Report Title: CO_2 Sequestration in Coalbed Methane Reservoirs: Experimental Studies and Computer Simulations

Type of Report: Final

Reporting Period Start Date: 9/20/2001

Reporting Period End Date: 11/30/2002

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Date Report Was Issued: 12/15/2002

DOE Award Number: DE-FG26-01NT41283

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ABSTRACT

One of the approaches suggested for sequestering CO_2 is by injecting it in coalbed methane (CBM) reservoirs. Despite its potential importance for CO_2 sequestration, to our knowledge, CO_2 injection in CBM reservoirs for the purpose of sequestration has not been widely studied. Furthermore, a key element missing in most of the existing studies is the comprehensive characterization of the CBM reservoir structure. CBM reservoirs are complex porous media, since in addition to their primary pore structure, generated during coal formation, they also contain a variety of fractures, which may potentially play a key role in CO_2 sequestration, as they generally provide high permeability flow paths for both CO_2 and CH_4. In this report we present an overview of our ongoing experimental and modeling efforts, which aim to investigate the injection, adsorption and sequestration of CO_2 in CBM reservoirs, the enhanced CH_4 production that results, as well as the main factors that affect the overall operation. We describe the various experimental techniques that we utilize, and discuss their range of application and the value of the data generated. We conclude with a brief overview of our modeling efforts aiming to close the knowledge gap and fill the need in this area.

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INTRODUCTION AND SCIENTIFIC DISCUSSION

CO₂ Sequestration: Fossil fuels, which supply over 85% of the world's energy needs, are also a major contributor to environmental pollution. They are, in particular, the main source of anthropogenic CO_2, the major player in the "Green House" effect. It is estimated that, if CO_2 emissions were to continue and grow, this will have far reaching environmental consequences for our planet. It is clear that the United States (the world's largest emitter of CO_2) and the rest of the industrialized world must develop new technologies for controlling and sequestering CO_2.

One of the approaches that have been suggested is injecting and sequestering the CO_2 in coalbed methane (CBM) reservoirs. In doing so one displaces the natural gas stored in these reservoirs, which can then be utilized as a clean form of energy. The advantage of this approach over other long-term storage/sequestration ideas is that the value of the natural gas produced may help to alleviate partly or in whole the CO_2 sequestration costs.

The Structure of CBM Reservoirs: During the conversion of plant materials into coal, gases were generated that were either adsorbed on the coal surface or dispersed in the pores around the coal seam. CH_4 is the major component (about 95%), the remaining gases being C_2H_6, CO_2, N_2, He, H_2, and H_2S. Most of the CB methane is in a sorbed state. Its amount is determined by the confining pressure and the surface area within the micropores, which is very large, ranging from 20 to 200 m^2/gr [1] implying that a CBM reservoir can produce much larger amounts of CH_4 than a conventional gas reservoir of comparable size at about the same temperature and pressure.

CBM reservoirs in addition to gas contain also large amounts of water, which is typically released during the maturation process. The moisture content of coal varies greatly dependent on the coal rank, from 75-90 % in peat, 30-50 % in lignite, 7-10% in high volatile bituminous, to 1-5 % in low-volatile bituminous. There are four different types of moisture found in coal [2].

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They include: (1) Free or adherent moisture, which is the moisture retained in a free state (not bonded to coal) in the pore structure of coal; (2) inherent or bed moisture, that is physically adsorbed in the micropores and capillaries; (3) chemically bound moisture, that is organically bound in the structure of coal; and (4) water of hydration, that is associated with the inorganic constituents of coal. Of these types of moisture the important one during CO_2 CBM reservoir sequestration is the adherent moisture, which affects gas permeability, and the inherent moisture, which interferes with gas adsorption.

Fractures play a fundamental role in CBM reservoirs, as they provide high permeability paths for CH_4 production. There are four different types of fractures found in such fields [3]. They include (i) faults and shear zones, (ii) extension and compression related joints, (iii) mining induced fractures, and (iv) the coal cleat system. Coal cleats play an important role during CBM CO_2 sequestration. Two different types of cleats are found in a coal sample, the primary cleats (otherwise also known as the face cleats) and the secondary cleats, known as the butt cleats. The *face* cleats control the flow of CH_4 to the production well and usually form an interconnected network, and the *butt* cleats control transport of gas from the micropores to the face cleats. Factors that determine cleat spacing is coal rank, petrographic composition, mineral matter content, and stress/strain history.

The displacement of CH_4 by CO_2 is the result of three processes (i) adsorption/desoprtion in the coal matrix, (ii) diffusion to the cleats, (iii) and flow through the cleats and the larger coal fractures. The coal matrix has a microporous structure with pores ranging for 0.4 nm to 2 nm and permeability of the order of microdarcy [4, 5]. The cleats on the other hand have permeability of the order of milidarcy About 90% of methane adsorbs in the matrix, with only 10 % adsorbed in the cleats. CH_4 production from CBM reservoirs is a two-step process: First, CH_4 must desorb

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from the pore surfaces, and second the gas (and water present) must flow through the fractures to the production well [6].

The Simulation of CBM Reservoirs: Conventional simulation of CH_4 production in CBM reservoirs uses double-porosity (DP) models [7], which consider production from a network of fractures embedded in a porous matrix. The flow to the production wells is assumed to occur only through the fracture network represented by a simple-cubic network. In reality, the fracture network and matrix in CBM reservoirs differ from these idealized models in many important ways: (1) As noted above fractures develop over a wide range of scales; (2) the pores of CBM reservoirs are so small that the conventional diffusion theory may not applicable; (3) the matrix may not be necessarily disconnected and isolated (as assumed in the DP model); (4) the fracture and pore networks have complex and multiscale structures. Recent success in modelling petroleum reservoirs using such multiscale models of fractures and pores [8, 9] suggests that the same approach can be used for modelling of CBM reservoirs.

