

## VOLUMETRIC BEHAVIOUR OF COAL DUE TO CO<sub>2</sub> AND EFFECTS OF STRESS

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### Introduction

The Kyoto Protocol (1997) committed many countries to reduce their CO<sub>2</sub> emissions. Between 2008 and 2012, the Netherlands should reduce its contribution to the total by 6% relative to the level of CO<sub>2</sub> in 1990. CO<sub>2</sub>-emission is coupled to energy demand as satisfied by hydrocarbon consumption.

International strategies are therefore to find methods to reduce the consumption of hydrocarbons, or to find a way to dispose the emitted CO<sub>2</sub> in the oil and gas extraction process itself. The latter is made possible by 'Enhanced Coalbed Methane (ECBM) production', a method where potential new gas plays and CO<sub>2</sub>-storage in the subsurface are combined. In this method, adsorbed CH<sub>4</sub> is driven out by CO<sub>2</sub>-introduction into underground coal layers. The methane is extracted from the subsurface by a well. A good overview of recent standpoints is given by White et al. (2005).

The idea is very simple, but field and laboratory experiments show that still many uncertainties must be overcome. For example, the process is known to be dependent on characteristics of uptake, retention of CH<sub>4</sub> and CO<sub>2</sub>, and structural and mechanical properties of coal layers. Among others, it is generally known that CO<sub>2</sub>-introduction at an axial stress leads to a reduction of coal permeability and macroscopically detectable expansion, called 'swelling' (e.g. Krooss et al., 2002). Earlier researchers focused on the adsorption behaviour of CO<sub>2</sub> in coal, and related the swelling to this physical adsorption. Because the observed effect could not be explained fully by Langmuirian models, the model was extended to especially cover high gas pressure behaviour and binary gas adsorption, also including CH<sub>4</sub> (Clarkson & Bustin, 2000). However, more recently studies come available that recognise chemical processes, including more aggressive types of chemical leaching (van Bergen et al., this conference; Ozdemir et al., 2004). The aim of this research is to investigate the volumetric behaviour in coal due to interaction with CO<sub>2</sub> under *in situ* conditions, and to gain understanding of the processes involved.

### Sample description

The experiments outlined below were performed on both natural coals as well as on activated carbon (as reference sample). A high volatile bituminous coal was taken from a Polish mine and an anthracite from a mine in the United Kingdom. The sample from Poland was taken from the same coal seam that is used for injection in the RECOPOLE field experiment in Poland (van Bergen & Pagnier, this conference). This will allow us to relate the laboratory results to the field observations in a later stage. The high volatile bituminous coal was taken from layer 364 at a depth of 640-740 m in the Brzeszcze mine in the Upper Silesian Basin. The mined coal in this basin is of Pennsylvanian (Upper Carboniferous) age (Nowak, 2004). Vitrinite reflectance data show a VR<sub>r</sub> of 0.78% (standard deviation of 0.05), indicating that the coal is high-volatile bituminous. Maceral compositions vary: vitrinite content ranges between 59.8% and 66.0%; liptinite varies between 7.6% and 9.8%; and inertinite shows values in the range between 26.4% and 30.0% (Table 1). Bulk chemistry data were acquired using the RockEval-method. Heating steps of 0-250 (°C) and 250-550 (°C) pyrolyse and oxidise coal material, from which Total Organic Carbon (TOC), amount of volatilised hydrocarbons, amount of hydrocarbons produced by thermal cracking and amount of produced CO<sub>2</sub> can be deduced (Table 2). From the acquired concentrations, O/C- and H/C-ratios are calculated and plotted on a classic 'van Krevelen-diagram' (van Krevelen, 1993). The analysed samples gave rather high H/C-ratios (Fig. 1). However, these kind of results are often seen in Upper Silesian Basin coals and are called 'perhydrous coals' (Arenillas et al., 2003; Iglesias et al., 2000; Kotarba et al., 2005).

The activated coal is manufactured by Alfa Aesar and delivered in a -20 to +50 mesh grain fraction, with a moisture content of 2% and a 0.25%db dust fraction.

### Methods

#### Sample preparation

In order to eliminate as many physical heterogeneities as possible within the samples, the 364 natural coal and the activated carbon both were ground and sieved in three fractions, respectively <63 (µm), 63-212 (µm) and >212 (µm). In the analyses we use the 63-212 (µm) grain fraction because it is small enough to homogenise the sample to an acceptable level and large enough to maintain the micro-pore structure.

