

Low-high temperature flue gas direct injection in south African bituminous and anthracite coals: sorption capacity assessment

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Numerous studies have been carried out recently on the sequestration of carbon dioxide (CO₂), a greenhouse gas, produced due to human activities. Consequently, storage of CO₂ in storage sites, such as unmineable coal seams, has been identified as one of the promising options with the advantage of recovering coal-bed methane (CH₄). However, CO₂ injected into coal seams contains additional gases that may reduce storage capacity, cause changes in sorption behaviour and physicochemical properties of coal. This research was aimed at investigating the sorption behaviour of three South African coals (sorbents) upon pure CO₂ and flue gas (sorbates) sorption. Measurements were conducted on 10 g samples with a grain size <2 mm. A synthetic industrial flue gas containing 12% CO₂, 5.5% O₂, 82% N₂, 0.38% SO₂ and 0.12% NO₂ was used in the study. Sorption isotherms were measured at a temperature ranging from 30 to 60°C and pressures up to 9 MPa using a high-pressure CO₂ volumetric adsorption system (HPCVAS). Sorption of CO₂ by coal was highly reduced in the presence of additional gases due to competition for sorption sites. The reduction in CO₂ (in flue gas) sorption capacity of coal was up to 63% compared to sorption of pure CO₂.

Keywords: Carbon dioxide, coal, flue gas, preferential sorption, sorption capacity.

SINCE the industrial evolution, large amounts of greenhouse gases (GHGs), including some radioactive gases have been emitted into the atmosphere¹. This has led to climate change which is one of the main risks threatening humanity. The continuous burning of fossil fuel increases atmospheric CO₂ concentration each year and this can warm the planet. A natural question that arises with respect to sequestration of anthropogenic CO₂ is: how long should CO₂ emission be kept under control to ensure that

global temperature rise is within 2°C? The interconnection between climate change and CO₂ emissions has been a 'hot topic' amongst scientists, politicians, and the general public. This discussion has been coined the term 'greenhouse effect'².

Merely maintaining the atmospheric CO₂ concentrations between 450 ppm and 650 ppm by 2100 would require an extreme reduction in anthropogenic CO₂ emissions over the next 20–30 years. Eventually, reducing GHG emissions will be a supreme mitigating action, necessitating more efficient and cleaner energy sources than fossil fuels, and other changes in current humanity activities³. At the United Nations Climate Change Conference held in Paris in 2015, 195 countries (including South Africa) settled on a plan to decrease CO₂ emissions and other GHGs. This was done to limit the global temperature rise below 2°C (this is relative to pre-industrialization evolution climate; thus, future global warming should be limited to below 1.4°C because the global temperature has already increased by 0.6°C at the end of the twentieth century)⁴.

Investigations have shown that South Africa, a developing country, is amongst the top 15 emitters of CO₂ in the world⁵. Due to the increasing worldwide focus on climate change, there has been an increasing awareness that South Africa needs to assume low-carbon intensive routes to avoid foreseeable social and financial penalties⁶. Since the Kyoto Protocol in Copenhagen in 2009, South Africa has committed to reducing its GHG emissions by at least 34% till 2020 and by 42% till 2025, subject to receiving sufficient financial support and necessary technology from international fraternity⁷.

Carbon capture and storage (CCS) technology is one of the integral parts of the intergovernmental panel on climate change (IPCC)⁸ strategies to reduce the amount of CO₂ in the atmosphere⁹. With growing awareness about the importance of CCS in resolving global warming, efforts have been made in political, engineering and academic sectors to develop knowledge capacity and

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technical know-how in CCS¹⁰. In 2010, the South African Centre for Carbon Capture and Storage (SACCCS) launched an atlas on geological storage of CO₂ in South Africa. This was followed with the identification of storage sites and their capacities^{11,12}. From the investigation, an overall potential CO₂ storage capacity of 150 gigatonnes (Gt) was reported and CO₂ storage capacity of about 1 271.9 million tonnes (Mt) was found in coal fields.

Injection of CO₂ into unmineable coal seams is one of the most attractive systems to sequester CO₂; however, precise knowledge of injection and sorption-induced coal property changes are essential for safe and successful implementation of this storage technique¹³. Injecting CO₂ into unmineable coal seams consists of two beneficial parts, (1) enhanced coalbed methane recovery and (2) CO₂ sequestration. In conventional geological reservoirs, CO₂ is thought to be trapped by four mechanisms including capillary or residual, structural, mineral and dissolution trappings. However, adsorption trapping of CO₂ is the most dominant storage mechanism in coal matrix¹⁴.

For geological storage of CO₂ in unmineable coal seams, little attention has been focused on direct injection of flue gases from power plants or other flue gas emitting sources. There is also limited understanding of flue gas sorption behaviour into unmineable coal seams, particularly, for South African coals¹⁵. Therefore, this article presents the effect of impurities in CO₂ stream on CO₂ sorption capacity of selected South African coals. Synthetic flue gas (containing 12% CO₂, 5.5% O₂, 82% N₂, 0.38% SO₂, and 0.12% NO₂) has been evaluated/used to mimic the industrial flue gas from coal-fired power plant (instead of pure CO₂) for experimental purposes. The sorption was measured under reservoir *in situ* and supercritical CO₂ conditions. This provided an experimental basis for conclusive predictive assessments of flue gas and CO₂ sequestration.

