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EFFECT OF SO_2 CO-FEEDING ON CO_2 ADSORPTION CAPACITY OF SOUTH AFRICAN COALS DURING CO_2 SEQUESTRATION

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Abstract

The effect of SO_2 in feed stream on CO_2 sorption capacity of unmineable South African coal seams during CO_2 sequestration was studied. Laboratory studies were carried out using a synthetic flue gas (99.5% CO_2/ 0.5% SO_2 and 98.5% CO_2/1.5% SO_2) in a high pressure volumetric experimental setup connected with an on-line gas-chromatograph was used. The experiments were performed in dry and moisture-equilibrated (1.5 - 4.5 %) state at 35 °C and pressured up to 90 bars. The adsorption experimental data was fitted on existing adsorption models to understand the adsorption behaviour of the coal seams. The results showed that the presence of SO_2 and moisture of the coal significantly reduce the sorption capacity of CO_2. However, pressure increase from sub-critical to super-critical positively enhanced the CO_2 adsorption capacity of the coal samples studied. These results support the need for desulphurization of the flue gas before compression and storage in unmineable coal seams. In addition, the type of coal (properties), injection pressure and coal seam moisture play a vital role in the sequestration process.

Keywords: Carbon dioxide; Sequestration; Sorption capacity; South African coal seams; Sulphur dioxide.

1. Introduction

Carbon dioxide (CO_2) sequestration in deep unmineable coal seams or abandoned coal mines with enhanced coal bed methane (ECBM) has become a subject of increasing importance around the world as a way of reducing atmospheric CO_2 emissions from point sources (coal-fired power plants and natural-gas-burning sources). Carbon capture and storage (CCS) has been identified as a major option in mitigating CO_2 emissions [1]. The technology is the only industrial-scale process capable of capturing large quantities of CO_2 at point source and burying it underneath the earth's surface [2]. Regarding CO_2 properties in relation to storage conditions, CO_2 will approach its supercritical state (31.1°C and 73.9 bars) with increasing depth. The targeted coal seams for CO_2 injection in South African coals are at depths of approximately 800 to 1000 m to achieve the supercritical CO_2 state at reservoir conditions [3]. These conditions need to be accounted for when measuring adsorption capacity for a potential CO_2 storage coal seam site as adsorption capacities of coal will differ with depth [4] therefore, accu-rate data obtained from laboratory experiments are essential to understanding the situation.

The separation and compression of CO_2 for sequestration from point sources are estimated to cover approximately 75 % of the total cost of CCS [5]. One option is to lower the cost by permitting a less pure CO_2 stream for injection [1,5-7]. However, the type and amount of impurities present in the flue gas and CO_2 stream prepared for storage depend on the types of fuels and type of capture technology, respectively [8]. Experimental data on the injection of the CO_2

mixtures containing O_2, Ar, SO_2, CO, H_2 and other impurities on coal are limited. Under-standing the effect of these impurities on the sorption capacity of coal as a storage material will be of importance for CCS processes [8]. Knauss *et al.* [5], evaluated the impact of storing impure CO_2 on geological formations and showed that if CO_2 is co-injected with SO_2, the SO_2 will be oxidized to sulphate. In addition, the authors claimed that only insignificant quantities of this gas could be tolerated due to the extremely low pH (0-1) generated. Wang *et al.* [1], showed that the presence of SO_2, NO_X, and H_2S (even in small amounts (SO_2 up to 1 %)) has significant chemical effects on the coal seam and cap rock.

On the storage side, the most important advantage of CO_2 sequestration in the coal seam is its permanent sorption on the solid medium over geologic times, although the adsorption capacity and stability of the adsorbed CO_2 are affected by the nature of the coal and the environment location. There are several factors that may limit or improve the degree of adsorption which includes temperature, pressure, coal moisture content, coal rank and changes in the coalbed water pH [9]. Numerous studies of CO_2 adsorption on coal and the factors that affect its stability under in-seam conditions have been carried out [9-13]. Gas sorption studies are often carried out on dry coal, but as coal seams are naturally water saturated [10], it is required that sorption isotherms should be measured in the presence of moisture for accurate sorption capacity evaluation.

