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Mechanical and flow behaviours and their interactions in coalbed geosequestration of CO₂

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Studying gas transport mechanisms in coal seams is crucial in determining the suitability of coal formations for geosequestration and/or CO_2 -enhanced coal bed methane recovery (ECBM), estimating CO_2 storage capacity and recoverable volume of methane, and predicting the long-term integrity of CO_2 storage and possible leakages. Due to the dual porosity nature of coal, CO_2 transport is a combination of viscous flow and Fickian diffusion. Moreover, CO_2 is adsorbed by the coal which leads to coal swelling which can change the porous structure of coal and consequently affects the gas flow properties of coal, i.e. its permeability. In addition, during CO_2 permeation, the coal seam undergoes a change in effective stress due to the pore pressure alteration and this can also change the permeability of the coal seam. In addition, depending on the *in situ* conditions of the coal seam and the plan of the injection scheme, carbon dioxide can be in a supercritical condition which increases the complexity of the problem. We provide an overview of the recent studies on porous structure of coal, CO_2 adsorption onto coal, mechanisms of CO_2 transport in coalbeds and their measurement, and hydro-mechanical response of coal to CO_2 injection and identify opportunities for future research.

Keywords: coalbed geosequestration; carbon dioxide; diffusion; adsorption; reservoir geomechanics

1. Introduction

Geosequestration is the process of pumping CO_2 into deep geological formations such as coalbeds to reduce or offset greenhouse gas emissions into the atmosphere. Coalbeds are of interest because they have naturally stored methane which can be displaced by injecting CO₂ and can help produce a clean and valuable hydrocarbon that can partly offset the sequestration expenses. Thus, it is also called CO₂-enhanced coalbed methane recovery (ECBM). The economic feasibility of carbon dioxide sequestration into coal seams in some areas and formations has been investigated by several authors and it has been suggested that this option might be economically viable (Gentzis 2000, Yamazaki et al. 2006, Robertson 2009, Shimada and Yamaguchi 2009). A number of demonstration projects of CO₂ injection into coalbeds have been undertaken in the United States, Europe and Asia (Reeves 2001, Yamaguchi et al. 2006, Van Bergen et al. 2006, Wong et al. 2007, Botnen et al. 2009). However, industrial scale operations have not commenced because of concerns related to gaps in understanding and a limited ability to predict gas flow mechanisms as well as coal behaviour in response to CO₂ injection.

It is currently believed that when CO_2 is injected into a coal seam, it flows inside the macro-porous system of cleats and then starts to diffuse into the coal matrix to reach the micropores and be stored there in an adsorbed state. The adsorption of CO_2 by the coal causes physico-chemical changes that result in an increase in coal matrix volume, which is termed *swelling*. Swelling can lead to changes in the hydraulic and mechanical properties of coal. This leads to a reduction in CO_2 injectivity and raises doubts about the integrity of storage sites. In order to develop an efficient strategy for coal seam sequestration, a comprehensive understanding of the variables that affect the transport and mechanical properties and their interactions is required.

In this review, gas transport mechanisms in coalbeds and also changes in their mechanical and flow properties due to CO_2 injection will be discussed. First, the porous structure of coal and the mechanisms and properties of gas adsorption are introduced. Then, a comprehensive review of flow mechanisms, including permeation and diffusion, and how these are influenced by the intrinsic properties of coal is presented. The change in mechanical and flow properties of coal, due to sorption-induced swelling, is also of a considerable importance and some authors' experimental data are presented. Finally, an overview of the current knowledge and research gaps are identified.

2. Molecular and porous structure of coal

Coal is an organic sedimentary rock that contains varying amounts of carbon, hydrogen, and other elements including mineral matter. Coal can be considered as a polymer of a

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Figure 1. (a) Conceptual coal model in which aromatic compounds are connected to each other via aliphatic bridges (Haenel 1992) and (b) molecular structural model of bituminous coal (with carbon content of 83%) (Marzec 1985). Note that the aromatics-hydrocaromatics units shown in 'a' represent the clusters of rings in 'b'.

certain molecular weight (Ward and Suarez-Ruiz 2008), with a structure composed of an accumulation of aromatic macromolecular chains which are inter-linked to form a body of solid material. Conceptual and structural models of bituminous coals are illustrated in Figure 1. The molecular structure of coal depends on the origin and rank of a particular coal (Ishihara *et al.* 2004), and a number of different models have been proposed (Nishioka 1993). For carbon contents greater than 85% many properties of coal can be related to the molecular size of the structural units.

The molecular structure leads to a porous material with a wide range of pore sizes, that includes many microscopic pores resulting in a large internal surface area (Pashin 2008). The range of pore sizes and their interconnectedness influence mechanical properties, gas storage and flow and have been of interest to researchers in coal science for many years (Alexeev *et al.* 1999, Hall *et al.* 2000).

In general, coals have significant specific surface area, up to $215 \text{ m}^2/\text{g}$ (Gürdal and Yalçin 2001) with open porosities varying from 2.5-18.0% (Gan et al. 1972). The porosity is generally considered to comprise of nanopores or micropores (<2 nm), mesopores (2-50 nm), and macropores (>50 nm) in which fluids can be stored and flow (Harris and Yust 1976, Balek and Koranyi 1990, Radlinski et al. 2004, Sereshki 2005, Pashin 2008). When considering the flow and mechanical behaviour there does not appear to be any advantage from considering micropores and mesopores separately and the term micropores is used subsequently for all pores less than 50 nm. A major part of the stored gas resides in the micropores (Parkash and Chakrabartty 1986). The nature of the porosity varies with carbon content and rank, with macropores predominant in the lower carbon (lower rank) coals, whereas higher carbon (higher rank) coals contain predominantly micropores (Gan et al. 1972). The porosity of coal decreases with carbon content until reaching a minimum (of around 3%) at approximately 89% carbon content, and then increases with further carbon content increase (Speight 2005).

To date many techniques and methods have been used to observe and measure the porosity of coals, and this has resulted in ongoing debate about the interconnectedness of the pores. Some assume that coal has an interconnected network of pores (Harris and Yust 1976, Harpalani and Zhao 1991, Gamson *et al.* 1993, Radovic *et al.* 1997), while others believe that pores are isolated from each other. For example Alexeev et al. (1999) estimated 60% of the pore space is closed, and fluid can only migrate from one pore to another by diffusion through the solid coal matrix (Larsen and Wernett 1992, Larsen *et al.* 1995). These contrasting opinions are a consequence of technological limitations which prevent direct observation of the porous structure (Sharma *et al.* 2000).

A system of natural orthogonal fractures, also known as cleats, form the vast majority of the macropore space in coal (Pashin 2008). Cleat formation is controlled by intrinsic tensile forces, fluid pressures, and tectonic stresses (Gamson *et al.* 1993, Su *et al.* 2001). Most cleat surfaces are perpendicular to the bedding. The major set is variously termed the *primary*, *main, face* or *master* cleats, and the minor set named the *secondary, butt, back, cross* or *bord* cleats (Figure 2) (Spears and Caswell 1986). The secondary cleats end at intersections with through-going primary cleats and are believed to have formed later (Laubach *et al.* 1998). In some coals, a third cleat set is present which is commonly curvi-planar, very short in length and not aligned with either primary or secondary cleats (Gamson *et al.* 1993).

Transport of gas through coal depends primarily on the spacing and aperture of the cleats (Laubach *et al.* 1998). Cleat spacing is usually sufficiently close (millimetres to centimetres) that numerous visible fractures are present in coal cores (Laubach *et al.* 1998). Cleat spacing tends to increase with increasing mineral content (Spears and Caswell 1986), and decreases with porosity so that cleat spacing reduces with rank reaching a minimum for medium volatile bituminous coals, where porosity is a minimum, and then increases for higher carbon contents (Laubach *et al.* 1998). Cleat apertures range from



Figure 2. Schematic illustration of coal cleat geometries. (a) Cleats pattern in plain view. (b) Cleat hierarchies in cross-section view (Laubach et al. 1998).

hairline fractures narrower than one micron to major fractures wider than 20 millimetres (Pashin 2008). Some minerals may fill the cleats and affect the permeability of coal (Pashin 2008). These minerals in the cleats constitute a significant fraction of total mineral matter in the coal (Spears and Caswell 1986).

