

## EFFECT OF MOISTURE ON THE SORPTION OF CO<sub>2</sub> BY COAL

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### INTRODUCTION

It is well known that coal deposits contain varying amounts of moisture adsorbed or occluded within void spaces [1]. Coal seams are also known to contain varying amounts of gases such as methane and CO<sub>2</sub> [2]. Even though the presence of moisture is likely to reduce the gas storage capacity of coals [3,4], the reasons for such an occurrence are not well understood. Knowledge of the gas storage capacity of coals is of fundamental importance for coalbed methane studies. Therefore, it is of interest to investigate in detail the role of moisture in affecting the sorption of gases by coals. The presence of moisture in coals can affect the sorption of gases in the following ways: (a) gas dissolution; (b) pore blockage/filling; and (c) structural changes due to coal swelling. These effects have been addressed by (a) using CO<sub>2</sub> as sorbing gas (since it is present in coalbeds, it dissolves in water and it is often used to characterize the coal structure), and (b) using two coals having different swelling tendencies in water.

### EXPERIMENTAL

Table 1 shows the ASTM proximate and elemental analyses of the coals used in this study. In both cases, coal powders (-20 Tyler mesh) were studied under dry and moist conditions. Dry conditions were achieved by subjecting the samples to evacuation at ca. 10<sup>-3</sup> torr and 115°C overnight. Moist coals were prepared using an "incipient wetness" technique [5], which consisted in adding drops of distilled/deionized water to 1 g of coal and stirring until a muddy material remained. The amounts of water required

for achieving incipient wetness (Table 2) were 1.9 and 6.6 times greater than the equilibrium moisture contents for Mary Lee and (the more easily wetted) New Mexico coals, respectively.

Low pressure (0-830 torr) volumetric CO<sub>2</sub> sorption experiments were performed at 25°C using a Carlo Erba Sorptomatic 1800 apparatus. When moist samples were used, it was necessary to correct the equilibrium pressures for the contribution due to water evaporation. This was done by assuming that water evaporation reached equilibrium well within the time frame of the measurements. In addition, a further correction was applied to the CO<sub>2</sub> equilibrium pressure data to account for the amount of CO<sub>2</sub> dissolved in the water contained by the coal. In this case, both equilibrium CO<sub>2</sub> dissolution and the applicability of Henry's Law were assumed.

Moisture-induced swelling effects were assessed by performing experiments following a procedure described by Green et al. [6]. In essence, the volume expansion caused by the addition of water to 1 g of ~100 Tyler Mesh coals (after centrifugation) was measured, and was expressed as swelling ratios (Table 2).

## RESULTS AND DISCUSSION

**CO<sub>2</sub> Sorption Capacity of Dry vs. Moist Coals.** Figure 1 shows the CO<sub>2</sub> sorption isotherms for both dry and moist samples of Mary Lee and New Mexico coals. For both coals it is shown that the CO<sub>2</sub> adsorption capacity decreases in the presence of moisture. Similar results were reported for CO<sub>2</sub> sorption on lignites [3] and for CH<sub>4</sub> sorption on bituminous coals [4]. At very low relative pressures, the (typically concave downwards) shapes of the isotherms are affected by nonequilibrium conditions, as evidenced by the shapes of the respective Dubinin-Radushkevich (D-R) plots (Figure 2) [7]. The corresponding D-R equivalent surface areas for both dry coals (Table 2) are of reasonable magnitude compared to reported values [8]. Moist coals also provide D-R surface area estimates in close agreement with those of their dry counterparts (Table 2). Therefore, the equivalent CO<sub>2</sub> D-R

surface areas appear to be independent of the presence of moisture in the coals. Similarly, micropore volumes (obtained by extrapolation of D-R plots to saturation pressure) are comparable for both moist and dry samples of each coal. Hence, at pressures close to saturation the presence of moisture appears to have little bearing on the  $\text{CO}_2$  sorption capacity of coals. On the other hand, at low pressures there are clear differences in  $\text{CO}_2$  sorption capacity between dry and moist samples of each coal, with the latter taking up less  $\text{CO}_2$  than the former.

**Contribution by  $\text{CO}_2$  Dissolution to  $\text{CO}_2$  Sorption.** Figure 3 shows the variation in the calculated equilibrium amounts of  $\text{CO}_2$  dissolved in the moisture of each coal (assuming that the moisture consists of pure water) with  $\text{CO}_2$  partial pressure. These values, obtained using the amounts of water required to reach incipient wetness (Table 2), are seen to be very small in comparison with the total  $\text{CO}_2$  uptakes of each coal (Figure 3). Incipient wetness water values provide upper limits for the moisture contents of these coals, and are presumably comparable to the maximum moisture holding capacities of similar coals. Therefore, it is concluded that the dissolution of  $\text{CO}_2$  does not contribute significantly to the  $\text{CO}_2$  sorption by bituminous coals, at least at low relative pressures.