Against this background, this study investigated the effect of SO_2 on the sorption capacity of coal during CO_2 sequestration. The volumetric method which determines sorption from the pressure change during gas transfer between a calibrated reference volume and a measuring cell was used in this study. In addition, effect of the moisture content of the coal on the CO_2 sorption capacity of the coal was investigated as well. Due to the versatility of adsorption modelling to explain adsorption behaviour of solid materials, Langmuir and Extended Langmuir adsorption models were used in this study to model the experimental data and explain the adsorption behaviour of the coal.

2. Experimental

2.1. Samples and adsorption set-up

Two South African coal samples were used in this study. One sample was obtained from Springlake Colliery (Coal A) in KwaZulu Natal and the other from Ermelo Coalfield (Coal B) in Mpumalanga. The proximate and petrographic analysis was conducted on these samples to know their compositions.

The high pressure adsorption set-up used in this study consists of a sample cell and the reference cell, where both cells have accurately measured volumes of 43.79 and 465.11 cm^3, respectively, estimated by the Helium expansion technique [14] These cells were placed in an isothermal oven to ensure a constant temperature throughout the experiments. A Gas Chroma-tograph (GC) is attached to the setup which was used to measure gas composition in the competitive adsorption tests. Carbon dioxide or binary gas mixture is admitted to the system in incremental pressure steps up to a maximum pressure of 90 bars while the temperature is kept constant at 35°C. A total of nine pressure steps were used. A detailed description of the apparatus and procedure has been outlined by Mabuza [15]. The excess sorption or Gibbs sor-ption was used to compute the results because sub to supercritical pressures (3.5 to 90 bar) were used in this study.

2.2. Adsorption experiments

In preparation of the samples for isotherm measurements, the coal samples were crushed and sieved to a particle size of +4.75 mm-5 mm. The volumetric method was used to measure the adsorption isotherms.

To obtain various moisture contents on the coal samples, the as-received samples were dried in situ under vacuum. Each sample was dried under vacuum at 120°C for 1 hour 30 minutes. Moisture equilibration was done prior to the sorption measurements. The degassed samples of similar mass (+/- 6 g) were equilibrated with moisture at different time intervals, which allowed the adsorption of moisture at different percentages between the range of 1.5 % and 4.5 %, respectively. The moisture content of each sample was determined using a Moisture Analyser MOC63u supplied by Shimadzu. Immediately after moisture equilibration, sorption experiments were conducted. The moisture content was calculated from the weight change of the sample mass using Eq. (1):

$$\text{Moisture \%} = \frac{W_2 - W_1}{W_2} \times 100 \qquad (1)$$

where, w_1 and w_2 are the initial and final weights of the coal sample, respectively.

Sorption of pure CO_2 (99.6 % CO_2 supplied by Afrox) and binary gas mixtures (99.5 % CO_2/ 0.5 % SO_2 and 98.5 % CO_2/ 1.5 % SO_2 also supplied by Afrox) were studied on both dried and moisture-equilibrated samples using a High Pressure Volumetric Adsorption System (HPVAS). In the system, the isothermal oven was set at 35°C and 15 minutes allowed to achieve thermal equilibrium. The sample cell and reference cell were evacuated to establish a definite starting state. These cells were separated, a certain quantity of gas was admitted to reference cell and 5 - 15 minutes was allowed for pressure and thermal equilibration while the pressure was monitored. The sorbate gas was then admitted to the sample cell and sorption started resulting in pressure drop and this pressure drop was accurately observed until equilibrium was achieved, this was estimated to take 60 minutes. After recording the equilibrium pressure, the cells were separated again and the same procedure was repeated until the maximum pressure was reached. In this study, nine (9) incremental pressure steps were required for each test so as to produce a reasonable adsorption isotherm.