An understanding of the molecular structure and the nature of the pores, which affect the mechanical response, and the gas flow and storage, is required in CO_2 sequestration and ECBM applications. For example, cleat aperture, spacing and connectedness are important in controlling gas flow whereas the porosity of the matrix controls storage capacity. As will be shown in the following sections, these parameters are influenced by interactions between CO_2 and the coal structure.

3. Adsorption of CO₂ onto coal

Gas adsorption and desorption or simply gas sorption is a process in which gas molecules "interact" with a surface (Sereshki 2005, Pashin 2008). Molecules and atoms can attach themselves onto surfaces in two ways: physisorption and chemisorption. In physisorption (physical sorption), there is a reversible weak Van der Waals attraction of the adsorbate to the surface. Chemisorption is an irreversible process where gases are held on the surface of coal by chemical forces (Ozdemir 2004, Pashin 2008). Physical adsorption can occur alone, but chemisorption is always accompanied by physical adsorption (Dollimore *et al.* 1976).

The mechanism of gas sorption in coal is still not completely understood (Melnichenko *et al.* 2009), and many sorption isotherms have been used to describe it. Of these the Langmuir and Dubinin (Dubinin-Radushkevich and Dubinin-Astakhov) have been the most widely reported as can be seen in Table 1. Each isotherm is based on assumptions about the nature of the absorbent surface and the number of particles that may be sorbed. For example, the Langmuir isotherm assumes that under constant pressure and temperature, there is a dynamic equilibrium between sorbed and non-sorbed phases and sorption is limited to a single layer. Langmuir's equation is given by:

$$V = \frac{V_L P}{P_L + P} \tag{1}$$

Where P is the equilibrium gas or vapour pressure, V is the volume of gas adsorbed, V_L is the Langmuir monolayer volume (maximum monolayer capacity) and P_L is the Langmuir pressure corresponding to $0.5 \times V_L$ The isotherm parameters V_L and P_L are determined by a process of curve fitting to experimental data. A summary of recent experimental studies on CO₂ sorption in coal is given in Table 1. In many studies the Langmuir isotherm has been shown to provide reasonable predictions of the sorption of CO2 and multi-component gas mixtures (containing CO₂) to coal under below-critical conditions (Laxminarayana and Crosdale 1999, Busch et al. 2003a, Yamazaki et al. 2006, Jodlowski et al. 2007, Saghafi et al. 2007, Prusty 2008) and supercritical conditions (T>31 °C and P > 7.38 MPa) which are relevant to sequestration in deep coal seams (Busch et al. 2003b, Busch et al. 2006, Yu et al. 2008).

The Dubinin equations have also been used to describe the sorption of CO_2 in the gaseous state (e.g. Charriére *et al.* 2010, Pone *et al.* 2009b) and also modified for supercritical CO_2 (Sakurovs *et al.* 2007, Day *et al.* 2008c). Early studies (e.g. Clarkson *et al.* 1997) showed that Dubinin model (D-A) fits the experimental data better than Langmuir model for both CO_2 and CH_4 below the critical point. Sakurovs *et al.* (2007) developed a modified Dubinin model, in which the gas pressure is replaced by gas density and also a proportionality term has been added to the equation to account for the gas adsorption on the

Table 1.	Experimental data for adsor	ption of CO ₂ on coal for differen	it isotherm models in recent	publications

	Gas Type				
Adsorption isotherm model	Composition	PVT	Reference(s)		
Langmuir	Pure Gas Only	Subcritical	(Yamazaki <i>et al.</i> 2006, Laxminarayana and Crosdale 1999, Saghafi <i>et al.</i> 2007, Ceglarska-Stefanska and Brzoska 1998)		
		Supercritical	(Li et al. 2010, Goodman et al. 2007)		
	Multi-component Gas	Subcritical	(Busch et al. 2003a, Ceglarska-Stefanska and Zarebska 2005, Prusty 2008)		
Dubinin-Astakkov	Pure Gas Only	Subcritical	(Pone et al. 2009b, Siemons et al. 2007, Harpalani et al. 2006, Ozdemir et al. 2004)		
		Supercritical	(Sakurovs <i>et al.</i> 2010, Ottiger <i>et al.</i> 2006, Clarkson <i>et al.</i> 1997, Bae and Bhatia 2006)		
	Multi-component Gas		(Sakurovs et al. 2010)		
Dubinin-Radushkevich	Pure Gas Only	Subcritical Supercritical	(Jodłowski <i>et al.</i> 2007, Clarkson and Bustin 1999) (Sakurovs <i>et al.</i> 2007, He <i>et al.</i> 2010, Day <i>et al.</i> 2008c, Clarkson <i>et al.</i> 1997, Bae and Bhatia 2006)		
Others	Multi-component Gas Pure Gas Only Multi-component Gas	Subcritical Supercritical	(Jodlowski <i>et al.</i> 2007, Bae and Bhatia 2006) (Fitzgerald <i>et al.</i> 2005, Mazumder <i>et al.</i> 2006)		



Cas Density (kg m)

Figure 3. Langmuir and D-R isotherms for adsorption of carbon dioxide at pressures up to 15 MPa (DR+k and Langmuir+k means the modified isotherm with the absorption term) (Sakurovs *et al.* 2007).

interior of coal in addition to its exterior. This model (DR+k model in Figure 3) is able to fit the experimental data precisely under high pressure and supercritical conditions with up to 1% accuracy (Sakurovs *et al.* 2007, Sakurovs *et al.* 2010).

There trends between sorption and coal rank is somewhat complicated, and this is believed to be a consequence of counteracting trends of increasing carbon content leading to increasing sorption, and reducing porosity with increasing carbon content which reduces the surface area available for sorption. However, some experimental data showed a U-shaped trend between maximum adsorption capacity of coal and vitrinite reflectance (R_{max}) with a minimum at $R_{max} = 1.1-1.2$ which corresponds to a total carbon content of around 85% (Day *et al.* 2008a, Pini *et al.* 2010). The effect of competition for sorption sites results in reductions in the maximum amount of CO₂ that can be sorbed when the coal is initially moist and when the pores are filled with methane. There is little data on the effect of coal rank on competitive sorption.

Although adsorption has been one of the most studied aspects of ECBM and CO_2 sequestration, questions remain about adsorption-desorption mechanisms and the selectivity of multi-component fluids, under environmental conditions of deep coal seams.

4. Gas flow in coal

4.1 Mechanisms

Gas-phase flow in porous media consists of viscous and diffusive components. As described earlier, coal is a naturally fractured medium, usually characterized by a dual porosity system composed of *micropores* and *macropores*. It is generally assumed that flow of gas through cleats (macropores) is a laminar viscous flow which is described by Darcy's law, whereas, gas transport through the coal matrix (micropores) is assumed to be controlled by diffusion (Shi and Durucan 2003).

Darcy's law states that the average velocity of the gas, u, is directly proportional to the gas-phase pressure gradient, ∇P , and the gas-phase permeability, k, as illustrated below:

$$u = -\frac{k}{\mu} \left(\nabla P - \rho g \nabla z\right) \tag{2}$$

where μ is the gas-phase viscosity, ρ is the density of the gas, and g is the gravity. It should be noted that the actual velocity of the gas in fractures, ν , is related to the average velocity by $\nu =$ u/φ_f where φ_f is the fracture porosity. The mass flux equation can be written as (Henderson *et al.* 2005)

$$q = \frac{\partial \left(\phi_f \rho\right)}{\partial t} + \nabla. \left(\rho u\right) \tag{3}$$

This form of Darcy's equation considers the compressibility of the gas which can be described by an equation of state (i.e. $\rho = f(P,T)$) such as Peng-Robinson (Henderson *et al.* 2005). The relationship between gas viscosity and pressure and temperature can also be considered. It should be noted that supercritical gas, immediately above the critical point is still compressible and therefore, the gas compressibility can be an important property. Many models developed so far, have neglected this fact and have assumed the supercritical gas as an incompressible fluid.

