



Relationships between CO₂ sorption capacity by coals as measured at low and high pressure and their swelling

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ABSTRACT

From a comparison of high and low pressure sorption behaviour of 28 bituminous and subbituminous coals for carbon dioxide, the sorption capacity calculated at high pressure is always substantially greater than that estimated from low pressure sorption measurements. The difference between maximum sorption capacity from high pressure measurements and that from low pressure measurements increases with decreasing rank. This difference can be quantitatively explained by swelling of the coal at high pressure that does not occur during low pressure measurements. When expressed as volume %, the maximum sorption capacity calculated from high pressure measurements was found to equal the sum of the maximum sorption capacity calculated from low pressure measurements and the volumetric swelling the coal undergoes on exposure to high pressure. This relationship implies that the volume occupied by the coal molecules is constant when it swells: the greater apparent coal volume that occurs on swelling in gases is entirely taken up completely by increased pore volume. Moreover, this relationship provides a natural explanation for the finding that when a coal that is swollen with gas is compressed, the coal releases it. If so, low pressure sorption measurements may provide a more direct estimation of coal sorption capacity in constrained coal seams, provided a robust method of predicting maximum sorption capacity from low pressure sorption behaviour can be established.

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1. Introduction

The success of using unmineable coal seams to store CO₂ depends on the ability of the coal to store and release gas. Some coals, when not constrained, can adsorb over 10% by weight of CO₂ under supercritical conditions (Day et al., 2010). In order to determine the amount of CO₂ that can be adsorbed at high pressure, measurements are usually performed on unconstrained coals. High pressure (>7 MPa) sorption measurements of CO₂ by coal are usually performed above its critical temperature (31 °C) to avoid the extreme pressure and temperature sensitivity of the gas density near the critical temperature and pressure, and to match temperature conditions commonly found in deep seams. At pressures above 7 MPa the excess sorption of CO₂ decreases approximately linearly with increasing gas density (Sakurovs et al., 2010), indicating that near-complete saturation has been achieved. Thus the maximum sorption capacity of the coal can be directly estimated from high pressure measurements.

However, some researchers have suggested that the sorption capacity of coal may well be different if the coal is constrained, which is assumed to be the case in the coal seam (Liu et al., 2011). This is because unconstrained coals swell in CO₂ and the swollen coal may have a greater sorption capacity for gas than a constrained coal. Such a

difference will affect calculations of the amount of CO₂ that can be stored in coal seams. For example, Moffat reported a decrease in sorption capacity of methane by coal in 1955, when the coal was confined in Woods metal (Moffat and Weale, 1955). Although unconstrained coals (even inertinite-rich ones (Day et al., 2010)) swell in CO₂ at high pressure, when constrained and CO₂ is added, differential swelling between the different macerals is observed: vitrinites expand and inertinites contract to compensate, even though the inertinites appeared to absorb more CO₂ (Karacan, 2003, 2007; Karacan and Mitchell, 2003; Pone et al., 2010). Hol (Hol et al., 2011) found that compression of powdered coal that had sorbed CO₂ resulted in CO₂ expulsion, the amount of which was proportional to the applied stress.

Swelling and sorption are correlated (Ceglarska-Stefanska and Czaplinski, 1993). In a study of the response to swelling three Australian bituminous coals using a number gases including CO₂, methane, xenon and ethane over a range of pressures (Day et al., 2010), the volume increase in swelling was closely dependent on the volume of gas sorbed in all cases. A similar relationship was also found between swelling and sorption in bituminous coals when moisture is added (Fry et al., 2009). This indicates a common mechanism which is responsible for both swelling and sorption. Kelemen and Kwiatek also found a strong relationship between swelling and sorption (Kelemen and Kwiatek, 2009). When their swelling and sorption data are converted to a common volumetric basis, the relationship

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between the two in their coals is similar to that found by Day et al. (Day et al., 2010).

Low pressure measurements of sorption of CO₂ by coals usually involve measurements in the pressure range 0 to 0.1 MPa, at 0 °C. Even strongly swelling coals swell very little (around 0.1% by volume) at subatmospheric pressures even in CO₂ (Bustin et al., 2008; Walker et al., 1988). Thus measurements of sorption capacity performed at low pressure would not be influenced by swelling, unlike high pressure measurements. The data is commonly fit by the Dubinin–Radushkevich (DR) equation

$$W_{ads} = W_0 e^{-[\ln(P_{sat}/P)RT/E]^n} \quad (1)$$

where W_{ads} is the amount adsorbed at a given pressure P , W_0 is the maximum sorption capacity of the coal, P_{sat} is the pressure at which CO₂ condenses at 0 °C (3.49 MPa), R is the gas constant, T the temperature, E the apparent heat of sorption. In the DR equation, n is fixed at 2. In the Dubinin–Astakhov version, n is allowed to vary. Because measurements are performed at pressures well below saturation pressure, the maximum sorption capacity of the coal using this method is of necessity obtained by extrapolation.

However, despite gas sorption by coals having been measured at both subatmospheric and high pressure, there has been no systematic comparison made between the maximum sorption capacity calculated by the two different techniques. Several papers (Belmabkhout et al., 2004; Clarkson and Bustin, 1999; Gensterblum et al., 2009, 2010) provide both low and high pressure sorption results on their materials but do not compare the results directly. In this study we compare low and high pressure volumetric sorption capacity of a number of coals and find that the high pressure sorption measurements always give a higher sorption capacity than those calculated from low pressure sorption measurements. We find that the swelling of coal at high pressure can account for the difference in sorption capacity determined by the different techniques.