Experimental

Sample description and preparation

Three South African coals from at least three different coalfields located in the main Karoo basin were used in this study. These coals are from Ermelo (Coal EML), Somkhele (Coal SML) and Springlake (Coal SPL) and were selected based on their coal rank and coal maceral compositions. They also represent major commercial coal fields in South Africa. In addition, these coalfields have been earmarked as potential future CO₂ storage sites by Viljoen *et al.*¹² (see Figure 1). The CO₂ storage potential estimates for Somkhele, Ermelo, and Springlake coalfields are 82.9, 331.8 and 43.1 Mt respectively. This amounts to about a third of the entire CO₂ storage potential in South African coalfields.

Coal samples were collected *in situ* using a hammer and a crow bar from respective coalfields. The samples were placed in plastic bags, sealed on site and transported to laboratory. To avoid atmospheric exposure and prevent oxidation, samples were flushed with an inert nitrogen gas and then stored in a refrigerator (<3°C temperature condition).

CO₂ sorption experiments

A high-pressure volumetric sorption system (HPVSS) was designed, constructed and commissioned to estimate the flue gas and CO₂ sorption capacity of the coal samples. A schematic of the HPVSS is shown in Figure 2.

The experimental set-up consists of sample drying vessel, reactor cell, reference cell and a digital control system for pressure and temperature recordings. The reference and reactor cells were made of stainless steel with volumes of 467.2 cm³ and 43.79 cm³ respectively. The pressure in the reference and reactor cells was controlled and monitored by a digital control system connected to a WIKA pressure transducer (model A-10). An SRI gas chromatograph (GC) (model 8610) supplied by Chromspec Chromatography was connected to the HPVSS experimental set-up by a 1/8 inch stainless steel tube and was used to measure the flue gas composition before and after each sorption test. A data logging system connected to the pressure and temperature transducers was used to collect the pressure and temperature data every five seconds.

Pure CO₂ sorption isotherms were measured at 30, 40, 50 and 60°C and at pressures up to ~9.0 MPa. This temperature profile is based on the coal reservoir temperature and pressure profiles reported by Zang¹⁶, with the targeted CO₂ sequestration depth of 800 m and above 30°C. Therefore, this was taken as the lowest temperature. Each sorption test involved eight consecutive procedures: sample degassing; moisture equilibrating the sample; filling the reactor cell with coal; reactor cell evacuation using a vacuum pump; void volume (V_{void}) determination of the reactor cell filled with a coal sample; injecting CO₂ into the reference cell; expanding CO₂ into the reactor cell and, data recording. Each coal sample was degassed under vacuum conditions at 130°C and, subsequently, moisture equilibrated to 4% using deionized water before sorption measurements. Sorption capacity and other properties such as density, pore size, surface area and porosity for coals could be affected by the presence of moisture within the sample¹⁷; other elucidations cannot be precluded entirely; however, residual moisture seems to play the most dominant role in affecting the sorption capacity on coals¹⁸. Each sample was then placed inside the sample cell and, thereafter, subjected to vacuum for 15 min so evacuate any former gases. The

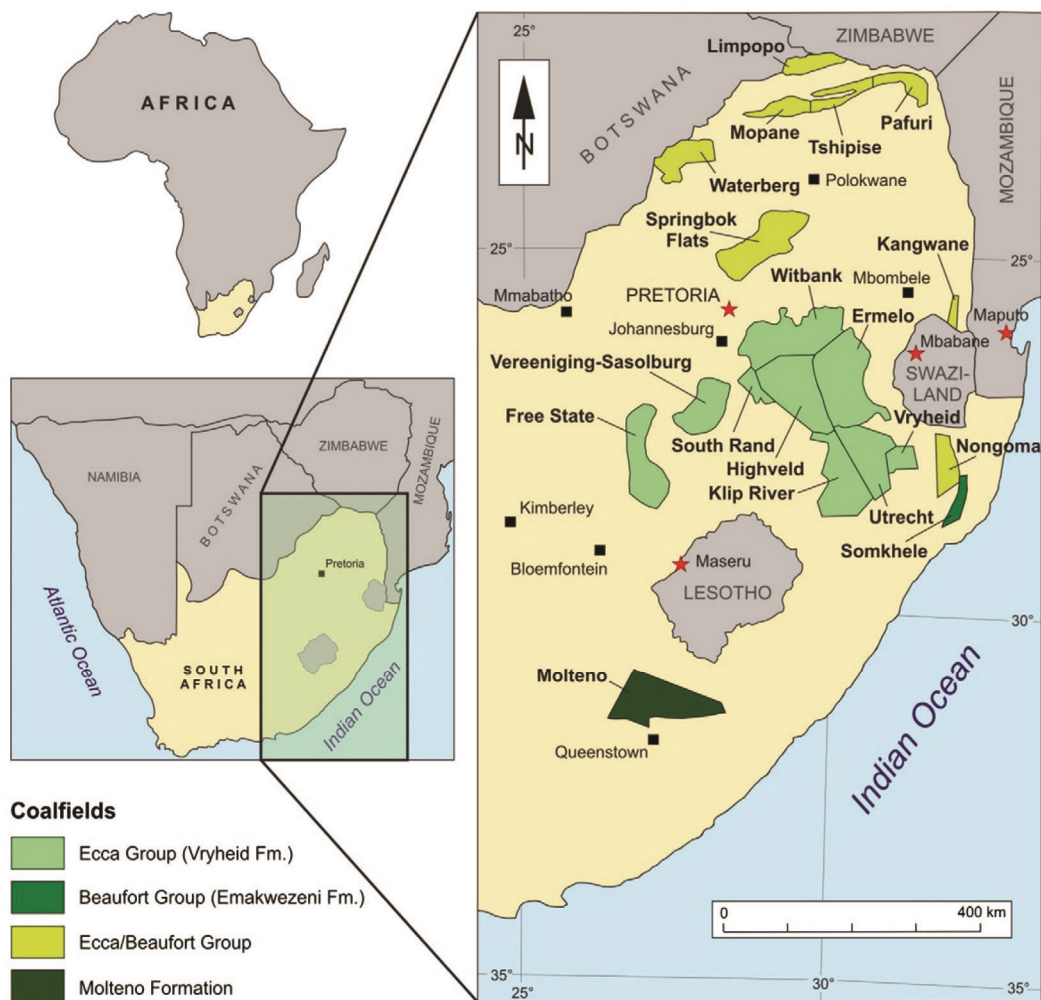


Figure 1. Map showing the location of south African coalfields⁴⁶.