Diffusion is the process of fluid movement in matrix blocks of rock due to the concentration gradient. There are different kinds of gas diffusion mechanisms occurring in porous media but it is generally assumed that continuum diffusion is the dominant mechanism in coalbed methane recovery (Cui *et al.* 2004). Diffusion processes in porous media are conventionally described by Fick's first and second laws: the first for steady and the second for non-steady flux. The Maxwell-Stefan formulation is an extension of first Fick's law for multi-component gas mixtures. The first Fick's law is written:

$$q_d = -D_e \nabla c \tag{4}$$

Where q_d is the diffusive flux that is used as a source/sink term for mass conversation in dual porous model, D_e is the effective diffusion coefficient, and ∇c is the concentration gradient. The second Fick's law has a similar form but uses the second derivative of concentration as follows:

$$q_d = -D_e \nabla^2 c \tag{5}$$

For most studies, gas fluxes due to viscous flow and diffusion are calculated separately and then simply added together. This approach is favoured because it is much easier and needs less computational effort than fully coupled analyses. Webb (2006) explained how diffusion and advection can have interaction on each other. However, some studies have shown that such an approach may lead to inaccuracy and have recommended the use of the Dusty Gas Model (DGM), in which the porous media is included as a dusty gas component of the gas mixture and also other diffusion processes (in addition to continuum diffusion) can be considered (Webb 2006).

4.2 Permeability

The permeability of coal seams has been investigated by a number of authors and a wide range of values have been published. The permeability in mining applications is usually in the range of 0.1 mD to 100 mD (9.87×10^{-14} to 9.87×10^{-11} m²) (Sereshki 2005). For sequestration, low values can be expected because the target coal seams are significantly deeper, and the elevated stress levels will cause smaller cleat apertures. For example, Pinetown *et al.* (2008) reported that permeability of coal in the Sydney Basin varied from 0.1 to 50 mD, decreasing for deeper seams so that permeability was commonly less than 1 mD below 400 meters in depth. Also, due to the anisotropic nature of coal and the different continuities and apertures of face and butt cleats, horizontal permeability (parallel to bedding) is typically an order of magnitude larger than the vertical permeability (Gash *et al.* 1992).

Permeability is influenced by the intrinsic properties of coal. Several studies (Smyth and Buckley 1993, Clarkson and Bustin 1997, Robertson and Christiansen 2005) have shown that permeability is affected by coal rank in a similar manner to porosity, reaching a minimum for medium volatile bituminous coals and increasing for higher and lower rank coals. However, an exception is lignite which can have very low permeability despite a relatively high porosity due to the lack of a well developed and interconnected cleat system (Botnen *et al.* 2009). There is little data on the permeability of the intact coal matrix although values of 0.04–0.7 mD have been reported (Flores 2004).

4.3 Diffusivity of CO₂

The value of the effective diffusion coefficient depends on the coal rank and type, gas type, porous network, and environmental conditions (pressure and temperature). For many coals the effective diffusivity of methane ranges from 2.9×10^{-11} to 3.7×10^{-9} m²/s (according to Olague and Smith 1989). The diffusivity of CO₂ is usually higher than that of methane by a factor of 2–3 for dry coal and by a factor of 5–6 for moist coal (Busch *et al.* 2004). It has been suggested that the relative difference between diffusion of CH₄ and CO₂ is due

to the different behaviours of carbon dioxide and methane (Charriére *et al.* 2010), and the role of gas molecule size and pore space structure (Cui *et al.* 2004). The smaller size of CO_2 molecules leads to a faster movement and easier entrance into narrower pore throats compared to larger molecules of CH₄ (Cui *et al.* 2004). Also, Larsen (2004) stated that CO_2 has a more favourable interaction enthalpy than hydrocarbons (such as methane) which results in faster diffusion into coal.

Environmental conditions can also affect the rate of diffusion. For example, increase in moisture content decreases the diffusivity of both methane and CO_2 (Clarkson and Bustin 1999) because water molecules can block the pathways of gas molecules inside the coal matrix. Increasing temperature has a positive effect on the rate of diffusion (e.g. Krooss *et al.* 2002, Busch *et al.* 2004, Charrière *et al.* 2010), due to the fact that at higher temperature, gas molecules have higher energy and tend to move faster. Moreover, Cui *et al.* (2004) reported that increase in gas pressure continuously decreases the apparent diffusion coefficient; however, the influence of pressure on the effective diffusivity is not well established.

Although data for effective diffusivity are available, their reliability is suspect because most values have been determined indirectly from studies of the desorption kinetics from samples of powdered coal. The monitored sorption kinetics is used to determine the apparent diffusion coefficient of gas in coal. This "indirect" method is based on a number of assumptions and simplifications, such as assuming spherical particles with the same size (unipore) or a range of sizes (bidisperse), and considering Henry's law for isotherms (Ruckenstein et al. 1971, Clarkson and Bustin 1999, Shi and Durucan 2003). More recently, some studies have used solid core samples (e.g. Pan et al. 2010) which may be more accurate as they retain the original porous structure. Recently, a new direct method that does not need assumptions about the average particle size and porous structure of matrix has been developed at CSIRO laboratories (Saghafi et al. 2007). It measures the gas flux through solid coal disks of 6-12 mm in diameter and 2-6 mm in thickness (Figure 4). The system consists of a coal disk and two gas chambers at each side initially filled with different gases (e.g. CO_2 and N_2). Monitoring of the gases concentrations as they

diffuse in the opposite direction to the chambers where concentration is lower enables the diffusion coefficient to be determined. Using sorption data obtained from a separate adsorption analysis allows theoretical curves to be produced for different diffusivities by matching with the measured flux curve. Further development of this method to enable measurement of both adsorption and diffusion in an integrated diffusion-sorption test would eliminate the errors due to using different coal samples with different preparation processes. A summary of the recent studies on diffusion of CO_2 in coal is shown in Table 2 where it can be seen that most of diffusion studies have been conducted using sorption kinetics techniques and there is a knowledge gap in diffusion of multicomponent gases in coal, especially under supercritical conditions. It may be noted that the direct measurements tend to give higher values of diffusivity, and point to a need for further tests to provide more reliability in diffusivity values.

5. Mechanical properties of coal

Mechanical properties (strength and stiffness) vary with coal rank and type, and the direction of loading relative to the bedding planes. At low confining stresses the strength of coal is controlled by its tensile strength and the cleat spacing, which increases with rank (Figure 5b) (Esterle 2008), and is affected by sample size because the larger samples contain more cleats and therefore the strength and stiffness decrease significantly (Medhurst and Brown 1998, Esterle 2008). Owing to its mode of deposition and cleat orientation, coal is an anisotropic material and the strength, and stiffness, is higher perpendicular to the direction of bedding (Pomeroy and Morgans 1956). The strength has been described by the Hoek-Brown criterion (e.g. Medhurst and Brown 1998, Gentzis *et al.* 2007, Masoudian *et al.* 2011). The generalized Hoek-Brown failure criterion is given below.

$$\sigma_1' = \sigma_3' + \sigma_c \left(\frac{m\sigma_3'}{\sigma_c} + s\right)^a \tag{6}$$



Temperature controlled container

Figure 4. Schematic Diagram of measurement apparatus for gas diffusivity in coal, used in CSIRO, gas flow from chamber 1 to chamber 2 through the coal disk (Saghafi *et al.* 2007).