**Contribution by Pore Blockage/Filling to  $\text{CO}_2$  Sorption.** To account for the moisture-related decrease in  $\text{CH}_4$  sorption by bituminous coals, Joubert et al. suggested that some water molecules can effectively block pore entrances through specific interaction with oxygen functional groups in the coals [4]. These authors based their reasoning on the observation that the moisture-induced suppression in  $\text{CH}_4$  sorption (and in Langmuir equivalent  $\text{CH}_4$  surface area) was proportional to the oxygen content of the coals [4]. The same trend is observed for  $\text{CO}_2$  sorption in the present study (see Table 2 and Figure 1). However, the moisture-induced decrease in  $\text{CO}_2$  sorption in our case is independent of the D-R equivalent  $\text{CO}_2$  surface areas and, especially, the D-R micropore volumes of these coals (Table 2). The latter

observation suggests that the access of CO<sub>2</sub> to the coal pores is not restricted by the presence of moisture.

**Contribution by Coal Swelling to CO<sub>2</sub> Sorption.** Swelling ratios for the coals investigated differ significantly (Table 2), and are comparable to those reported for low rank coals [3,9]. In the presence of moisture, the more swelling coal, New Mexico, was found to experience a much more drastic reduction in CO<sub>2</sub> sorption capacity than the relatively non-swelling coal, Mary Lee (Figure 1). Studies of swelling-related structural changes in lignites using N<sub>2</sub> sorption [3] indicate that drying induces a collapse of macro- and mesopores, as well as undetectable changes in microporosity which parallel an increase in CO<sub>2</sub> sorption. The latter is in agreement with our observations at low relative pressures (Figure 1). Since CO<sub>2</sub> sorption at low pressures occurs by the preferential volume filling of the narrowest micropores (i.e., those with the highest sorption potentials) [7], the above results are best interpreted by postulating that the micropore diameters decrease upon drying. It follows that micropore diameters should increase when in contact with moisture, especially for swelling coals. This would explain why moisture limits the CO<sub>2</sub> sorption capacity of coals in the following way: (a) in the absence of moisture, CO<sub>2</sub> can penetrate and fill all accessible micropores; (b) in the presence of moisture, average micropore diameters increase, without necessarily involving a loss in micropore volumes (Table 2); (c) the increase in average micropore diameters limits the number of narrower pores that serve as sorption sites for CO<sub>2</sub> at low relative pressures, and hence causes a decrease in the low-pressure CO<sub>2</sub> sorption capacity of the coals (Figure 1); (d) the increase in average micropore diameters is more marked for swelling coals (Table 2), and consequently their CO<sub>2</sub> sorption capacity is more sensitive to the presence of moisture; (e) at higher relative CO<sub>2</sub> pressures, enough CO<sub>2</sub> is available to populate the wider micropores (i.e., those with lower adsorption potentials), and eventually at saturation conditions all accessible micropore volume is filled with CO<sub>2</sub> regardless of the presence of moisture.

## CONCLUSIONS

The CO<sub>2</sub> sorption capacity of two bituminous coals at low pressures (up to 830 torr) decreases in the presence of moisture. This contrasts the fact that their micropore volumes, obtained from the corresponding D-R plots, are comparable for both moist and dry coals. The contribution of CO<sub>2</sub> dissolution to its sorption was found to be negligible. The reduction in CO<sub>2</sub> sorption capacity is very significant for the more swelling coal compared to that of the less swelling coal. This remarkable reduction is possibly related to an increase in the average diameter of micropores as a result of swelling, rather than to blockage of pores by moisture.

