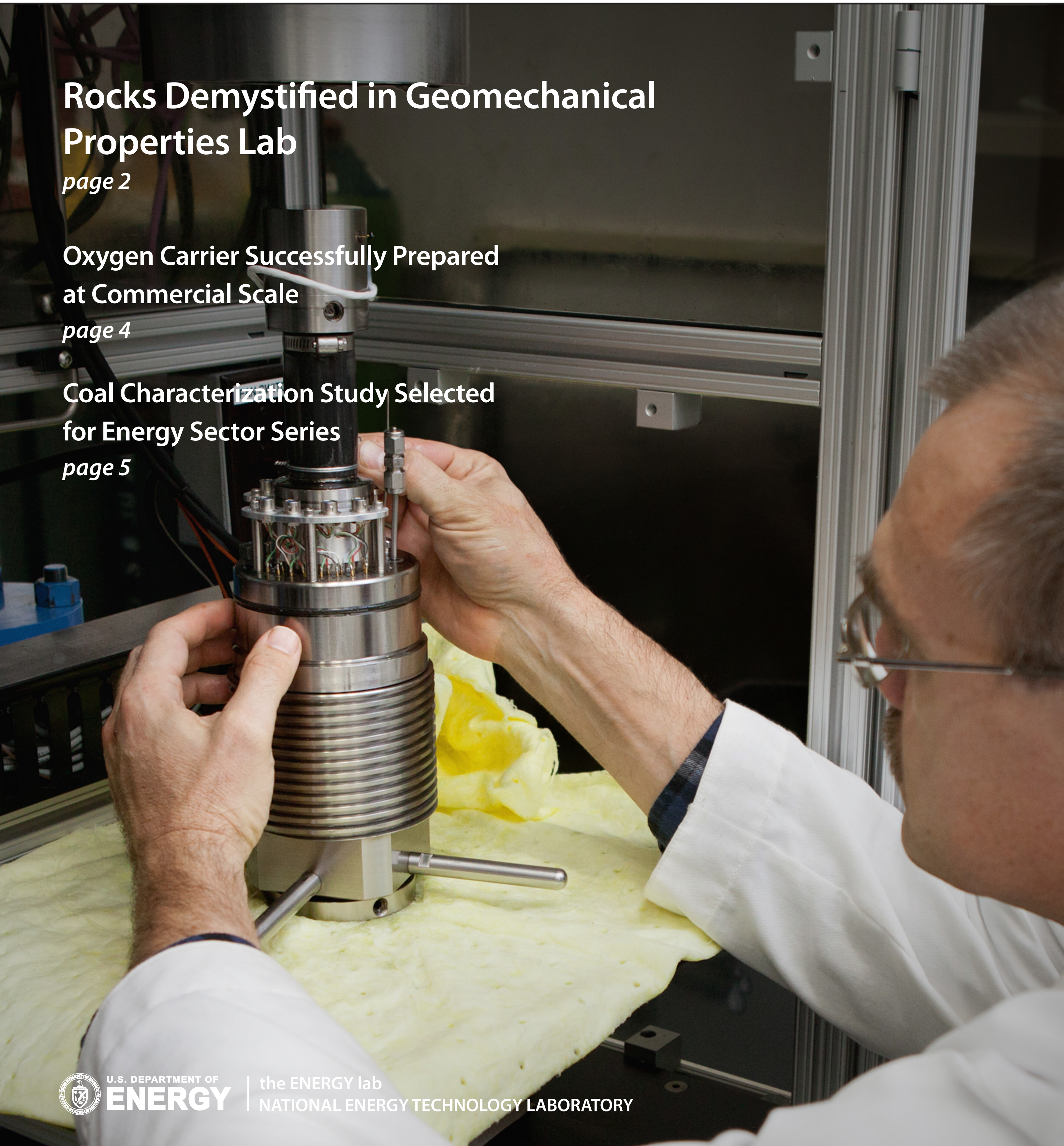
netlognews

NETL's Quarterly R&D newsletter — January 2014, Issue 32



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Cover image: *NETL's Geological Sequestration Core Flow lab.*

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newlognews is a quarterly newsletter highlighting recent achievements and ongoing research at NETL. Any comments or suggestions, please contact Paula Turner at paula.turner@netl.doe.gov or call 541-967-5966.

NETL scientist Igor Haljasmaa at work in the Core Flow lab.