Because compaction experiments are performed under a dry vacuum, the samples were dehydrated in an oven at 40 (°C) for 2 days and stored in a desiccator under an argon atmosphere at ambient gas pressures. This is to prevent chemical interaction between coal material and the air.

#### Experimental Set-up

Our experimental set-up consists of an Instron 1362 servo-mechanical loading frame. Based on a 30 (mm) compaction vessel and a static load capacity of 100 (kN), it is capable in producing axial stresses up to 140 (MPa). The apparatus is able to control either its position (thereby fixing the vessel volume) or its applied load. To guarantee the system is not disturbed by sudden perturbations due to CO<sub>2</sub>-introduction, the apparatus holds at constant position. It therefore counteracts all stress that is exerted on its piston. A furnace controls the vessel temperature, set at 40 (°C) constant, which is hot enough to introduce supercritical CO<sub>2</sub>. Furthermore, a bottle of He provides pressure up to 10 (bar), to conduct He-porosity measurements. When all compaction due to creep mechanisms has ceased, the material is unloaded and its He-porosity is measured. All CO<sub>2</sub>-experiments begin after this pre-treatment. CO<sub>2</sub> is introduced at a bottle pressure of 5.6 (MPa), backed up with a nitrogen-filled gas pressure booster to provide pressures up to nearly 10 (MPa) constant. This pressure is held constant. During eventual release of the CO<sub>2</sub>, gas samples are taken to be analysed in a gas chromatograph. Volumetric properties as well as sample temperature and applied load are measured. All data are logged digitally (16 bit) and visually by a chart recorder.

#### Experimental program

The demand to work with physically homogeneous coals requires the presence of structures that are comparable at the start of each experiment. Ideally this has to be achieved in terms of grain stacking, macro-porosity, grain size, temperature and gas pressures. In order to achieve this, we decided to pre-compact all samples in a vacuum at a fixed applied stress. To be sure a suitable pre-compaction uniaxial stress is selected, stepwise compaction within the range 5-80 (MPa) was conducted to assess the porosity vs. compaction behaviour of the high volatile bituminous coal aggregate (Fig. 2). The porosity decreases from 40% to 20% due to this compaction. Above 65-70 (MPa), these values tend to flatten out at around 20%, indicating that additional stress does not result in further porosity reduction. On the basis of these results further experiments were chosen to start after pre-compaction of the sample at 65 (MPa). Next, four CO<sub>2</sub>-coal interaction experiments were conducted. Two tests ran on the high volatile bituminous coal aggregate, one on the anthracite and one on the activated carbon. All four were pre-compacted at 65 (MPa) for 1-2 days and then unloaded to around 0.3 (MPa). After a volumetric equilibration of a few hours at 0.3 (MPa), an appropriate starting material is produced that has suitable dimensions to be used in strain analyses. 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**

In order to guarantee that the experiments deal with a physically stable grain aggregate a dry compaction of coal grains at 65 (MPa) was conducted prior to CO<sub>2</sub>-coal interaction experiments. In the case of the high volatile bituminous coal, this results in formation of a grain pellet. Activated carbon remained a powder.

The two-stage introduction of CO<sub>2</sub> into the samples (Fig. 3<sup>a-b</sup>) leads to a saturation of the sample with CO<sub>2</sub>. The plots show both a theoretically calculated pore pressure (on the basis of the CO<sub>2</sub> pressure) and recorded applied stress. For a constant sample volume, a definition of a constant effective stress ( $\sigma_e = \sigma_{\text{applied}} - P_f$ ) theoretically implies that an increase in pore pressure is balanced by an increase of applied stress. Noticeably, all large alterations in stress state occur within 10 (min) after addition of the CO<sub>2</sub>. The intensity of stress varies, depending on the material.

When the piston is shifted upward, a volume of fluid is generated above the sample. This allows the sample to equilibrate in free space. In all cases, the axial stress drops to its expected value based on

pore pressure (i.e. around 10 (MPa)). Axial strain relative to the sample dimensions after pre-compaction, is taken relative to time (Fig. 4). Not all samples show a clear trend in volumetric behaviour. But in any case all axial strain remains in the range of 4-6%.