The amount of CO_2 in the gas phase in both the reference and sample cell was calculated using the Gibbs excess method which assumes a constant ratio of condensed phase volume and void volume throughout the experiment and requires no further assumptions [16]. The Gibbs excess adsorption (n^{ex}) and the absolute adsorbed amount in moles (n^{abs}) were calculated using Eq. (2):

$$n^{excess} = \frac{n_{total} - \rho V_{void}}{m_{sample}} \qquad (2)$$

where n^{excess} is the excess adsorbed amount of CO_2 (mmol/g); n_{total} is total moles adsorbed (mmol/g); $\boldsymbol{\rho}$ is the sample density (mmol/cm^3); V_{void} is the void volume (cm^3) and m_{sample} is the mass of the sample (g).

The amount of absolute adsorbed was calculated using Eq. (3). The adsorbed phase density is usually assumed to be constant through the experimental range [17] and for this study, the value of 22.6 mmol/mL for CO_2 was used to the model.

$$n^{abs} = \frac{n^{excess}}{1 - \left(\frac{\rho_{gas}}{\rho_{ads}}\right)} \qquad (3)$$

where n^{abs} is the absolute adsorbed amount of CO_2 (mmol/g); ρ_{ads} is the gas adsorbed phase density of CO_2 in (mmol/cm^3).

The adsorption isotherms are shown in Figure 1, plotted as the total amount of excess adsorbed CO_2, n^{excess}, versus the measured equilibrium pressure.

For the preferential desorption measurements with the binary CO_2 - SO_2 gas mixtures, gas samples were extracted during desorption steps and injected to the GC for chromatographic analysis. After equilibrium pressure had been reached for each pressure step, the remaining gas in the sample cell was sampled via a sampling valve connected between the sample cell and GC.

2.3. Adsorption modelling

Adsorption modelling is a useful method of predicting and comparing the adsorption performance though existing adsorption models. There are several two-parameter isotherm models which are expressed mathematically for CO_2 adsorption on coal. The Langmuir model is the most frequently used model in modelling the adsorption data in CO_2 adsorption. Extended Langmuir (EL) model was used for preferential adsorption data in this study. The

Langmuir model is the most common model that defines adsorption according to monolayer adsorption (the adsorbed layer is one molecule in thickness) where adsorption can only occur at a fixed number of definite limited sites, that are identical and equivalent with no lateral interactions between adsorbed molecules of adjacent sites [18]. The Langmuir model equation is:

$$V_{ads} = \frac{PV_m K_L}{1+PK_L} \qquad (4)$$

where V_{ads} is the volume of gas adsorbed/mass of adsorbate at pressure P in (mmol/g); gas pre-ssure in (bars) while V_m is monolayer volume of gas in mmol/g and the Langmuir constant (K_L).

The linearized form of the Langmuir model was used to describe the relationship between the excess adsorbed CO_2 and the equilibrium pressure due to its mathematical simplicity. The EL model is an extension of the Langmuir model used to model adsorption data of binary and multicomponent gasses. The model is more accurate for two components [19], hence its application was appropriate for this study. The EL model equation for component ***i*** is:

$$V_{ads} = \frac{V_m K_L y_i P}{1+\sum K_L P y_i} \qquad (5)$$

where V_{ads} and V_m are the adsorbed gas and maximum adsorbed gas volumes; K_L and P are the Langmuir coefficient and pressure.

3. Results and discussion

3.1. Proximate and petrographic analysis

Table 1 shows that proximate and petrographic analysis of the coal samples used in this study. During coalification process, the fine pores of coal are closed forming sealed pores which are not accessible to water [20] but accessible to gas adsorption, hence high rank coals adsorb a high amount of CO_2 compared to low rank coals. The presence of mineral matter in a coal sample also hinders CO_2 adsorption surface areas [20]. Coal B which is a low rank coal had high moisture content and mineral matter which negatively affects adsorption capacity of the coal. Inertinite present in coal promotes hydrophilic sites which in turn decreases the adsorption of CO_2. From Table 1, vitrinite rich Coal A had the highest CO_2 adsorption capacity due to low moisture content and mineral matter compared to inertinite rich Coal B.