Rocks Demystified in Geomechanical Properties Lab—Carbon dioxide (CO_2), a greenhouse gas, is being captured from power plants and injected deep beneath the surface of the earth. The ability to do this is now much closer to reality than it is to science fiction. Scientists working in the Geological Sequestration Core Flow Lab (GSCFL) at NETL are making it possible to predict how Earth's rocks will behave when the CO_2 is placed in deep storage.

Contrary to the old adage "solid as a rock," rocks contain holes that are naturally filled with fluids like air, water, oil, or natural gas. To remove fluids, as we do when recovering oil and natural gas resources, the fluid has to be able to move through the rock. The percent of the rock that is made up of holes – or pores – is its porosity, and the ease with which fluid flows through a rock is its permeability. Under normal geologic conditions, porosity in rocks is less than 20 percent and an attractive permeability for recovering fluids is more than 100 millidarcies (a darcy is the unit of measure for permeability). The higher the permeability and porosity, the more appealing the formation is for CO_2 storage as well.

Equipment in the GSCFL has recently been significantly upgraded to measure broader ranges of porosity and permeability, as well as other geomechanical characteristics such as sonic velocity, Young's modulus, and Poisson's ratio. These measurements can help NETL scientists determine which fluids are in the pores and how the rock reacts to the stress of injecting or withdrawing fluids from the earth, as happens with gas and oil production, hydraulic fracturing of reservoirs, sequestration of carbon dioxide, and in geothermal projects. Read more about this facility in NETL's LabNotes.

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Drilling fluids, image courtesy of J. Veil, Argonne National Laboratory.

New Drilling Fluids Prepared for High-Temperature Drilling

—In rotary drilling operations for oil or natural gas, a drilling fluid or mud is pumped down the drill string, through the drill bit, and back to the surface around the outside of the drill pipe, through the annulus. A drilling fluid removes cuttings; lubricates and cools the drill bit; seals permeable formations; suspends solids even when drilling (and consequently fluid flow) is halted; and controls subsurface pressure to prevent formation damage as well as blow out. The mud must have a high viscosity to suspend solids, and this is usually attained by thickening a base fluid, such as water or oil. Since fluid properties change during drilling due to the incorporation of drilled solids and formation fluids, one must have the ability to alter rheological properties with the help of additives. A drilling fluid must be low cost, nontoxic, and stable during drilling.

Two main categories of drilling fluids are water-based (brines or muds) or oil-based (oil-dispersions or invert-emulsions). Water-based fluids or muds are more common and relatively less expensive. However, they are suitable only for relatively low temperature and pressure drilling operations. For high temperature and high pressure (HTHP) drilling, oil-based fluids or muds are more suitable and use diesel, mineral oil, or a linear paraffin as the base fluid.

NETL-Regional University Alliance (NETL-RUA) researchers completed an experimental study using nanoparticles to prepare model drilling fluids for HTHP applications. Invert emulsions are used to drill for oil and gas when good wellbore stability and high-temperature tolerance are required. These drilling fluids contain a solid phase and two immiscible liquid phases stabilized with a polymeric surfactant.

In ultra-deep drilling, due to high temperature, the surfactant degrades causing phase separation. The use of a combination of hydrophobic nanoparticles and organically modified nanoclay results in stable water-in-oil invert emulsion model drilling fluids. These gel-like fluids have the desired plastic viscosity and yield stress suitable for HTHP drilling applications. Testing showed that the nanoparticle-stabilized emulsions remain stable with only small changes in rheological properties. This study showed that nanoparticles can be used to prepare stable drilling fluids, which have the potential to be used in HTHP drilling operations. This study was published in The *Canadian Journal of Chemical Engineering*, vol. 91, pp. 1641-1649 (2013).

