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Physical and structural effects of carbon dioxide storage on vitrinite-rich coal particles under subcritical and supercritical conditions

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ABSTRACT

The effects of CO_2 sequestration on the chemical and physical properties of coal have been shown to be influenced by the coal's maceral composition. Whilst inertinite-rich coal particles have insignificant changes upon exposure to subcritical CO_2 conditions for extended time periods (6 months), vitrinite-rich coal particles had changes in the structure and physical properties. In the present paper, changes in the structural and physical characteristics of a South African vitrinite-rich dry coal were studied after exposure to subcritical (42 bar, 25 °C), and supercritical (125 bar, 35 °C) CO_2 conditions for 6 months. The samples were characterised pre- and post-CO_2 exposure. The characterisation techniques used were: CO_2 adsorption capacity (using a custom built high pressure volumetric system), surface area and pore size distribution analysis using both N_2 and CO_2 gas and the Brunauer–Emmett–Teller method (BET) and Fourier-Transform Infrared Spectroscopy (FTIR). Structural and physical changes in the coal were observed; these changes differed for subcritical and supercritical conditions. It was found that the surface area and number of micro-pores decreased sharply for the supercritical treated coal sample when compared to the untreated and subcritical treated coal sample. The adsorption capacity of the supercritical treated coal was also reported to be lower than the subcritical treated coal over the same period.

1. Introduction

The global focus on climate change is continuously increasing. This has led to developing countries like South Africa exploring the use of lower carbon-intensive energy trajectories (Naidoo, 2009). South Africa has an abundance of coal reserves, and with the limitations and expense associated with renewable energy as a bulk energy supplier, emphasis is being given to clean coal technologies (Raubenheimer, 2007). One promising option is Carbon Capture and Storage (CCS). This process involves the separation of CO_2 from industrial and energy related sources and its transportation to a storage location for long term isolation from the atmosphere. Although geological storage of anthropogenic gases as a greenhouse mitigation option was first proposed in the 1970s, little research was done until the early 1990s (IPCC, 2005). Potential geological storage locations include, but are not limited to: depleted oil and gas reservoirs, deep unused saline water-saturated reservoir rocks, oil shales and deep unminable coal seams (Xu et al., 2007; Bachu, 2003; Holloway and Survey, 1993). Deep unminable coal seams may possess the advantage of significantly reducing transport costs in the CCS process as most of the locations of the major point source emissions are within the vicinity of the coal reserves (Viljoen et al., 2010), particularly in South Africa (Cloete, 2010). With the possibility of enhanced coal bed methane recovery (ECBM) as a potential viable funding mechanism, unminable coal seams are an even more promising storage option.

Gas storage in coal seams is however quite complex due to the intricate and heterogeneous nature of the coal, as evidenced by the substantial dedication of literature to the subject (Maphala and Wagner, 2012; Cao et al., 2011; Mastalerz et al., 2010; Gathitu et al., 2009; Ozdemir, 2009; Karacan, 2003, 2007; Goodman et al., 2005; Larsen, 2004; Crosdale et al., 1998). However, there is still much that is not understood about coal-CO_2 interactions (Mirzaeian and Hall, 2006; Larsen, 2004). Most studies reported in literature are conducted at short adsorption periods (up to 2 weeks) and/or low pressures (<60 bar) (Perera et al., 2011; Romanov and Soong, 2008; Sakurovs et al., 2007). In the effort to predict the long term effects of CO_2 storage in coal seams, it is essential to gather information on coal-CO_2 interactions and their effects on the coal structure and its properties (Larsen, 2004). These interactions have been reported to be dependent on the coal's maceral composition (Maphala and Wagner, 2012; Cao et al., 2011; Mastalerz et al., 2010). Crosdale et al. (1998) found that maceral composition plays an influential role in the development of the pore structure relating to gas sorption. Lithotypes in combination with mineral matter were also shown by Morse et al. (2010) to influence both

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the gas adsorption as well as the micro and meso-porosity of coals. Mastalerz et al. (2010) report structural and physical changes only in vitrain, as compared to fusain and clarain after saturation with CO_2. The swelling properties of vitrinite have also been observed by some authors as compared to the inertinites and clays, which tend to be compressed with exposure to CO_2 (Day et al., 2008; Goodman et al., 2005; Karacan, 2003; Karacan and Mitchell, 2003; Patel and Reucroft, 1986). Structural changes in coal after CO_2 exposure have been reported in literature at pressures as low as 3.5 bar (Goodman et al., 2005). The identification and characterisation of such changes in coals is crucial as initial exposure to CO_2 may significantly affect its adsorption properties and characteristics in the long term (Yang et al., 2011; Goodman et al., 2005). Limited literature is available on the topic and hence calls for further research (Yang et al., 2011; Fokker and van der Meer, 2004). Maphala and Wagner (2012) considering the different behaviour of macerals under subcritical CO_2 storage, showed minimal changes in the physical properties of inertinite rich coal particles, compared to vitrinite rich coal particles. As a continuation to this study, the present paper investigates the effect of long term CO_2 storage in a dry South African vitrinite-rich coal of medium rank C classification. The coal was exposed to supercritical CO_2 conditions in a Parr type reactor for 6 months. The coal was characterised pre-and post-treatment, the results are compared to those obtained under subcritical treatment of the same sample (Maphala, 2012).