Table 1. Properties of the coals investigated.

Component	Coal A	Coal B
Proximate Analysis (wt%, adb)		
Moisture	1.5	4.47
Volatile matter	5.4	49.8
Ash	6.1	17.94
Fixed Carbon	87.2	27.8
Petrographic Analysis (vol. %)		
Vitrinite	55.30	9.60
Inertinite	43.30	71.60
Liptinite	0.00	8.60
Mineral Matter	1.50	10.20
Vitrinite Reflectance	3.49	0.64
Coal Rank	High Rank B	Medium C

adb - air dried basis

3.2. Effect of SO_2 and moisture on CO_2 adsorption

The CO_2 adsorption isotherms on dry coals in Figure 1 show that the highest excess sorption capacities of Coal A and B observed to have maximum values of 1.65 and 1.00 mmol/g, respecttively, within the limited pressure ranges used in this study. The 35°C isotherms show a sharp increase in excess CO_2 sorption capacity between 3.5 to 60 bar after which it approaches an asymptotic behaviour for both dry and moisture-equilibrated coal samples at high pressures as illustrated in Figure 1. The adsorption amount increases with respect to pressure, often described by the Langmuir model [21-22].

Table 1 shows that Coal B had high as-received moisture content compared to Coal A meaning more moisture was removed during the degassing process therefore expected to have high adsorption capacity of CO_2. But Coal B had the least maximum adsorption capacity of 1.00 mmol/g compared to Coal A, this could be due to the fact that during the drying process, shrinkage takes place and the extent of shrinkage is greater than the volume of water removed [9]. In high rank Coal A, the accessible volume seemed to be relatively unaffected by the moisture removal, therefore, the adsorbing CO_2 filled the available volume because the structure was more rigid. Whereas with low rank Coal B, during drying, only a portion of the volume previously occupied by water was re-occupied by CO_2 and the rest of the volume was lost because the structure had relaxed [9]. Low rank coals has many adsorption sites that are active for water adsorption and not favorable for CO_2 adsorption [20].