Coal Origin		Experimental		Diffusion			
Country	Basin	Method	Sample	P _{max} (MPa)	Model	Value $(10^{-10} \text{ m}^2/\text{s})$	Ref.
Australia	Sydney	Sorption Kinetics	Solid Core	4.0	Fickian Unipore		(Pan <i>et al.</i> 2010)
		Direct	Solid Disk	0.3	Fickian	0.7–7.2	(Saghafi <i>et al.</i> 2007, Saghafi 2010)
Canada	Cretaceous Gate	Sorption Kinetics	Powdered Sample	0.6	Fickian Unipore / Bidisperse		(Clarkson and Bustin 1999)
France	Lorraine	Sorption Kinetics	Powdered Sample	5.15	Fickian Unipore	0.019	(Charriére <i>et al.</i> 2010)
Great Britain	Selar Cornish / Nottinghamshire	Sorption Kinetics	Powdered Sample	12.0	Fickian Unipore	0.01–10	(Siemons <i>et al.</i> 2007)
Poland	Upper Silesian	Sorption Kinetics	Powdered Sample	1.74	Fickian Unipore	0.788	(Busch et al. 2004)
South Africa	Highveld	Direct	Solid Disk	0.3	Fickian	3.7-15.1	(Saghafi et al. 2008)
United States	Black Warrior	Sorption Kinetics	Powdered Sample	3.4	Fickian Unipore / Bidisperse		(Gruszkiewicz <i>et al.</i> 2009)



 Table 2.
 A summary of studies on CO2 diffusion into coal during last decade

Figure 5. The relationship between carbon content and (a) elastic modulus and (b) compressive strength of coal (Szwilski 1985).

Where *a*, *m* and *s* are fitting parameters and σ_c is the uniaxial compressive strength (UCS) of coal. As expected, the strength is higher at greater confining stress, and becomes increasingly controlled by frictional shearing.

Some properties do not show a significant dependency on coal type, for example, a Poisson's ratio of 0.346 is reasonably representative of a wide range of coal grades (Szabo 1981). It should be noted that, bulk modulus of coal is numerically close to Young's modulus according to the value of Poisson's ratio (Suuberg *et al.* 1995).

The graphs in Figure 5 show the minimum UCS and a modulus minimum occurs at around 85% carbon content, where porosity and cleat spacing are also minimum. Similar trends have been reported in other studies, for example (White and Mazurkiewicz 1989) have shown that an increase in moisture content (from 3.7% to 12%) causes a decrease in mean strength and elastic modulus by 12.5% and 35%, respectively for bituminous coals. As the strength data are generally obtained from small specimens it would be expected that the strength trend is unaffected by the cleat spacing. In other rocks low porosity is associated with high strength, so the minimum strength at this carbon content demonstrates the importance of the cross-linking of the coal molecules which is also a minimum at this carbon content. Moving away from the minimum,



Figure 6. The relationship between coal brightness (medium rank, high volatile) and mechanical strength (Medhurst and Brown 1998).

the cross-linking and porosity both increase, and this leads to increases in strength and stiffness. However, as carbon content decreases, a local maximum in the stiffness can be seen at a carbon content of 80%, which is believed to reflect the increasing importance of the increasing porosity as coal rank reduces.

Only very limited data are available for strength and stiffness at higher confining stresses, some of which are depicted in Figure 6. It can be seen that dull coals (higher ash content) have higher strengths than bright coals (lower ash content). We can also further anticipate that the strength will be increasingly controlled by frictional interactions as stress level increases and the effects of the cross-linking will reduce.

5.1 Effects of CO₂ on strength and stiffness

Research has shown that vapour and gas sorption can affect the mechanical properties of solid bodies (Czaplinski and Holda 1982), and it has been suggested that this reduces their strength (Ates and Barron 1988). It is also well known that coal swells in the presence of carbon dioxide (e.g. Reucroft and Patel



Figure 7. The effect of temperature on elastic modulus of a typical polymer (Mahieux 1999).

1986, Stacy and Jones 1986, Walker et al. 1988). It is currently believed that these changes are a consequence of CO₂ lowering the glass transition temperature of the coal polymer structure (Larsen 2004). Coal behaves as a glassy polymer at room temperature (Lucht et al. 1987, Green et al. 1991), where the molecular structure of coal is "frozen" in place. When the temperature exceeds its glass transition temperature ($T_g =$ 580-623 K), the coal changes from a glass to a rubber (Lucht et al. 1987). Because solvents, gases and vapours (e.g. carbon dioxide) in contact with coal, act as a plasticizer and increase the coal's ability to rearrange to a new structure with a lower energy state the glass transition temperature decreases. The effect of this change of state on the stiffness of a typical polymer is shown in Figure 7. In its glassy state, an increase in temperature slightly decreases the elastic modulus. However, the polymer stiffness decreases dramatically around the glass transition temperature. Thus one may expect that depending on the amount of adsorbed gas, the rearrangement of coal structure will lead to a partial loss in strength and stiffness.

Only limited data are available regarding the effect of gas sorption on the stiffness and strength of coal. Czaplinski and Holda (1982) and Aziz and Ming-Li (1999) provide indirect evidence of significant strength reductions in the presence of CO₂. More recent triaxial tests on brown and bituminous coal (Masoudian *et al.* 2011, Viete and Ranjith 2006) have shown significant reductions in strength (13% to 20%) and stiffness (26% and 15%) at low confining stress; however as stress level increased the influence of CO₂ appeared to decrease. Some typical data are shown in Figure 8.

The stress-strain curves for CO_2 -saturated and watersaturated samples compressed under 1.0 MPa confining stress, are depicted in Figure 9. It can be seen that the strain energy (the area below stress-strain curve) is significantly lower for the CO_2 -saturated sample. This is consistent with the effects of CO_2 leading to a solid structure with lower energy level (higher entropy).



Figure 8. The effect of CO₂ saturation on (a) compressive strength and (b) Elastic modulus of coal (Masoudian et al. 2012).



Figure 9. The stress-strain curve for two coal samples: one saturated with CO₂ and the other saturated with water (Masoudian et al. 2013).

5.2 Sorption-induced swelling/shrinkage of coal

Swelling data are available for a variety of coals subjected to a wide range of temperatures and pressures. It is considered that swelling is a function of gas volume adsorbed onto coal, and factors that affect the adsorption are expected to affect the swelling as well. For example, increases in moisture content, which reduce sorption, reduce the amount of swelling (Van Bergen et al. 2009), and swelling is roughly proportional to the amount of adsorbed CO₂ up to intermediate pressures (Day et al. 2008b). However, Day et al. (2008b) also report that further increases in pressure result in continuing adsorption but no increase in swelling. Increases in volume have ranged from 0.36% at low pressures to 1.9% at pressures of 5 MPa (Reucroft and Patel 1986, Walker et al. 1988) and 1.7-1.9% was observed under high pressure and high temperature conditions Day et al. (2008b). With decreasing temperature, swelling tended to occur at lower pressures. Shrinkage has been reported to occur in confined coal samples after CO₂ saturation (e.g. Pone *et al.* 2009a). Moreover, the mechanical properties can also affect the extent of swelling with higher Young's modulus leading to reduced swelling (Durucan et al. 2009), and the greatest swelling occurring in the plane perpendicular to the bedding plane (Day et al. 2008b).

Many researchers have proposed mathematical models for the volume change due to gas adsorption, which are based on the Langmuir (Robertson and Christiansen 2005, Pan and Connell 2007, Mazumder and Wolf 2008) and Dubinin (Day *et al.* 2008b) adsorption isotherms. The observation that adsorption continues at high pressures without swelling (Day *et al.* 2008b) indicates these models can be inaccurate under *in situ* conditions.

5.3 Effects of CO₂ injection on permeability

In situ stress and sorption-induced swelling are important controlling parameters during geosequestration and ECBM recovery. The former may change as a result of depletion (in CBM) or injection (ECBM and/or CO_2 geosequestration) and the latter may change due to the sorption of gas onto the coal. The reduction of permeability as a result of CO_2 injection has been observed in demonstration projects (Reeves *et al.* 2003, Wong *et al.* 2007), and laboratory studies with methane have indicated permeability reductions of more than two orders of magnitude (Somerton *et al.* 1975).