Idealized CBM reservoir models typically fail to account for the swelling/deformation of the coal matrix, which occurs when CO_2 is injected in the reservoir, and which may result in the closure of some of the fractures. If the swelling continues, the reservoir may undergo further deformation, up to the point that the coal material may convert into a rubbery state. During CO_2 injection, a CBM reservoir can, thus, be found in three distinct states: (a) A rigid state, before CO_2 injection; (b) a semi-rigid state, in which some of the fractures have been closed; and (c) a rubbery state, when large amounts of CO_2 have been injected, with most of the fractures closed. Large deformation of CBM reservoir, caused by injection of CO_2, can be clearly detected in the laboratory by variations in effective permeability. At low pressures, and for small CO_2 amounts injected, the effective permeability is constant. However, as the pressure increases, and more

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CO_2 is injected, the permeability starts to vary with the pressure. In addition, there is a large hysteresis between adsorption and desorption.

Idealized models also fail to properly account for the phenomena that occur in the microporous region of the coal matrix. Experimental studies [10] with CO_2, CH_4, and N_2 indicate that the equilibrium gas and adsorbate phase compositions differ greatly. The most strongly adsorbed gas is CO_2, followed by CH_4 and N_2. It is widely believed that production of CH_4 occurs by single-phase desorption from the pores which are so small that do not allow the influx of water from the system of cleats. This gives rise to the phenomenon of hindered diffusion [11], in which a large molecule diffuses in a pore with a comparable size. For diffusion of a molecule with a hydrodynamic radius R_m in a pore of radius R_p, one has

$$\frac{D}{D_\infty} = f(\lambda), \tag{1}$$

where D is the effective diffusivity of the molecule, D_∞ its diffusivity in an unbounded fluid, $\lambda = R_m / R_p$, and f is a function which depends on the pore and molecular shapes. Despite the existence of such rigorous results, the standard approach to modeling transport in CB reservoirs is to assume that gas-phase transport occurs by a classical diffusion process.

THE PRELIMINARY RESULTS

The emphasis in this short-term (six months) project was on creating the needed infrastructure, and for developing a detailed plan for further experimental and modeling work; the latter plan is outlined in the "proposed additional work" section . This work was carried out collaboratively with Dr. Mark Knackstedt of the Research School of Australian National University and his team, who are assisting us with the High Resolution X-Ray CT (XRXCT) microimaging tests. Coal cores were kindly provided to us by Dr. David Morse of the Illinois

Geological Survey. There are key aspects in CBM CO_2 sequestration that still need to be investigated thoroughly in the laboratory. They include (i) understanding of the CBM core structure, (ii) its transport and sorption characteristics, and (iii) its behavior under CO_2 sequestration conditions. The techniques that we have developed and utilized to address these issues are described below:
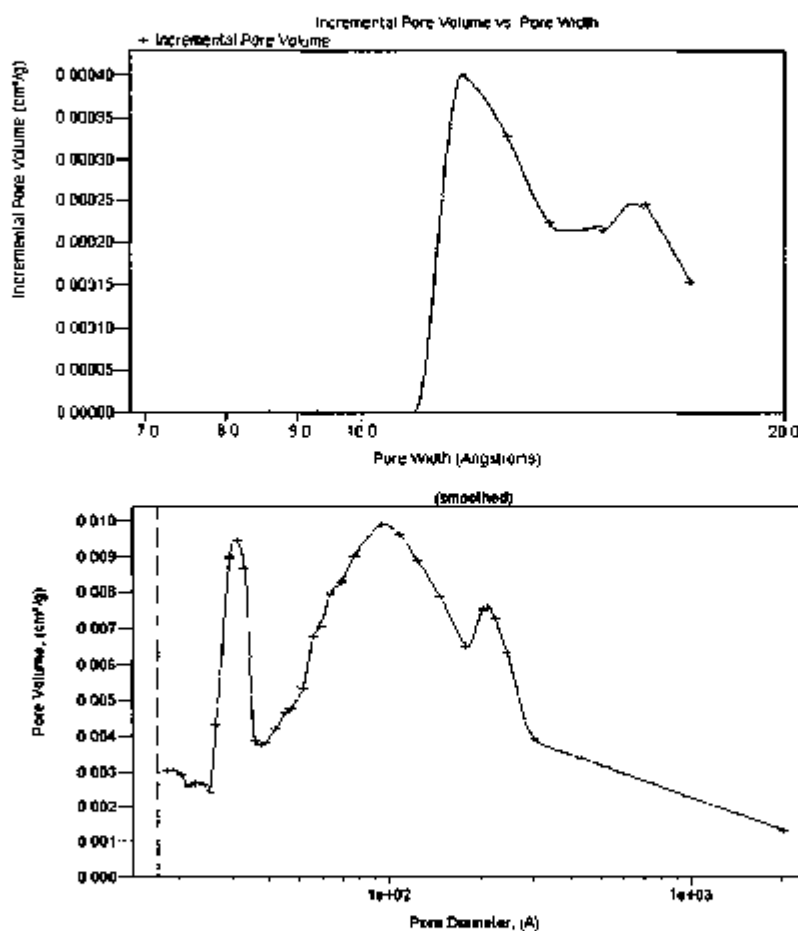
Understanding the CBM Core Structure: The challenge here is the multiple length scales characterizing the CBM coal structure. In the laboratory one can analyze up to the cleat length scale. Unfortunately, no technique can, alone, provide a complete characterization of the pore structure. We have utilized in this project three different techniques. They include:

1. Adsorptions of single probe gases. Two different probe gases are used in our investigations, namely N_2 at 77 K and CO_2 at 273 K. To analyze the pore size distribution (PSD) different techniques are utilized depending on the region of the pore space. Figure 1, for example shows the results of the PSD analysis for one of the core coal samples. Our sorption apparatus operates down to very low pressures, which allows to probe deep into the nanoporous region. This is important for CBM CO_2 sequestration, as most of the CH_4 is adsorbed in the nanoporous (< 2nm) region. Using CO_2 as a probe gas is important, as one would like to probe the nanoporous region potentially accessible by CO_2. N_2 adsorption gives the baseline PSD.