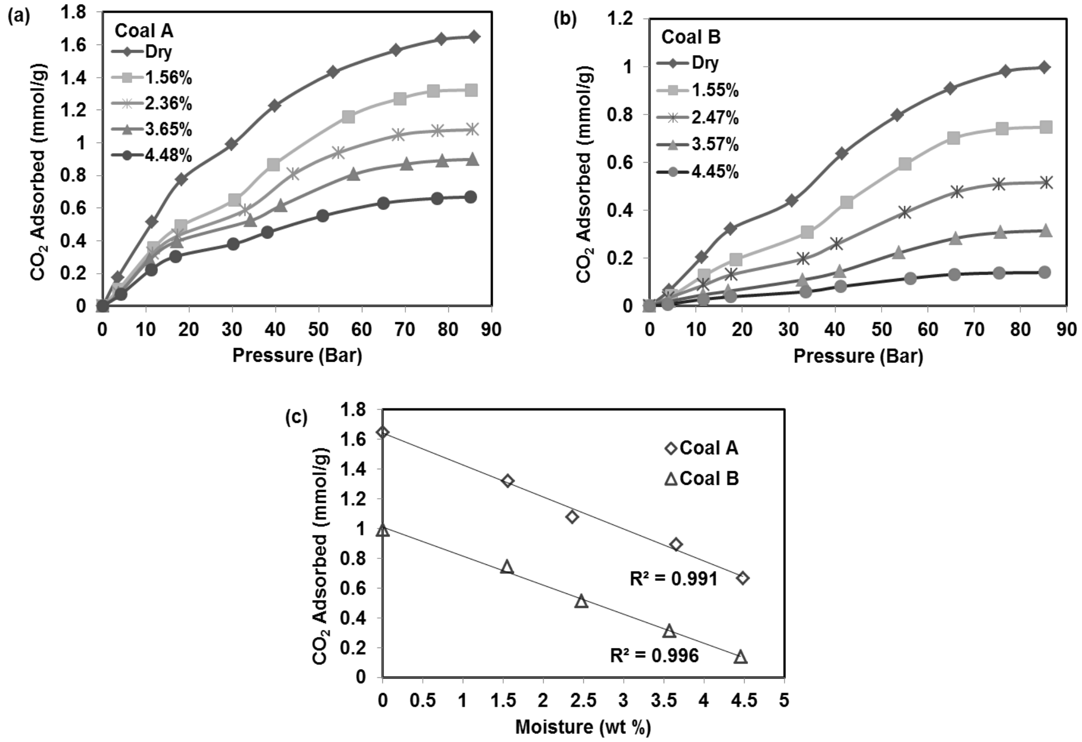

Figure 1. Adsorption isotherms of CO_2 on dry and moisture equilibrated coals: (a) Coal A and (b) Coal B. Maximum CO_2 sorption capacity as a function of moisture content for both coals A and B are shown in (c).

In-order to accurately model in situ conditions, sorption isotherms are typically measured on both dry and moisture-equilibrated coal samples. The effect of moisture on the CO_2 adsorption capacity of two South African coals was studied. The CO_2 sorption capacity of moisture-equili-brated coal samples in all cases was less compared to dry coal samples, and the degree of effect was variable through the range of the samples. The effect of moisture content on CO_2 adsorption capacity is illustrated in Figure 1, where an increase in the moisture content resulted in a decrease in CO_2 adsorbed for both coals investigated. In Coal A, the adsorption capacity was reduced by 60 % on a sample with a moisture content of 4.48 % compared to the dry sample. For low rank Coal B, the CO_2 adsorption capacity was substantially decreased by 80 % for moisture content of about 4.45 % compared to the dry sample. Figure 1 (c) which is a plot of maximum excess sorption capacity versus moisture content for both coals investi-gated shows how adsorption capacity decreases linearly with moisture increase.

CO_2 adsorption capacity increases with coal rank in moist coals. Although water molecules are small compared to CO_2 molecules with cross sectional areas of 0.11 and 0.20 nm^2, respectively [10], therefore, should be capable of accessing more of the pore volume, the surface areas stated by the water adsorption data are considerably lower than the equivalent CO_2 values. This, therefore, indicates that only a small section of the total surface area is accessed by water because water molecules are limited to polar sites. Low rank coals hold a greater section of polar sites and their water surface areas are higher than for high rank coals hence the explanation why the decrease in CO_2 sorption capacity in the presence of water is highest in low rank coals.

In general, it can be observed that CO_2 sorption capacities for moisture-equilibrated coal samples are usually lower than for the dry coal samples. According to a study by Mavor *et al.* [23], as little as 1 % moisture reduce the adsorption capacity by 25 %. Clearly, the results of the CO_2 experiments of this study indicate a reduction of 20-25 % relative to the dry coal samples at a moisture content of around 1.5 % which supports earlier studies. Ozdemir and Schroeder [9], discussed a possible mechanism of CO_2 adsorption on moisture-equilibrated coal samples and mentioned that coal has a cross-linked layered macromolecular structure related with both covalent and noncovalent interactions. Water molecules are kept within the coal, and since the pores are water filled, only the outer surface is exposed to the adsorbing gas. Therefore, the adsorption of CO_2 on coal only occurs typically on the outer portion of pores rather than inside the inner portion of these pores where the surface potential for adsorption is high and this result in decreased CO_2 adsorption capacities on moist coals. Low rank coals have high inertinite content in them. Inertinite enhances the reduction of CO_2 adsorption capacity on coal by increasing the adsorption capacity of water because they contain a number of macro-porosity (30 nm to 10 µm pore diameter) [24]. Inertinite also contains more oxygen functional groups which promote hydrophilic sites hence Coal B displayed the least CO_2 adsorption capacities than Coal A. The proximate analysis reveals that Coal B has a high content of inertinite than Coal A (see Table 1).