Subsequent analysis of the pore fluid shows that a number of dissolved components produce a bad odour in the released gas. Gas chromatographic results clearly show the presence of COS and CS<sub>2</sub>-compounds in different amounts, lowest for gas samples from the anthracite (Fig. 5<sup>a-c</sup>). Aliphatic (C<sub>x</sub>) compounds are abundant in the extracted gas from the anthracite and the high volatile bituminous coal. These compounds could clearly be recognised up till (iso-)pentane and are nearly absent in activated carbon gas.

## Discussion

Coal material has a very complex physical and chemical structure, and heterogeneities can be expected down to the molecular level. However, it was attempted to make the samples as homogeneous as possible, without destroying the finest pore structure. There the samples are crushed and sieved to a known grain size. Subsequently, the sieved powder was pre-compacted to re-introduce a macro-pore system in the coal. This sample preparation was conducted to generate a physically identical starting material each test. Although some physical heterogeneity in the sample will remain we are confident that these remaining inhomogeneities did not play a role of any significance in the processes leading to the results above. When upscaling laboratory results, one has to take into account that sieving may have lead to maceral fractionation (Busch et al., 2004). Here the bigger grain size fractions tend to be enriched in liptinite and vitrinite and smaller grain size fractions in inertinite. The performed maceral analyses may therefore reveal slightly lower or higher maceral contents. Vitrinite reflectances however do not show such a variation. Additionally, upscaling always is hampered by the individual differences in coal characteristics. For example, the perhydrous character of the high volatile bituminous coal implies the presence of a higher H-index and a relatively dominating activity of aliphates. Based on our results, it is too early to make any generic comments on this.

During all experiments, conducted on different samples, an increase in applied stress is observed once CO<sub>2</sub> is added. According to the definition of effective stress ( $\sigma_e = \sigma_{\text{applied}} - P_f$ ), compensation of the pore pressure by an equal applied force holds the effective stress constant. However, subtracting the pore pressure from the axial stress reveals that an excess stress is measured. This implies the sample itself is executing a net force to the apparatus. The activated carbon exposes only little excess stress behaviour (1 (MPa)) compared with the anthracite (3.5 (MPa)) and high volatile bituminous coal (4.5 (MPa)) (Fig. 6). This behaviour occurs within 10 (min) and is independent of the CO<sub>2</sub> gas pressure: i.e. the excess stress of at 5.6 (MPa) is similar to that of 9.5 (MPa). The independence of gas pressure increase is an indication that at least part of the sensed excess stress is caused by a chemical reaction that requires a volume increase. The machine artificially restricts the sample to expand. The observed differences per test can be explained by differences in chemical reactivity of the specific sample. It is expected that CO<sub>2</sub> will have the most intense effect on the weakest bonds in the coal structure. Most likely, these are represented by the non-branched aliphatic chains.

Although the actual relation between excess stress and volumetric change is yet unclear, a higher reactivity seems likely to be measured in terms of a greater excess stress, since the apparatus restricts the sample to constant volume. Activated carbon does not contain any compounds that are likely to react, since these are stripped off in the manufacturing process, implying a low reactivity. CO<sub>2</sub>-interaction tests therefore show a low excess stress and gas chromatographic analyses indicate the absence of aliphatic compounds. The observed difference between high volatile bituminous coal and anthracite could be explained by their difference in degree of coalification. Generally, in the process of coalification compounds are removed from the coal structure in the reverse order of their bond strength. The lower rank high bituminous coal contains more weak bonds than the anthracite, and is therefore likely to be more reactive. This can be measured in terms of difference in excess stress. 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>. Nevertheless, there is no clear relation between excess stress and observed free expansion (Fig. 4). After evacuating the sample from CO<sub>2</sub> the first time, the high volatile bituminous and the anthracitic 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. When dealing with purely reversible processes, a release of the CO<sub>2</sub> gas pressure to vacuum initiates total relaxation of the system (it will return to its initial volumetric state). In the case a material remains in an expanded state under vacuum, the process

responsible for this condition is irreversible. Conclusively, we propose that CO<sub>2</sub> is permanently incorporated in the coal structure by chemical reaction.

