R & D

# facts

U.S. Department of Energy
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Carbon Sequestration

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## Carbon Dioxide Storage in Coal Seams


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### Background

The Department of Energy's (DOE) National Energy Technology Laboratory (NETL) is engaged in a broad research and development (R&D) effort to develop and assess technology that will be used to safely and reliably store carbon dioxide ($CO_2$) in coal seams, oil reservoirs, and saline formations, and to monitor sequestration effectiveness.

The following three tasks of this project address the storage capacity of coal seams and the trapping mechanism in which $CO_2$ is stored in the coal seam:

- **Task 1:** Explore coal structure changes under $CO_2$ sequestration conditions via scanning electron microscopy (SEM).
- **Task 2:** Probe the direct physical and chemical interaction of $CO_2$ sorption on coals provided by field projects using in situ infrared spectroscopy.
- **Task 3:** Conduct the gravimetric-volumetric analysis of coal swelling and shrinking at high $CO_2$ pressures.

### Description

#### Task 1

The results of attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy results suggest that the coal undergoes a structure rearrangement in the presence of $CO_2$. If this is true, the data obtained using fresh (unexposed to $CO_2$) coal samples may likely be irrelevant to $CO_2$ sequestration because exposure to $CO_2$ may induce structure changes and the coal may be different before and after the initial $CO_2$ exposure. The ATR-FTIR measurements provide an indirect measurement of this structure rearrangement. NETL plans to use SEM to directly study the rearrangement of the coal. This information will be valuable for predicting what will happen to the coal seam when $CO_2$ is injected for long-term storage.

### Task 2

The results of the interlaboratory comparison of the $CO_2$-coal sorption isotherm have suggested that the reproducibility of $CO_2$-coal isotherm is within 30 percent in the subcritical regime of pressures up to 8 MPa (orders of magnitude). However, once the supercritical boundary is crossed, the sorption isotherms begin to deviate substantially. We plan to use ATR-FTIR to study the interaction between $CO_2$ and coals in the supercritical regime while constructing a sorption isotherm. The isotherm in the supercritical regime is important especially when deep, unmineable coal seams are targeted for carbon storage purposes. The isotherm must be understood well enough to have reliable predictive value; otherwise the $CO_2$ storage capacity of potential candidate coal seams must be measured experimentally. This redundancy needs to be addressed

### Task 3

The interaction between $CO_2$ and coals provides a thermodynamic driving force for $CO_2$ dissolution in coals. $CO_2$ dissolves in coals and swells them at higher pressures. This must be understood well enough to have reliable predictive value; otherwise the $CO_2$ storage capacity of each potential candidate coal seam must be measured experimentally. Without knowing the swelling amount, accurate measurements of $CO_2$ sorption by coals are not possible. Traditional experimental methods do not account for the related changes in void volume. New methods should be developed to account for swelling and shrinking of coal in response to sorption. The study should address how the $CO_2$-coal interactions change with coal rank and maceral type and how they affect the structural changes in the $CO_2$-coal system.

## Primary Project Goal

The project will address the trapping mechanism and storage capacity for $CO_2$ storage in coal seams. The project will also provide insight into how coal swelling may restrict flow of $CO_2$ into coal seams and suggest injection techniques that will enhance $CO_2$ contact within the coal seam.

This project supports the Carbon Sequestration Program's Goals of demonstrating the ability to predict $CO_2$ storage capacity with +/-30 percent accuracy by 2012. The tasks will also help to develop an understanding of trapping mechanism for coal seams and target unmineable coal seams (those too deep and too thin to be mined economically), aid in providing an improved understanding of coal properties and their changes with $CO_2$ sorption under reservoir conditions, and improve predictive modeling capability for $CO_2$ injection in coals.

## Objectives

- **Task 1 –** To explore coal structure changes that occur when coals are exposed to $CO_2$. Data obtained using fresh (unexposed to $CO_2$) coal samples may likely be irrelevant to $CO_2$ sequestration because exposure to $CO_2$ may induce structure changes and the coal may be different before and after the initial $CO_2$ exposure.

- **Task 2** – To measure $CO_2$ sorption isotherms on coals at pressure greater than 8 MPa. Special effort will be made to measure $CO_2$ sorption on field site samples. This data is necessary for estimating coal seam capacity for $CO_2$ and isotherms needed to model in $CO_2$-coal uptake and permeability.

- **Task 3 –** To provide accurate storage capacity estimates for non-rigid materials by measuring swelling of the samples in situ with combined volumetric and gravimetric techniques.

## Benefits

The project has resulted in development of a new theory of coal swelling and how the $CO_2$ adsorption process affects swelling. It will provide guidelines for both efficient sequestration of carbon dioxide in coal seams and enhanced methane production. Through a better understanding of the fundamental chemistry involved in the $CO_2$ adsorption/methane ($CH_4$) desorption process, it will be possible to select optimum conditions for $CO_2$-enhanced coalbed methane production/ sequestration. The enhanced methane production associated with $CO_2$ sequestration will help to defray sequestration costs. Additionally, capturing carbon dioxide and sequestering it will prevent harmful emissions into the atmosphere that may further increase global warming.

