

FT/IR INVESTIGATION OF CO₂ INTERACTION WITH COAL UNDER HIGH PRESSURE

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Introduction

Subsurface coal seams contain significant amounts of gas, that is largely adsorbed in the internal surface of the coal pores. From the 1970s onwards there has been a growing interest to produce this gas, coalbed methane, as a fuel. Due to a concerted effort by the US government and private organisations to demonstrate commercial production, the coalbed methane industry in the USA grew from a little-known, high-cost operation to a competitive main-stream natural gas resource (Ayers, 2002). At the end of the 1980's, this industry searched for methods to enhance production. The successes of Enhanced Oil Recovery (EOR) gave the coalbed methane industry, especially Amoco (now BP), the idea that gas injection could also be successfully applied in coalbeds to enhance coalbed methane production. The primary benefit of ECBM with gas injection is the increased production rates of methane. This means that the time to produce the gas is significantly reduced, therefore provide a shorter return on investment. Another benefit is that the recovery factor, although still depending strongly on the pressure drop by water production, will be increased due to the desorption reactions induced by the injected gas. In case of a gas with a lower adsorption capacity than methane (helium or nitrogen) extra methane will desorb from the coals due to a lowered partial pressure of methane in the cleat system. In case of a gas with a higher adsorption capacity than methane there will be an exchange reaction at the coal surface. Due to the adsorptive behaviour of coal it was soon recognized that Enhanced Coalbed Methane recovery (ECBM) with gas injection was a completely different process than EOR. Laboratory experiments showed that the adsorption capacity of coal was different for different gases (e.g. Fulton et al., 1980; Reznik et al., 1984; Puri and Yee, 1990; Stevenson et al., 1991; Arri et al., 1992; Hall et al., 1994; Stevens et al., 1999; Wolf et al., 1999; Krooss et al., 2002). Helium does not adsorb, nitrogen adsorbs less than methane, and the adsorption for gaseous carbon dioxide is about twice as high as for methane. From a production point of view, helium was considered to be the ideal gas for ECBM, since one would only need a small amount of gas for enhancement. Because helium is too expensive, the cheap N₂ was considered second best. CO₂ was more expensive and, based on these early laboratory experiments, one needs about four times the amount of N₂ for comparable enhancement. However, the commitment of the Kyoto protocol forces many countries to reduce their greenhouse gas emissions, including CO₂. For ECBM, with CO₂ injection, this meant that the strong adsorption of CO₂ on coal changed from a disadvantage, from a production point of view, to a valuable extra benefit for a production project. Especially in Europe, this focused research towards injection of CO₂ as enhancement gas.

In CO₂-ECBM operations, CO₂ is injected into the subsurface coal seams. The general idea 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. The desorbed methane can be subsequently produced, either from the same well as used for injection (huff-puff) or from other wells in the proximity of the injection well. Both laboratory experiments and field tests in Canada and the United States have suggested that for each CH₄ molecule produced, at least two CO₂ molecules can be sequestered (e.g. Puri & Yee, 1990; Stevenson et al., 1991; Hall et al., 1994). Laboratory experiments showed that this ratio of 1:2 could be even larger at depths greater than about 800 meters, where the gaseous CO₂ changes to supercritical CO₂ (Hall et al., 1994; Krooss et al, 2002).

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 (see Van Bergen & Pagnier, this conference). However, although these field projects are taking place and much laboratory work has already been done, 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

An experimental program was set-up in order to investigate the processes as outlined above. Two types of experiments were executed: uni-axial deformation experiments, as presented by Hol (this conference) and

qualitative FT/IR investigation of gas interaction with coal under high pressure. A transparent high pressure cell was developed that allows "direct" measurements of the adsorption on coal, by using FT/IR spectroscopy (Fig. 1). With FT/IR functional groups of the coal structure can be identified in the spectrum (Fig. 2). Possible changes in the composition of the coal are likely to be recognized in the coal. There is a special focus on the type of interaction between the gases (CH_4 and CO_2) with the coal. However, not all issues are solved in the experimental phase, especially in the preparation of thin sections from coal with microtome.

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_2 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_2 physisorption and concluded that in the investigated coal there was only one type of sorption site for CO_2 . However, as presented by Hol et al. (this conference), there are strong indications for other coal samples that 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_2 . This implies that the coal is chemically altered by the CO_2 , and that it will not return to its initial state after pressure release (irreversible process).

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. With FT/IR spectroscopy, one has the possibility to observe actual changes that occur in the coal. 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 Hol et al. (2005). A possible effect of chemical change could be that the coal is becoming more "plastic" or "rubbery" (Larsen, 2004). Supercritical CO_2 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_2 . These changes are substantial, comparable to heating of the material over 100 °C for several days. Off 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 RECOPOOL field in Poland that this could indeed play an important role.

Other chemical reactions seem likely, considering the supercritical phase of the CO_2 . 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_2 seem to be confirmed by the GC-MS analyses of gas from the CO_2 -coal experiments by Hol et al. (this conference).