2. Flow perporometry: Though probe gas adsorption is the principal technique for characterizing the nanoporous and mesoporous region, its usefulness does not extend beyond the 1000 region. To characterize the structure beyond this pore size range we have made use of the technique of flow perporometry, which is a method used to measure the PSD of coal core samples. A thin (several mm) CBM core sample is fixed onto a metal ring and placed and sealed tightly in between two half-cells of the flow perporometry cell. Inert gas (He) is first pushed

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through the sample by pressurizing one of the chambers, while the other chamber is maintained at 1 atm; for a given pressure gradient the flow rate and corresponding pressure gradient are noted. The experiment is then repeated for a broad range of pressure gradients. The sample is then saturated with a wetting fluid (e.g., distilled water) and the experiment is repeated for the same range of pressure gradients. By comparing the gas flows at the various pressure drops the

Figure 1. PSD for coal core. Top figure nanoporous region using DFT analysis. Bottom, mesoporous/macroporous region using the BJH technique.

Sample's PSD can be deduced. Figure 2 below shows the PSD of the CBM sample whose nanoporous and mesoporous regions were analyzed in Fig. 1.
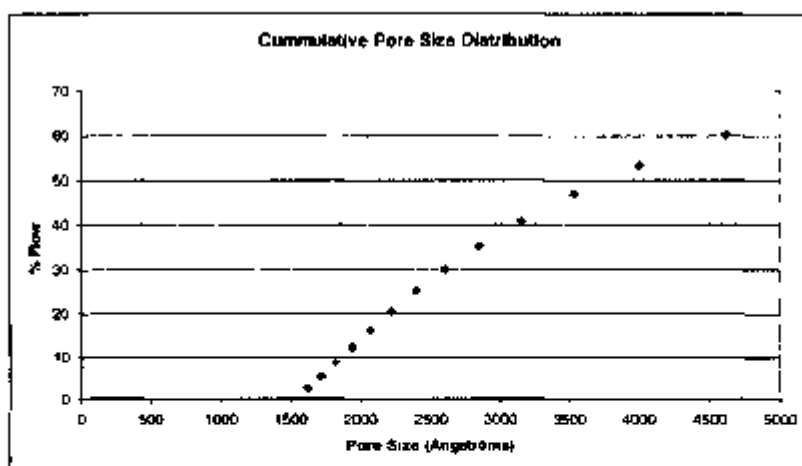
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Figure 2. PSD using flow perporometry

3. <u>High resolution X-Ray CT microimaging:</u> Though useful for the characterization of the pore structure of CBM samples in the macroporous region, flow perporometry is not accurate beyond the pore range of 700-800 nm. CBM core pores in that region contain only a small fraction of the sorbed methane, but play a vital role in the transport processes during CO_2 sequestration. To characterize this pore region we collaborate in our studies with Mark Knackstedt at ANU using the technique of HRXCT microimaging. A schematic of the XRXCT microimaging facility is shown in Figure 3.

Figure 3. Schematic of the HRXCT microimaging facility
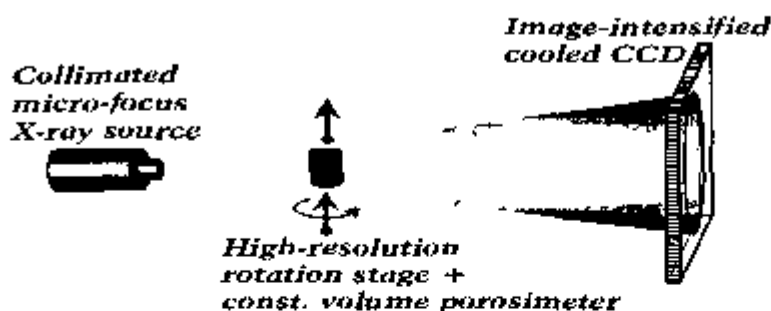
Conventional medical CT instruments provide resolution on the order of 1-2 mm for meter- to decimeter-scale objects. Although useful for the measurement of porosity and density correlations in rocks, these instruments lack the resolution required for the study of pore-scale structure in coal cores. At ANU Mark A. Knackstedt, and his group have constructed a HRXCT

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facility for the 3-D structural analysis of porous media at the micron and submicron scale (~ 700 nm), and for the study of transport and fluid flow in these materials. The facility has both the X-ray source and the detector optimized for high resolution and enables one to maximize the field of view (FOV). The observation of sparse features such as the poorly connected fluid channels within the porous sample requires this high resolution over large volumes. The experimental CT facility is capable of generating images comprising up to 8 billion voxels, providing us with an unparalleled ability to investigate *in situ* the pore structure of coal cores over a range of length scales. The CT instrument employs a cone-shaped X-ray beam, which produces a series of 2-D projected images of the sample volume recorded as a function of rotation angle. Recovering the full 3-D internal structure of a sample involves rotating the object 360° and obtaining several thousands of projections (for scales $>1000^3$). The many projections are reconstructed with an advanced algorithm to generate a 3-D density map. After the phases (pores and the various regions of the coal matrix) have been identified one can generate 3-D visualisations of the pore space and, if present, different density phases. After the image of the porous sample is identified, its effective transport properties can be computed. This is done, using finite element or finite difference techniques, by discretizing the transport equations and superimposing the appropriate grid on the 3-D image, hence avoiding any approximation regarding the shape or size of the pores.. Hence, the effective transport properties of the CBM samples are predicted directly from microtomographic images. This technique also allows one to illustrate the local transport paths within a porous structure, an experimentally intractable problem, thus providing an insight into the pore-scale mechanism of flow and transport. Figure 4 below shows a series of 2-D images from a CBM sample (from the same core with samples of Figs 1 and 2) analyzed at the ANU

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facility. On the top of each image key observations are noted. Obvious from these cross-sections is the presence of a persistent fracture network and several mineralization regions.