The change in permeability during fluid flow in fractured rocks has been widely investigated, and a variety of relationships (cubic-power, cubic-log, exponential) have been proposed between the effective stress change caused by the changing pore fluid pressure and permeability. The effective stress change causes deformation of the rock matrix and the cleats, so the closure of the cleats will depend on the compressibility of both. Confined swelling due to adsorption of CO_2 will lead to further stress changes which will affect the effective stress acting on the cleats. A number of empirical coal permeability models that capture these effects, some more directly than others, are presented in Table 3. The change in permeability as a function of change in effective stress (due to change in pore pressure as a result of fluid production/injection) is a well-studied problem

Table 3. A summary of coal permeability models

Model Name/Ref	Porosity/Permeability Equations	Eq No.	Description
Somerton et al. (1975)	$\frac{k}{k_0} = \exp\left[-3 \times 10^{-3} \sigma k_0^{-0.10} \left(\sigma_h - \sigma_{h0}\right) + 2 \times 10^{-4} \sigma^{1/3} k_0^{1/3}\right]$	Equation (4)	Empirical Methane permeability
Seidle <i>et al.</i> (1992)	$\frac{k}{k_0} = \exp\left[-3c_f\left(\sigma_h - \sigma_{h0}\right)\right]$	Equation (5)	$\sigma_h - \sigma_{h0}$: change in the stress
Seidle and Huitt (1995)	$\frac{k}{k_0} = \left[1 + \frac{\varepsilon_L}{3} \left(1 + \frac{2}{\phi_0}\right) \left(\frac{P_0}{P_L + P_0} - \frac{P}{P_L + P}\right)\right]^3$	Equation (6)	ε_L : maximum sorption strain
Palmer and Mansoori (1996)	$\frac{k}{k_0} = \left[1 + \frac{P - P_0}{M\phi_0} + \frac{\varepsilon_L}{\phi_0} \left(\frac{K}{M} - 1\right) \left(\frac{PP_L + P}{-} \frac{P_0}{P_L + P_0}\right)\right]^3$	Equation (7)	K and M are the bulk and axial modulus, respectively
ARI (1990)	$\frac{k}{k_0} = \left\{ \left[1 + c_f \left(P - P_0 \right) \right] - c_m \times \left(\frac{1 - \phi_0}{\phi_0} \right) \left(\frac{\Delta P_0}{\Delta C_0} \right) \left(C - C_0 \right) \right\}^3$	Equation (8)	<i>C</i> is gas concentration, c_m and c_f are matrix and pore compressibility
Shi and Durucan (2005)	$\frac{k}{k_0} = \exp\left\{-3c_f\left[\frac{\nu}{1-\nu}\left(\sigma-\sigma_0\right) + \frac{E\varepsilon_L}{3\left(1-\nu\right)}\left(\frac{P}{P_L+P} - \frac{P_0}{P_L+P_0}\right)\right]\right\}$	Equation (9)	E and ν are Young's modulus and Poisson's ratio
Liu and Rutqvist (2010)	$\begin{cases} \Delta \sigma = -\frac{\nu}{(1-\nu)} \Delta P + \frac{E\left(\Delta \varepsilon_s - \Delta \varepsilon_f\right)}{(1-\nu)} \\ \Delta \varepsilon_s = \varepsilon_L \left(\frac{P}{P_L + P} - \frac{P_0}{P_L + P_0}\right) \\ \Delta \varepsilon_f = \frac{\phi_0}{2} \left[1 - \exp\left(c_f \Delta \sigma\right)\right] \\ \frac{k}{k_0} = \exp\left[-3c_f \Delta \sigma\right] \end{cases}$	Equation (10)	

in petroleum reservoir engineering and two sets of equations have been suggested: exponential and cubic. The exponential models (Equations (4), (8), (12) and (13)) define an exponential relationship between permeability and effective stress while in cubic models (Equations (6), (10) and (11)) the relationship between porosity and permeability is considered to be cubic. All of these equations have also included the effect of coal matrix swelling on effective stress or porosity. Although these models are easy to implement, they are limited by the assumptions of an isotropic elastic matrix, with constant values independent of stress level and sorption, uniaxial strain and constant vertical stress, constant cleat compressibility and the lack of a rigorous model for the prediction of sorptioninduced swelling and shrinkage and thus were not able to predict the field data properly in some circumstances (Pekot and Reeves 2003, Palmer 2009, Liu and Rutqvist 2010). Thus, studies need to be conducted to increase the accuracy and applicability of permeability prediction. Pan and Connell (2012) identified a range of research gaps in permeability prediction in CBM and/ECBM studies through an extensive review on published experimental and modelling investigations and suggested that future works should be concentrated on finding a balance between complexity and accuracy of permeability models.

6. Summary

A wide range of experimental and theoretical studies have been performed to investigate the mass transport mechanisms occurring in CO₂-ECBM and geosequestration. However, the available data cannot be simply applied to *in situ* conditions at elevated temperature and pressure, and to date, few studies have considered the mechanical behaviour of coal while injecting CO₂. It is considered that the geomechanical aspects of coalbed geosequestration are important in assessing the storage capacity, gas flow and safety and therefore cannot be neglected. The review has indicated a number of shortcomings in our understanding of the response of coalbeds during sequestration of CO₂ that are summarised below.

- Adsorption: The assumed adsorption model has a significant effect on the estimated gas storage. There remain uncertainties about competitive sorption and the effects of temperature, pressure and phase, and how these vary with coal rank, porosity and stress level.
- Swelling: It is well established that volume changes occur when coal is saturated with CO₂. However, the magnitude and sign of the volume change and how these are related to properties of the coal need further investigation.
- Gas permeability: Gas storage and production estimates depend on the permeability and its change as CO₂ is adsorbed. Uncertainties remain about the coupling of swelling and mechanical changes which affect the permeability estimates, and there are limited experimental and numerical studies that describe the permeability of water/gas mixtures in coal.

- Gas diffusion: The database on diffusion of CO₂ into coal is limited and the influence of coal rank and porosity is not well understood. Further experiments on solid coal specimens are required to extend the database and confirm the effects of state.
- Geomechanical aspects: More efforts are required to understand the effect of CO₂ adsorption on mechanical properties of coal. This paper has demonstrated the influence of CO₂ on the mechanical deformation mechanisms that occur during geosequestration. Although some recent studies have coupled the mechanical deformation of coal when modelling CO₂ sequestration, no study has considered the change in mechanical properties due to CO₂.

References

- Alexeev, A.D., Vasilenko, T.A. and Ulyanova, E.V., 1999. Closed porosity in fossil coals. *Fuel*, 78, 635–638.
- Ates, Y. and Barron, K., 1988. The effect of gas sorption on the strength of coal. *Mining Science and Technology*, 6, 291–300.
- Aziz, N.I. and Ming-Li, W., 1999. The effect of sorbed gas on the strength of coal – an experimental study. *Geotechnical and Geological Engineering*, 17, 387–402.
- Bae, J.-S. and Bhatia, S.K., 2006. High-pressure adsorption of methane and carbon dioxide on coal. *Energy and Fuels*, 20, 2599–2607.
- Balek, V. and Koranyi, A.D., 1990. Diagnostics of structural alterations in coal: Porosity changes with pyrolysis temperature. *Fuel*, 69, 1502–1506.
- Botnen, L.S., Fisher, D.W., Dobroskok, A.A., Bratton, T.R., Greaves, K.H., McLendone, T.R., Steinerf, G., Sorensena, J.A., Steadmana, E.N. and Harjua, J.A., 2009. Field test of CO₂ injection and storage in lignite coal seam in North Dakota. *Energy Procedia*, 2013–2019.
- Busch, A., Krooss, B.M., Gensterblum, Y., VanBergen, F. and Pagnier, H. J. M., 2003a. High-pressure adsorption of methane, carbon dioxide and their mixtures on coals with a special focus on the preferential sorption behaviour. *Journal of Geochemical Exploration*, 78–79, 671–674.
- Busch, A., Gensterblum, Y. and Krooss, B.M., 2003b. Methane and CO₂ sorption and desorption measurements on dry Argonne premium coals: pure components and mixtures. *International Journal of Coal Geology*, 55, 205–224.
- Busch, A., Gensterblum, Y., Krooss, B.M. and Littke, R., 2004. Methane and carbon dioxide adsorption–diffusion experiments on coal: upscaling and modeling. *International Journal of Coal Geology*, 60, 151–168.
- Busch, A., Gensterblum, Y., Krooss, B.M. and Siemons, N., 2006. Investigation of high-pressure selective adsorption/desorption behaviour of CO₂ and CH₄ on coals: An experimental study. *International Journal of Coal Geology*, 66, 53–68.
- Ceglarska-Stefanska, G. and Brzoska, K., 1998. The effect of coal methamorphism on methane desorption. *Fuel*, 77, 645–648.
- Ceglarska-Stefanska, G. and Zarebska, K., 2005. Sorption of carbon dioxide-methane mixtures. *International Journal of Coal Geology*, 62, 211–222.
- Charrière, D., Pokryszka, Z. and Behra, P., 2010. Effect of pressure and temperature on diffusion of CO₂ and CH₄ into coal from the

Lorraine basin (France). *International Journal of Coal Geology*, 81 (4), 373–380.