### Conclusions

Firstly, we must emphasise that in this paper the idea is supported that in association with macroscopically observable 'swelling', the overall internal structure and texture of the coal is modified; either by physical or chemical processes. This means that internal behaviour leads to macroscopically observable effects. This may sound obvious, but often the term 'swelling' is used in association with 'adsorption'. Suggesting that adsorption is the only process responsible for coal expansion. With the here presented experiments it is shown that expansion of coal material is observed, accompanied by a sample expansion, capable of doing work and releasing aliphatic (C<sub>x</sub>) compounds when due to saturation with CO<sub>2</sub>. It is observed that these volumetric effects due to coal-CO<sub>2</sub> interaction show a permanent and non-permanent component. Most likely, the non-permanent component is related to a reversible adsorption process, where the permanent component is caused by a chemical reaction. Based on its chemical composition, it was expected and observed that activated carbon would show no permanent volumetric effect as a result of interaction with CO<sub>2</sub>. Conversely, the permanent volumetric changes in both the high volatile bituminous coal and the anthracite are a result of their chemical composition. These permanent changes might be coupled to irreversible chemical processes.

Based on ideas in polymer science, Larsen et al. (1997) and Larsen (2004) already suggested plasticizing processes in coal when CO<sub>2</sub> is introduced. A structural re-arrangement due to chemical interaction might change the physical properties of coal, which leads to changes in volumetric behaviour. On the other hand, Ozdemir et al. compensate for volumetric behaviour and produce a model that account only for adsorption.

The integration of different analytical techniques is essential in gaining insight in physio-chemical processes and effects in coal. Together with the work of van Bergen et al. (this conference), this study is the result of such a multi-disciplinary approach. Physical oriented compaction experiments can reveal apparently unquantifiable observations that can be unravelled in terms of processes with the use of chemical oriented techniques like the mass spectrometer and infrared microscope (Mastalerz, 2001; Mastalerz et al. 2004; Goodman et al., 2005), and vice-versa.

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Material	% Vitrinite	% Liptinite	% Inertinite	% Minerals	n°	VR <sub>r</sub> %	St.dev.	n°
High Vol. Bit. Coal <sup>d</sup>	66,0	7,6	26,4	0,0	500	0,79	0,05	50
High Vol. Bit. Coal <sup>b</sup>	59,8	9,8	30,0	0,4	500	0,77	0,05	50

Table 1: Macerals and Vitrinite Reflectances for a high volatile bituminous coal sample from the Upper Silesian Basin in Poland (two analyses).

Material	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	T <sub>max</sub>	TOC %	HI	OI	PI	MINC %	PC %	RC %	Quant	Total C %	Total S %
High Vol. Bit. Coal <sup>b</sup>	0,91	182,48	2,33	430	64,01	285	4	0,00	24,73	15,64	48,37	9,70	82,59	0,464
High Vol. Bit. Coal <sup>d</sup>	0,73	163,88	2,01	430	67,61	242	3	0,00	15,40	14,09	53,52	8,30	74,21	0,285

Table 2: RockEval and Carbon/Sulfur data for a high volatile bituminous coal sample from the Upper Silesian Basin in Poland (two analyses).