2. Experimental

The coal sample used was obtained from a northern coalfield in South Africa. The sample was crushed and screened to +500–1000 μm particle size fraction. Density fractionation was carried out to concentrate the vitrinite maceral. Organic solvents, chloroform and benzene, were used for density fractionation. These solvents were selected due to their negligible effect on the coal properties after density fractionation as compared to inorganic solvents as determined by a preliminary analysis where samples were characterised pre and post density fractionation for different types of solvents (Maphala, 2012). Following density media separation, each sample was dried in a vacuum-drying oven at 50 °C for 24 h. The samples were well mixed and standard characterisation methods: Proximate, ultimate, and petrographic analyses (maceral content) were employed; the results are presented in Table 1.

2.1. Characterization methods

Following Maphala and Wagner (2012), additional characterisation methods were performed before and after the long term CO_2 treatment. These characterisation methods were designed to access the structural and physical properties of the coal and consisted of: Surface area and pore size distribution analysis using the Brunauer–Emmett–Teller (BET) method, density measurements using Helium Pycnometry for CO_2 sorption capacity measurements and Fourier Transform Infrared spectroscopy (FTIR).

Table 1
Proximate, ultimate and petrographic analysis results for the vitrinite-rich coal particles pre-treatment.

Component	wt.%
Petrographic analysis (vol.%, mmf)	
Vitrinite	97.0
Liptinite	1.3
Inertinite	1.7
Rank classification (UN ECE)	Medium rank C
Proximate analysis (wt.%, daf)	
Ash	4.9
Moisture	3.8
Volatile matter	35.6
Fixed carbon (by difference)	55.7
Ultimate analysis (wt.%, daf)	
Carbon	68.25
Hydrogen	5.14
Nitrogen	1.52
Oxygen (by difference)	15.31

mmf — mineral matter free, daf — dry ash-free, UN ECE-United Nations Economic Commission for Europe hard coal classification scheme.

Applying the BET method, a Micrometrics 2020 ASAP surface area analyser was employed using NO_2 and CO_2 gases as the probe gas to determine surface area and pore size distribution. The NO_2 was used to analyse the meso-pore, macro-pore and larger micro-pore structures whereas the CO_2 was used to evaluate the smaller micro-pores (Prinz et al., 2004). All samples were degassed for 2 h at 105 °C to remove moisture and adsorbed gases on the sample surface prior to analysis. The surface area of the coal samples as determined by the BET method and Langmuir model are outlined. The Langmuir model is defined by Eq. (2):

$$V_{ads} = V_m \frac{bP}{1+bP}. \tag{2}$$

Where V_{ads} is the volume of the gas adsorbed, V_m is the volume available for monolayer covering (at constant T and $P \to \infty$), P is the equilibrium gas or vapour pressure, b is the Langmuir parameter which is an empirical constant. The BET model is an extension of the Langmuir model that accounts for the formation of multilayers (Brunauer et al., 1936), and is hence an improved parameter that will be reported in the present paper. The BET equation has the following form:

$$\frac{p}{(p_0-p)m^a} = \frac{C-1}{Cm_1}\left(\frac{p}{p_0}\right) + \frac{1}{Cm_1}. \tag{3}$$

Where ${}^{p}/_{p_0}$, is the relative pressure, and C is a constant related to the net heat of adsorption. The surface area was obtained by fitting the models to low pressure adsorption isotherms with CO_2 used as the adsorbate. The micro-pore area and micro-pore volume of the sorbent were determined according to the thickness plot (T-plot) method. Pore diameter distributions were obtained by the H–K (Horvath–Kawazoe) method based on the desorption isotherm.

FTIR was used for investigating the functional groups. A Bruker FTIR spectrometer equipped with a NICPLAN microscope was employed in both transmission and reflected modes. All spectra were obtained at a resolution of 4 cm^{-1} and 128 scans were co-added (a ratio to a gold plate background of 128 scans was calculated). Kramers–Kronig transformation was applied to the reflectance spectra. Similar to Maphala and Wagner (2012), the bands were assigned according to Painter et al. (1978).

The CO_2 adsorption capacities were measured using a Volumetric Adsorption System (VAS) (Maphada, 2012). The VAS was designed for the present study and custom built by Chemvak CC in South Africa. The unit consists of a gas storage cell and an adsorption cell connected to a pipe bearing and an air controlled pneumatic valve, as demonstrated in Fig. 1. Both cells were completely placed within a thermostat (oven) and provided with pipes for gas supply and evacuation, as well as with thermocouples and manometers to measure the temperature and pressure inside the cells, respectively. Isotherms were generated in the range of 5–45 bar at a temperature of 28 °C. Successive pressure increments of 10 bar were used and each point in the isotherm was run until equilibrium adsorption. The method for isotherm construction is well documented (Romanov and Soong, 2008; Painter et al., 1978). The number of moles adsorbed at each pressure step is calculated as the difference in the total number of moles injected onto the sample cell and the number of moles when equilibrium is reached at each pressure step as defined by Eq. (1):

$$n^{exc} = n^t - \rho V_o. \tag{1}$$