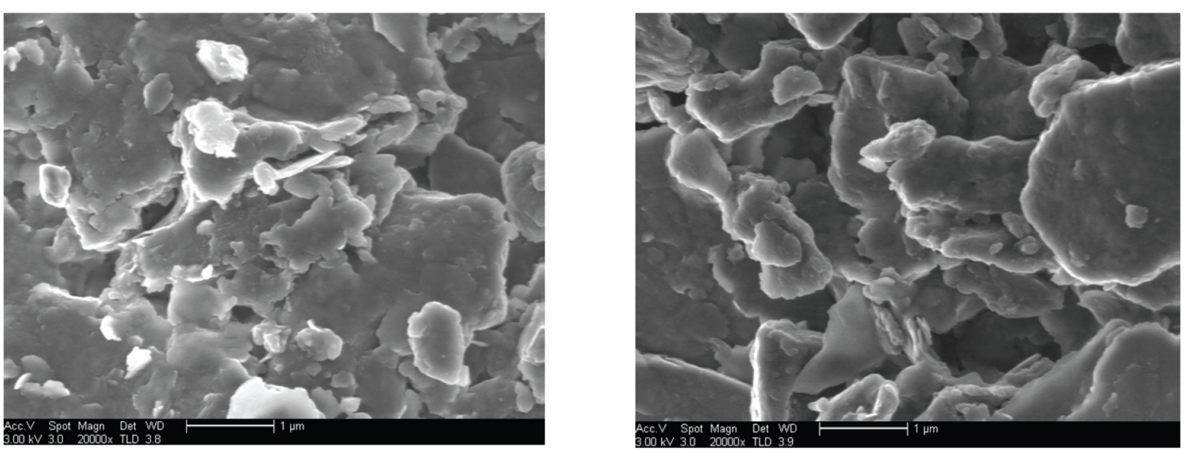
## Accomplishments

### Task 1

Preliminary measurements with SEM on powdered coals have been collected (see figures below). The SEM images suggest that the surface area of the coals has increased upon $CO_2$ exposure. We plan to continue the measurements with chunk coals to simulate intact coal that would be found in a coal seam.

### Task 2

Sorption isotherms, which describe the coal's gas storage capacity, are important for estimating the carbon sequestration potential of coal seams. Sorption isotherms will be measured with a new ATR-FTIR spectroscopic cell purchased for the Pittsburgh NETL campus. This cell is similar to the one described in the ACS journal, Journal of Physical Chemistry B 2002, 106,754-759, where supercritical interactions on polymers are discussed.




Before $CO_2$ exposure　　　After $CO_2$ exposure

*Figure 1. SEM images of coal powder. Left side: coal before $CO_2$ exposure. Right side: Coal exposed to 1400 psig $CO_2$ at 40 °C.*

Current measurements for $CO_2$ interactions with coal samples from the Argonne National Laboratory's premium coal bank, field samples, and activated carbon at pressures up to 20 MPa are in progress.

## Task 3

NETL has developed an R&D framework for improving conventional geo-mechanical approaches to modeling carbon sequestration in coal beds by taking into account coal properties at the macromolecular level. The framework accomplishes this by incorporation of the local porosity changes driven by macromolecular thermodynamics of plastic deformations. The model of sorption-induced coal swelling, published in the ACS journal (Romanov, 2007), serves to provide a new direction for those modelers who are interested in the predictive rather than correlative power of their models. The proposed strain-volume fraction relationship for osmotically driven network relaxation offers a direct way of taking into account the molecular level interactions and incorporating them into the geomechanical models. Improved modeling could avoid costly and unexpected problems, such as coal swelling around injectors and reduced injection efficiency that can stall or even terminate site development.

Many types of materials (polymer, coal, clay, etc.) change their volume and structure after absorption of gaseous and liquid substances. Various types of volume changes affect the accuracy of sorption measurements by two major methods – gravimetric and manometric. NETL onsite researchers investigated the errors associated with the volumetric effects, specifically, the case of carbon dioxide sorption on coal. It was demonstrated that the resulting error in buoyancy correction in the gravimetric method is equivalent to the corresponding error in assumed void volume in the manometric method. With a volumetric apparatus, the coal swelling will change the ratio of container volume to sample volume, thus introducing error. In a gravimetric apparatus, coal swelling will alter the buoyancy of the sample, thus introducing error. Data on coal swelling as a function of $CO_2$ pressure are needed. Once obtained, they can be used to correct the published $CO_2$ sorption data. If the molar volume of the $CO_2$ dissolved in coals can also be measured, a complete picture of $CO_2$ on and in coals can be assembled. The study suggests that the integration of the two methods, combined with the binary gas mixture technique of in situ volume measurement, will dramatically improve the accuracy of sorption measurements for materials such as coal and clay.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