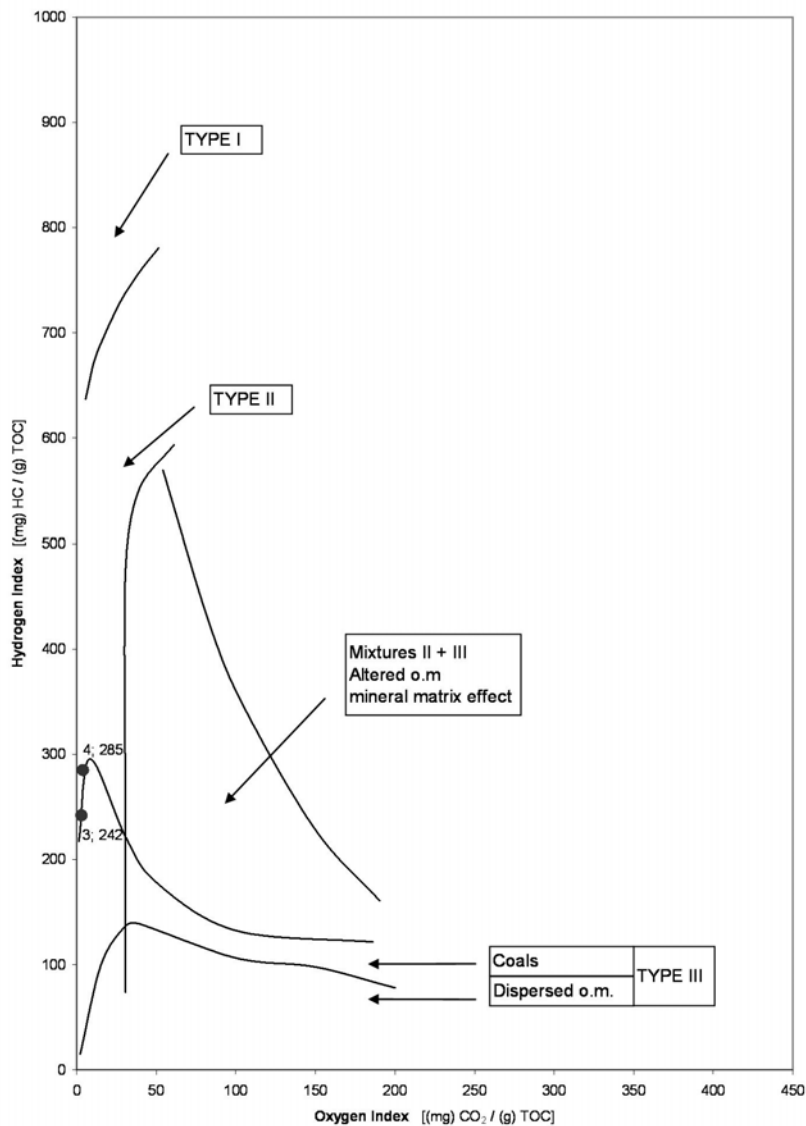


Figure 1: Pseudo-van Krevelen diagram plotting Hydrogen and Oxygen indexes for a high volatile bituminous coal. The coal plots in a Type-III field, with a high Hydrogen index, indicating a 'perhydrous' character.

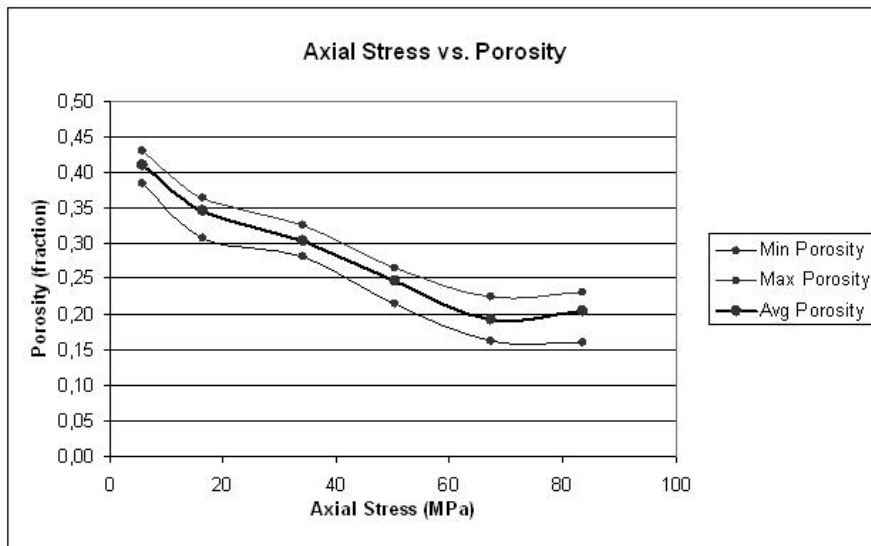


Figure 2: He-porosity evolution during compaction of the High Volatile Bituminous Coal. Minimum and maximum curves are due to measured pressure variations.