2. Experimental

Twenty-eight coals of bituminous and subbituminous rank were selected for this study. Five of these came with lumps large enough for blocks to be prepared for swelling measurements.

For sorption measurements the coals were crushed with minimum fines to less than 1 mm and the +0.5 mm–1 mm size fraction was used for all characterisation (analytical data in Table 1). Prepared samples were dried under vacuum at 60 °C to a pressure of less than 1 mbar, or overnight, whichever was longer.

For swelling measurements, coal blocks with nominal dimensions of 30 × 10 × 10 mm were cut from lumps of coal using a diamond-tipped saw. Two blocks were made from each sample; one with the long axis perpendicular to the bedding plane and the other with the long axis parallel to the bedding plane. Coal 9 was relatively friable and several trials were necessary to make a coherent block. There was no surface evidence of cleating in the blocks examined.

The helium density of each coal sample ($\rho_{C,He}$) was determined using a Quantachrome Ultra Pycnometer 1000 helium pycnometer. Samples were degassed in the isotherm apparatus to less than 0.5 mbar under vacuum prior to measurement.

2.1. Low pressure measurements

Pore volume (p_L) of these coals was obtained using a Micromeritics Tristar 3020 surface area and porosity analyser. The CO₂ excess sorption was measured at 0 °C over the gas pressure range 0 to 0.1 MPa and fitted using the Dubinin–Radushkevich (DR) model (Eq. (1)), which is the common fitting model used to fit low pressure CO₂ sorption data. Pore volume values thus calculated were converted from ml/g to ml/ml by multiplying by the helium density of the coal. The density of adsorbed CO₂ was assumed to be 1028 kg/m³, which is the van der Waals density of CO₂ and close to the sorbed phase density measured by several different techniques (Sudibandriyo et al., 2003).

Table 1
Analytical and CO₂ sorption data for coals.

	$\rho_{C,He}$ g/cm ³	Ash % db	Carbon daf, %	Hydrogen daf, %	VM daf, %	$R_{v,max}$ %	Vitrinite mmf, %	Liptinite mmf, %	p_H vol. %	p_L DR-equal weighted vol. %	p_L DR-linearised vol. %	p_L DA-fit vol. %
1	1.519	17.6	83.86	4.55	28.4	0.81	10.6	5.0	11.97	9.47	9.02	8.82
2	1.505	18.7	83.52	4.77	31.1	0.80	20.2	4.9	11.37	8.80	8.79	9.09
3	1.353	6.6	85.87	5.09	29.3	1.06	65.1	2.2	9.61	6.67	6.58	6.82
4	1.422	7.7	82.99	4.66	31.7	0.69	29.7	3.9	15.23	8.84	8.69	9.13
5	1.350	12.0	81.70	5.74	41.4	0.79	84.2	4.1	8.47	5.19	5.57	4.30
6	1.357	5.1	89.67	4.75	19.7	1.61	81.7	0.1	8.50	5.91	6.26	4.96
7	1.295	2.5	85.95	5.63	35.2	1.11	95.5	2.0	6.40	5.29	6.86	3.56
8	1.594	20.3	80.68	3.93	31.2	0.62	23.9	1.6	16.81	8.48	8.46	8.42
9	1.552	20.8	71.84	3.45	32.7	0.62	23.9	1.6	15.59	10.35	10.33	11.73
10	1.391	8.3	85.61	4.93	30.0	0.90	33.9	2.3	9.99	8.49	10.71	5.90
11	1.375	8.9	88.80	4.95	24.5	1.27	48.7	0.4	7.83	6.50	6.54	6.44
12	1.357	6.4	88.35	4.83	23.5	1.29	59.1	0.2	9.36	7.61	7.61	7.83
13	1.312	4.1	85.92	5.56	36.4	0.98	72.5	7.0	6.51	4.62	4.84	4.12
14	1.368	9.1	89.22	5.37	27.7	1.21	85.4	0.3	9.38	6.42	6.53	5.95
15	1.348	7.4	87.90	5.24	27.0	1.16	69.1	1.1	9.00	7.36	6.27	9.68
16	1.313	5.6	84.11	5.73	36.1	0.95	82.7	4.1	8.55	5.01	5.06	4.68
17	1.293	5.2	81.22	5.31	45.8	0.70	68.3	14.1	8.90	5.31	5.28	5.15
18	1.365	5.7	89.61	4.73	22.8	1.34	35.6	3.3	7.45	5.53	5.73	4.96
19	1.331	7.4	83.59	5.40	37.3	0.89	88.7	2.2	8.83	5.87	6.09	5.41
20	1.324	5.3	84.37	5.55	38.5	0.90	89.4	3.5	7.53	4.56	3.53	4.53
21	1.481	16.9	88.93	4.55	21.7	1.40	28.1	0.0	7.76	6.14	4.87	6.12
22	1.376	8.4	88.76	4.87	20.4	1.63	83.9	0.0	8.63	6.71	5.47	6.96
23	1.367	8.8	88.82	5.01	23.4	1.43	76.7	0.0	8.47	5.94	5.15	5.76
24	1.334	5.1	86.30	5.50	31.2	1.03	63.6	1.7	9.24	6.49	6.09	5.82
25	1.316	7.2	86.64	5.50	32.7	0.99	90.9	0.7	10.05	5.65	4.93	5.37
26	1.542	24.8	81.78	5.32	38.8	0.81	28.7	6.7	6.80	4.22	4.57	4.75
27	1.473	21.3	83.23	5.03	37.5	0.77	61.8	4.8	9.73	6.50	5.79	6.09
28	1.363	5.8	88.96	4.73	24.8	1.22	47.6	4.2	7.77	6.55	5.62	6.48

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