

WORKSHOP

**CO₂-ENHANCED COALBED METHANE
PRODUCTION**

(CO₂-ECBM)

28 – 30 November 2005

at

Delft University of Technology
Department of Geotechnology

**WORKSHOP:
CO₂-ENHANCED COALBED METHANE PRODUCTION (CO₂-ECBM)**

Date: 28 – 30 November 2005

Venue: Delft University of Technology - Department of Geotechnology

Editor: Karl-Heinz. A.A. Wolf

Attendance list

- Prof. Dr, Satya Harpalani: Southern Illinois University, U.S.A
- 2 Ajayendra Kumar MSc.: Southern Illinois University, U.S.A
- 3 Dr. Bernd Krooss: RWTH-Aachen, Germany
- 4 Dr. Andreas Busch: RWTH-Aachen, Germany
- 5 Dr. Dirk Prinz: RWTH-Aachen, Germany
- 6 Yves Gensterblum Dipl. Geol.: RWTH-Aachen, Germany
- 7 Dr. Dan Bossie Codreanu: IFP-Paris
- 8 Dr. Shi Quan: Imperial College London, U.K.
- 9 Dr. Huges Legrain: University of Mons, Belgium
- 10 Prof. Dr. Guy DeWeireld: University of Mons, Belgium
- 11 Mrs. Klara Orešnik: ERICo, Velenje, Slovenia
- 12 Mr. Janez Kozinc: ERICo, Velenje, Slovenia
- 13 Prof. Yu Li: Chinese Academy of Science, Tayuen, China
- 14 Frank van Bergen: NITG-TNO, Utrecht, The Netherlands
- 15 Drs. Henk Pagnier: NITG-TNO, Utrecht, The Netherlands
- 16 Prof. Dr. Chris Spiers: Utrecht University, The Netherlands
- 17 Prof. Dr. Collin Peach: Utrecht University, The Netherlands
- 18 Drs. Sander Hol: Utrecht University, The Netherlands
- 19 Drs. Jelle van Sijl: : Utrecht University, The Netherlands
- 20 Dr. Jos Maas: Shell-SIEP, Rijswijk, The Netherlands
- 21 Dr. Niels van Wageningen: Shell-SIEP, Rijswijk, The Netherlands
- 22 Dr. Hans Bruining: Technische Universiteit Delft
- 23 Nik Siemons Dipl. Geol.: Technische Universiteit Delft
- 24 Drs. Patrick van Hemert: : Technische Universiteit Delft
- 25 Saikat Mazumder MSc.: : Technische Universiteit Delft
- 26 Ir. Willem Jan Plug: Technische Universiteit Delft
- 27 Raoul van Lier: Technische Universiteit Delft
- 28 Inge Moors: Technische Universiteit Delft
- 29 Jorge Gonzalez: : Technische Universiteit Delft
- 30 Dr. Jesper Spetzler: Technische Universiteit Delft
- 31 Dr. Daniela Sijajic: : Technische Universiteit Delft
- 32 Drs. Karl-Heinz Wolf: Technische Universiteit Delft

Programme ECBM-WORKSHOP

Monday 28th of November – Wednesday the 30th of November

Venue:

Geotechnology Department, Delft University of Technology,
Mijnbouwstraat 120, 2628 RX Delft - The Netherlands

Program proposal:

Sunday:

Foreign guests welcomed in the Hotel

Monday: The seam and its environment

- 9.00 Coffee
- 9.30 Introduction by K-H Wolf
- 10.00 Shi Quan: Phenomenon around a borehole?
- 11.00 Discussion: Bernd Krooss
- 12.00 Lunch
- 13.30 Homogenization by Hans Bruining
- 14.30 Up scaling by Dan Bossie
- 15.30 Discussion: Niels van Wageningen
- 16.30 Lab tour

- 19.00 Diner for all

Tuesday: Size and sorption

- 9.00 Coffee
- 9.30 Dirk Prinz and Andreas Busch: coal structures and sorption behavior
- 11.00 Discussion: Hughes Legrain
- 12.00 Lunch
- 13.30 Patrick van Hemert and Nikolai Siemons: Pitfalls in sorption experiments and theory
- 15.30 Discussion: Jos Maas

- 19.00 Diner for all

Wednesday: Combining methods, new thoughts

- 9.00 Coffee
- 9.30 Satya Harpalani and Ajayendra Kumar: An American Story
- 11.00 Discussion: Hans Bruining
- 12.00 Lunch
- 13.30 Saikat Mazumder, Frank van Bergen: Case II diffusion
- 15.00 Discussion followed by a summary on the 3 days, with discussion by Satya Harpalani
- 17.00 Finalization

MONDAY 28th of November

The seam and its environment

9.00 hrs: Coffee

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10.00 hrs: Shi Quan: Phenomenon around a borehole?

11.00 hrs: Discussion: Bernd Krooss

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14.30 hrs: Up scaling by Dan Bossie

15.30 hrs: Discussion: Niels van Wageningen

16.30 hrs: Lab tour

Numerical Simulation of Enhanced CBM Recovery: Recent Advances and Challenges

Ji-Quan Shi
Imperial College London, UK

Coalbeds as (unconventional) gas reservoirs are characterised by two distinctive porosity systems: a well-defined and almost uniformly distributed network of natural fractures (also known as cleats) and matrix blocks containing a highly heterogeneous porous structure between the cleats. As such, coalbed reservoirs generally conform rather well to the Warren and Root type of dual-porosity reservoir models, which are developed for naturally fractured petroleum reservoirs.

Virgin seams are often saturated with water. During primary recovery by pressure depletion, methane production is facilitated by dewatering the target seams to allow desorption of the adsorbed methane, which then migrates through the coal matrix into the cleats. The transport of gas through a coal seam is considered a two-step process. It is generally assumed that flow of gas (and water) through the cleats is laminar and obeys Darcy' law. On the other hand, gas transport through the porous coal matrix is controlled by diffusion. Coalbed reservoir simulators typically solve water and gas two-phase flow equations in the cleats, coupled with an equation describing the rate of mass transfer between the matrix and cleats.