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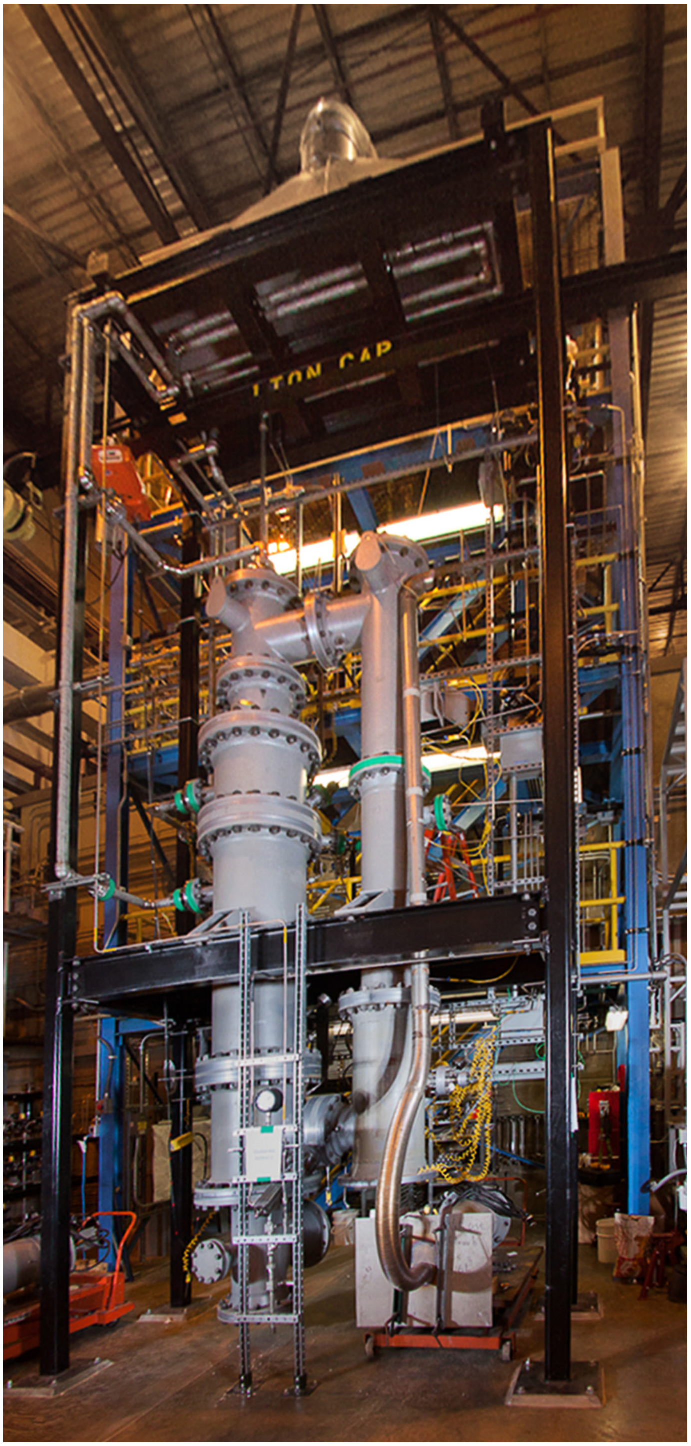


NETL's Chemical Looping Reactor.

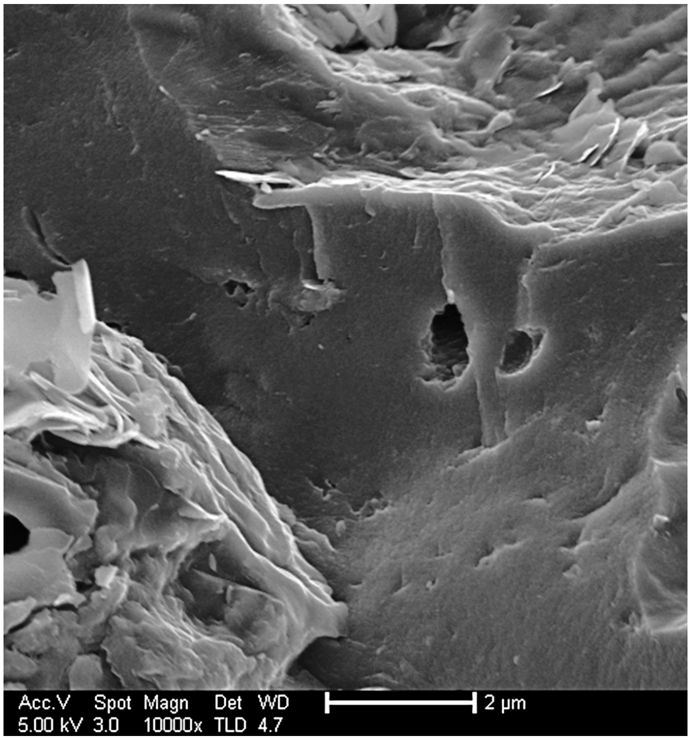
Oxygen Carrier Successfully Prepared at Commercial Scale—A commercial-scale batch of a magnesium oxide (MgO)-promoted hematite oxygen carrier developed at NETL has been successfully prepared at NexTech Materials in Lewis Center, Ohio. Development of efficient oxygen carriers is essential to advance chemical looping combustion (CLC), a potential pathway to emissions-free fossil energy. Natural minerals such as hematite, an iron-oxide mineral, have been evaluated for methane CLC, but the reaction rates are not sufficient for development of a commercial process. Incorporation of MgO into natural hematite strongly modifies the reduction behavior in comparison to MgO and hematite alone.

