



## CARBON DIOXIDE STORAGE IN COAL SEAMS

### Background

The following four tasks address the storage capacity of coal seams and the trapping mechanism in which CO<sub>2</sub> is stored in the coal seam:

- **Task 1:** Inter-laboratory comparison of CO<sub>2</sub> adsorption isotherms
- **Task 2:** Infrared study of CO<sub>2</sub> sorption on coal
- **Task 3:** Dilatometry and manipulation of coal sorption capacity by CO<sub>2</sub> pressure cycling
- **Task 4:** Gravimetric-volumetric method of measurement of CO<sub>2</sub> adsorption on coal

### Task 1

It is important to ensure that information obtained from adsorption isotherms will be useful for assessing the technical feasibility of CO<sub>2</sub> sequestration in coal seams. The specific area of interest is the comparison of adsorption isotherm data obtained in various laboratories. Inter-lab precision is needed to ensure that any differences in results obtained from different laboratories are due to physical phenomenon and not to the details of the analysis procedure itself. The comparison of value from one lab to another is confounded not only by differences in coal samples and experimental methods but also by a lack of knowledge of what reproducibility can be expected between two labs with the same sample and under the same conditions.

### Task 2

To create models that will accurately describe the behavior of both the CO<sub>2</sub> and coal when CO<sub>2</sub> is injected into coal seams, the interactions between CO<sub>2</sub> and coal must be understood at a level that allows their prediction for coals of different rank and type. One reason is that these interactions in part govern how much CO<sub>2</sub> will be sorbed by coal and thus are needed to calculate the seam's capacity to hold CO<sub>2</sub>. The interaction between CO<sub>2</sub> and coal provides a thermodynamic driving force for CO<sub>2</sub> dissolution in coals, making it important to understand how the interactions change with coal rank and maceral type. This must be understood well enough to have reliable predictive value; otherwise the CO<sub>2</sub> storage capacity of potential candidate coal seams must be measured experimentally in order to select the best.



### **Task 3**

At high pressure, CO<sub>2</sub> dissolves in coal, causing swelling and changes in physical properties, such as hardness. This must be understood before large-scale injections of CO<sub>2</sub> can be performed. When carbon dioxide dissolves in coal, it works as a plasticizer that makes coal softer and more deformable. Its interactions with coal determine its success as a plasticizer and therefore must be understood at a level that allows for accurate predictions. If this cannot be done, swelling and plastization will have to be measured for all candidate coals which is a massive and expensive undertaking because the softening and swelling affect pumping rates of CO<sub>2</sub> into coal, which impacts the design of CBM recovery and CO<sub>2</sub> sequestration systems. In cases of extreme softening, there may be geological consequences. The long-term solubility of CO<sub>2</sub> in coals may be reduced if the softened coals undergo a known structure rearrangement and affect the coal's ability to retain CO<sub>2</sub>.

When coals swell, cleats and cracks in coal are pushed closed reducing the flow rates of CO<sub>2</sub> into the coal. The closure and drop in flow rate must be part of the models used to design ECBM well placement and CO<sub>2</sub> sequestration injection well placement. To build the necessary predictive capability into the models, both coal swelling and softening must be predicted which requires fundamental knowledge of how CO<sub>2</sub> and coal interact. In addition, swelling and softening measurements must be made on a variety of coals to provide a data set to validate the models' predictions.

### **Task 4**

In order to be sequestered into coal seams, CO<sub>2</sub> has to be in a supercritical state (above 32 °C, 7.4 MPa). However, only recently have there been any studies of the extent of adsorption of supercritical carbon dioxide by coal. Physical properties of coal may be anisotropically altered by carbon dioxide, or the acidic solution in water may react with the organic or mineral matter present in the coal matrix. Coal is also known to swell in the presence of CO<sub>2</sub>, which may be significant with respect to interpreting data. All traditional methods assume homogeneous properties of the sorbate and constant volume of the sample; usually limited to single gas adsorption.

There are two main methods currently employed for measuring isotherms on coal: volumetric/manometric and gravimetric techniques. In either gravimetric or volumetric apparatus, swelling of the coal sample and the corresponding volume changes cannot be directly measured during the test. The combination of the volumetric and gravimetric techniques, on the other hand, utilizes the advantages of both and gives a very accurate direct method of adsorption measurement.

## **Primary Project Goal**

The project will address the trapping mechanism and storage capacity for CO<sub>2</sub> storage in coal seams. The project will also provide insight into how coal swelling may restrict flow of CO<sub>2</sub> into coal seams and suggest injection techniques that will enhance CO<sub>2</sub> contact within the coal seam.

## **Objectives**

- **Task 1** - To ensure information obtained from laboratory-measured sorption isotherms will be useful for assessing the technical feasibility of CO<sub>2</sub> sequestration in coal-seams. The data obtained in the project could also provide the basis for an ASTM or ASTM-like laboratory method when coal seam sequestration becomes commercial.
- **Task 2** - To address the CO<sub>2</sub>-coal storage capacity at pressures up to 15 MPa and better understand the CO<sub>2</sub>-coal trapping mechanism.
- **Task 3** - To understand softening and swelling of coal under conditions relevant to carbon sequestration.
- **Task 4** - To obtain information for accurate estimates of CO<sub>2</sub> sorption by coal and to develop a model to generate adsorption isotherms via numerical techniques established for data analysis.