Transport and Sorption Characteristics: In order to study the transport/sorption characteristics, but also in order to carry out simulated CBM reservoir CO_2 sequestration experiments we have constructed a new experimental apparatus, shown in Fig. 5. At the heart of the system is a stainless steel autoclave capable of withstanding pressures up to 2000 psi, placed inside a temperature controlled oil-bath. The CBM sample is placed within this autoclave. The way the CBM sample is positioned depends on the type of experiments to be carried out. For adsorption/desorption experiments of single and mixtures of gases, the sample is placed inside the autoclave the remaining volume is filled with inert quartz beads, and then the sample is exposed to the relevant gases at predetermined intervals and sequence. The flow of the gas exiting the autoclave is monitored with a mass flow-meter and its composition is continuously analyzed with a mass spectrometer. The composition of gases into the autoclave is set using mass flow controllers and the pressure is maintained constant by a pressure controller. For the measurement of the flow permeability (and for some of the CO_2 sequestration experiments) the core is embedded in a high temperature epoxy matrix. To do so, the original core is carefully machined into a cylinder and the epoxy coating (typically ¼ in thick) covers the whole core with exception of the top and bottom surfaces. When the epoxy cures (a multi-step preparation approach is followed to assure that the epoxy during the curing step does not infiltrate the core from its sides) the top and bottom surfaces are machined flat. A stainless steel tubing is then embedded ~2 in deep into the core on the bottom surface. An additional ¼ mm thick coating of epoxy is the placed there to seal the sample bottom. During the experiments the pressure the top

and bottom surfaces are exposed to, are independently controlled and the flow rate of the gas exiting the core is measured.

Early in image, no visible pores
Lots of mineralization with no clear
preferential direction

Mineralization now aligned. Note fracture
pattern. This pattern persists over several slices

Mineralization moves along the
core with same alignment but
fractures persist still in same place

further along   fractures filled

Again, change in mineralized regions
but fracture network shows similar structure

note the big fractures (black) near
the mineralization

Figure 4: HRXCT images

For most porous media Darcy's law, which for a compressible fluids in steady state is expressed as,

$$Q = 0.003164 * T_{sc} * A_c * k * (p_1^2 - p_2^2) \qquad (2)$$

$$p_{sc} * T * Z * L * \mu$$

Where k = permeability, md

μ = Fluid viscosity, cp; A_c=sample area

L = length of the porous body; T=temperature

Z = compressibility factor; T_{sc}, P_{sc}=standard temperature and pressure

Q = output flow rate

P_1, P_2 = Upstream and downstream pressures

Assuming all other parameters/variables are constant (with the exception of the top and bottom pressures), then Darcy's law predicts a linear relationship between Q and $(p_1^2 - p_2^2)$

$$Q \sim k * (P_1^2 - P_2^2)$$

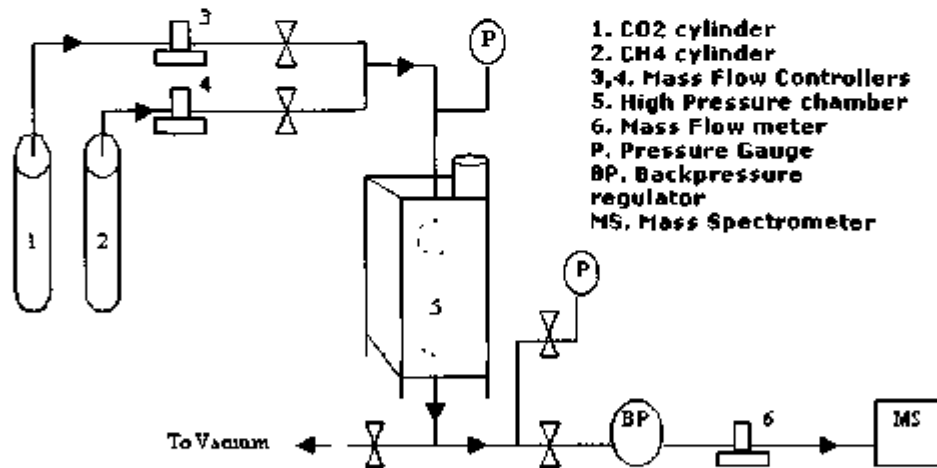

1. CO2 cylinder
2. CH4 cylinder
3,4. Mass Flow Controllers
5. High Pressure chamber
6. Mass Flow meter
P. Pressure Gauge
BP. Backpressure regulator
MS. Mass Spectrometer

Figure 5. CO₂ sequestration laboratory system.

Q vs p^2/z

♦ Series1 ■ Series2

Q (ml/sec)

3

2

1

0

0.E+00   1.E+05   2.E+05   3.E+05
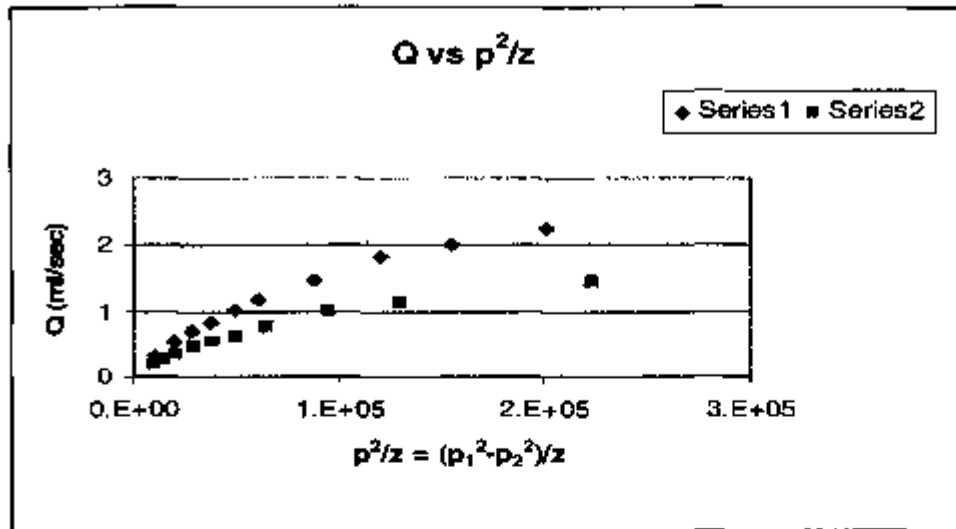
p^2/z = (p$_1^2$-p$_2^2$)/z

Figure 6. CO_2 flow through the core.