Fixed-bed and fluidized-bed reactor data show that incorporation of 5 percent MgO with 95 percent hematite doubles the oxygen-transfer capacity of hematite and increases the global reaction rate by a factor of five.

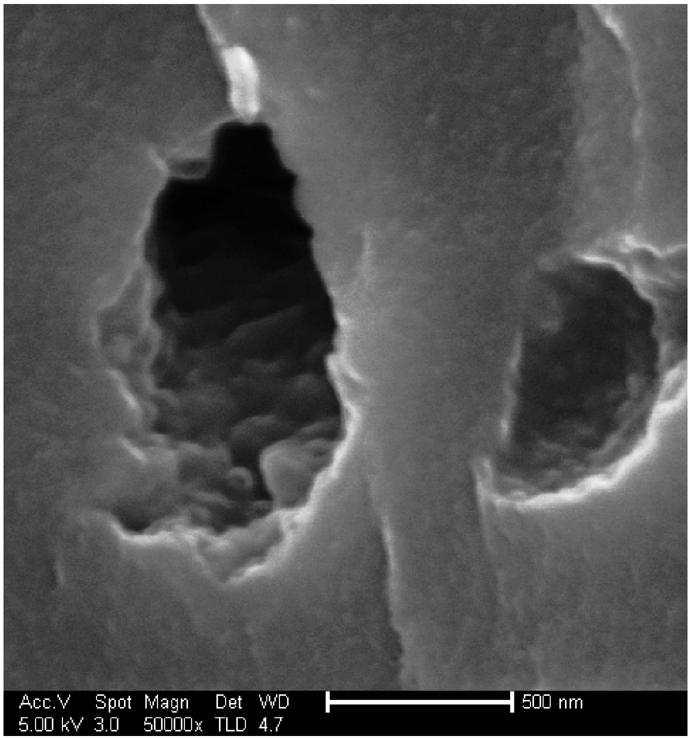
NETL researchers worked with NexTech to successfully scale-up its lab procedure and produce a 400-pound batch of the promoted hematite suitable for testing in fluidized beds. The commercial batch has reactivity similar to that of the lab-scale preparation, and its attrition resistance is superior to that of commercial fluid-bed cracking catalysts. The material will be tested in NETL's pilot-scale 50-kilowatt chemical looping reactor. A U.S. patent application has been submitted for this oxygen carrier.

Information about NETL's chemical looping program is available here.

Contact: Ranjani Siriwardane, 304-285-4513



SEM image of submicron-size coal pores at 10,000x.

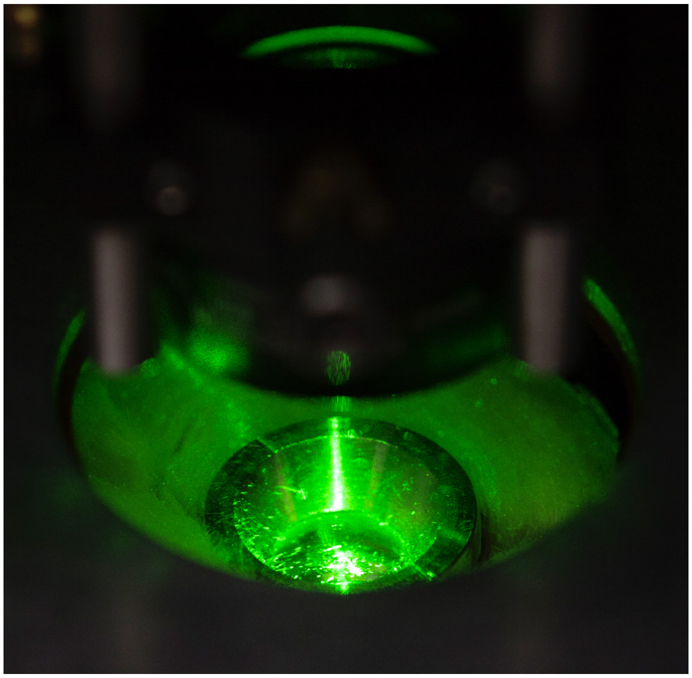


SEM close-up of coal pores at 50,000x.