An important feature of coalbed reservoirs is that coal matrix shrinks (expands) on desorption (adsorption) of gas. Matrix shrinkage associated with methane desorption is responsible for preventing the collapse of coalbed permeability caused by increasing compaction with reservoir pressure depletion during primary methane production. Recently published permeability data show that the absolute permeabilities have increased by a factor of up to 7 with continuing pressure depletion in the San Juan Basin coalfields.

During enhanced methane recovery/CO₂ sequestration in coal, adsorption of CO₂ gas, which has a greater sorption capacity than methane, would cause matrix swelling and thus, in contrast to gas desorption, could potentially have a detrimental impact on cleat permeability of coal. Field evidence suggests that the well injectivity has indeed declined at the early stages of CO₂ injection and then rebounded at the Allison pilot in the San Juan Basin. The loss in well injectivity is attributed to an estimated two-order of magnitude reduction in permeability.

The use of numerical models is essential in the development of ECBM technology, which is still in its infancy. It has been recognized that an ECBM simulator should have all the basic capabilities that a commercial coalbed methane simulator for primary CBM recovery has, as well as the capability to handle:

- multi-component gas mixtures,
- matrix swelling effects due to CO₂ adsorption on coal,
- mixed gas adsorption,
- mixed gas diffusion,
- non-isothermal effect for gas injection.

Considerable advances in the numerical simulation of enhanced as well as primary CBM recovery have been made in the last few years, especially in terms of permeability modelling. However, many researchers still believe that CO₂ injection in coalbeds is extremely complex and not fully understood. A full understanding of all the complicated mechanisms involved in the CO₂ storage/ECBM recovery processes is needed in order to establish full confidence in the numerical models used.

Up-Scaling in Coal

**Dan Bossie-Codreanu,
Institut Francais du Petrole (IFP) – Paris**

Coal is currently viewed as made up of 3 main scales, namely macro, meso and micro. The macro scale corresponds to Darcy flow while meso and micro scales are considered as scales in which Fick's law applies. Most of the numerical models currently used in coal bed methane apply this kind of formalism. Experimentally, the distinction between macro and meso-micro scales is relatively easy to establish. On the other hand, within the meso-micro scale, a clear distinction between these sub-scales is more difficult to establish. Thus the first part of our presentation is devoted to a review of some techniques and findings concerning this kind of characterization. As we will see, the natural following step is to transform some of the observations made on cores, images or natural analogues into petrophysical properties, which in return will have to be input to numerical cells. The fact that observations in the field are made up at smaller scales than numerical cells establishes the need for up-scaling techniques and methodologies.

The next part then will be to review how to take observations at the small scale and transform them into petrophysical "representative" values assigned at the numerical scale. The shortcomings of such techniques and what we think are new avenues are provided.

Given the fact that a "practical up-scaling" is highly dependent

- on the type of numerical model used.
- the ability to gather representative field data
- the capacity to obtain mixed scale data (cores, logs, well-tests)

we review the basic equations governing coal flow modeling. Clearly stating these equations will lead us to understand where the up-scaling needs are. A critical discussion concerning these equations is given, and based on field observations a critical review of these equations is also made. The possible implications of changes in these equations on up-scaling issues is discussed.

The three steps above (geological observation, transformation of the geological features into petrophysics and laying down of the basic modeling equations) bring us to propose a general framework of petrophysical characterization at any scale based on fractal geometry and percolation theory. Along with this approach more classical averaging techniques are given. An other aspect of the methodology we favor is the easiness of implementation within an integrated reservoir study.

In order to demonstrate this, we are reviewing the different steps "normally" involved in an integrated study. Thus we will discuss :

- the pertinence or not of using a geostatistical approach to coal and the subsequent needs to up-scale,

- the layering aspects and ways to achieve it.
- the integration of various scales of data

By comparing classical approaches to the one proposed, we show that basic upscaling can be achieved at the characterization level, that geostatistical approaches are to be used only in certain cases and that natural layering in coal is governed by cleat structure (we will define this term) and at worst based on a petrophysical fine scale layering which can be obtained using simple techniques. Consequently more classical approaches in coal are unwarranted.

By debunking the up-scaling needs at various scales, a general framework of characterizing coal is finally given. Improvements, critical paths and further research activities aiming at improving the above are also discussed, which will conclude this presentation.

Abstract Hans Bruining

TUESDAY 29th of November

Size and sorption

9.00 hrs: Coffee

9.30 hrs: Dirk Prinz and Andreas Busch: coal structures and sorption behavior

11.00 hrs: Discussion: Hughes Legrain

12.00 hrs: Lunch

13.30 hrs: Patrick van Hemert and Nikolai Siemons: Pitfalls in sorption experiments
and theory

15.30 hrs: Discussion: Jos Maas

Sorption behaviour of coals

Andreas Busch

Institute of Geology and Geochemistry of Petroleum and Coal, Aachen University

(RWTH Aachen), Lochnerstr. 4-20, D-52056 Aachen, Germany

1. Sorption Kinetics

Apart from thermodynamic data on equilibrium sorption capacity and selective sorption, numerical modeling of CBM processes requires information on the kinetics (rates, characteristic times) of sorption processes. In order to cover this issue which is of relevance in different EU-projects (ICBM, RECOPOL), the kinetics of CO₂ and CH₄ sorption on dry and moist Carboniferous coals have been investigated at different temperatures (32 and 45°C). The tests were conducted with eight different particle size fractions (< 0.063 mm up to ~8 mm) and equilibration was monitored at 3 to 6 different pressure levels.

The goal was to provide simple, semi-empirical approaches applicable in reservoir models for CBM production and CO₂ injection.