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Table 1. Proximate and Ultimate Analyses of Coals Used

PSU NUMBER	PSOC 1469	PSOC 1446
SEAM NAME	MARY LEE	NEW MEXICO # 8
STATE	ALABAMA	NEW MEXICO
COUNTY	WALKER	SAN JUAN
TOWNSHIP / CITY	GOODSPRINGS	FRUITLAND
RANK	HV bit. A	HV bit. C
PROXIMATE ANALYSIS		
% MOISTURE	1.9	11.2
% ASH	20.6	18.5
% VOLATILES	27.3	33.5
% FIXED CARBON	50.2	36.8
ULTIMATE ANALYSIS (daf)		
% CARBON	84.9	77.3
% HYDROGEN	5.7	5.0
% NITROGEN	1.8	1.6
% SULPHUR	1.0	1.1
% OXYGEN (diff.)	6.6	15.0

Table 2. Properties of Coals Used

PSU NUMBER	PSOC 1469	PSOC 1446
% OXYGEN (daf, diff.)	6.6	15.0
% EQUILIBRIUM MOISTURE	7.2	12.1
INCIPIENT WETNESS VOLUME (cc/g)	0.14	0.80
MICROPORE VOLUME (cc/g)		
DRY	0.14	0.07
MOIST (CORRECTED)	0.15	0.08
BET N <sub>2</sub> SURFACE AREA (m <sup>2</sup> /g)		
DRY	26	16
CO <sub>2</sub> SURFACE AREA (m <sup>2</sup> /g)		
DRY	162	105
MOIST (CORRECTED)	156	93
MICROPORE SLIT WIDTH (nm)		
DRY	1.8	1.4
MOIST (CORRECTED)	1.9	1.8
SWELLING RATIO	1.09	1.29

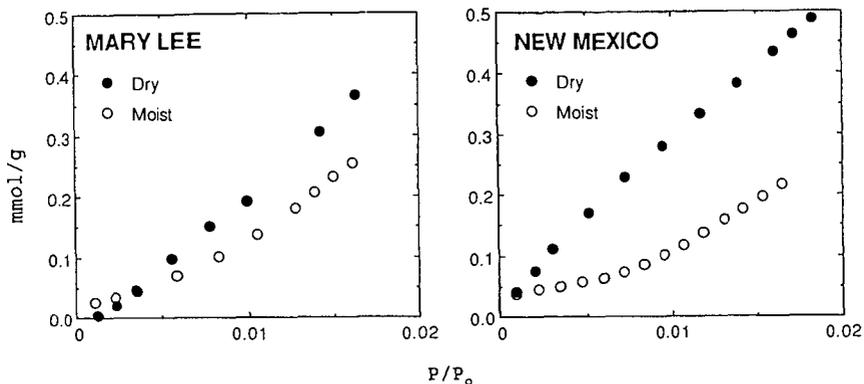


Figure 1. CO<sub>2</sub> adsorption isotherms.

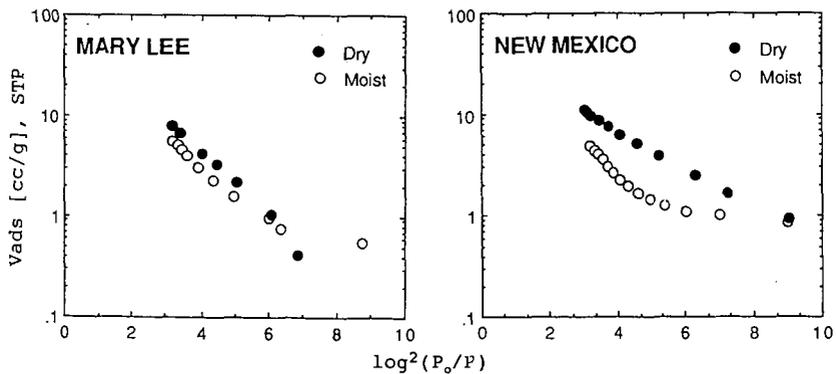


Figure 2. Dubinin-Radushkevich plots.

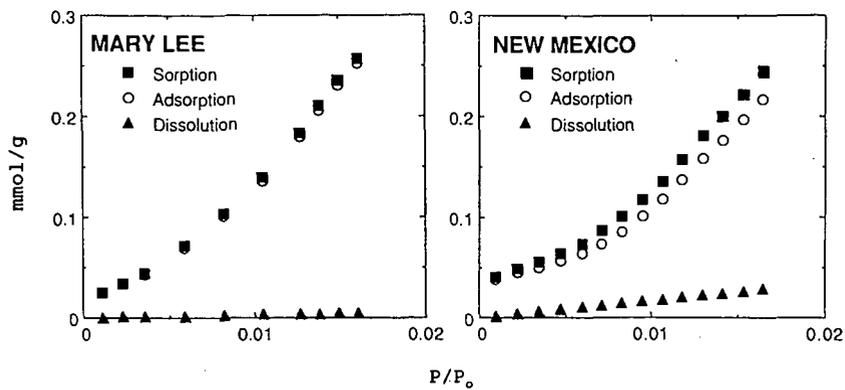


Figure 3. Contribution by dissolution to CO<sub>2</sub> sorption isotherms.