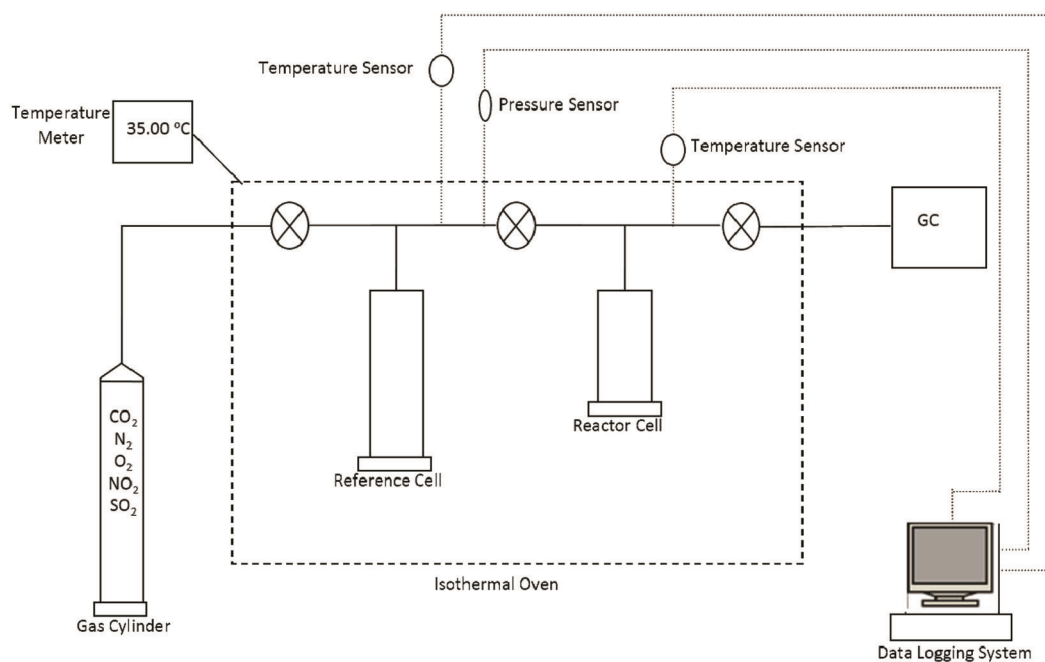


Figure 2. Schematic of the high pressure volumetric sorption system.

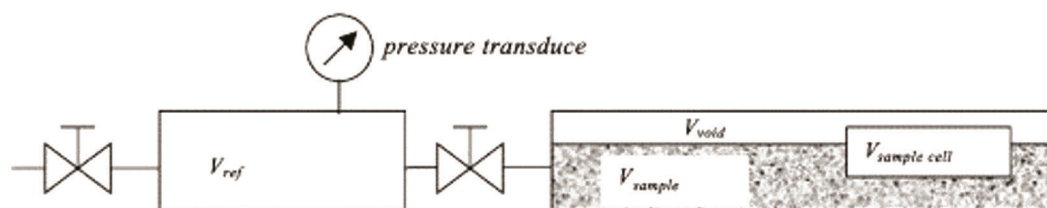


Figure 3. Focused area of HPCVSS showing the definitions for the volumetric method for gas sorption measurements^{28,34}.

void volume (Figure 3), V_{void} , in the sample cell was estimated using the helium expansion approach described by Sudibandriyo¹⁹.

Helium was evacuated and the sorbate (pure CO₂ or flue gas) was introduced into the system. Nine incremental pressure steps were preferred for the sorption tests where pressure was increased at intervals of ~1.0 MPa until 9.0 MPa was reached. During the initial (trial) tests run up to 24 h, it was discovered that 90 min was adequate for the equilibrium point to be reached. The recorded pressure and temperature data was used to estimate the amount of gas sorbed per gram of coal tested.

Flue gas sorption isotherms measurements

The flue gas sorption tests of CO₂/O₂/N₂/SO₂/NO₂ on South African coals at 30°C and 60°C, and pressures up to 9.0 MPa were conducted at 12/5.5/82/0.38/0.12 mole % feed composition. The procedure was exactly similar to that of pure gas sorption isotherm measurements. The only significant distinction was that after equilibrium pressure was reached for each pressure step, the gas remaining in the sample cell was diverted via the sample valve connector (connected between the reactor cell and the GC) to the GC. This was done to determine the un-sorbed amount of each individual gas. Initially, the flue gas was sampled from the cylinder and analysed using the GC to determine the composition of gas received from the supplier.

Results

Proximate and petrographic analysis

Table 1 shows the maceral composition and proximate analysis of the three coals under investigation. Coal SML has high vitrinite content (84 vol%) and low inertinite (11.5 vol%), Coal EML has high inertinite content (74.2 vol%) with low vitrinite content (12.8 vol%), and Coal SPL has almost 50/50 vol% for each of vitrinite and inertinite contents. Coal SPL will be used as a control particularly when discussing the effects of coal macerals. It should also be noted that Coal EML has significantly high mineral and volatile matters of 9.8 vol% and 59.8 wt% respectively.