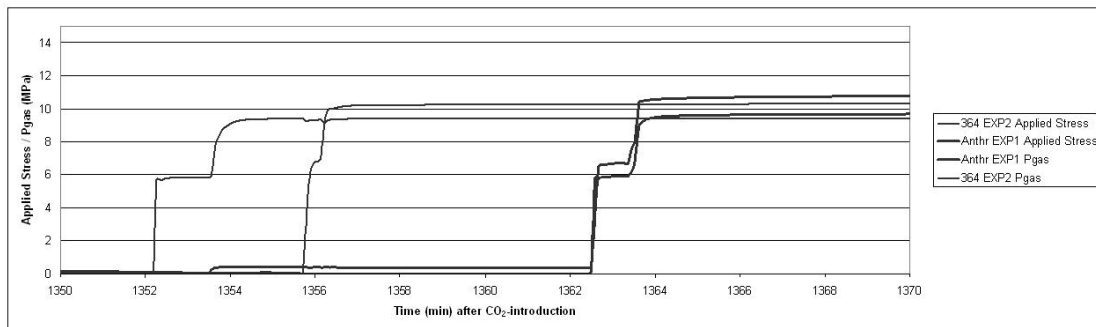
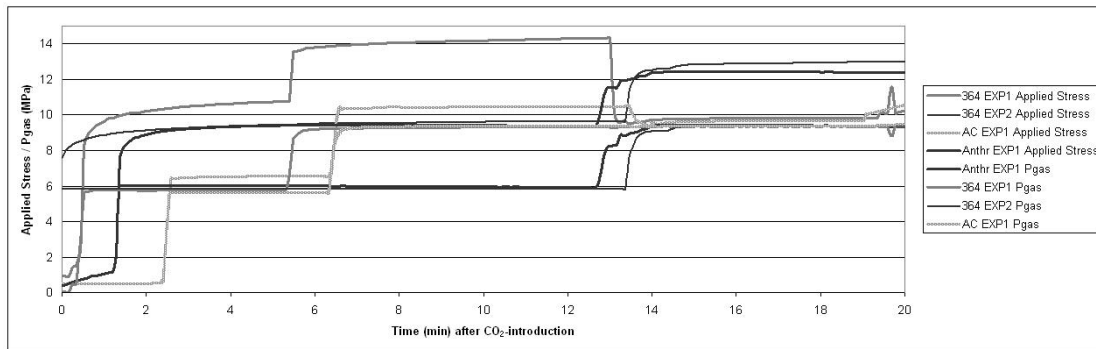


Figure 3: <sup>a</sup>Applied stress and gas pressure in (MPa) during first introduction of CO<sub>2</sub> at fixed vessel volume. Gas pressure was applied in two stages; 5.6 and 9.5 (MPa). <sup>b</sup>Applied stress and gas pressure in (MPa) during second introduction of CO<sub>2</sub> at fixed vessel volume. Gas pressure was introduced in one stage at 9.5 (MPa).

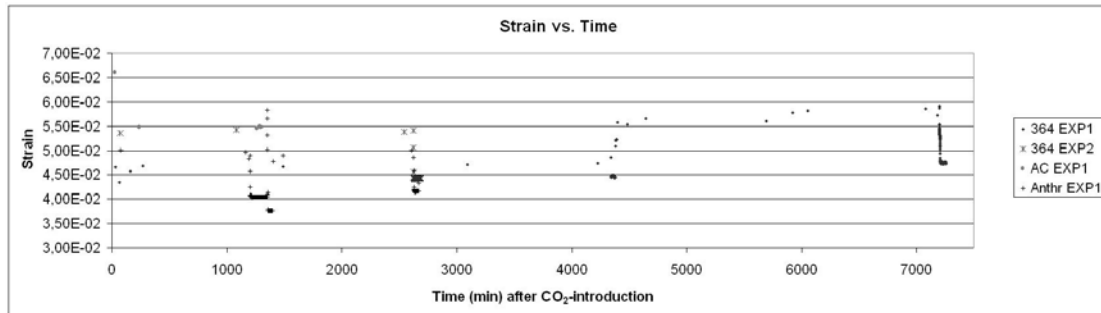


Figure 4: Axial Strain (taken relative to sample dimensions after pre-compaction) is plotted in time. Vertical trends coincide with gas pressure application or release.

