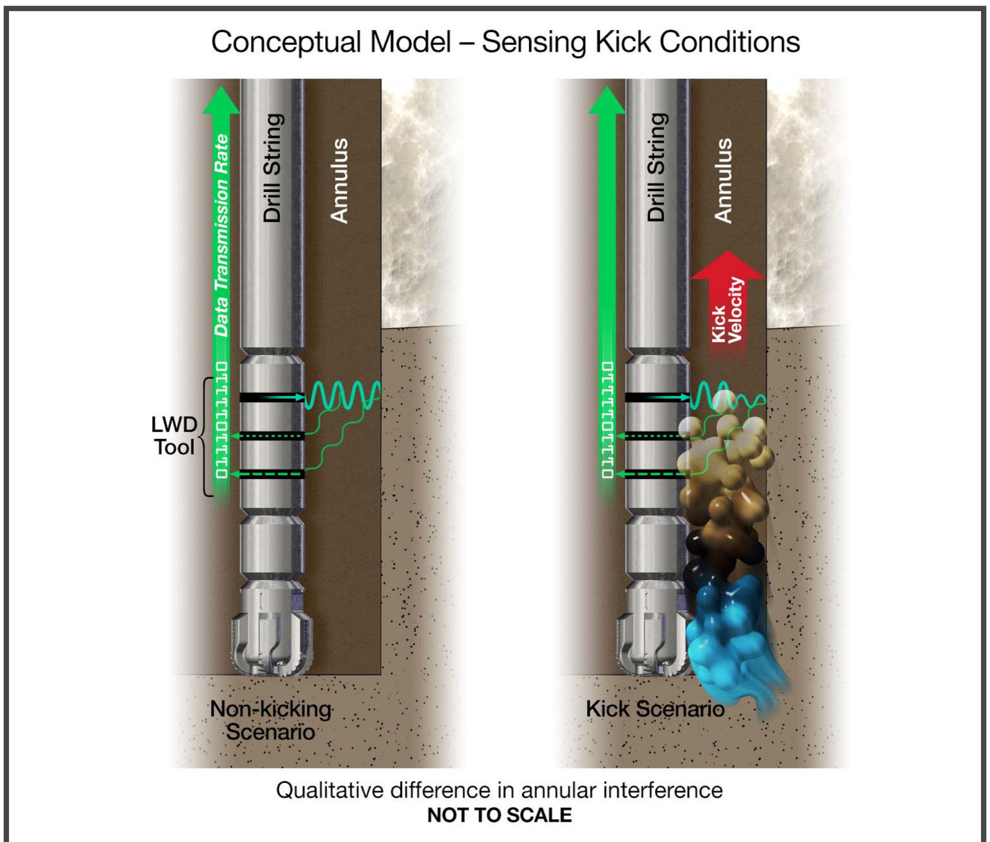
The technique uses highly sensitive, near-bit measurements from the logging-while-drilling (LWD) instrumentation that is already in use during drilling. Collected data that may be affected by kick fluids are transmitted to the surface, where they are compiled into a statistical algorithm. The algorithm develops data trends. Significant deviations from the expected measurement value are flagged by the algorithm, generating a notification which is sent to the driller. The algorithm sensitivity is modular and can be adjusted to satisfy specific drilling needs. This feature will minimize false detections, reducing costly rig downtime and work stoppages.

No modifications or additions to the drillstring are necessary to implement this technique, making it inexpensive and efficient to implement. The technique will use multiple, overlapping LWD measurements, reducing uncertainty whether a detected event is significant or not.

Early results are encouraging. Researchers are attempting to collect borehole data with documented kick events from operators to verify which LWD logs provide the best real-time, raw data to detect pre-kick trends. Opportunities also exist for an industry-NETL partnership to further develop this technology.

For additional information about NETL's kick detection system, please visit edx.netl.doe.gov/offshore.

Contact: Kelly Rose



A kick within the wellbore, pictured on the right, can damage equipment and endanger workers and the environment.

Creative Freedom Helps Intern Develop Novel Gas Separation Membranes

ORISE Post-Doctoral Chemist Larry Hill

A "I love that the scientific literature only has so many answers," **Larry Hill** said. "The best thing about science is answering your questions yourself in the lab."

Larry, an ORISE post-doctoral chemist at NETL, started his journey to becoming a scientist at Southeastern Louisiana University (Hammond, LA) near his hometown of Abita Springs. While doing his undergraduate work, he became interested in Dr. Jeffrey Pyun's work synthesizing nanoparticles—much smaller than the width of a hair—at the University of Arizona (Tucson, AZ). He was "blown away" by the variety of analytical equipment—important to nanoparticle and polymer development—and the collaborative environment that the University of Arizona offered. He pursued a Ph.D. there, and it was through Dr. Pyun that Larry heard about the ORISE internship opportunity at NETL.

For his fellowship with mentor **Dave Hopkinson**, Larry synthesizes materials that can be used for carbon capture to help prevent the greenhouse gas from acting as an agent of climate change. So far, few membrane materials have been developed that can be processed to make thin films to separate large amounts of CO_2 from flue gas for long periods of time. The resulting thin films lack the right mix of chemical and mechanical stability to meet Department of Energy goals. Larry starts with commercially available engineering thermoplastics: processable polymers with the right gas selectivity, chemical stability, and strength for long-term use. With some chemical modification, these materials could also become more permeable to CO_2. To design and create novel membrane materials, Larry is fine-tuning polymers—long strings of molecules—to make the membrane thinner but stronger.

For this sort of work, collaborating with other scientists at NETL and area universities can be a major advantage. "Sometimes just talking with someone can help you come up with a possibility you didn't think of before," Larry said. "Plus, equipment at a partner's site can provide you with characterization methods that you wouldn't have working isolated in your own lab." Understanding the material's characteristics is vital to building relationships between its structure and properties, which can then be used to design the structure of next-generation materials.