Figure 6 shows the relationship between Q and $(p_1^2 - p_2^2)/z$ for one of the CBM samples (from the same core with the samples of the prior figures). Note in this figure that up to a certain pressure gradient the flux through the core obeys Darcy's law; beyond a certain pressure gradient, however, this is no longer true. A simple explanation of this behavior is swelling of the coal matrix due to CO_2 sorption. Other causes are also plausible, and this remains an important aspect of our future investigations.

Behavior under CO_2 sequestration conditions: The apparatus of Fig. 5 is also utilized to study CBM core behavior during CO_2 sequestration. Prior to initiating these experiments the core is first conditioned under appropriate conditions. Typically, the core is evacuated overnight. If experiments with dry cores are desired, then the autoclave is pressurized at a certain pressure with CH_4; the autoclave inlet is then closed and the core is allowed to equilibrate in the CH_4 atmosphere until it no longer appears to adsorb CH_4. The autoclave is then loaded with additional CH_4 and the procedure is repeated

Figure 7. Autoclave pressure vs. time. Total methane uptake 0.038 gr CH_4/gr of sample

for many cycles until the core completely saturates with methane at the desired pressure and temperature conditions. An experiment of loading the coalbed core with CH_4 at 200 psi is shown in Fig. 7. Once the sample is completely saturated with CH_4, the CO_2 sequestration experiment may begin. With the existing system one can control the flow rate and CO_2 delivery pressure into the core. As the CO_2 flows

Figure 8. CH_4/CO_2 molar ratio exiting the core. P_{inp}=400 psi, P_{bot}=350 psi.

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into the core the exit gas stream's flow rate and composition are continuously measured. From these values one can calculate individually the flow rates of 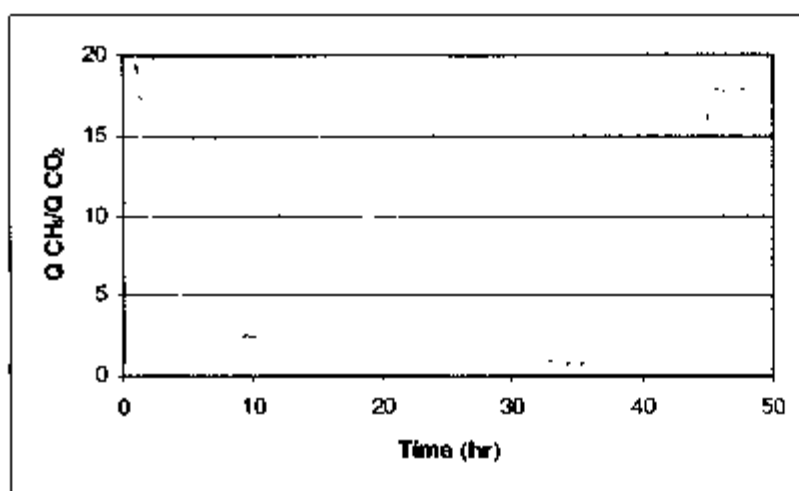CH_4 and CO_2 exiting the core. The ratio of CH_4 and CO_2 flow rates exiting the coalbed core as a function of time (t=0 is the point when the core is exposed to CO_2) is shown in Fig. 8. The analysis initially indicates a high CH_4 content with little CO_2 in it. Over a few hours, the trend is reversed The data on the exit flow rates of CH_4 and CO_2 provide valuable information concerning the CBM core characteristics during CO_2 sequestration. For carrying out experiments with wet CBM cores the experimental apparatus allows one to load the core with water under the desired temperature and pressure conditions. One can also carry sequestration experiments utilizing simulated flue gas rather than CO_2 alone. Both these experiments are planned during the Phase 2 of this project.

PROPOSED ADDITIONAL WORK

As noted above, an efficient method of increasing CH_4 production from a CBM reservoir is by injecting CO_2 into the reservoir. Experiments indicate that CO_2 is most strongly adsorbed on the surface of the coalbed's micropores, and thus its injection into the reservoir causes desorption of CH_4 from the pores' surface. The very large surface area of the micropores implies that one can sequester huge amounts of CO_2 in a CBM reservoir, and at the same time produce larger amounts of CH_4 than what otherwise would be produced by the conventional method. To our knowledge, CO_2 injection in CBM reservoirs has been studied by only a few groups [12]. However, in contrast to our own study, the emphasis in most of these investigations was on increasing CH_4 production, rather than on CO_2 sequestration. A key element missing in most of these studies is a meaningful characterization of the CBM reservoir structure. Without such structural information it would be difficult to predict, (1) how much CO_2 can be sequestered in a

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CBM reservoir; (2) how much CH_4 can be produced as a result of CO_2 injection; and (3) how the morphology of a CBM reservoir affects CO_2 sequestration. Furthermore, to date, no attempt has been made to combine modern ideas involving realistic models and statistical concepts with computer simulations and well-conceived experiments of CO_2 injection into a CBM reservoir and its sequestration therein. This is the key emphasis in future research by our group. Our study will aim to investigate the injection of CO_2 in the reservoirs, its adsorption on the rough micropore surfaces, and its sequestration there, and the enhanced CH_4 production that results from the CO_2 injection, as well as the main factors that affect the overall operation.