A qualitative investigation of the data revealed the following results:

- Sorption equilibration proceeds significantly faster for CO₂ than for CH₄
- Sorption rates decrease with an increase in grain size fraction for CO₂ and CH₄
- Equilibration times for measurements with CO₂ and CH₄ on moist coal are significantly longer than on dry coal
- Equilibration times decrease with temperature for both gases

Various attempts were made to parameterise the experimental equilibration curves. Generally, it was found that parameterisation requires at least assumption of a two-step, bisdisperse process. This can be envisaged to reflect the fact that transport and successive sorption in macro- and micropores, respectively occurs at different time scales.

For practical purposes the sorption process was tentatively described by a linear combination of two 1st order rate functions with different rate constants. Half-life times ($\tau_{1/2}$) as characteristic parameters of the combined adsorption/diffusion processes have been calculated and plotted as a function of grain size. These plots document that particle sizes above 0.5 to 1 mm sorption half-life times remain essentially constant. Further half-life sorption times of the slow sorption step for CH₄ and CO₂ has been calculated as a function of surface coverage. This approach has been chosen to evaluate the effect of surface coverage on the combined adsorption/diffusion effect. Contrary to the rapid sorption step that exhibits only little variation in half-life sorption time, the slow step shows much stronger fluctuations. For both gases it can clearly be documented that at high surface coverage (high pressures) a sharp increase in characteristic times (half-life sorption times) can be observed.

In combination with the sorption kinetic experimental data the simple modeling approach used in this study provides a first step for the implementation of sorption kinetics into CBM/ECBM

reservoir simulators and to extrapolate from laboratory to reservoir scale. The model has been implemented into the reservoir simulation software SIMED. Results demonstrate the necessity of more sophisticated kinetic models for the reasonable simulation of CO₂-ECBM processes.

2. CO₂ Sorption isotherms

To investigate CO₂ sorption on natural coals with respect to CO₂ storage it is useful to measure experimentally sorption isotherms at reservoir conditions (T=25-60°C, P<200 bar). Many data have been published in the literature, only a few cover the conditions necessary for simulation of the processes. It is stated here that CO₂ isotherms cannot be modelled by Langmuir or IAST approaches to higher pressures since the interaction of natural coals with CO₂ are not fairly understood so far (swelling of coal, CO₂ as dissolvent, density of the sorbed phase). Further, measurements on dry samples may be used for comparison studies, however to use these data for reservoir simulation seems meaningless because water plays a major role in the sorption of CO₂ on coal. In this context, three different studies will be presented that will discuss these issues in more details and shall help as a guideline for establishing a reliable method to measure HP scCO₂ isotherms.

- A Round Robin inter-laboratory comparison on moisture equilibrated coals from the Argonne Premium Coal Program has been performed in 2005. The results of the data will be presented
- CO₂ isotherms on different samples at various conditions will be presented
- A very recent study in the scope of the German national Geotechnologien Programme investigated the sorption behaviour of clays. Since the results are very promising but not very well understood, they will be presented as well.

Interaction of Water and Pore Structure on the Methane Adsorption Capacity of Coals of Varying Rank

Prinz, D., Institute of Petroleum and Coal, RWTH Aachen, Germany.

The production of methane from coal seams as well as the sequestration of carbon dioxide have recently become important topics of applied science, whereas the release of methane during mining activities has been an important subject of interest for many decades. The storage and release of gases in coals depends to a great extent on their inner surface and porosity. However, calculation of porosity of coals proved to be very difficult, e.g. due to the small diameter of micropores, which have the dimension of a few Ångstrom.

In addition, classical methane adsorption isotherms experiments have been measured at pressures and temperatures typical for coal mining conditions. For the evaluation of coalbed methane potential in depths, extending mining activities, much higher pressures and temperatures have to be applied.

In this context, a volumetric apparatus was used allowing the measurement of isotherms on dry and moisture-equilibrated coals at high pressures (up to 15 MPa). Additionally, absolute adsorption isotherms from the moisture equilibrated sample measurements were calculated in order to get information about the absolute adsorption capacities.

Low-pressure nitrogen isotherms at 77K on dry coals, low-pressure carbon dioxide isotherms at 273K on dry and 275K on moisture equilibrated coals were measured. Using the theory of micropore filling, micropore volumes and structural parameters were computed. As a second approach, small angle neutron scattering was used to evaluate structural parameters of coals (e.g. specific surface, pore radi distribution).

The measurements were performed on 10 coal samples covering a vitrinite reflectance range between 0.76 to 2.23 % (high volatile bituminous B to semi-anthracite).

Results from the measurements validate that the coal structure consist of two phases. The crystalline phase, which is inaccessible to water and the amorphous phase, which can be penetrated with water to a certain degree. Adsorption isotherms on moisture-equilibrated coals suggest that the presence of water in coals reduces the adsorption space to the ultramicropores of the crystalline phase. Furthermore, only the low rank coals are characterized by a broad pore size distribution, whereas the high rank coals do not show any significant meso- or macroporosity.

Can we measure sorption isotherms under reservoir conditions?

Patrick van Hemert

Delft University of Technology, Department of Geotechnology
(P.vanjemert@citg.tudelft.nl)

In the last decade many attempts have been made to measure single and binary sorption isotherms of coal under reservoir conditions (e.g. $\sim 45^\circ\text{C}$ and ~ 150 bar).

It is my intent to show that these measurements require high precision and accuracy in pressure and temperature measurements. Also these measurements are very dependent on the equation of state used. This can be very problematic when measuring mixtures, because the density properties of many mixtures can usually not be predicted with the required accuracy.

A prototype model will be used to calculate the influence of experimental and physical uncertainties on the sorption measurements. Afterwards a group discussion with the required uncertainty for lab and field applications will be held.

As an example two pictures are included to give an indication of the sensitivity of the isotherm measurements (see figure 1 and 2). The sorption properties of a 20-80% $\text{CO}_2\text{-H}_2$ mixture is investigated. Physical assumptions are linear independent sorption, and Redlich-Kwong-Soave behavior for the gas (binary interactions parameters = 0).