Table 1. Proximate and petrographic analysis of the coals used

Analysis type	Coal ID		
	Coal SML	Coal EML	Coal SPL
Petrographic analysis (vol%, inc. mm)			
Vitrinite	84.0	12.8	55.3
Inertinite	11.5	74.2	43.3
Liptinite	0.0	3.3	0.0
Mineral matter	4.5	9.8	1.5
Vitrinite reflectance (Ro)	2.24	0.64	3.49
Proximate analysis (wt%, adb)			
Fixed carbon	74.1	27.8	75.0
Moisture	1.0	4.5	1.5
Ash	17.3	17.9	12.8
Volatile matter	7.6	59.8	10.7

adb, Air dried basis; inc. mm, Including mineral matter; Ro, Random.

Table 2. Summary of pure CO₂ sorption capacities

Sample ID	Sorption capacity (mmol/g) Temperature (°C)			
	30	40	50	60
Coal SML	4.16	3.41	2.92	2.54
Coal SPL	3.85	3.18	2.63	2.37
Coal EML	3.46	3.02	2.78	2.25
Reference	Figure 4 a	Figure 4 b	Figure 4 c	Figure 4 d

High-pressure pure CO₂ sorption

The sorption isotherms of high-pressure pure CO₂ experiments conducted on moisture equilibrated South African coals are shown in Figure 4. These experiments reached a maximum CO₂ pressure of ~9.0 MPa at all four temperatures. All isotherms increased monotonously from low to sub-critical pressures and exhibited a monotonous asymptotic behaviour at high pressures (<6.0 MPa). The behaviour was consistent for all isotherms across different temperatures.

Table 2 summarizes the CO₂ sorption capacities at all the 4 temperatures investigated in this study. At the final pressures of the sorption isotherms (see Figure 4), the sorption capacity of CO₂ was determined to range from ~2.25 to 4.16 mmol CO₂/g coal (~0.099–0.183 tonnes of CO₂ per tonne of coal). The highest sorption capacities

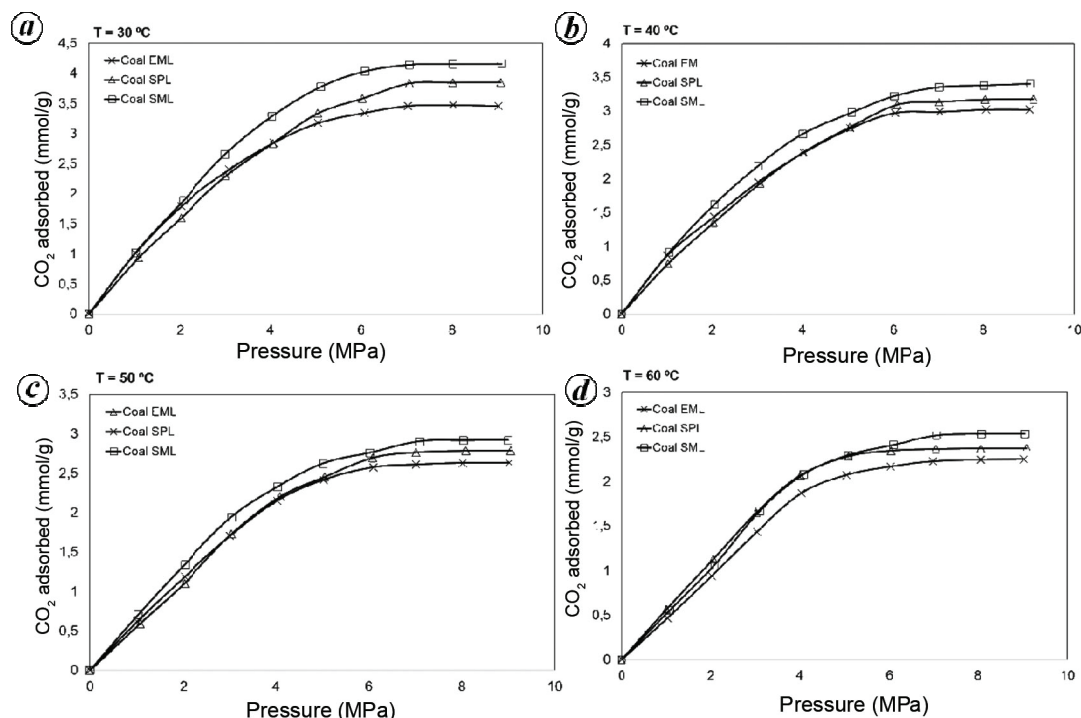


Figure 4. Excess sorption isotherms for pure carbon dioxide on moisture equilibrated South African coals at: (a) 30°C, (b) 40°C, (c) 50°C and (d) 60°C.