There is a number of aspects of CO_2 sequestration in CBM reservoirs that makes it a unique problem for study. The reservoir consists of pore and fracture networks with a heterogeneous morphology. The fracture network, in particular, has a multiscale hierarchical structure; this has two important implications. One is that CO_2 adsorption is very different from what is expected from a conventional reservoir. The second implication is that the CBM reservoir is drained in a qualitatively very different way from that predicted from the simple-cubic fracture networks commonly used in the current double-porosity models. Other factors that complicate the study of CO_2 sequestration in CBM reservoirs is that the coal matrix itself deforms as a result of CO_2 injection, and that the transport of CH_4 and CO_2 in the nanopores is by configurational (hindered) diffusion. In the study of CO_2 injection all these unique factors must be taken into account.

Injection and adsorption of CO_2 in CBM reservoirs, and the accompanying diffusion and flow of CH_4 and water towards the production wells, are multiphase phenomena. These reservoirs, as noted previously, contain a large number of fractures of different length scales. There is now much evidence [13, 14], for example, that tectonic fracturing processes lead to the

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creation of fracture networks with multiscale, self-similar characteristics. For flow and transport in such reservoirs, the Darcy permeability and the transport coefficients are not constant, but vary with distance from the source (well) [9]; *local* formulations, used previously for CBM reservoirs, are inadequate for describing the transport processes. The complexity of such phenomena in fractured reservoirs requires the development of models significantly more elaborate than the dual-porosity approaches; and validating these models with careful measurements, so that they can be used for both local as well as regional studies. Our group has previously developed a network model of pores with rough surfaces [15] that successfully models the effect of surface roughness on adsorption, flow, and diffusion through a porous medium; we have also carried out extensive modeling and simulations of hindered diffusion in porous media [16]. These will be important components of the overall CBM CO_2 injection model. In what follows, we describe the methodology for Phase 2 of our study, which when completed will provide the necessary tools for a comprehensive study of CO_2 invasion of CBM reservoirs, for its adsorption there, and the simultaneous CH_4 production.

Task I: Characterization of Coalbed Methane Reservoir Core Samples

The focus in this Task is on experimentally determining the local connectivities of the CBM core pore space, and its pore matrix and cleat fracture network. In this Task we will continue our collaborative efforts with Mark Knackstedt at ANU using the HRXCT microimaging technique [17] for mapping out the spatial distribution of the macropores and the cleat fractures of CBM samples. This technique generates 3-D images of CBM reservoir samples with a resolution <1 μm and allows the identification of the macropore and fracture networks; during Phase 2 this technique will be used for computing the effective permeabilities and relative permeabilities (during two-phase flow of gas and water in the sample). Our preliminary

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investigations (see Fig. 4) indicate the presence of very complex macropore and cleat fracture network structures. In addition, they indicate that the CBM sample's matrix is highly nonuniform with many mineralized regions. The distinct advantage of the HRXCT technique is that it provides 3-D information with unparalleled resolution, compared to what conventional techniques using serial sectioning of samples provide; in addition it is a non-destructive technique. Serial sectioning of CBM samples, on the other hand, is a delicate operation, as such materials are fragile.

In this Task we will also make use of flow perporometry for characterizing the mesoporous region, and $N_2/CO_2/CH_4$ physisorption to characterize the nanoporous space, as previously detailed. Data interpretation will utilize a technique [18] which combines detailed molecular simulations of sorption at the microscale level together with pore network simulations of dynamic sorption/desorption phenomena at the macroscale level. In Phase 2, use will also be made of small-angle x-ray scattering (SAXS) investigations, which will provide complementary information in probing the nanoporous region [19].

Task II: Experimental Studies of Sorption and Transport

In this Task we will study the sorption of binary mixtures of CO_2 and CH_4, as well as ternary $CO_2/CH_4/N_2$ mixtures. The binary mixture has been chosen to simulate CH_4 displacement by CO_2, while the ternary mixture is to simulate CH_4 displacement by flue gas. The sorption behavior under a broad range of pressure conditions, typical of those encountered in CBM processes, will be investigated for the CBM cores using the apparatus of Fig. 5. Both intact and finely ground samples will be studied in order to determine the contributions to sorption (if any) of the macropore and cleat fracture networks.

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The transport characteristics of the CBM samples, e.g., the permeabilities of (single/ideal and mixture) of the aforementioned three gases, will be measured both with steady-state permeation flow-through experiments (in which the core is encased in an epoxy matrix), and in uptake-type experiments. For the uptake-type experiments both whole core and ground samples will be utilized. Different regions of the pore space contribute differently to transport during transient and steady-state experiments. For example, dead-end porosity contributes little to steady-state transport, but actively participates during transient experiments. Further, during steady-state experiments a constant partial pressure environment prevails within the pore structure; the same is not true during uptake-type experiments. Of particular interest is the effective permeability pressure-dependence. Fractured samples are generally anisotropic, and hence are characterized by a permeability tensor. Experiments will be carried out to measure the effective permeabilities in all the sample's principal directions; this information will be very useful for reservoir simulations.

Of particular interest in this Task will be the effect of the deformation of the CBM samples due to sorption on the effective transport properties. Such behavior manifests itself with nonlinear permeation behavior. In addition, what one often finds is that the permeation behavior is sample-history dependent, i.e., that it makes a difference whether the sample was previously evacuated, exposed to CO_2, etc. In real applications the water present, mostly in the coal matrix's mesoporous and macroporous regions and in the cleat fractures, will tend to interfere with both the sorption and transport characteristics. The apparatus of Fig. 5 allows one to condition the samples *in situ* with H_2O at various temperature and pressures. After completing the experiments described above for dry samples, we will then examine the sorption and transport behavior of wet (at various saturation levels) samples. We plan to measure the relative permeabilities of both

water and gas in CBM samples. The measurement technique is well-established [9]. Similar to single-phase flow and measurements of the absolute permeabilities, of particular interest will be the pressure-dependence of the relative permeabilities.