The following experimental uncertainties were used as input parameters (random errors assumed as normally distributed):

T (systematic error)=0.5 K

T (random error)=0.05 K

P (systematic error)=1%

P (random error)=0.05 bar

x (systematic error)=0

x (random error)=1 %

Participants are encouraged to supply different gas mixtures, EOS's, model sorption isotherms and experimental uncertainties during the workshop. The code should be in MATLAB 6.5; please contact the author in the case of any doubt. Extensive Sorption models and/or EOS's should be provided to the author in advance.

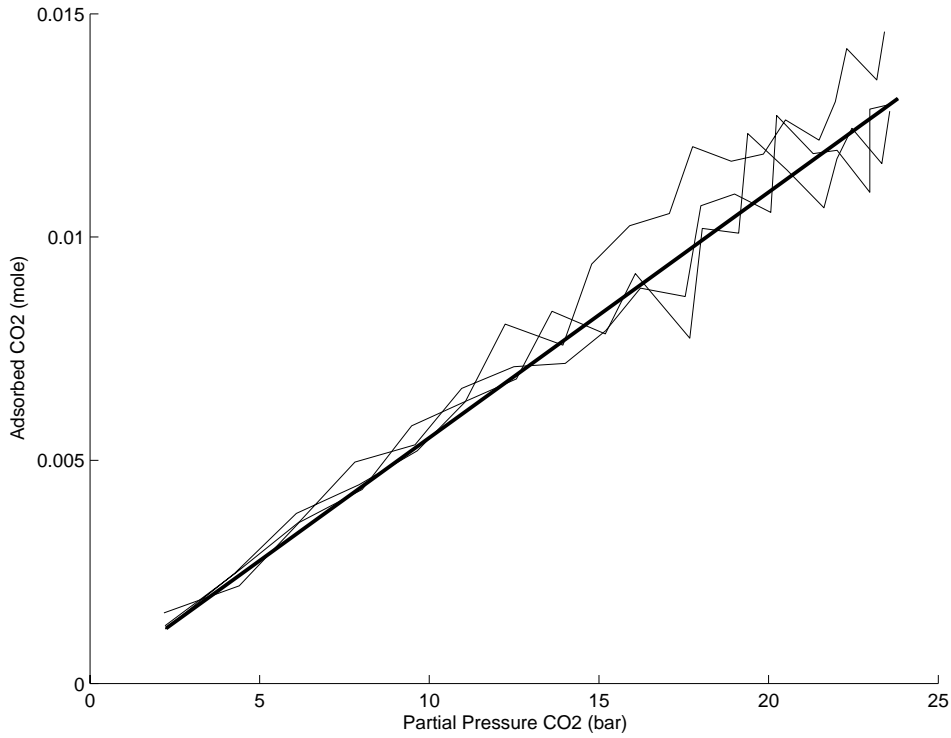


Figure 1: CO2 sorption isotherms. The thick line is the perfect sorption isotherm (model input) ; the thinner lines are three random realizations of measurements with the aforementioned uncertainties (model output).

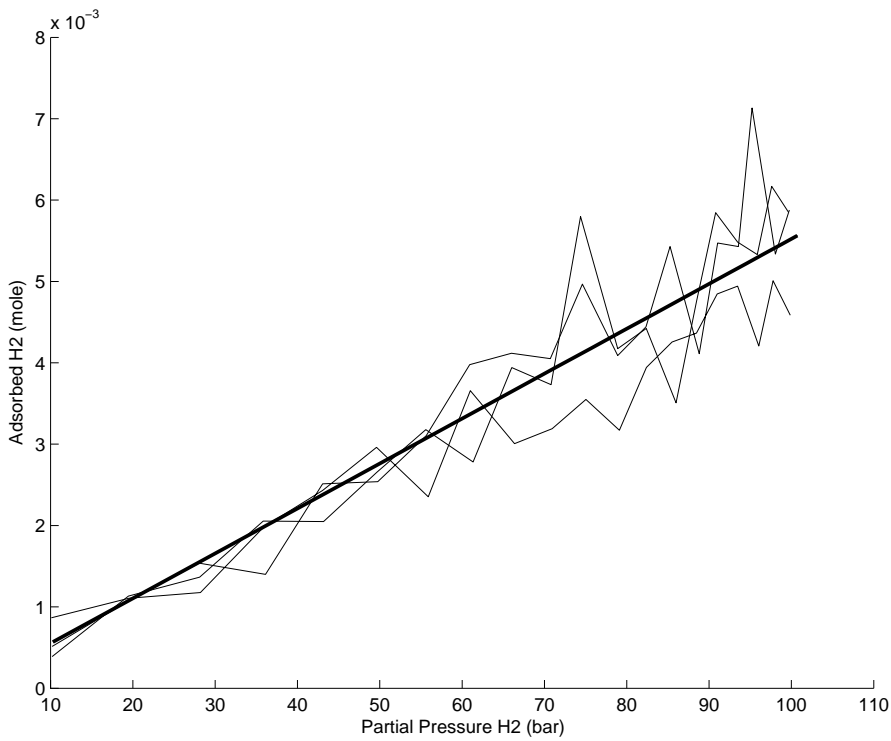


Figure 2: H2 Sorption isotherms. The thick line is the perfect sorption isotherm (model input); The thinner lines are three random realization of measurements with the aforementioned uncertainties (model output).

Pitfalls in sorption experiments

Nikolai Siemons

Delft University of Technology, Department of Geotechnology

High pressure adsorption experiments assess the adsorption capacity of an adsorbent. Different methods are utilized to measure adsorption at constant temperature as a function of pressure. Here, the volumetric method was used to determine the amount of molecules adsorbed as a function of pressure. As adsorption of molecules of the free gas phase occur, the gas pressure drops. From this pressure drop, the adsorbed mass can be determined, when the system reaches equilibrium.

The accuracy of volumetric adsorption measurements strongly depend on the following parameters:

1. Accurate measurement of pressure and temperature
2. Accurate equation of state (EOS) of the adsorbing gas
3. Exact determination of the volumes of the experimental set-up

A Parameter study of the temperature and pressure measurements have revealed that even a slight offset of the thermo-element has a remarkable impact on the calculated gas densities which are crucial for the evaluation of the experiments. The temperature device (thermocouple) was then calibrated by CO₂ expansion experiments at different pressures.