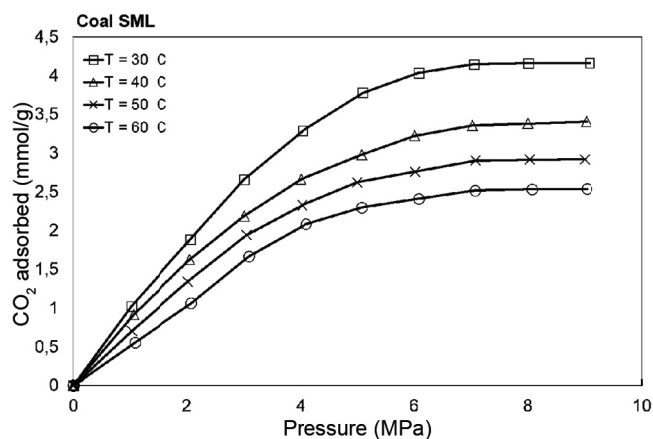


Figure 5. Excess sorption isotherms for pure carbon dioxide on moisture equilibrated Somkhele coal at 30°C, 40°C, 50°C and 60°C.

were observed at 30°C with maximum sorption capacity ranging from ~3.46 to 4.16 mmol CO₂/g coal (~0.152–0.183 tonnes of CO₂ per tonne of coal). Coal SML consistently displayed the highest sorption capacity among all samples. This was more evident at higher pressures (<6.0 MPa).

The samples were compared for their high-pressure pure CO₂ sorption capacity at different temperature (Figure 5). Since Coal SML was established to have the highest sorption capacities, it was used as a basis to evaluate this effect. It was observed that maximum sorption capa-

city consistently decreases with an increase in isothermal temperature.

High-pressure flue gas sorption

The sorption experiments reached a maximum flue gas pressure of ~9.0 MPa; however, results of flue gas sorption conducted at temperatures of 30°C and 60°C are presented. The feed composition used was 12%CO₂/5.5%O₂/82%N₂/0.38% SO₂/0.12%NO₂. The total flue gas sorption capacity on coals ranges from ~2.34–3.96 mmol CO₂/g-coal (~0.081–0.128 tonnes CO₂ per tonne of coal; Figure 6). The coal sample is differed their preference for sorption of other individual gases (see Figure 7).

It was observed that the sorption capacity of each component increased with an increase in gas pressure. All isotherms consistently exhibit a monotonous increasing trend until the final pressure (~9 MPa) without reaching any asymptotic stage. The O₂, SO₂ and NO₂ trends increase slowly with increasing pressure compared to those of CO₂ and N₂.

In the current study, Luo *et al.*²⁰ approach for assessing selective sorption of CO₂ and CH₄ gases on Jurassic shale from China was adopted for assessment of the occurrence of preferential sorption of CO₂, N₂, O₂, SO₂ and NO₂ gases on moisture equilibrated South African coals. All coal samples revealed a preferential CO₂ sorption trend at both 30°C and 60°C with the exception of Coal SPL (Figure 6c) which exhibited a slight (non-significant)

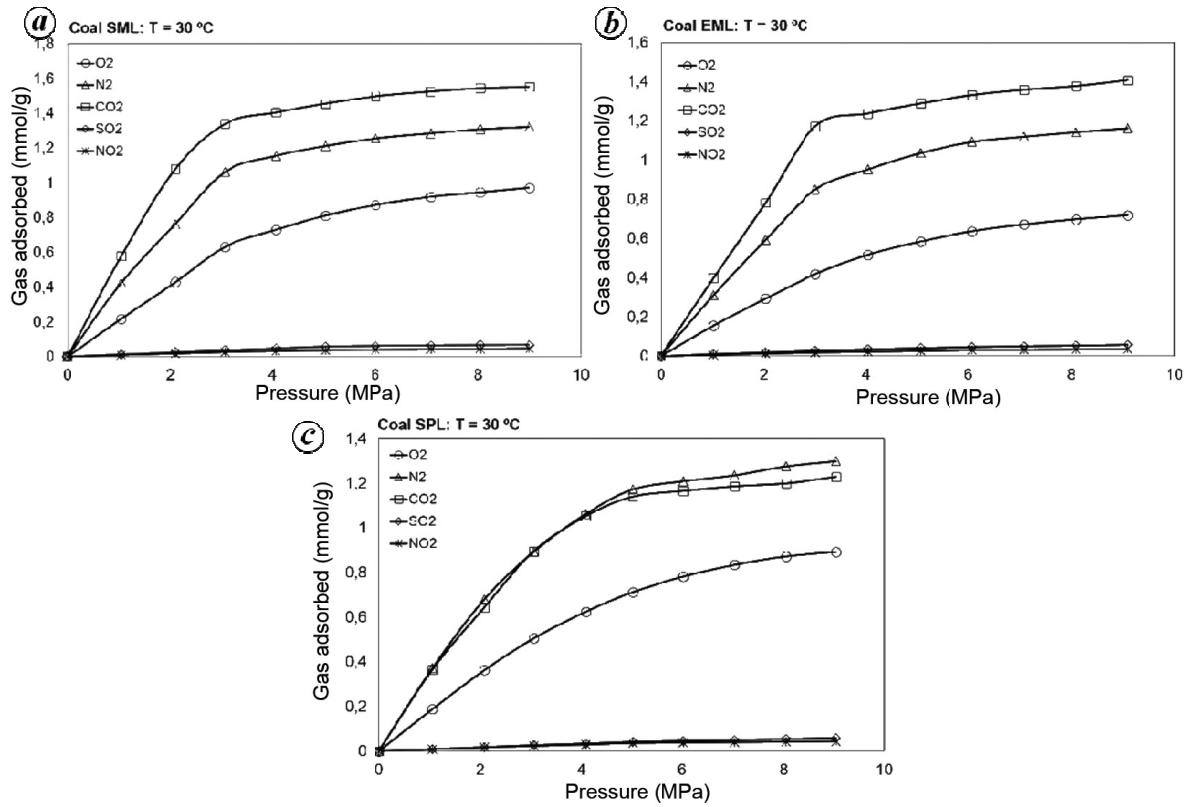


Figure 6. Sorption isotherms for flue gas on moisture equilibrated at 30°C: (a) Coal SML, (b) Coal EML and (c) Coal SPL.