3.3. CO_2 adsorption modelling

Langmuir model which assumes surface monolayer coverage was used to interpret CO_2 adsorption capacity of coal samples investigated in this study. The monolayer coverage capacity (N_{sm}), Langmuir constant (a) and linear regression correlation coefficients are shown in Table 2. The data fit well with correlation coefficients of 0.99 for dry samples, and 0.98 for moisture-equilibrated coal samples under an isothermal temperature of 35°C and the pressure range studied. The Langmuir parameters are shown in Table 2 and Figure 2 where the Langmuir monolayer coverage for Coal A ranges between 1.06 mmol/g and 2.43 mmol/g with dry sample having the highest monolayer coverage for Coal B.

Table 2. Langmuir parameters of the two coals investigated

	Moisture %	N_{sm}	a (bar^{-1})	R^2
Coal A	Dry(0)	2.43	0.026	0.99
	1.56	2.60	0.012	0.98
	2.47	1.87	0.017	0.98
	3.57	1.41	0.021	0.98
	4.32	1.06	0.021	0.98
Coal B	Dry(0)	2.68	0.008	0.99
	1.55	2.16	0.007	0.98
	2.47	2.07	0.004	0.98
	3.57	1.64	0.003	0.98
	4.45	1.27	0.002	0.98

Coal B had a monolayer coverage ranging between 1.27 mmol/g and 2.68 mmol/g following the same trend as Coal A; with a dry sample having the highest monolayer coverage. This trend corresponds to the adsorption capacities presented in Figure 1, whereby dry samples have the highest adsorption capacity whilst high moisture content coal samples have the lowest CO_2 adsorption capacity. In Figure 2, the relationship between the experimental values and the calculated values was presented which was used to further confirm the validity of the Langmuir model. From both graphs, it was observed that the Langmuir isotherm regression overlay significantly well with the experimental data, therefore, Langmuir model was correlated with the present CO_2 adsorption data.

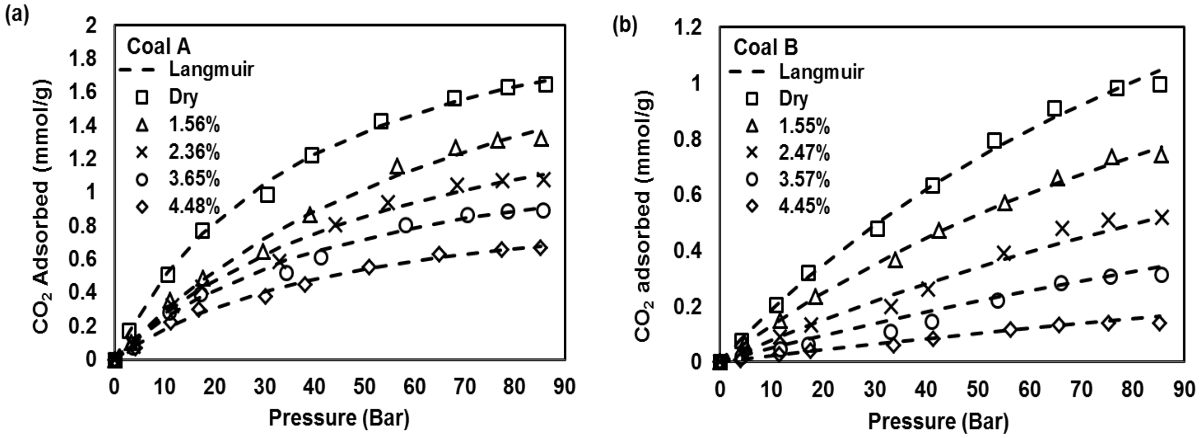

Figure 2. CO_2 adsorption isotherms on both coals showing the fits of Langmuir model: (a) Coal A and (b) Coal B

The adsorption isotherms of binary gas mixtures were investigated on Coal A samples only. This was due to the fact that Coal A samples had the highest adsorption capacities on both dry and moisture-equilibrated states (see Figure 1). Coal B samples followed the same trend as observed in Figure 1 but with lower adsorption capacities compared to Coal A samples. Figure 3 shows the CO_2-SO_2 gas mixture isotherms for two moisture contents plotted as a function of equilibrium pressure. From the adsorption capacities of pure CO_2, the addition of approximately 1.5 % and 4.5 % moisture decreased the adsorption by 20 % and 60%, respectively. For that reason, the low and high moisture content were discussed in this section.