Task III: Experimental Studies of CO_2 Sequestration in CBM reservoir cores

Though measurements of the kind described in the two Tasks above are invaluable in defining the characteristics of the core samples matrix and its pore and cleat fracture networks, by themselves they cannot be used to describe the CO_2 sequestration in CBM cores. This phenomenon involves simultaneous transport of CO_2 and CH_4 (and potentially other gases like N_2) and adsorption and desorption processes of all such species on the pore surface and space, all of which are by definition non-equilibrium processes. To understand how much the coal pore surface and pore space contribute to the ability of CO_2 to selectively displace CH_4 from the coal microporous space, one must directly probe and investigate these non-equilibrium processes.

In this task we will carry out CO_2 sequestration experiments using the experimental system of Fig. 5. The procedure we will follow was described in detail previously. The core sample will be first appropriately pre-conditioned (e.g., for wet samples by treating *in situ* with water at predetermined temperature and pressure), and then will be loaded with CH_4. The sample will then be exposed to CO_2 (or its mixture with other gases) to initiate the CO_2 sequestration experiment. During the experiment the amount of gas that escapes the core and its composition are continuously monitored. Experiments will be carried out for a range of pressures and temperatures to simulate the conditions found in the real CBM reservoirs. Of key importance is also the effect of the level of water saturation of a given sample.

Task IV: Modeling CO$_2$ Sequestration In CBM Reservoirs

As previously noted, one of the challenges one faces when modeling CO$_2$ sequestration in CBM reservoirs is the presence of multiple and widely varying length scales. In investigating phenomena that occur in systems that contain several disparate length scales one may utilize either sequential or parallel multi-scale modelling methods. In the sequential methods, which are used more extensively than the parallel multi-scale modelling methods, beginning with the smallest length scale of the problem, the results of one series of computations are used as the input to the next (larger) up the length scale hierarchy. Hence, the essential idea is to pass (as input) information (output) from the finer to coarser scales. This is the approach that will be followed in this Task, at least as a first step. The parallel multi-scale approach is not, as yet, as well developed as the sequential approach, because it requires very significant computing power. In this method, the different computational methods that are appropriate for describing phenomena at each individual length scale are coupled for a simultaneous attack on a given problem. If it were not for the fact that the parallel multi-scale approach turns out to be often computationally intractable, it would have been the technique of choice in modeling inherently multi-scale engineering processes, like CO$_2$ sequestration in CBM reservoirs. The reason for this is that for many of these processes, one must know what is happening simultaneously in different regions and length scales of the system in order to understand and predict the macroscopic behavior. What makes the parallel approach the "less frequent route to travel" is that it often turns out to be computationally not feasible.

In Phase 2 of this project the emphasis will be on applying and validating the sequential multiscale modelling approach with the CBM cores, which are the focus of three experimental Tasks above. Extending the modeling methodology proposed in Task IV beyond this length scale

(e.g., CBM reservoir modeling) is rather straightforward; the challenge lies in generating a comparable set of experimental data at these length scales with those to be generated in Tasks I-III above. We will first describe the method at the macropore and cleat fracture length scales, and continue with the coal matrix length scales.

The macropore and cleat fracture length scale: The macropores and cleat fractures can be obtained from the 3D HRXCT images which can then be used to compute the effective (and relative) permeabilities of the core samples. These are the permeabilities that the flow-through experiments in Task II will generate; the computations in this Task will complement the experimental studies, and also serve as a useful check of our overall effort. The technique we use for carrying out such computations is novel [17]: We first lay out a 3-D finite-element (or finite differences) grid on the 3-D images; we then identify macropore, cleat fracture, and solid matrix areas, and solve for the effective permeabilities (by solving the Stokes' equation). This way, one needs not to make assumptions regarding the shape and/or sizes of the macropores and cleat fractures. In addition, all the components of the effective permeability tensor are computed very accurately. This procedure will be carried out for all samples for which HRXCT data will be available. Since CO_2 may deform the samples, the pressure-dependence of the permeabilities will be also computed; these computations will then be combined with the experimental data to develop correlations for the pressure and porosity dependence of the effective permeabilities, to be used (passed along as input) in the CBM reservoir length scale simulations. Two-phase relative permeabilities can be computed in a similar manner [9, 17], by simulations in which the 3-D image is saturated by one fluid and invaded by a second fluid. This way, the saturation dependence of the relative permeabilities will be determined.

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The Coal Matrix: CO_2 sequestration in CBM reservoirs is the outcome of a complex series of events, which involve transport through the macropore and cleat fracture networks, diffusion through the mesopore and micropore regions of the coal matrix, and adsorption of CO_2 onto (or desoprtion of CH_4 from) the surface of the micropores. Macropores and cleat fractures and the coal matrix itself represent two distinct classes of transport paths, in the sense that each has its own distinct characteristics. We have shown previously [20] that transport in a disordered medium with multiple families of transport paths is distinctly different from that in a porous medium with only one type of transport paths.

Consider first diffusion, which is simpler to simulate than both diffusion and flow. Since we use networks of cleat fractures and pores to represent the core, we utilize a set of discrete equations of the following form

$$\frac{\partial C_i}{\partial t} = \sum_j \frac{D_{ij}}{l_{ij}} \left[C_j(t) - C_i(t) \right] + E_i C_i(t) \tag{3}$$

where $C_i(t)$ is a two-dimensional column vector, the sth component of which gives the concentration of the gas at time t in path s at network site i. By path we mean either the macropore and cleat fracture or the coal matrix pore networks, which are very different. D_{ij} is a matrix whose elements are the diffusivities in the paths between sites i and j. The *exchange matrix* E_i gives the rate of diffusive exchange between the different transport paths at site i. l_{ij} is the length of the path (fracture or pore) between i and j.

We have already discussed the approach in characterizing the macropore and cleat fracture transport path using the 3-D HRXCT images. For this transport path computations will need no assumptions regarding the shapes and sizes of the pores and fractures, but will be quite intensive. For the coal matrix path the data available (probe gas physisorption, SAXS, flow perporometry) do not provide for direct imaging. Techniques developed by our group and others

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[21], on the other hand, allow us to determine the pore size distribution of the pore network and its connectivity. In the coal matrix path for micropores diffusion may be hindered, the corresponding diffusivities in the matrix D would obey Eq. (1). To reiterate, our approach consists of (1) generating the fracture and coal matrix networks based on the experimental data, and (2) solving Eqn. (3) for the two coupled networks.