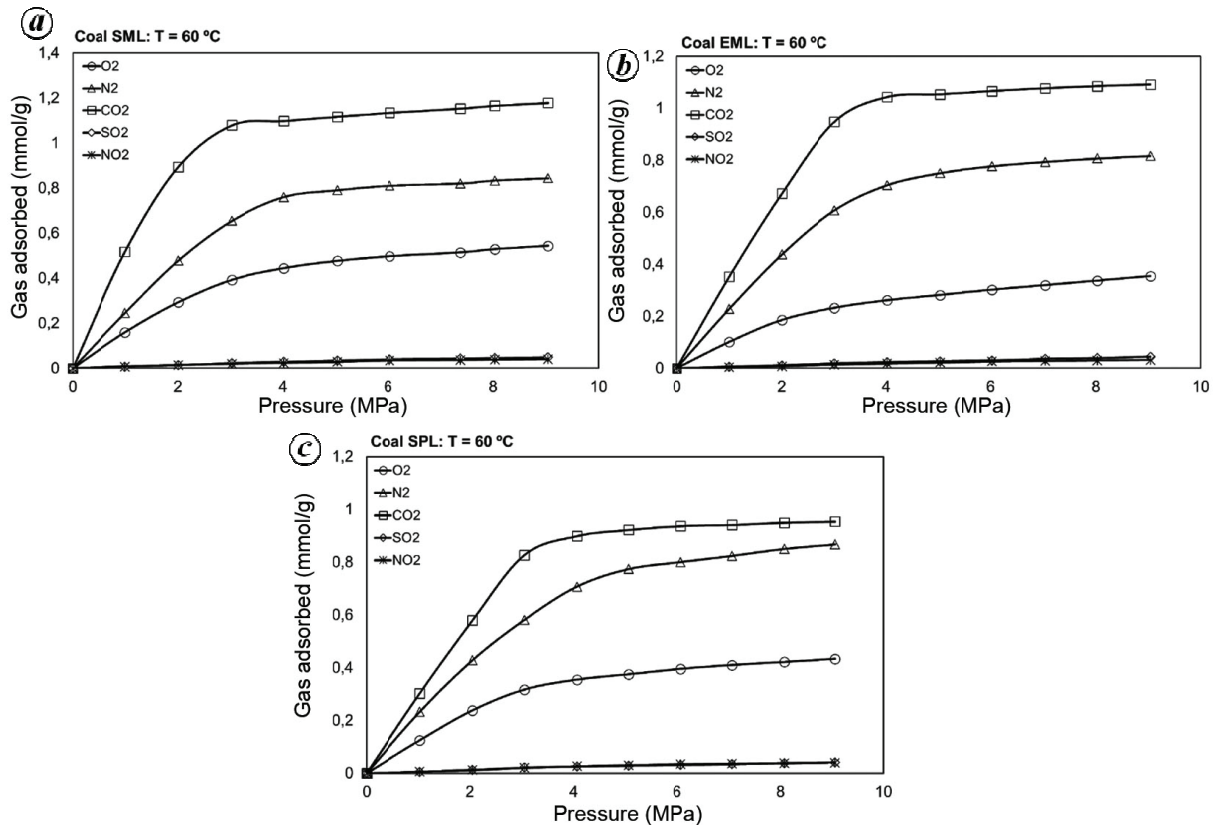


Figure 7. Sorption isotherms for flue gas on moisture equilibrated at 60°C: (a) Coal SML, (b) Coal EML and (c) Coal SPL.

preferential N₂ sorption trend at 30°C. This (coal SPL trend) is more evident at high pressures (subcritical to supercritical).

The CO₂ sorption capacities calculated from experimental data range from ~1.30 to 1.55 mmol CO₂/g-coal (~0.054–0.068 tonnes of CO₂ per tonne of coal), and the total gas sorption capacity range from ~3.38 to 3.96 mmol gas/g-coal (see Table 3). As with pure CO₂ injection, Coal SML is observed to have the highest total gas and CO₂ sorption capacities of 3.96 mmol gas/g-coal and 1.55 mmol CO₂/g-coal respectively. Coal EML has the lowest sorption capacities of ~3.38 mmol gas/g-coal and 1.41 mmol CO₂/g-coal. This trend was also observed for pure CO₂ injection.

Comparison of CO₂ sorption capacities for pure CO₂ and flue gas injection

Figure 8 compares sorption capacities for pure CO₂ and flue gas on Coal SML. Coal SML was used as basis to perform this comparison due to its high sorption capacity as discovered in this study. Same trends were obtained for the other two coals (EML and SPL). CO₂ sorption capacity was significantly higher when pure CO₂ was injected than when flue gas was injected under similar conditions of temperature and pressure. This difference was calculated to be ~63% average.

In the context of total gas uptake (Figure 9), the maximum amount of gas that could be sorbed by Coal SML at 30°C and pressures up ~9.0 MPa was 4.16 (0.183 tonnes of CO₂ per tonne of coal) and 3.96 mmol gas/g-coal (0.123 tonnes of gas per tonnes of coal) for pure CO₂ and flue gas respectively. The difference was calculated to be ~5% in mole basis (~30% mass basis).

Discussion

Proximate and petrographic analysis

As mentioned earlier, Coal SML has high carbon content with low volatile and mineral matter contents. This makes it more favourable for sorption of CO₂. According to Beamish *et al.*²¹, microporosity in coals decreases with increasing volatile constituents that block the micropore structure. This means that the lower the volatile matter present in coal, the less the blockage in micropore structure for CO₂ sorption.