- Clarkson, C.R. and Bustin, R.M., 1997. Variation in permeability with lithotype and maceral composition of Cretaceous coals of the Canadian Cordillera. *International Journal of Coal Geology*, 33, 135–151.
- Clarkson, C.R. and Bustin, R.M., 1999. The effect of pore structure and gas pressure upon the transport properties of coal: a laboratory and modeling study. 2. Adsorption rate modeling. *Fuel*, 78, 1345–1362.
- Clarkson, C.R., Bustin, R.M. and Levy, J.H., 1997. Application of the mono/multilayer and adsorption potential theories to coal methane adsorption isotherms at elevated temperture and pressure. *Carbon*, 35, 1689.
- Cui, X., Bustin, R.M. and Dipple, G., 2004. Selective transport of CO₂, CH₄, and N₂ in coals: insights from modeling of experimental gas adsorption data. *Fuel*, 83, 293–303.
- Czaplinski, A. and Holda, S., 1982. Changes in mechanical properties of coal due to sorption of carbon dioxide vapour. *Fuel*, 61, 1281–1282.
- Day, S., Duffy, G., Sakurovs, R. and Weir, S., 2008a. Effect of coal properties on CO2 sorption capacity under supercritical conditions. *International Journal of Greenhouse gas Control*, 2, 342–352.
- Day, S., Fry, R. and Sakurovs, R., 2008b. Swelling of Australian coals in supercritical CO₂. *International Journal of Coal Geology*, 74, 41–52.
- Day, S., Sakurovs R. and Weir, S., 2008c. Supercritical gas sorption on moist coals. *International Journal of Coal Geology*, 74, 203–214.
- Dollimore, D., Spooner, P. and Turner, A., 1976. The BET method of analysis of gas adsorption data and its relevance to the calculation of surface areas. *Surface Technology*, 4, 121–160.
- Durucan, S., Ahsan, M. and Shi, J., 2009. Matrix shrinkage and swelling characteristics of European coals. *Energy Procedia*, 1, 3055–3062.
- Esterle, J.S., 2008. Mining and beneficiation. *In*: I. Suarez-Ruiz and J.C. Crelling, eds. *Applied coal petrology*. Burlington, MA: Elsevier, pp. 61–83.
- Fitzgerald, J.E., Pan, Z., Sudibandriyo, M., Robinson, J.R.L., Gasem, K.A.M. and Reeves, S., 2005. Adsorption of methane, nitrogen, carbon dioxide and their mixtures on wet Tiffany coal. *Fuel*, 84, 2351–2363.
- Flores, R.M., 2004. Coalbed methane in the Powder River Basin, Wyoming and Montana: An assessment of the Tertiary-Upper Cretaceous coalbed methane total petroleum system. U.S. Geological Survey Digital Data Series DDS–69–C. Denver, CO: U.S. Geological Survey.
- Gamson, P.D., Beamish, B.B. and Johnson, D.P., 1993. Coal microstructure and micropermeability and their effects on natural gas recovery. *Fuel*, 72, 87–99.
- Gan, H., Nandi, S.P. and Walker, P.L., 1972. Nature of the porosity in American coals. *Fuel*, 51, 272–277.
- Gash, B. W., Volz, R.F., Potter, G. and Corgan, J.M., 1992. The effects of cleat orientation and confining pressure on cleat porosity, permeability and relative permeability in coal. In *Proceedings of the SPWLA/SCA Symposium*, Oklahoma City, OK, June 15–16, 1992. Oklahoma City: Society of Core Analysts.
- Gentzis, T., 2000. Subsurface sequestration of carbon dioxide an overview from an Alberta (Canada) perspective. *International Journal of Coal Geology*, 43, 287–305.

- Gentzis, T., Deisman, N. and Chalaturnyk, R.J., 2007. Geomechanical properties and permeability of coals from the Foothills and Mountain regions of western Canada. *International Journal of Coal Geology*, 69, 153–164.
- Goodman, A.L., Busch, A., Bustin, R.M., Chikatamarla, L., Day, S., Duffy, G.J., Fitzgerald, J.E., Gasem, K.A.M., Gensterblum, Y., Hartman, C., Jing, C., Krooss, B.M., Mohammed, S., Pratt, T., Robinson, Jr, R.L., Romanov, V., Sakurovs, R., Schroeder, K. and White, C.M., 2007. Inter-laboratory comparison II: CO₂ isotherms measured on moisture-equilibrated Argonne Premium coals at 55 °C and up to 15 MPa. *International Journal of Coal Geology*, 72, 153–164.
- Green, T. K., Pan, W.-P. and Clark, M., 1991. Glass transition temperature of modified coals. Preprints, Division of Fuel Chemistry, American Chemical Society, 36 (1), 814–819.
- Gruszkiewicz, M.S., Naney, M.T., Blencoe, J.G., Cole, D.R., Pashin, J.C. and Carroll, R.E., 2009. Adsorption kinetics of CO₂, CH₄, and their equimolar mixture on coal from the Black Warrior basin, West-Central Alabama. *International Journal of Coal Geology*, 77, 23–33.
- Gürdal, G. and Yalçin, M.N., 2001. Pore volume and surface area of the Carboniferous coals from the Zonguldak basin (NW Turkey) and their variations with rank and maceral composition. *International Journal of Coal Geology*, 48, 133–144.
- Haenel, M.W., 1992. Recent progress in coal structure research. *Fuel*, 71, 1211–1223.
- Hall, P.J., Brown, S.D.and Calo, J.M., 2000. The pore structure of the Argonne coals as interpreted from contrast matching small angle neutron scattering. *Fuel*, 79, 1327–1332.
- Harpalani, S., Prusty, B.K. and Dutta, P., 2006. Methane/CO₂ sorption modeling for coalbed methane production and CO₂ sequestration. *Energy and Fuels*, 20, 1591–1599.
- Harpalani, S. and Zhao, X., 1991. Microstructure of coal and its influence on flow of gas. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 13, 229–242.
- Harris, L.A. and Yust, C.S., 1976. Transmission electron microscope observations of porosity in coal. *Fuel*, 55, 233–236.
- He, J., Shi, Y., Ahn, S., Kang, J.W. and Lee, C.-H., 2010. Adsorption and desorption of CO₂ on Korean coal under subcritical to supercritical conditions. *The Journal of Physical Chemistry B*, 114, 4854–4861.
- Henderson, N., Flores, E., Sampaio, M., Freitas, L. and Platt, G.M., 2005. Supercritical fluid flow in porous media: modeling and simulation. *Chemical Engineering Science*, 60, 1797–1808.
- Ishihara, A., Qian, E.W., Sutrisna, I.P. and Kabe, Y., 2004. *Coal and coal-related compounds: structures, reactivity and catalytic reactions.* Oxford: Elsevier Science and Technology Books.
- Jodłowski, G.S., Baran, P., Wojcik, M., Nodzenski, A., Porada, St. and Milewska-Duda, J., 2007. Sorption of methane and carbon dioxide mixtures in Polish hard coals considered in terms of adsorption-absorption model. *Applied Surface Science*, 253, 5732–5735.
- Krooss, B.M., Van Bergen, F., Gensterblum, Y., Siemons, N., Pagnier, H.J.M. and David, P., 2002. High-pressure methane and carbon dioxide adsorption on dry and moisture-equilibrated Pennsylvanian coals. *International Journal of Coal Geology*, 51, 69–92.
- Larsen, J.W., 2004. The effects of dissolved CO₂ on coal structure and properties. *International Journal of Coal Geology*, 57, 63–70.
- Larsen, J.W., Hall, P. and Wernett, P.C., 1995. Pore structure of Argonne Premium coals. *Energy and Fuels*, 9, 324–330.