In order to calculate the gas density of the free gas phase, the high resolution EOS of Span &

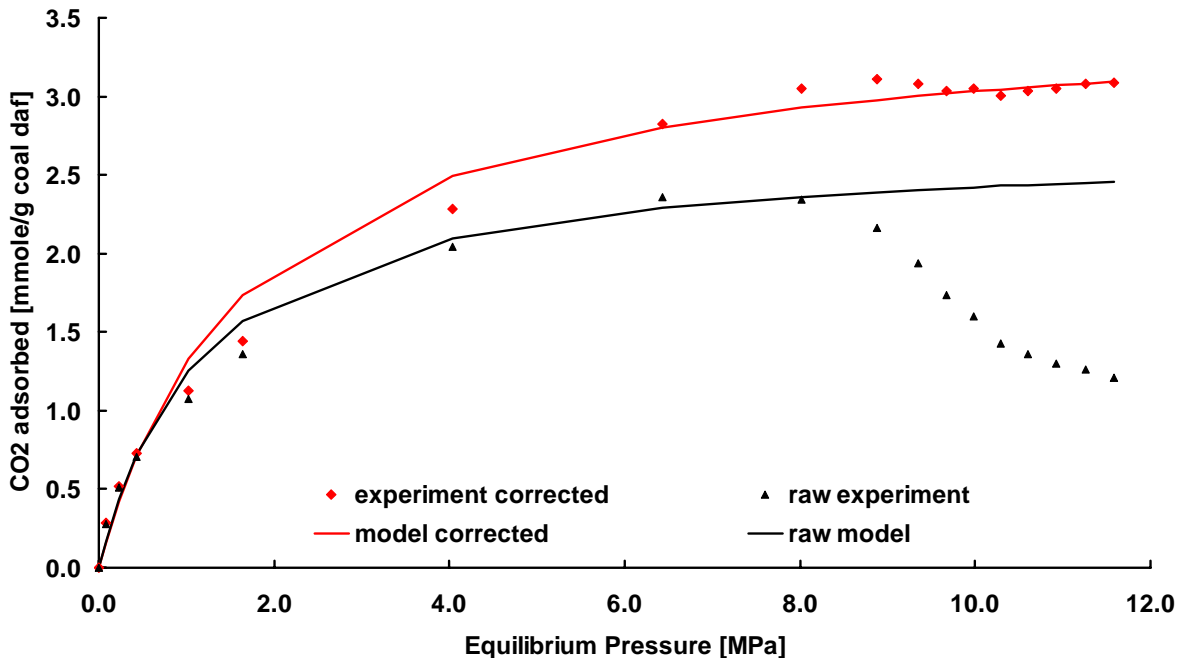


Figure 1: Low rank adsorption isotherm of CO₂ at 45° C. The void volume value was reduced by ca. 15% for all points.

Wagner was used.

The main problem however, is the volume change during the adsorption of CO₂. Firstly is questionable if the He void volume determined equals the CO₂ void volume at the start of an adsorption experiment.

Secondly, the void volume in the sample cell is reduced by coal swelling and the generation of a layer of adsorbed molecules, depending on the prevailing gas pressure.

The way, the set-up is designed, it is impossible to distinguish between these effects and assess their contribution to the overall volume change that is also unknown. For this reason, a bulk volume change correction was applied which has been constraint to a monotonically increasing adsorption behavior. The corrected void volume value, however, is applied to all pressure steps and can be interpreted as an average volume correction over the whole experiment.

WEDNESDAY 30th of November

Combining methods, new thoughts

9.30 hrs: Satya Harpalani and Ajayendra Kumar: An American Story

11.00 hrs: Discussion: Hans Bruining

12.00 hrs: Lunch

13.30 hrs: Saikat Mazumder, Frank van Bergen: Case II diffusion

15.00 hrs: Discussion followed by a summary on the 3 days,
with discussion by Satya Harpalani

17.00 hrs: Finalization

IMMEDIATE RESEARCH ISSUES IN SEQUESTRATION OF CO₂ IN DEEP AND UNMINEABLE COALS

Satya Harpalani and Ajayendra Kumar
College of Engineering
Southern Illinois University
Carbondale, Illinois
USA

ABSTRACT

In a recent survey (2005) carried out to identify the "... four to five highest priority knowledge gaps of technology barriers that affect the prospects for efficiently storing CO₂ in deep coals and.....challenges posed by the simultaneous recovery of coalbed methane", *swelling of coal and permeability loss due to CO₂ injection* was cited by most respondents as the highest priority item. *Technologies to overcome loss of permeability/injectivity* was the second, followed by the *ability to find and characterize favorable settings, relationship of ECBM and CO₂ storage in coals, monitoring of CO₂ flow and retention, and effect of CO₂ on coal properties and behavior.*

It has been shown repeatedly during the last thirty years that solid coal shrinks with release of methane, and swells when exposed to CO₂. It is generally believed that the matrix shrinkage has had a profound positive effect on CBM production in the San Juan Basin, which is very deep. It is also believed that CO₂ injection has had a negative impact on flow characteristics of coal in the Basin although some believe that this is only a temporary effect. Laboratory work has clearly shown that shrinkage/swelling is a real phenomenon although there appears to be somewhat of an uncertainty whether the effect has a universal effect on all coals at all locations. For example, what is its impact on shallow coals, that is, where stresses are relatively low? Is the effect of matrix strain primarily one of permeability loss/gain due to its impact on cleat characteristics, or the indirect impact due to significant changes in the effective stress resulting from the strain, or a combination of the two? In fact, there even appears to be a degree of uncertainty about the laboratory conditions for the experimental work related to estimation of the sorption-induced volumetric strain. It is not clear whether the effective stress should be maintained constant during the experiment, or allowed to vary. It is equally unclear if the strain should be kept constant instead, that is, the sample should *not* be allowed to swell/shrink, and if so, then how can the strain be estimated.