One of Larry's favorite things about the work he does is the flexibility it gives him. "Lab work needs creativity to develop solutions," Larry said. "When I can freely explore a couple of different ways to approach the goal, I end up with a much better way of attaining it."

Contact: Larry Hill

NETL's In-House Research Program:
Carbon Capture

Capturing carbon dioxide (CO_2) before a fossil-fueled power plant releases it to the atmosphere is one way to reduce greenhouse gas emissions. The practice, though, is still too costly for widespread use, and the materials it relies on are not always efficient or durable enough. Through the Carbon Capture Program, researchers work to develop technologies that make carbon capture a more affordable, attainable prospect for electric utilities. The researchers' goal is to help reduce the cost of carbon capture to less than $40 per tonne of captured CO_2. Specifically, they are developing technologies that will undergo bench-scale testing in actual flue or fuel gas (two types of gases that power plants emit). Their tasks include:

- Synthesizing, integrating, and optimizing new carbon capture systems—using computer models and computational tools—in order to assess their potential to make carbon capture less expensive.

- Subjecting solvents[1], sorbents[2], and membranes[3] to realistic conditions in the laboratory (including high temperatures, pressures, and moisture content) and exposing them to a small portion of a plant's fuel/flue gas—known as a slipstream—to evaluate how well they isolate CO_2 and to address the technical challenges they present.

- Using toolsets available through the Carbon Capture Simulation Initiative to analyze carbon capture systems and determine the performance targets that they must meet to attain the Department of Energy's carbon capture goals.

- Building an apparatus that can be used to rapidly identify materials with carbon capture potential, so that they may be investigated sooner.

- Inventing and evaluating breakthrough solvents, sorbents, and membranes on the laboratory scale and, with guidance from computational simulations, pursuing those materials that warrant further development.

- Identifying carbon capture processes beyond conventional gas-processing operations, analyzing their feasibility, planning their laboratory-scale verification, and (when appropriate) verifying them in the lab.

Contact: David Hopkinson

[1] liquid materials that separate CO_2 from a gas mixture and release it after a change in temperature or pressure, producing a pure stream of CO_2

[2] solid materials that strip CO_2 from a gas mixture and release it after a change in temperature or pressure, yielding pure CO_2

[3] selective barriers, often composed of a polymeric film, that permeate one gas species more quickly than another gas species

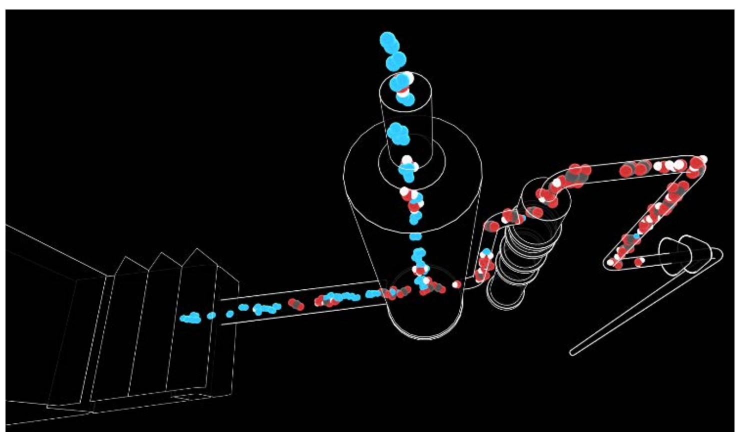
FUNDAMENTAL FACTS

Fuel Gas or Flue Gas?

Fuel gas, as the name suggests, is any type of fuel that exists as a gas under normal conditions. Natural gas is one example. Coal can also be used to produce fuel gas. In gasification plants, coal is converted into a fuel gas called synthesis gas (syngas), which is composed of carbon monoxide, hydrogen, carbon dioxide (CO_2), and water. The syngas can then be used to fuel a gas turbine, to power fuel cells, or to synthesize chemicals.

Flue gas, by contrast, is the "smoke" emitted from stacks of power plants. In reality, flue gas is not smoke, but rather the products of combustion comprising water vapor (which forms steam as the gas stream contacts cooler outside air) and other gases such as nitrogen and CO_2.

NETL's carbon capture research is investigating membranes both for purifying fuel gas and separating CO_2 from flue gas. When applied to fuel gas, membranes can block contaminants and impurities, which not only prevents damage to costly components, it also enables the engine or turbine to use the fuel gas more efficiently.



Flue gas contains the products of combustion. Shown here, CO_2 (represented as red and gray molecules) is separated from flue gas.

Membranes applied to flue gas for carbon capture allow CO_2 to pass through while blocking all other gas species. In this way, CO_2 can be separated for storage and prevented from entering the atmosphere.

Contact: Larry Shadle

APPLAUSE

Patent Issued

Method of Preparation of a CO_2 Removal Sorbent with High Chemical Stability During Multiple Cycles, **Ranjani V. Siriwardane** (DOE/NETL); and **Shira Rosencwaig** (EnVerid Systems, Inc.), 9,079,160, issued July 14, 2015.

Kudos!

R&D Magazine has announced the finalists for the 53rd annual R&D 100 Awards. The annual awards, known as the "Oscars of Invention," are selected by an independent panel of more than 70 judges. This year's selections include a technology developed by NETL and its strategic partners, Schneider Electric and West Virginia University. Known as **EYESIM™**, this immersive virtual reality software program provides operator simulation training to improve power plant operations and safety. The lifelike, real-time virtual learning environment allows personnel to improve their safety skillset for increased operational efficiency and a reduction of costly errors.

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
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