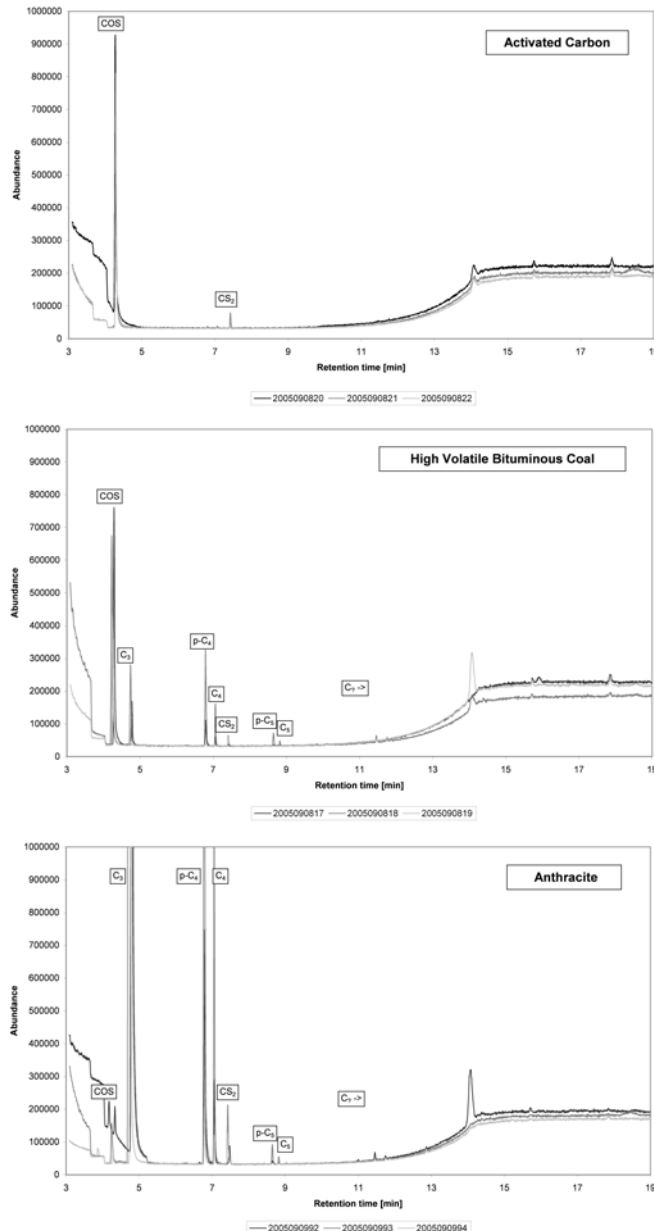


Figure 5: Molecular abundances relative to retention time, measured in a gas chromatograph. Activated carbon<sup>a</sup>, high volatile bituminous coal<sup>b</sup>, and anthracite<sup>c</sup> are plotted, indicating clear peak abundances for COS, CS<sub>2</sub> and aliphates up to C<sub>5</sub> or higher.



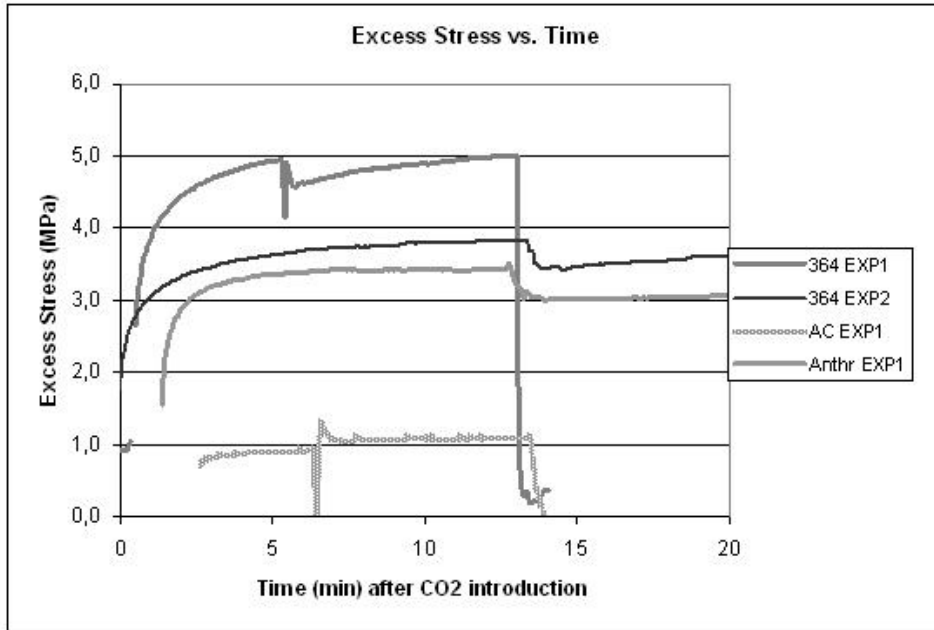


Figure 6: Excess stress in time, during first introduction of CO<sub>2</sub>. Note the decreasing excess stress with increasing amount of carbon in the material. Also note an increase in CO<sub>2</sub> pressure from 5.6 to 9.5 (MPa) does not lead to a higher excess stress.