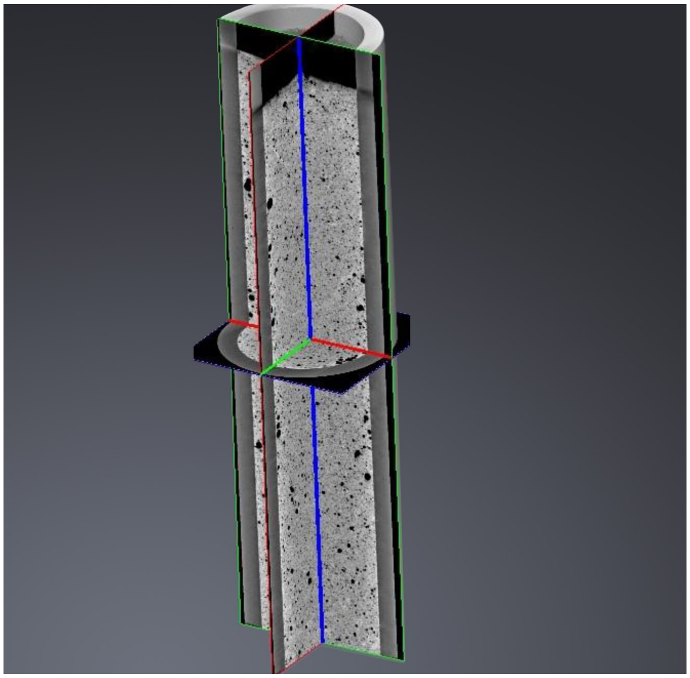
Coal Characterization Study Selected for Energy Sector Series—Using high-resolution, field-emission scanning electron microscopy (SEM), and by applying a novel relocation technique to locate surface features of the unconfined coal cores, NETL researchers have examined the solvent and swelling effects of supercritical CO_2 on coal structure and porosity. Submicron size pores were imaged and then precisely relocated after supercritical CO_2 exposure to investigate any irreversible CO_2 induced alterations or structural changes due to the solvent or swelling properties of CO_2. This relocation process is the first documented of its kind to study coal pore structure at high resolution. Their results also indicate that changes on the macropore scale, if any, are reversible and do not permanently impact the coal macropores.

The work, "Characterization of coal before and after supercritical CO_2 exposure via feature relocation using field-emission scanning electron microscopy," was published in *Fuel* (2013, 107, 777-786). This article was also selected as being of special interest to the energy sector by the Renewable Energy Global Innovations Series. The Series *"... alerts the scientific community to breaking journal articles considered to be of importance to the progress in renewable energy technologies.... Publications featured by Renewable Energy Global Innovations gain extensive exposure that help advance the implementation of new and promising renewable energy technologies."*

Contacts: Angela Goodman, 412-386-4962, and Barbara Kutchko, 412-386-5149



NETL's Raman gas sensor.



3D CT-Scans of 1-inch cement core.

New Raman Gas Sensor Technology Measures Fuel Gas

—An NETL patent application titled "Gas Sensing System Employing Raman Scattering" has recently been accepted. The Raman Gas Sensor technology was invented jointly by researchers at the University of Pittsburgh and NETL under the NETL-Regional University Alliance program. The Raman Gas Sensor is capable of measuring all fuel gas species plus H_2, N_2, O_2, and H_2O simultaneously and continuously in less than 1 second. The gas sensor employs the use of Raman spectroscopy and a unique signal-intensifying capillary tube to quantitatively measure these gases.

This level of performance and rapid response resulting from the high signal-to-noise ratio enables the sensor to be used in a feed-forward configuration for gas turbine and reciprocating engine control systems to determine fuel composition before the fuel arrives in the combustion chamber. The sensor also has potential applications in wellhead sensing and in many areas of the chemical industry for continuous monitoring. The patent has been exclusively licensed by an instrument manufacturer, and sales are expected to commence within a 3-year timeframe.