Table 3. Total gas sorption capacity when injecting flue gas at 30°C

Sample ID	Total gas capacity (mmol/g)	CO ₂ sorption capacity (mmol/g)	Reference
Coal SML	3.96	1.55	Figure 6 a
Coal SPL	3.53	1.30	Figure 6 b
Coal EML	3.38	1.41	Figure 6 c

Effects of coal maceral composition

A common trend was observed for the CO₂ sorption capacities of the three coal samples. CO₂ sorption capacities increased with increase in vitrinite content up to pressures of ~9 MPa and temperatures up to 60°C. This trend is in line with previous observations^{22,23}.

Clarkson and Bustin²² on Western Canadian Cretaceous coals, found an increase in CO₂ sorption capacities attributed to an increase in vitrinite content of the coal. They concluded that the pore structure and gas sorption capacity (GSC) are essentially influenced by the coal composition. Recently, Maphala²³ performed long-term CO₂ sorption measurements on inertinite-rich and vitrinite-rich South African coals. They found that CO₂–coal interaction is dependent on maceral composition of the coal, a vitrinite rich coal has stronger CO₂–coal interaction than inertinite-rich coal.

Vitrinite maceral mainly contains micropores and inertinite predominantly contains macropores and mesopores²⁴. Due to its abundant microporosity, which

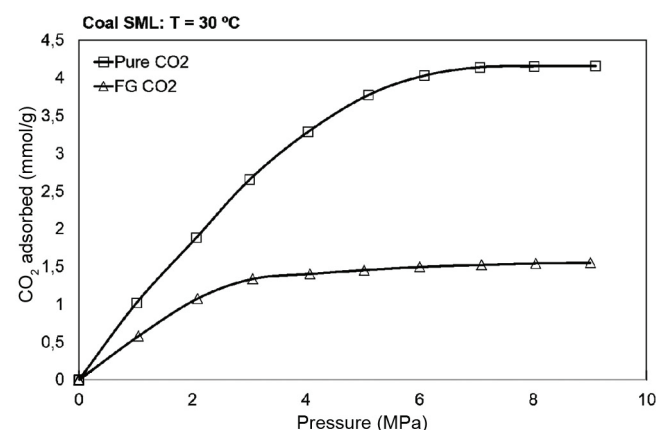


Figure 8. Comparison of sorption capacities of pure CO₂ and flue gas at 30°C for moisture equilibrated Coal SML.

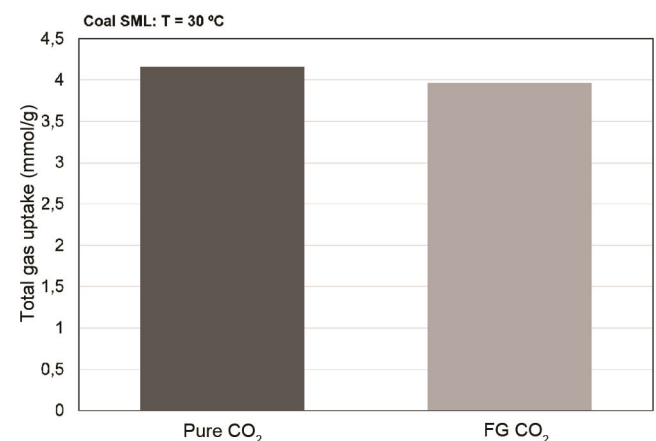


Figure 9. Comparison of total gas uptake for Coal SML at 30°C for pure CO₂ and flue gas.

results in high coal total pore area, vitrinite content is classified as the single most significant maceral composition in gas sequestration studies²⁵. Harris and Yust²⁶ linked the microscopic composition of coals to porosity and pore size. Vitrinite therefore contains numerous sorption sites compared to inertinite and liptinite. According to Crosdale *et al.*²⁷, the variation in CO₂ sorption capacity is linked to pore structure development, mainly micropores, which depend on the coal type and rank. Furthermore, Busch *et al.*²⁸ ascribe an increase in crystalline phase in coal to an increase in CO₂ sorption capacity. The increase in crystalline phase indicates a dramatic decrease in the amount of the volatile matter, and consequently increase in vitrinite character.

The effect of maceral composition on GSC is still a matter of argument. Even though there is currently unfound grounds of the role of coal type (especially the maceral composition) on gas sorption capacity and behaviour, many researchers in this field^{22,23,29–33} have speculated that coal maceral composition influences the GSC³⁴.

Effects pressure and temperature

Both pure CO₂ and flue gas sorption isotherms exhibit behaviour of a normal Langmuir Type I isotherm up to a pressure of ~9.0 MPa (see Figures 4–8). The phenomenon at which sorption isotherms display a monotonous asymptotic behaviour is observed when the bulk density of the gas phase starts to rise faster than the adsorbed phase density as a function of pressure³⁵. This phenomenon is demonstrated in Figure 10 for Coal SML.

The present results show a distinct unfavourable effect of temperature on gas sorption capacity of coals up to pressures of ~9.0 MPa. This is in agreement with previous studies^{34,36,37}. According to Krooss *et al.*³⁴, the negative effect arises because the sorbed phase volume decreases with increasing temperature (see Figure 11). At lower temperatures the difference in densities between free gas phase and sorbed phase tends to be smaller (see Figure 10) and the sorption on coal is no longer justified.