A change in the properties of coal, when exposed to CO₂, is another topic that needs immediate attention. Is there really plasticization of coal when it is exposed to CO₂ at high pressures, leading to some sort of a glass-to-rubber transition, and if so, what does it do to the physical structure of coal (cleats, pores)?

The objective of this session is to determine whether these issues/concerns are real, or self-inflicted, and come to some sort of a consensus on how to best conduct experimental research to answer some of the questions in the most meaningful way.

CO₂ induced swelling and anomalous diffusion mechanisms in coal

S. Mazumder, J. Bruining and K-H.A.A Wolf
Delft University of Technology, The Netherlands

The similarities in structure between coal and glassy polymers have led to the application of theories of sorption behavior of polymers to coals. In particular, coals are heterogeneous, comprising macerals with different physical and chemical properties.

During penetrant transport at low or moderate temperatures, as penetrant enters the macromolecular network of coal, the network density decreases resulting in an increase of the large molecular chain motions (Peppas et al., 1985). This increase of the penetrant concentration of the network can be viewed as an effective decrease of the glass transition temperature (Hsieh, 1984). Structural changes induced during this process include swelling, micro cavity formation and primary phase transition requiring rearrangements of each chain segments. Such changes are dominated by relaxation phenomenon.

The diffusion of gas into coal may vary between two analytically treatable extremes. If the diffusion is controlled by the concentration the diffusion mechanism is Fickian. Where the diffusion doesn't fit the Fickian diffusion model it is termed as non Fickian, anomalous or Case II diffusion. Alfrey, Gurnee and Lloyd have presented a second limiting case for this type of sorption, where the rate of transport is entirely controlled by molecular relaxation. This type of transport mechanism is designated as CaseII transport. CaseII transport is characterized by the following features:

- (a) The penetrant is observed to advance through the adsorbent with a sharp and well defined diffusion front. Ahead of the front the penetrant concentration is zero and behind the front the penetrant is at equilibrium concentration where the penetrant substantially swells the adsorbent.
- (b) The boundary between the swollen matrix and the glassy material advances at a constant velocity.
- (c) The initial weight gain of the sample is directly proportional to time (linear propagation with time).
- (d) The swollen matrix behind the advancing front is at a uniform state of swelling.
- (e) Many authors do point out that the Fickian flux of solvent must be supplemented by a flux due to stress gradient which exists across the moving boundary.
- (f) Some process of molecular relaxation is possible for control of the front velocity.
- (g) Peterlin suggests that the sharp diffusion front, characteristic of the CaseII process, is preceded by a region of penetrant at low concentration which forms a precursor to the front, and results from essentially Fickian diffusion into the glassy material ahead of the front. He recognizes that the velocity of the front is controlled by some independent material property, and suggests time dependent rupture and disentanglement of molecular chains as possible process.
- (h) Thomas and Windle proposed that the rate controlling step at the penetrant front is the time dependent mechanical deformation of the glassy polymer in response to the thermodynamic swelling stress.

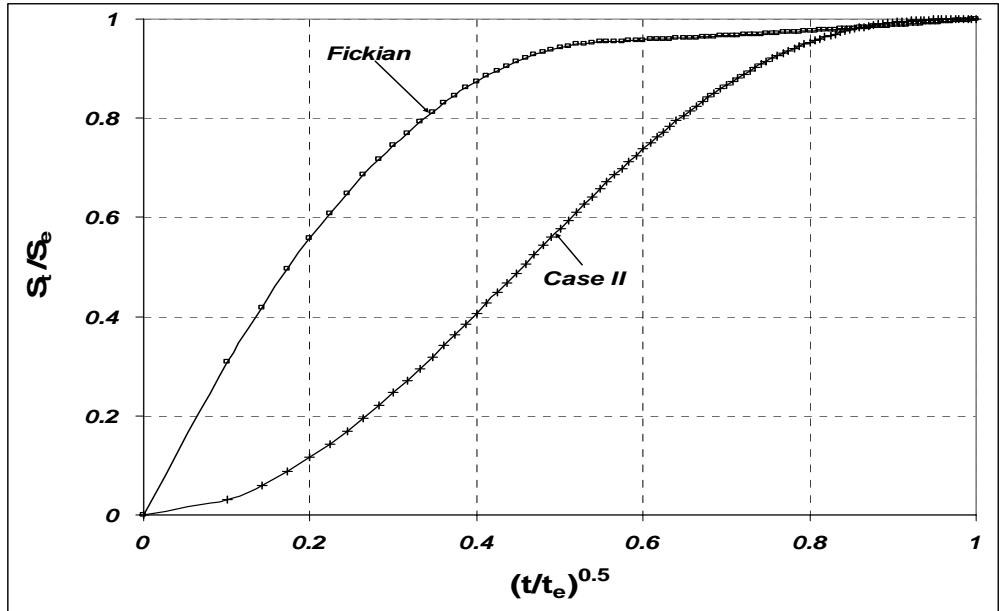


Figure 1. Assuming swelling of coal to be proportional to mass uptake, when plotted against dimensionless time clearly shows the difference between Case II diffusion and Fickian diffusion.

A calculation of the diffusion exponent from one of the swelling experiments with CO₂ on coal suggests that the diffusion process is anomalous. This is shown in Fig. 2.