- Larsen, J.W. and Wernett, P.C., 1992. The Argonne coals do not have an extended inter-connected pore network. *symposium on chemistry, structure and reactivity of coals, tar sands and oil shale.* San Francisco, CA: American Chemical Society Symposium, Division of Fuel Chemistry.
- Laubach, S.E., Marrett, R.A., Olson, J.E. and Scott, A.R., 1998. Characteristics and origins of coal cleat: a review. *International Journal of Coal Geology*, 35, 175–207.
- Laxminarayana, C. and Crosdale, P. J., 1999. Role of coal type and rank on methane sorption characteristics of Bowen Basin, Australia coals. *International Journal of Coal Geology*, 40, 309–325.
- Li, D., Liu, Q., Weniger, P., Gensterblum, Y., Busch, A. and Krooss, B.M., 2010. High-pressure sorption isotherms and sorption kinetics of CH₄ and CO₂ on coals. *Fuel*, 89, 569–580.
- Liu, H. and Rutqvist, J., 2010. A new coal-permeability model: internal swelling stress and fracture–matrix interaction. *Transport in Porous Media*, 82, 157–171.
- Lucht, L.M., Lamon J.M. and Peppas, N.A., 1987. Macromolecular structure of coals. 9. Molecular structure and glass transition temperature. *Energy and Fuels*, 1, 56–58.
- Mahieux, C.A., 1999. A systematic stiffness-temperature model for polymers and applications to the prediction of composite behavior. Thesis (PhD). Virginia Polytechnic Institute and State University.
- Marzec, A., 1985. Macromolecular and molecular structure of coal and the possible role of pyrolysis-field desorption mass spectrometry in its elucidation. *Journal of Analytical and Applied Pyrolysis*, 8, 241–254.
- Masoudian, M.S., Airey, D.W. and El-Zein, A., 2012. The effect of CO₂ on micro structure and mechanical properties of Australian black coal. *11th Australia and New Zealand Conference on Geomechanics (ANZ 2012)*, July 15–18, 2012. Melbourne: Australian Geomechanics Society, pp. 728–733.
- Masoudian, M.S., Airey, D.W. and El-Zein, A., 2013. A chemohydro-mechanical model for sequestration of CO₂ in coalbeds. *Geotechnique*, 63(3), 235–243.
- Masoudian, M.S., Airey, D.W., Gainey, A., Morris, T. and Berger, J., 2011. The mechanical properties of CO₂-saturated coal specimens 12th International Congress on Rock Mechanics (ISRM), October 18–21, 2011. Beijing, China. Leiden: CRC Press, 338– 341.
- Mazumder, S., VanHemert, P., Busch, A., Wolf, K.-H.A.A. and Tejera-Cuesta, P., 2006. Flue gas and pure CO₂ sorption properties of coal: a comparative study. *International Journal of Coal Geology*, 67, 267–279.
- Mazumder, S. and Wolf, K.H., 2008. Differential swelling and permeability change of coal in response to CO₂ injection for ECBM. *International Journal of Coal Geology*, 74, 123–138.
- Medhurst, T.P. and Brown, E.T., 1998. A study of the mechanical behaviour of coal for pillar design. *International Journal of Rock Mechanics and Mining Science*, 35, 1087–1105.
- Melnichenko, Y.B., Radlinski, A.P., Mastalerz, M., Cheng, G. and Rupp, J., 2009. Characterization of the CO₂ fluid adsorption in coal as a function of pressure using neutron scattering techniques (SANS and USANS). *International Journal of Coal Geology*, 77, 69–79.
- Nishioka, M., 1993. *Investigation of coal structure*. Pittsburg, CA: U.S. Department of Energy.
- Olague, N.E. and Smith, D.M., 1989. Diffusion of gases in American coals. *Fuel*, 68, 1381–1387.

- Ottiger, S., Pini, R., Storti, G., Mazzotti, M., Bencini, R., Quattrocchi, F., Sardu, G. and Deriu, G., 2006. Adsorption of pure carbon dioxide and methane on dry coal from the sulcis coal province (SW Sardinia, Italy). *Environmental Progress*, 25, 355–364.
- Ozdemir, E., 2004. Chemistry of the adsorption of carbon dioxide by Argonne Premium coals and a model to simulate CO₂ sequestration in coal seams. Thesis (PhD). University of Pittsburgh.
- Ozdemir, E., Morsi, B.I. and Schroeder, K., 2004. CO₂ adsorption capacity of argonne premium coals. *Fuel*, 83, 1085–1094.
- Palmer, I. 2009. Permeability changes in coal: Analytical modeling. International Journal of Coal Geology, 77, 119–126.
- Palmer, I. and Mansoori, J. 1996. How permeability depends on stress and pore pressure in coalbeds: a new model. *1996 SPE annual technical conference and exhibition*, October 6–9, 1996. Denver, CO: Society of Petroleum Engineers, pp. 557–564.
- Pan, Z. and Connell, L.D., 2007. A theoretical model for gas adsorption-induced coal swelling. *International Journal of Coal Geology*, 69, 243–252.
- Pan, Z. and Connell, L.D., 2012. Modelling permeability for coal reservoirs: A review of analytical models and testing data. *International Journal of Coal Geology*, 92, 1–44.
- Pan, Z., Connell, L.D., Camilleri, M. and Connelly, L. 2010. Effects of matrix moisture on gas diffusion and flow in coal. *Fuel*, 89 (11), 3207–3217.
- Parkash, S. and Chakrabartty, S.K., 1986. Microporosity in Alberta Plains coals. *International Journal of Coal Geology*, 6, 55–70.
- Pashin, J.C., 2008. Coal as a petroleum source rock and reservoir rock. *In*: I. Suarez-Ruiz and J.C. Crelling, eds. *Applied coal petrology*. Burlington, MA: Elsevier, pp. 227–262.
- Pekot, L.J. and Reeves, S.R., 2003. Modeling the effects of matrix shrinkage and differential swelling on coalbed methane recovery and carbon sequestration. *International coalbed methane symposium*, 5–9 May 2003. Tuscaloosa, AL: Advanced Resources International, pp. 1–15.
- Pinetown, K.L., Faiz, M.M., Saghafi, A., Stalker, L. and VanHolst, J., 2008. Coal seam gas distribution in the Hunter coalfield, Sydney basin. *PESA eastern Australasian basins symposium III*, September 14–17, 2008 Sydney: Petroleum Exploration Society of Australia, pp. 1–24.
- Pini, R., Ottiger, S., Burlini, L., Storti, G. and Mazzotti, M., 2010. Sorption of carbon dioxide, methane and nitrogen in dry coals at high pressure and moderate temperature. *International Journal of Greenhouse Gas Control*, 4, 90–101.
- Pomeroy, C.D. and Morgans, W.T.A., 1956. The tensile strength of coal. *British Journal of Applied Physics*, 7, 243–246.
- Pone, J.D.N., Hile, M., Halleck, P.M. and Mathews, J.P., 2009a. Threedimensional carbon dioxide-induced strain distribution within a confined bituminous coal. *International Journal of Coal Geology*, 77, 103–108.
- Pone, J.D.N., Hallecka, P.M. and Mathews, J.P., 2009b. Methane and carbon dioxide sorption and transport rates in coal at in-situ conditions. *Energy Procedia*, 1, 3121–3128.
- Prusty, B.K., 2008. Sorption of methane and CO2 for enhanced coalbed methane recovery and carbon dioxide sequestration. *Journal of Natural Gas Chemistry*, 17, 29–38.
- Radlinski, A.P., Mastalerz, M., Hinde, A.L., Hainbuchner, M., Rauch, H., Baron, M., Lin, J.S., Fan, L. and Thiyagarajan, P., 2004. Application of SAXS and SANS in evaluation of porosity, pore size distribution and surface area of coal. *International Journal* of Coal Geology, 59, 245–271.