Adsorption isotherms of CO_2 in the presence of SO_2 as an impurity are shown in Figure 3, where graphs (a), (b) and (c) are adsorption isotherms of CO_2 under the presence of 0.5 % SO_2. Graphs (d), (e) and (f) show the effect of 1.5 % SO_2 on the adsorption capacity of CO_2 on dry and moisture equilibrated coal samples. The adsorption capacity of the dry samples was high compared to the moist samples, and this was observed for both 0.5 and 1.5 % of the SO_2 present in the feed stream. The dry sample with 0.5 % SO_2 in the feed stream adsorbed 1.39 mmol/g of CO_2 which is less than the adsorption capacity obtained for pure CO_2 (Figure 1). The total reduction is approximately 20%, and an increase in the SO_2 concentration in the feed stream by 1.5 % further reduced the CO_2 adsorption capacity by approximately 50 %. The addition of moisture on the samples also had a negative impact on the CO_2- SO_2 adsorption capacity of the coal. From Figure 3, it can be observed that an increase in the moisture content decreased the CO_2 adsorption capacity significantly for both conditions. The experimental data of binary adsorption was modelled using EL model. In Figure 3, the dotted lines represent the theoretical calculated values using the EL model which provided an excellent fit to the expe-rimental data under all conditions with the correlation coefficient (R^2) of approximately 0.99. The EL model fitted the experimental data reasonably well for both Coal A and Coal B; the monolayer coverage decreased with an increase in moisture content meaning the presence of moisture decrease the adsorption capacity of the coal.