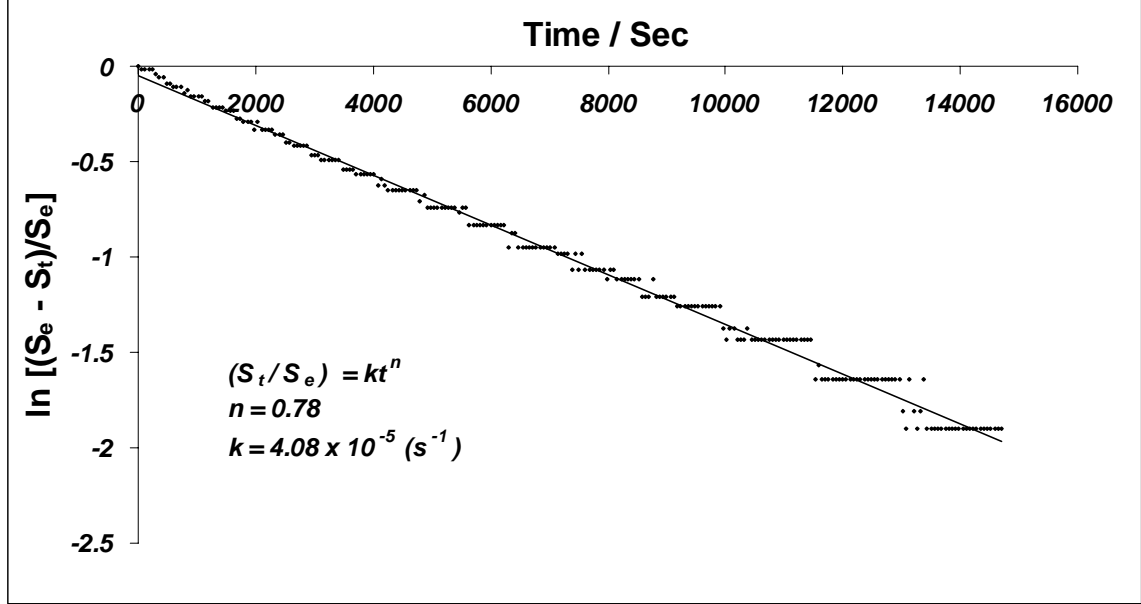


Figure 2. Calculation of the diffusion exponent (n).

CHEMICAL INTERACTION BETWEEN CO₂ AND COAL UNDER HIGH PRESSURE

Frank van Bergen^{1,2}, Sander Hol², Chris Spiers², Colin Peach²

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²Utrecht University, PO Box 80021, 3508 TA Utrecht, The Netherlands

Introduction

The general idea of CO₂-ECBM operations was that the injected CO₂ diffuses into the pores and adsorbs on to the pore surface, thereby replacing the methane at the internal coal surface. Although desk and laboratory studies looked promising, this technique was not yet a well-established and mature technology, and therefore implied some inevitable uncertainties. Therefore, field experiments were developed throughout the world. However, the processes that are going on *in situ* are not fully understood. A research programme was set-up in the Netherlands between Utrecht University, Shell International, Delft University of Technology and TNO to investigate the fundamental processes that play a role in these kinds of operations. This programme is part of the larger CATO (CO₂ Capture, Transport and Storage) project that was set-up to look into all potential storage options and the issues involved. This paper reports on the activities undertaken by Utrecht University and TNO in the scope of this project.

Coal swelling

Volumetric changes as a result of gas adsorption or desorption are a well known phenomenon. The matrix shrinkage and swelling can cause profound changes in porosity and permeability of coalbed methane reservoirs during depletion or when under injection processes (Pekot & Reeves, 2003). ECBM-CO₂ field experiments showed that the injectivity of CO₂ decreases in time, most likely due to a reduction of the permeability. This is generally attributed to a swelling of the coal after contact with the CO₂. This swelling was confirmed in laboratory experiments (e.g. Krooss et al., 2002; Mazumder, 2005).

Various models have been developed to describe these effects, such as presented by Sawyer et al. (1990) and Palmer and Mansoori (1996). The first model by Sawyer et al. (1990) uses gas concentration as an important parameter, because of the similarity between the curves of measured strain data vs. pore pressure and the Langmuir isotherm (Pekot & Reeves, 2003). The second model by Palmer and Mansoori (1996; 1998) is based on strain and the coal's rock mechanical properties. However, both models described shrinkage as a result of methane desorption, because the gas molecules that are adsorbed on the coal surface at a near liquid density occupy a certain volume. Laboratory data of CO₂ showed that CO₂ adsorption causes more strain and swelling than CH₄ (Pekot & Reeves, 2003). Much of this difference is attributable to the differing sorption capacity that any particular coal has for a particular gas, i.e. the more gas adsorbed by a coal at a given pressure, the larger the effect on strain, porosity and permeability (Pekot & Reeves, 2003). However, there are indications that another mechanism is also at work: similar amounts of gas result in different swelling behaviour (Pekot & Reeves, 2003). Pekot & Reeves (2003) do not give comments on the physical or chemical basis for the existence of differential swelling.

The above shows that the fundamental process of swelling process not fully understood. The observed swelling is so-far mainly attributed to the additional volume of the adsorbed phase, the

addition of the gas molecules to the solid phase. In our research, we are trying to differentiate between the physical adsorption and possible chemical adsorption that play a role when bringing coal in contact with CO₂.

Physisorption vs. chemisorption

Once a solid and a gaseous phase are brought together in one system, it is in most instances likely that there will be some interaction between the solid and the fluid. In this case, an adsorbate species is distributed between a solid phase and a gaseous one. The distribution, in general, is pressure and temperature dependent (Adamson & Gast, 1997). All gases below their critical temperature tend to adsorb as a result of general van der Waals interactions with the solid surface. In this physical adsorption (or physisorption) process, most important are the size and nature of interactions between the solid substrate and the adsorbent and on those between adsorbate molecules (Adamson & Gast, 1997). Physical adsorption equilibrium is very rapid in attainment, except when limited by mass transport rates in the gas phase or within a porous solid substrate. Also, this process is reversible; the adsorbate is removable without change by lowering the pressure (at constant temperature), although there may be hysteresis in the case of a porous solid (Adamson & Gast, 1997).

If the adsorption energy is large enough to be comparable to chemical bond energies, the process is called chemisorption. The adsorbate tends to be localized at particular sites, although some surface diffusion or mobility may still be present (Adamson & Gast, 1997). Chemisorption may be rapid or slow and may occur above or below the critical temperature of the adsorbate. It is distinguishable, qualitatively, from physical adsorption in that chemical specificity is higher and that the energy of adsorption is large enough to suggest that full chemical bonding has occurred. Gas that is chemisorbed may be difficult to remove, and desorption may be accompanied by chemical changes (Adamson & Gast, 1997). Because of its nature, chemisorption is expected to be limited to a monolayer. Physical adsorption is not so limited and, in fact, may occur on top of a chemisorbed layer as well as alongside it (Adamson & Gast, 1997). In fact, there is no sharp dividing line between these types of adsorption, although the extremes are easily distinguishable (Adamson & Gast, 1997).