Contact: Steven Woodruff, 304-285-4175; and Michael Buric, 304-285-2052

NETL Studies Foamed Cement to Help Stabilize Oil and Gas Wells

—In oil and gas well drilling, a steel casing is inserted into the wellbore and cemented in place to create a barrier between well fluids (oil or gas) being produced from the well and shallower rock formations, isolating the fluids from the environment. The cement, which is pumped into the space between the steel casing and the rock, also supports and stabilizes the casing. If the well is drilled through weak, porous, or highly fractured rock, cement can leak into the rock before it solidifies. This situation can lead not only to a loss of cement but to cracked or collapsed cement, creating a path through which the oil and gas can easily flow to the surface into drinking water aquifers and even into the ocean in deepwater drilling environments. In rare but extreme cases, a blowout of high-pressure gas or oil can result causing injuries, environmental damage, and property losses.

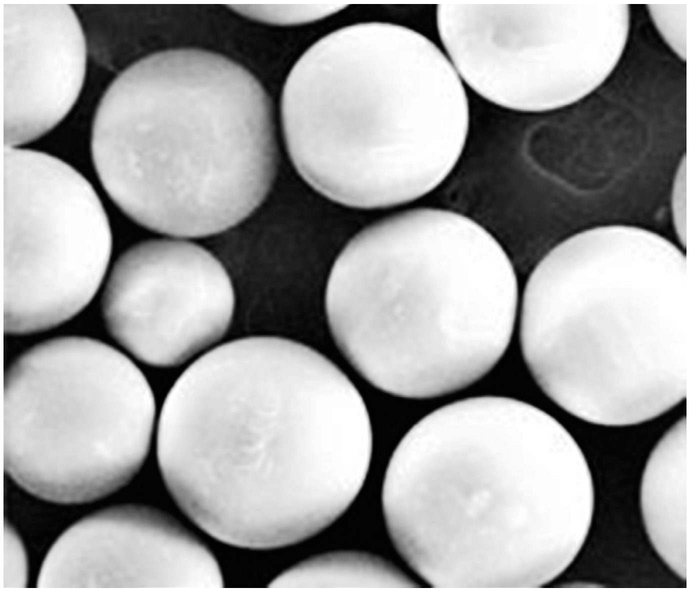
Low-density, foamed cements—cements containing microscopic bubbles of nitrogen or air—have been developed for wells where the rock is too weak to support conventional cement. Foamed cement is better able to withstand the temperature- and pressure-induced stresses common in these wells and provides a more reliable seal. To have the greatest strength and effectiveness, the gas in the cement must be evenly distributed.

NETL researchers are studying the physical properties of foamed cement under wellbore conditions to understand how they can be modified to lower the risk of spills.

Dr. Barbara Kutchko, who leads the research team, is using a computed tomography (CT) scanner to generate data and images of cements containing various amounts of air or nitrogen, at atmospheric and wellbore pressures. Just as in a medical procedure, the CT scanner produces and combines cross-sectional x-ray images to create a 3D view of the cements. The tests will help scientists and oil and gas companies understand the effects that cement production and placement have on the effectiveness of isolation of well fluids (oil and gas) from the environment.

A fact sheet is available describing our foamed wellbore cement deep water program.

Contact: Barbara Kutchko, 412-386-5149



BIAS sorbent pellets.

NETL Researchers Provide New Sorbent for Commercializing CO_2 Capture Process

—A recent NETL patent titled "Regenerable Solid Imine Sorbents" offers a new sorbent to test for commercializing an NETL-developed process to capture CO_2 from large-scale, fossil fuel-burning power plants. This process, called the Basic Immobilized Amine Sorbent (BIAS) process, uses regenerable, solid sorbents to capture CO_2 for permanent storage underground. The sorbent selectively reacts with CO_2 to extract it from the flue gas and is then heated to release the CO_2 for storage, thereby regenerating the sorbent for reuse. Inventors include McMahan Gray, Kenneth Champagne, and Daniel Fauth of NETL, along with a non-NETL inventor, Eric Beckman.

