

## CHEMICAL INTERACTION BETWEEN CO<sub>2</sub> AND COAL UNDER HIGH PRESSURE

Frank van Bergen<sup>1,2</sup>, Sander Hol<sup>2</sup>, Chris Spiers<sup>2</sup>, Colin Peach<sup>2</sup>

<sup>1,2</sup> TNO, PO Box 80015, 3508 TA Utrecht, The Netherlands

<sup>2</sup> Utrecht University, PO Box 80021, 3508 TA Utrecht, The Netherlands

### Introduction

The general idea of CO<sub>2</sub>-ECBM operations was that the injected CO<sub>2</sub> 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 (CO<sub>2</sub> 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-CO<sub>2</sub> field experiments showed that the injectivity of CO<sub>2</sub> 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 CO<sub>2</sub>. 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 CO<sub>2</sub> showed that CO<sub>2</sub> adsorption causes more strain and swelling than CH<sub>4</sub> (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 CO<sub>2</sub>.

### 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, CO<sub>2</sub>-coal interaction experiments were conducted on two different high volatile bituminous coal aggregates and on activated carbon. CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> is introduced to the sample.

### **Results**

The two-stage introduction of CO<sub>2</sub> into the samples leads to a saturation of the sample with CO<sub>2</sub>. The theoretical pore pressure was calculated on the basis of the CO<sub>2</sub> 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 exerts 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 CO<sub>2</sub> 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 CO<sub>2</sub> physisorption and concluded that in the investigated coal there was only one type of sorption site for CO<sub>2</sub>. 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 CO<sub>2</sub>. This implies that the coal is chemically altered by the CO<sub>2</sub>, 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 CO<sub>2</sub>. After evacuating the sample from CO<sub>2</sub> 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 CO<sub>2</sub> for a second time leads to an expansion again. Evacuation of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>. 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 CO<sub>2</sub>. 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 CO<sub>2</sub> seem to be confirmed by the GC-MS analyses of gas from the CO<sub>2</sub>-coal experiments.

Additionally, supercritical CO<sub>2</sub> 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.

### **Acknowledgements**

The technical staff members of the Laboratory for High Pressure and Temperature Research of Utrecht University, especially Peter van Krieken and Gert Kastelein, are thanked for their valuable support and suggestions in the experiments and interpretation. Harry Veld and Kathrin Reimer of TNO are acknowledged for their support and suggestions in the coal characterisation and gas analyses. The Central Mining Institute and the Brzeszcze mine in Poland and Delft University of Technology are acknowledged for providing the coal samples.

### **References**

- Adamson, A.W. & Gast, A.P., 1997. *Physical Chemistry of Surfaces*, 6<sup>th</sup> edition. Wiley-Interscience Publications, ISBN 0-471-14873-3, 784 pp.
- Amador-Hernandez, J. & Luque De Castro, M.D., 2000. On-line detection for supercritical-fluid extraction, *Journal of Biochemical and Biophysical Methods*, July 2000
- Goodman, A.L., Campus, L.M. & Schroeder, K.T., 2005. Direct evidence of Carbon Dioxide Sorption on Argonne Premium Coals using attenuated total reflectance – Fourier Transform Infrared Spectroscopy. *Energy & Fuels*, 2005, 19, 471-476.
- Kazarian, S.G. / Brantley, N.H. / Eckert, C.A., 1999. Applications of vibrational spectroscopy to characterize poly(ethylene terephthalate) processed with supercritical CO<sub>2</sub>. *Vibrational Spectroscopy*, Apr 1999.
- Krooss, B.M., F. van Bergen, Y. Gensterblum, N. Siemons, H.J.M. Pagnier, P. David, 2002. High-pressure methane and carbon dioxide adsorption on dry and moisture-equilibrated Pennsylvanian coals; *International Journal of Coal Geology* 51; p. 69-92

- Larsen, J.W., 2004. The effects of dissolved CO<sub>2</sub> on coal structure and properties, *International Journal of Coal Geology* 57, p. 63-70.
- Luque De Castro, M.D., Valcárcel, M., Tena, M.T., 1994. *Analytical supercritical –fluid extraction*, Heidelberg: Springer.
- Mazumder, S. , Wolf, K-H.A.A , Bruining, H., 2005. The Relationship between Coal Macromolecular structure and its Swelling. In: *Proceedings International RECOPOL workshop Szcyrk (Poland)*, March 10 & 11 2005.
- Palmer, I. and Mansoori, J., Dec. 1998: “How Permeability Depends on Stress and Pore Pressure in Coalbeds: A New Model,” paper SPE 52607, SPEREE, pp. 539-544.
- Palmer, I. and Mansoori, J., Oct. 1996: “How Permeability Depends on Stress and Pore Pressure in Coalbeds: A New Model,” paper SPE 36737, *Proceedings of the 71st Annual Technical Conference*, Denver, CO
- Pekot, L.J. and Reeves, S.R.: "Modeling the Effects of Matrix Shrinkage and Differential Swelling on Coalbed Methane Recovery and Carbon Sequestration", paper 0328, *Proceedings of the 2003 Coalbed Methane Symposium*, May 5-7, Tuscaloosa, AL.
- Sawyer, W. K., Paul, G. W., and Schraufnagle, R. A., June 1990: “Development and Application of a 3D Coalbed Simulator”, paper CIM/SPE 90-119, *Proceedings of the Petroleum Society CIM*, Calgary.