Approach

Uni-axial deformation experiments were executed in order to investigate the processes as outlined above. All samples were pre-compacted in a vacuum at a fixed applied stress. Next, CO₂-coal interaction experiments were conducted on two different high volatile bituminous coal aggregates and on activated carbon. CO₂ was then introduced in two steps; first at 5.6 (MPa), which in a second stage was increased to 9.5 (MPa). The sample is maintained at a fixed volume and the resulting stress changes are observed. After circa 1-2 hours, the load is removed and the volume of the sample is no longer constrained. We monitor the sample dimensions for a period of several hours to a day by bringing the piston to the sample at irregular intervals to monitor subsequent volume change. After stabilisation of the volumetric processes the CO₂ is released from the sample. Samples are taken from this gas for analysis with a gas chromatograph/mass spectrometer. The experiment is then repeated; the coal sample is again saturated with CO₂ at 5.6 and 9.5 (MPa). Note that there is no fundamental difference in approach between the first and the second time in the way CO₂ is introduced to the sample.

Results

The two-stage introduction of CO₂ into the samples leads to a saturation of the sample with CO₂. The theoretical pore pressure was calculated on the basis of the CO₂ pressure and compared to the applied stress. It appeared that the applied stress to keep the piston at its position was often larger than could be expected on the basis of the gas pressure. This implies that the sample executes an additional force on the piston. The displacement measurements, after removal of the piston, indicate that the volume of the sample is increasing. Gas chromatographic analysis clearly shows the presence of higher organic molecules (e.g. propane, (iso-)butane, (iso-)pentane, etc.) of the released gas from the experiments with the high volatile bituminous coal samples, while they are nearly absent in activated carbon gas.

Discussion

According to the classical idea in the CBM related literature, the gas is physically adsorbed on the coal surface. This can be considered as a reversible process: both the adsorbent and adsorbate return to their initial state once the pressure is released. Physisorption of CO₂ on coal was recently confirmed for lignite and low-volatile coal (Goodman et al., 2005). Goodman et al. (2005) calculated energy of adsorption consistent to those of CO₂ physisorption and concluded that in the investigated coal there was only one type of sorption site for CO₂. However, the GC-MS results of this study give strong indications that, for other coal samples, chemisorption does play an important role. In this latter case, it can be assumed that there is a chemical bonding between the coal and part of the CO₂. This implies that the coal is chemically altered by the CO₂, and that it will not return to its initial state after pressure release (irreversible process).

The results described above clearly indicate that all samples show a volumetric expansion as a result of contact with high pressure CO₂. After evacuating the sample from CO₂ the first time, the high volatile bituminous coal did not return to their initial dimensions. Only a small part of the expansion came back. Introduction of CO₂ for a second time leads to an expansion again. Evacuation of CO₂ shows that this last expansion is fully reversible. This indicates that possibly two processes are active; a reversible and an irreversible expansion. Possibly, these are related to physisorption and chemisorption, respectively.

In CBM research, much of the possible effects of chemisorption might be overlooked, because the majority of the research involved indirect volumetric or gravimetric experiments. Goodman et al. (2005) expected, in case of chemisorption, changes related to oxygen functionality but could not confirm this with ATR-FTIR. However, these observations do not have to be universal as shown by this study. A possible effect of chemical change could be that the coal is becoming more "plastic" or "rubbery" (Larsen, 2004). Supercritical CO₂ is known for its plasticizing effect on glassy polymers, by its ability to interact with basic sites in polymers (Kazarian et al., 1999). Kazarian et al. (1999) describe the changes in the ATR-IR spectra of PET (polyethylene) after treatment with supercritical CO₂. These changes are substantial, comparable to heating of the material over 100 °C for several days. Of course, it is questionable to what extent glassy polymers are analogue to coal, but this effect could play a role in coal. In that case, the consequences of the plasticizing effect would be substantial, e.g. critical in-situ fracking pressures might be increased or decreased. There are indications from the RECOPOL field in Poland that this could indeed play an important role.

Other chemical reactions seem likely, considering the supercritical phase of the CO₂. The use of a

supercritical fluid in a high pressure flow cell is not uncommon (Amador Hernandez & Luque De Castro, 2000), because "a supercritical fluid is considered an interesting solvent for solid samples extraction owing to the unusual combination of its physico-chemical properties: its gas-like high diffusivity, low viscosity and no surface tension facilitate its penetration through the small cavities of the solid matrix, while its solvent strength can be similar to that of liquids, depending on the pressure and temperature conditions (after Luque De Castro et al., 1994)". These solvent capabilities of CO₂ seem to be confirmed by the GC-MS analyses of gas from the CO₂-coal experiments.

Additionally, supercritical CO₂ is known to cause swelling on glassy polymers (Kazarian et al., 1999). In coal, both physi- and chemisorption will result, to some extent, in swelling of the coal and a change of coal structure. In fact, it has become increasingly appreciated in recent years that the surface structure of the adsorbent may be altered in the adsorption process (Adamson & Gast, 1997). As mentioned above, the swelling was confirmed in field and laboratory experiments.

Conclusively, chemical effects are likely to occur and are likely to result in physical changes of the coal, e.g. swelling. The coal changes and related swelling may have important implications for actual field operations. Swelling would affect permeability, as discussed earlier. Chemical solving of part of the coal may result in precipitation in other parts of the coal (comparable to scaling in some oil and gas operations), in the worst case in and around the pore throats thereby blocking gas exchange. Further research in the coming months will therefore focus on the relation between the coal composition and chemical and physical (swelling) implications, by undertaking FT/IR spectroscopy to observe actual changes that occur in the coal.

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