The R&D 100 Award-winning BIAS process was selected by the Electric Power Research Institute (EPRI) for screening in a micro-particle carbon dioxide capture process, which will evaluate the performance of various micro-particle media for use in a larger-scale commercial process. A five-kilogram BIAS was prepared by PQ Inc. and forwarded to EPRI for testing, and results are expected to be reported within the next six months. A positive outcome to the BIAS testing in EPRI's micro-particle capture process could lead to commercialization of this patented sorbent.

Contact: McMahan Gray, 412-386-4826

Recent NETL Publications

1.	Natesakhawat, Sittichai; Ohodnicki, Paul R., Jr.; Howard, Bret H.; et al. December 2013. Adsorption and Deactivation Characteristics of Cu/ZnO-Based Catalysts for Methanol Synthesis from Carbon Dioxide, *Topics in Catalysis,* 56, (18-20) SI, 1752-1763.
2.	Syamlal, Madhava; Benyahia, Sofiane. November 20, 2013. High-Resolution Methods for Preserving the Sum of Mass Fractions: Improved *X*-Scheme and an Alternative, *Int. J. Numerical Methods in Fluids*, 73 (8) 750-764.
3.	Bhavsar, Saurabh; Veser, Goetz. November 6, 2013. Bimetallic Fe-Ni Oxygen Carriers for Chemical Looping Combustion, *Industrial & Eng. Chemistry Research*, 52 (44) 15342-15352.
4.	Nielsen, Benjamin; Dogan, Omer N.; Howard, Bret H. November 2013. Comparison of the Corrosion of $Cu_{50}Pd_{50}$ and $Cu_{50}Pd_{44}M_6$ (M = Y, Mg or Al) Hydrogen Separation Membrane Alloys in Simulated Syngas Containing H_2S, *Corrosion Science*, 76, 170-181.
5.	Briggs, Brandon R.; Graw, Michael; Brodie, Eoin L.; et al. November 2013. Microbial Distributions Detected by an Oligonucleotide Microarray Across Geochemical Zones Associated with Methane in Marine Sediments from the Ulleung Basin, *Marine and Petroleum Geology*, 47, 147-154.
6.	Lawton, T.J.; Pushkarev, V.; Wei, D.; et al. October 31, 2013. Long Range Chiral Imprinting of C(110) by Tartaric Acid, *J. Phys. Chem.* C, 117 (43), 22290-22297.
7.	Li, Tingwen; Zhang, Yongmin. October 11, 2013. A New Model for Two-Dimensional Numerical Simulation of Pseudo-2D Gas-solids Fluidized Beds, *Chem. Eng. Sci.*, 102, 246-256.
8.	Alfonso, Dominic R. October 10, 2013. Further Theoretical Evidence for Hydrogen-Assisted CO Dissociation on Ru(0001), *J. Phys. Chem.* C, 117 (40) 20562-20571.
9.	Monazam, Esmail R.; Breault, Ronald W.; Siriwardane, Ranjani, et al. October 2013. Kinetics of the Reduction of Hematite (Fe_2O_3) by Methane (CH_4) During Chemical Looping Combustion: A Global Mechanism, *Chemical Engineering Journal*, 232, 478-487.
10.	Romanov, Vyacheslav N.; Hur, Tae-Bong; Fazio, James J.; et al. October 1, 2013. Comparison of High-Pressure CO_2 Sorption Isotherms on Central Appalachian and San Juan Basin Coals, *Intl. J. Coal Geology*, 118, 89-94.
11.	Monazam, Esmail R.; Breault, Ronald W.; Siriwardane, Ranjani, et al. October 2013. Thermogravimetric Analysis of Modified Hematite by Methane (CH_4) for Chemical-Looping Combustion: A Global Mechanism, *Ind. & Eng. Chem. Research*, 52 (42) 14808-14816.
12.	Baled, Hseen O.; Tapriyal, Deepak; Morreale, Bryan D.; et al. October 2013. Exploratory Characterization of a Perfluoropolyether Oil as a Possible Viscosity Standard at Deepwater Production Conditions of 533 K and 241 MPa, *Intl. J. Thermophysics*, 34 (10) 1845-1864.
13.	Pezzini, Paolo; Tucker, David, Traverso, Alberto. October 2013. Avoiding Compressor Surge During Emergency Shutdown Hybrid Turbine Systems, *J. Engineering for Gas Turbines and Power-Transactions of the ASME*, 135 (10) Article No. 102602.