Preferential sorption

The sorption capacity of pure CO₂ is generally higher than the sorption capacity of many flue gas impurities (including N₂, CH₄, SO₂, etc.); thus, under competitive sorption conditions, CO₂ is usually expected to be preferentially sorbed from any flue gas mixture. Differences were observed in the South African coals preferential sorption of flue gases at high pressures. There was strong preferential sorption of CO₂ over other gases. However, coal SPL deviated from this trend at low temperatures. This implies that, for this flue gas mixture, high sorption for CO₂ or N₂ depends on pressure, temperature, as well

as coal composition. Hence, the dependence of coal macerals cannot be established at this point. It is probable that the preferential sorption of CO₂ on coals is more complex than initially assumed.

Crosdale³⁸ showed that preferential sorption of CO₂ over other gases could be due to faster diffusion rate for CO₂ as compared to its counterparts. This was substantiated by Busch *et al.*²⁸ by proving that CO₂ consistently and significantly reached sorption equilibrium faster than CH₄. These findings evidently show that coals under investigation have high affinity for CO₂.

Implications of direct flue gas injection

Since the inception of the CCS technology and research, a number of researchers^{39–43} have published the cost estimate for this technology. According to Al-Juaied and Whitmore⁴⁴, CCS technology is estimated to cost US\$120–180 per tonne of CO₂. The cost of capturing CO₂ is typically the greatest cost of a CCS project due to high energy requirements⁴⁵. According to Rubin *et al.*⁴³,

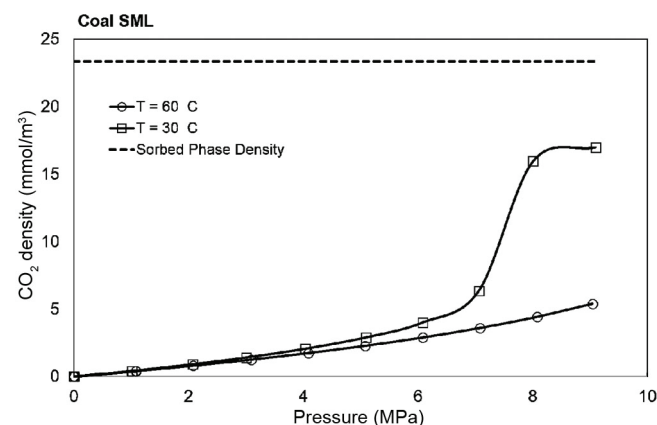


Figure 10. Carbon dioxide free gas and sorbed phase density profile at 30°C and 60°C.

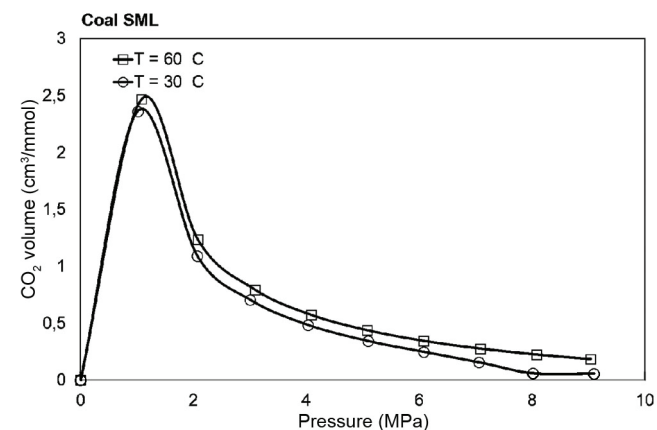


Figure 11. Carbon dioxide free gas volume profile at 30°C and 60°C.

the CO₂ capture costs range from US\$36 to US\$53 per tonne of CO₂; this accounts for approximately 30% of CCS technology costs. These figures are expected to remain unchanged over the next several decades and are based on post-combustion capture of existing supercritical pulverized-coal fired power plants using bituminous coals.

In the light of the above-mentioned CCS technology costs, omitting CO₂ capturing process by applying direct flue gas injection into geological formations (in this case unmineable coalfields) will make the CCS technology more affordable. This study shows that CO₂ storage potential for Somkhele, Ermelo and Springlake coalfields is 82.9, 331.8 and 43.1 Mt respectively. In principle, this means that up to ~10.2, 37.2 and 4.741 Mt of flue gas can be stored through sorption in Coals SML, EML and SPL respectively.

Conclusion

This study presents high-pressure pure CO₂ and flue gas sorption on three moisture equilibrated South African coals (Coal SML, coal SPL and coal EML) at 30–60°C and at pressures up to ~9 MPa. A comparison of the sorption capacities shows strong differences. The CO₂ sorption capacity is, on average, 37% more at lower temperatures (30°C) than at higher temperatures (60°C). The capacity increases with increase in pressure until a monotonous asymptotic stage is reached from subcritical (<6 MPa) to supercritical (9 MPa) pressures. It can be concluded that pressure and temperature are one of the major controlling factors during CO₂ storage in coals.

Though the effect of maceral composition of GSC on coal is still controversial, results show a positive correlation between the vitrinite content of coals and their CO₂ sorption capacity.

All coals exhibited a high preferential sorption for CO₂ for the temperature and pressure range investigated in this study. Furthermore, CO₂ sorption capacity of coal decreased by about 63% when flue gas was injected compared to the injection of pure CO₂, but the total gas sorption capacity of coal decreased by only 5% on mole basis. This means that if CO₂ is the only targeted gas for sequestration, flue gas injection is not recommended as an ideal option. However, if other gases are to be injected alongside CO₂ without discriminating, direct flue gas injection could be a promising option for CO₂ sequestration in coal seams.

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