Simulating Diffusion, Sorption and Two-Phase Flow: In reality, CO_2 sequestration in CBM cores involve, in addition to diffusion, sorption of CO_2 (and desoprtion of CH_4), and two-phase flow of water, CH_4 and CO_2. Eq. 3, as a result, is much more involved. In this Task we will use the two coupled networks generated as described previously; the effective values of the various flow and transport properties measured and/or computed (see above), will be used in the simulations for characterizing the networks and their effective properties. We will then study two-phase flow, transport and sorption in this system. The complexity of phenomena that occur and the presence of multiple transport paths, necessitate development of a comprehensive model. Since the CO_2 pressure-dependence of the effective and relative permeabilities will also be obtained through experiments and simulations, we will also carry out a series of simulations in in order to understand the effect of sample deformation/swelling on flow and sorption properties.

CONCLUSIONS

The basic project objective is the development of experimentally validated models for simulation of CBM reservoirs and for predicting the amounts of CO_2 sequestered, and the CH_4 produced. The ultimate goal is to develop a simulation package that consists of the following elements. (1) Computer simulators that take 3-D images of the samples, and compute their effective permeabilities and relative permeabilities as function of the samples' morphology and

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the pressure by which CO_2 is injected into the samples. (2) A second simulator that takes as inputs the results produced by the first simulator, and carries out simulations of diffusion, flow, and adsorption/desorption processes in CBM reservoirs.

REFERENCES

1. Mcculloch C.M, *et al.*, *US Bureau of Mines Report of Investigations 7910* (1974); Friesen W.L., and Mikula R.J., *J. Colloid Interface Sci.* 120, 263 (1987).

2. Levine J.R., *Proc. Coal Bed Methane Symposium*, Tuscaloosa, Alabama, 1991

3. Pattison C.I., Fielding C.R., McWaters R.H, and Hamilton L.H., in Coalbed Methane and Coal Geology, London Geological Society Special Publication, 109, United Kingdom, pp. 131-150, 1996.

4. Jones A.H, *et al.*, in *Geology and Coal-bed Methane Resources of the Northern San Juan Basin, Colorado and New Mexico*, edited by Fassett, J.E. (Rocky Mountain Association of Geologists Guide Book, 1988), p. 169

5. van Krevelen D.W., Coal, Elsevier Science Publishers, Amsterdam, the Netherlands, 1993.

6. Seidle J.P, and Arri L.E., Canadian Institute of Mining/SPE Paper 90-118, Alberta, Canada, June 10-13 (1990).

7. King G.R, *et al.*, *SPE Formation Evaluation* 1, 165 (1986); Smith D.M. and Williams, F.L., *Soc. Pet. Eng. J.* 24, 529 (1984).

8. Hewett T.A., paper SPE 15386, *61st annual Fall Meeting of SPE*, New Orleans, LA, October 5-8 (1986); Mathews J.L, *et al.*, *J. Pet. Tech* 41, 1136 (1989).

9. Sahimi M., *Transport in Porous Media* 13, 3 (1993); *Flow and Transport in Porous Media and Fractured Rock* (VCH publishers, Weinheim, Germany, 1995).

10. Stevenson M.D., *et al.*, SPE Paper 23026, Perth, Western Australia (1991).

11. Deen W.M, *AIChE J.* 33, 1409 (1987).

12. Fulton P.F., *et al.*, *Soc. Pet. Eng. J.* 20, 65 (1980); Reznik A.A., *et al.*, *Soc. Pet. Eng. J.* 24, 521 (1984); Arri L.E, *et al.*, SPE Paper 24363, Casper, Wyoming, May 18-21 (1992).

13. Barton C.C. and Hsieh P.A., *Physical and Hydrological-Flow Properties of Fractures*, Guidebook T385 (American Geophysical Union, Las Vegas, Nevada, 1989).

14. Sahimi M. and Goddard J.D., *Phys. Rev. B.* 33, 7848 (1986); Sahimi M., *et al.*, *Phys. Rev. Lett.* 70, 2186 (1993); Robertson M.C., Sammis C.G, Sahimi M., and Martin A.J., *J. Geophys. Res.* B100, 609 (1995); M. Sahimi and S. Arbabi, *Phys. Rev. Lett.* 77, 3689 (1996).

15. Sahimi M. and Imdakm A.O., *Phys. Rev. Lett.* 66, 1169 (1991).

16. Sahimi M. and Jue V.L., *Phys. Rev. Lett.* 62, 629 (1989); Sahimi M., *J. Chem. Phys.* 96, 4718 (1992); Ravi-Kumar V.S., Tsotsis T.T., and Sahimi M., *Ind. Eng. Chem. Res.* 36, 3154 (1997)

17. Knackstedt M.A, Sheppard A.P, Sahimi M., *Advances in Water Resources* 24, 257 (2001).

18. Seaton N.A., *et al.*, *Carbon* 27, 853 (1989); Liu H, *et al.*, *Chem. Eng. Sci.* 47, 4393 (1992); Stubos A.K., *et al.*, *Langmuir* 13, 2795 (1997).

19. Rassamdana H. and Sahimi M., *AIChE J.* 42, 3318 (1996).

20. Hughes B.D. and Sahimi M., *Phys. Rev. Lett.* 70, 2581 (1993); *Phys. Rev. E* 48, 2776 (1993); Sahimi M. and Tsotsis T.T, *Ind. Eng. Chem. Res.* 36, 3043 (1997).

21. Champagnie A.M, Tsotsis T.T., Minet R.G., and Wagner E., *J. Catal.* 134, 713 (1992); Yang, L., Zhou Y., and Tsotsis T.T., Proceedings of ICIM4 (in press).

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