Additionally, supercritical CO_2 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.

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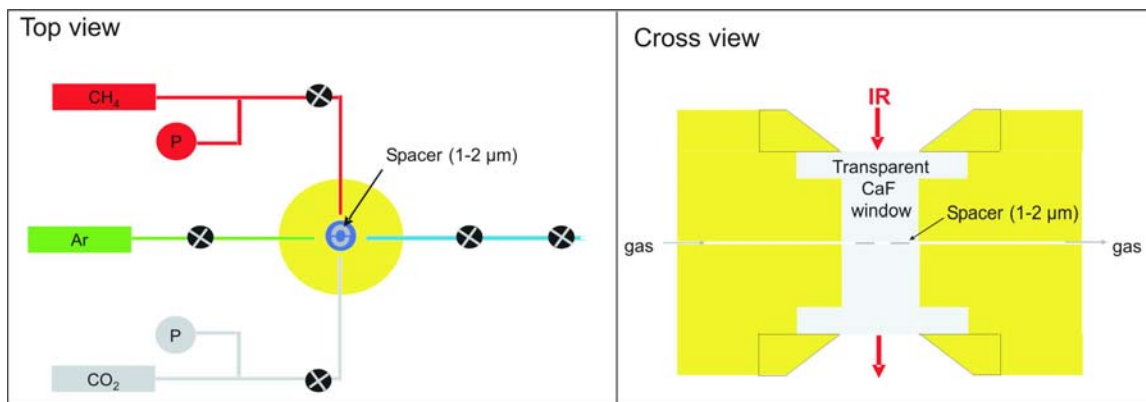


Figure 1 Setup of high-pressure infra-red cell

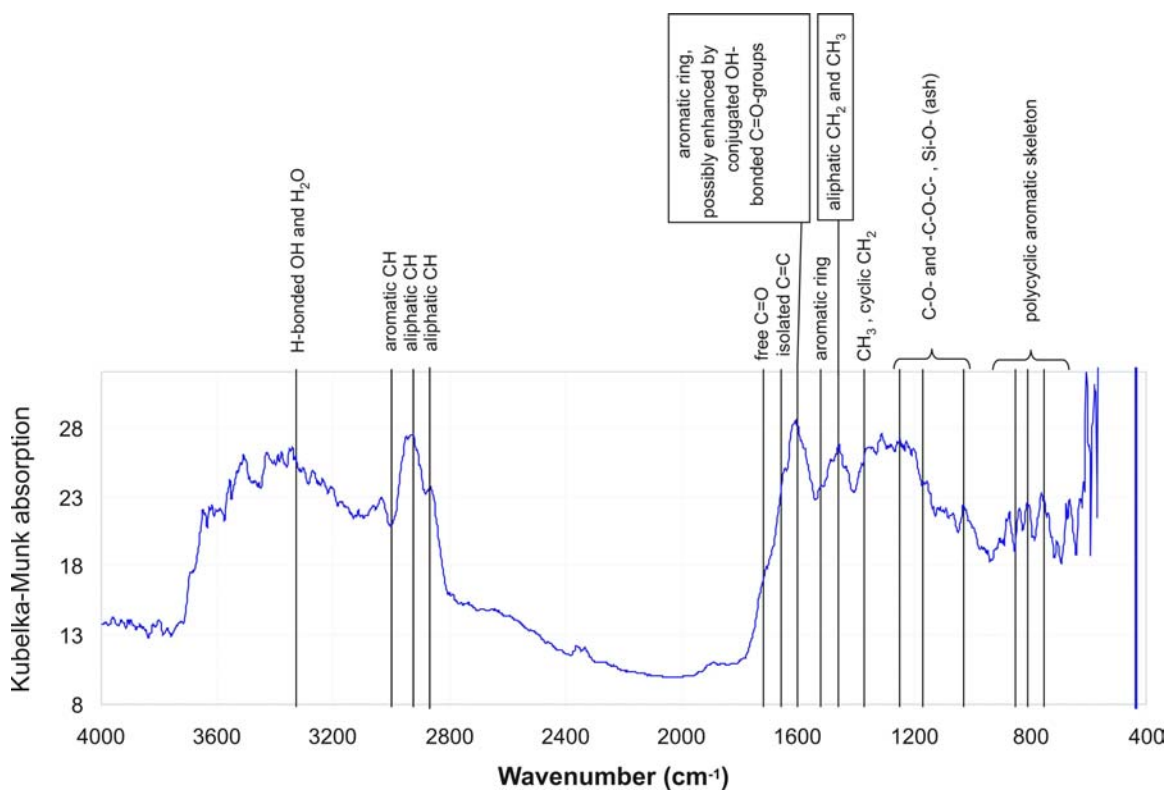


Figure 2 Infra-red absorption reflection spectrum of high volatile bituminous coal of powder from seam 364 of the Brzeszcze mine in Poland. Sample details are described in Hol et al. (this conference). Kubelka-Munk correction was applied to correct for reflection on powdered sample. Identification of peaks after Van Krevelen (1993).