Recent NETL Publications

14.	Cha, Jong-Ho; Seol, Yongkoo. October 2013. Increasing Gas Hydrate Formation Temperature for Desalination of High Salinity Produced Water with Secondary Guests, *ACS Sustainable Chemistry & Engineering*, 1 (10) 1218-1224.
15.	Li, Tingwen; Benyahia, Sofiane. October 2013. Evaluation of Wall Boundary Condition Parameters for Gas-Solids Fluidized Bed Simulations, *AIChE Journal,* 59 (10) 3624-3632.
16.	Gibson, LaTosha M.; Gopalan, Balaji; Pisupati, Sarma V.; et al. October 2013. Image Analysis Measurements of Particle Coefficient of Restitution for Coal Gasification Applications, *Powder Technology*, 247, 30-43.
17.	Agarwal, Sushant; Phuoc, Tran X.; Soong, Yee; et al. October 2013. Nanoparticle-Stabilised Invert Emulsion Drilling Fluids for Deep-Hole Drilling of Oil and Gas, *Canadian J. Chemical Engineering*, 91 (10) 1641-1649.
18.	Yang, Hyunjin; Aubry, Nadine; Massoudi, Mehrdad. September 30, 2013. Heat Transfer in Granular Materials; Effects of Nonlinear Heat Conduction and Viscous Dissipation, *Mathematical Methods in the Applied Sciences*, 36 (14) 1947-1964.
19.	Brant, A.T.; Giles, N.C.; Yang, Shan; et al. September 21, 2013. Ground State of the Singly Ionized Oxygen Vacancy in Rutile TiO_2, *J. Applied Physics*, 114 (11) Article No. 113702.
20.	Parthasarathy, Hariprasad; Dzombak, David A.; Karamalidis, Athanasios K. September 16, 2013. A Small-Scale Flow-Through Column System to Determine the Rates of Mineral Dissolution at High Temperature and Pressure, *Chemical Geology*, 354, 65-72.
21.	Guo Hai-Chao; Shi Fan; Ma Zheng-Fei; et al. September 2013. Molecular Simulations of Adsorption and Separation of Natural Gas on Zeolitic Imidazolate Frameworks, *Acta Physica Sinica*, 62 (17) 176802.
22.	Wu, Wei-Tao; Aubry, Nadine; Massoudi, Mehrdad. September 2013. Flow of Granular Materials Modeled as a Non-Linear Fluid, *Mechanics Research Communications*, 52, 62-68.
23.	Rubin, Edward S.; Short, Christopher: Booras, George; et al. September 2013. A Proposed Methodology for CO_2 Capture and Storage Cost Estimates, *AIChE Journal, 59* (9) 3247-3264.
24.	Rangarajan, Deepak; Curtis, Jennifer S.; Benyahia, Sofiane, et al. September 2013. Continuum Model Validation of Gas Jet Plume Injection Into a Gas-Solid Bubbling Fluidized Bed, *AIChE Journal, 59* (9) 3247-3264.

Patents Issued This Quarter

1.	Active Combustion Flow Modulation Valve. Jimmy D. Thornton (NETL), J. Peter Hensel (NETL), Nathaniel Black (University of Pittsburgh), Jeffrey Vipperman, David Lambeth, William Clark; **8,540,209**, issued September 24, 2013.
2.	Transpiration Purging Access Probe for Particulate Laden or Transpiration Purging Access Probe for Particulate Laden or Hazardous Environments. John Van Osdol; **8,596,798,** issued December 13, 2013.
3.	Method of Producing An Oxide Dispersion Strengthened Coating and Microchannels; Mary Anne Alvin (NETL); Minking Chyu (University of Pittsburgh); Brian Gleeson (University of Pittsburgh); Bruce Kang (West Virginia University); **8,609,187**, issued December 17, 2013.
4.	Cu-Pd-M Hydrogen Separation Membranes. Omer N. Dogan (NETL); Michael C Gao (URS); Rongxiang Hu (URS); De Nyago Tafen (URS); **8,608,829**, issued December 17, 2013.
5.	Minimization of Steam Requirements and Enhancement of Water-Gas Shift Reaction With Warm Gas Temperature CO_2 Removal; Ranjani V. Siriwardane (NETL); James Fisher, II (URS); **8,617,499**, issued December 31, 2013.

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