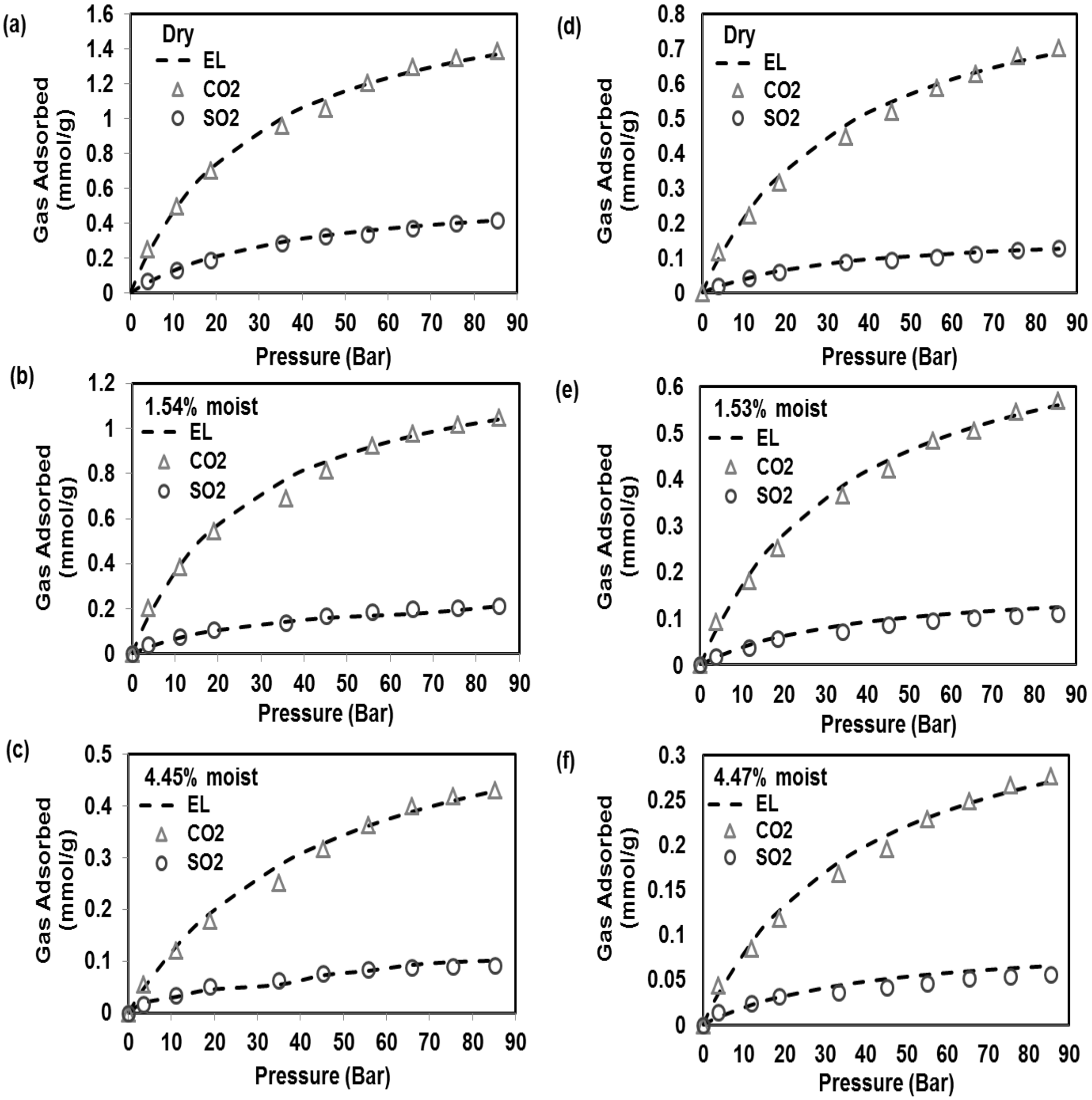

Figure 3. Binary gasses adsorption isotherms for Coal A showing the effect of SO_2 addition on moisture-equilibrated coal samples: (a - c) 0.5 % SO_2 and (d - f) 1.5 % SO_2

4. Conclusions

Based on this study, the adsorption isotherms of pure CO_2 and binary (CO_2-SO_2) gas mixtures were measured on dry and moisture-equilibrated states at isothermal temperature of 35°C and under supercritical pressures up to 90 Bar. The experimental data was fitted using Langmuir monolayer for single component and Extended Langmuir for binary and multicomponent. Langmuir and Extended Langmuir models fitted experimental data reasonably well indicating the suitability of these isotherm models to describe CO_2 adsorption in this study. This finding also implies that monolayer adsorption exists under the experimental conditions studied.

The presence of moisture was found to significantly decrease the CO_2 adsorption capacities of the coals. The adsorption capacities decreased linearly with an increase in moisture content resulting in a reduction of CO_2 adsorption capacity of approximately 20 % in moisture-equilibrated sample of Coal A compared to a dry sample of the same coal. In the low-rank Coal B, the reduction of CO_2 adsorption capacity was significant compared to the high rank Coal A, this could be that low-rank coals have bigger quantity of polar sites preferentially occupied by water instead of CO_2.

The presence of SO_2 in the feed stream of CO_2 for sequestration has a great effect on the adsorption capacity of CO_2 on coal. The CO_2 adsorption capacity was decreased by approximately 20% with a concentration stream of 0.5 % SO_2 and an addition of the SO_2 concentration to 1.5 % reduced the CO_2 adsorption capacity even further. The presence of moisture content also contributed to the CO_2 adsorption capacity by further reducing it. Therefore, the presence of SO_2 in the feed stream and moisture in the coal seams are expected to reduce the amount of CO_2 stored in coal seams and should be considered during CO_2 sequestration on coal seams. These results support the need for desulphurization of the flue gas before compression and storage of CO_2 in coal seams and will contribute to the measurements of CO_2 adsorption on South African coal seams particularly for the coals studied.

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