## Accomplishments

### Task 1

An inter-laboratory study comparing the CO<sub>2</sub> adsorption isotherms on moisture equilibrated Argonne coals is in progress. Seven participants located throughout the world have volunteered to participate in this study. All labs determined the isotherms for moisture-equilibrated Argonne coals (Pocahontas #3; Illinois #6; and Beulah Zap) using their own apparatus at 55 °C and pressures up to 13 MPa. The coals were moisture-equilibrated according to a revised version of the ASTM D 1412 standard method for moisture equilibration.

### Task 2

Carbon dioxide is a good plasticizer for many coals. Exposure to CO<sub>2</sub> gas changes subsequent CO<sub>2</sub> diffusion rates, CO<sub>2</sub> adsorption isotherms, and CO<sub>2</sub> solubility. The measurement on a single coal sample of sequential adsorption isotherms, of sequential diffusion rates measured, or sequential measurements of CO<sub>2</sub> may be affected by changes in the coal structure, caused by the initial exposure of the coal to CO<sub>2</sub>. After Pittsburgh No. 8 coal has been exposed once to CO<sub>2</sub> at 55 °C and 0.35 MPa, subsequent CO<sub>2</sub> sorption is much faster than the initial uptake and the amount of CO<sub>2</sub> sorbed increases (See Figure 1). Therefore, exposure of Pittsburgh No. 8 coal to CO<sub>2</sub> under these conditions results in changes in coal physical structure. The sorption of CO<sub>2</sub> by Pittsburgh No. 8 coal was studied by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). For coals that rearrange, the information gained by studying fresh coals may not be useful to CO<sub>2</sub> sequestration because their structure will be different after exposure to CO<sub>2</sub>. It is necessary to gather data on coals already rearranged due to CO<sub>2</sub> exposure.

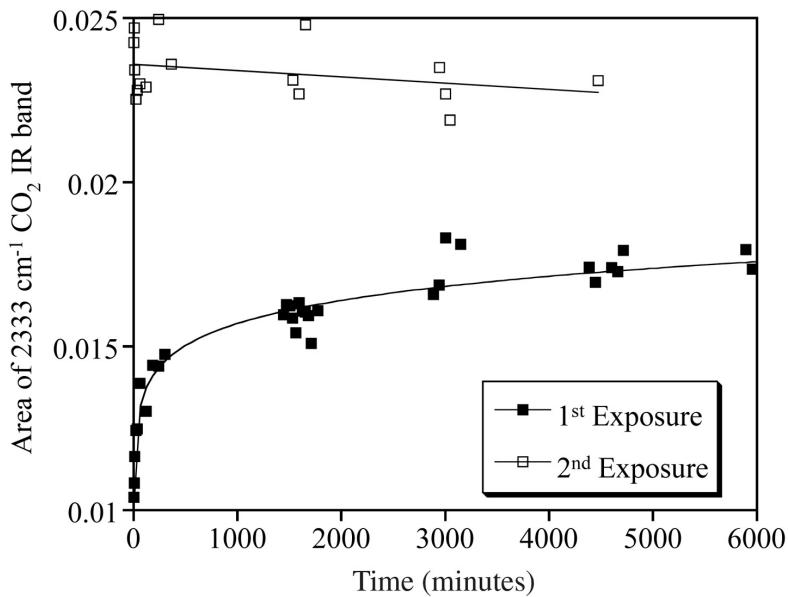


Figure 1. CO<sub>2</sub> sorption causes coal structure to change for Pittsburgh No. 8 coal.

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## Task 3

A high pressure dilatometer has been refurbished to test coal swelling and softening in the presence of CO<sub>2</sub>.

## Task 4

NETL has developed a new method that allows one to obtain information on coal swelling *in situ* and improve the accuracy of the adsorption isotherm in the region of supercritical CO<sub>2</sub> (See Figure 2).

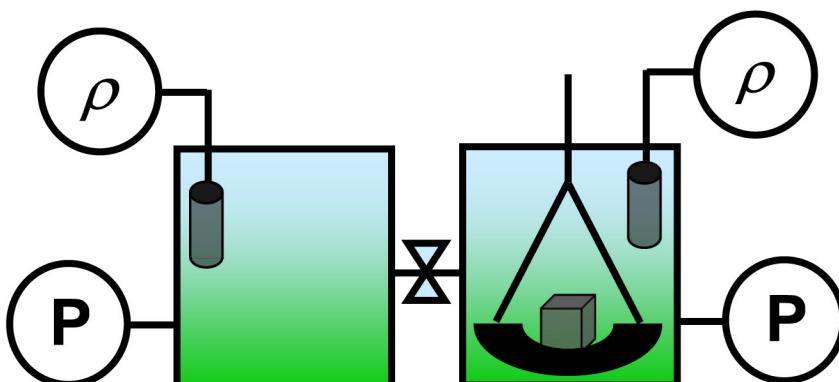


Figure 2. Adsorption isotherm unit.

By using the simultaneous pressure and density measurements one can determine the partial pressures of the two fluid components as long as their molar masses are very different.

## Benefits

The project has resulted in development of a new theory of coal swelling and how the CO<sub>2</sub> adsorption process affects swelling. It will provide guidelines for both efficient sequestration of carbon dioxide in coal seams and enhanced methane production. Through an understanding of the fundamental chemistry involved in the CO<sub>2</sub> adsorption / CH<sub>4</sub> desorption process, it will be possible to select optimum conditions for CO<sub>2</sub>-enhanced coalbed methane production / sequestration. The enhanced methane production associated with CO<sub>2</sub> sequestration will help to defray sequestration costs. Additionally, by capturing carbon dioxide and sequestering it, harmful emissions into the atmosphere that may further increase global warming are prevented.