- Radovic, L.R., Menon, V.C., Leon, C.A., Leon, Y., Kyotani, T., Danner, R.E., Anderson, S. and Hatcher, P.G., 1997. On the porous structure of coals: evidence for an interconnected but constricted micropore system and implications for coalbed methane recovery. *Adsorption*, 3, 221–232.
- Reeves, S.R., 2001. Geological sequestration of CO₂ in deep, unmineable coalbeds: an integrated research and commercial-scale field demonstration project. *SPE annual technical conference and exhibition*. New Orleans, LA: SPE 71749.
- Reeves, S.R., Taillefert, A., Pekot, L. and Clarkson, C., 2003. The Allison unit CO₂ – ECBM pilot: a reservoir modeling study. Topical report. Houston, TX: Advanced Resources International.
- Reucroft, P.J. and Patel, H., 1986. Gas-induced swelling in coal. *Fuel*, 65, 816–820.
- Robertson, E.P., 2009. Economic analysis of carbon dioxide sequestration in Powder River basin coal. *International Journal of Coal Geology*, 77, 234–241.
- Robertson, E.P. and Christiansen, R.L., 2005. Modeling permeability in coal using sorption-induced strain data. *In: Proceeding* of the 2005 SPE annual technical conference and exhibition, October 9–12, 2005, Dallas, Texas. paper SPE 97068. Society of Petroleum Engineers. http://www.onepetro.org/mslib/ servlet/onepetropreview?id=SPE-97068-MS
- Ruckenstein, E., Vaidyanathan, A.S. and Youngquist, G.R., 1971. Sorption by solids with bidisperse pore structures. *Chemical Engineering Science*, 26, 1305–1318.
- Saghafi, A., 2010. Potential for ECBM and CO₂ storage in mixed gas Australian coals. *International Journal of Coal Geology*, 82, 240–251.
- Saghafi, A., Faiz, M. and Roberts, D., 2007. CO₂ storage and gas diffusivity properties of coals from Sydney basin, Australia. *International Journal of Coal Geology*, 70, 240–254.
- Saghafi, A., Pinetown, K.L., Grobler, P.G. and van Heerden, J.H.P., 2008. CO₂ storage potential of South African coals and gas entrapment enhancement due to igneous intrusions. *International Journal of Coal Geology*, 73, 74–87.
- Sakurovs, R., Day, S. and Weir, S., 2010. Relationships between the critical properties of gases and their high pressure sorption behavior on coals. *Energy and Fuels*, 24, 1781–1787.
- Sakurovs, R., Day, S., Weir, S. and Duffy, G., 2007. Application of a modified Dubinin–Radushkevich equation to adsorption of gases by coals under supercritical conditions. *Energy and Fuels*, 21, 992–997.
- Sawyer, W.K., Paul, G.W. and Schraufnagel, R.A., 1990. Development and application of a 3D coalbed simulator. *CIM/SPE international technical conference*, June 10–13, 1990. Calgary. Society of Petroleum Engineers, 1–10, doi: 10.2118/90-119.
- Seidle, J.P. and Huitt, L.G., 1995. Experimental measurement of coal matrix shrinkage due to gas desorption and implications for cleat permeability increases. Beijing, China: SPE.
- Seidle, J.P., Jeansonne, M.W. and Erickson, D.J., 1992. Application of matchstick geometry to stress dependent permeability in coals. *SPE rocky mountain regional meeting*. Casper, Wyoming: SPE.
- Sereshki, F., 2005. Improving coal mine safety by identifying factors that influence the sudden release of gases in outburst prone zones. Thesis (PhD). University of Wollongong.
- Sharma, A., Kyotani, T. and Tomita, A., 2000. Direct observation of layered structure of coals by a transmission electron microscope. *Energy and Fuels*, 14, 515–516.

- Shi, J.Q. and Durucan, S., 2003. A bidisperse pore diffusion model for methane displacement desorption in coal by CO₂ injection. *Fuel*, 82, 1219–1229.
- Shi, J.Q. and Durucan, S., 2005. A model for changes in coalbed permeability during primary and enhanced methane recovery. *SPE Reservoir Evaluation and Engineering*, 291–300.
- Shimada, S. and Yamaguchi, K., 2009. Economic assessment of enhaced coalbed methane recovery for low rank coal seam. *Energy Procedia*, 1, 1699–1704.
- Siemons, N., Wolf, K.-H.A. and Bruining, J., 2007. Interpretation of carbon dioxide diffusion behavior in coals. *International Journal* of Coal Geology, 72, 315–324.
- Smyth, M. and Buckley, M.J., 1993. Statistical analysis of the microlithotype sequences in the Bulli seam, Australia, and relevance to permeability for coal gas. *International Journal of Coal Geology*, 22, 167–187.
- Somerton, W.H., Soylemezoglu, I.M. and Dudley, R.C., 1975. Effect of stress on permeability of coal. *International Journal of Rock Mechanics and Mining Science and Geomechanical Abstracts*, 12, 129–145.
- Spears, D.A. and Caswell, S.A., 1986. Mineral matter in coals: cleat minerals and their origin in some coals from the English Midlands. *International Journal of Coal Geology*, 6, 107–125.
- Speight, J.G., 2005. *Handbook of Coal Analysis*, New Jersey, John Wiley and Sons, Inc.
- Stacy, W.O. and Jones, J.C., 1986. The swelling and adsorption characteristics of Victorian brown coals. *Fuel*, 65, 1171–1173.
- Su, X., Feng, Y. Chen, J. and Pan, J., 2001. The characteristics and origins of cleat in coal from Western North China. *International Journal of Coal Geology*, 47, 51–62.
- Suuberg, E.M., Deevi, S.C. and Yunt, Y., 1995. Elastic behaviour of coals studied by mercury porosimetry. *Fuel*, 74, 1522–1530.
- Szabo, T.L., 1981. A representative poisson's ratio for coal. International Journal of Rock Mechanics and Mining Science and Geomechanical Abstracts, 18, 531–533.
- Szwilski, A.B., 1985. Relation between the structural and physical properties of coal. *Mining Science and Technology*, 2, 181–189.
- Van Bergen, F., Spiers, C., Floor, G. and Bots, P., 2009. Strain development in unconfined coals exposed to CO₂, CH₄ and Ar: effect of moisture. *International Journal of Coal Geology*, 77, 43–53.
- Van Bergen, F., Pagnier, H. and Krzystolik, P., 2006. Field experiment of enhanced coalbed methane-CO₂ in the upper Silesian basin of Poland. *Environmental Geoscience*, 13, 201–224.
- Viete, D.R. and Ranjith, P.G., 2006. The effect of CO₂ on the geomechanical and permeability behaviour of brown coal: implications for coal seam CO₂ sequestration. *International Journal of Coal Geology*, 66, 204–216.
- Walker, P.L., Verma, S.K., Rivera-Utrilla, J. and Khan, M.R., 1988. A direct measurement of expansion in coals and macerals induced by carbon dioxide and methanol. *Fuel*, 67, 719–726.
- Ward, C.R. and Suarez-Ruiz, I., 2008. Introduction to applied coal petrology. *In*: I. Suarez-Ruiz and J.C. Crelling, eds. *Applied coal petrology*. Burlington, MA: Elsevier, pp. 1–18.
- Webb, S., 2006. Gas transport mechanisms. In: C. Ho and S. Webb, eds. Gas transport in porous media. Theory and Applications of Transport in Porous Media. Dordrecht: Springer, pp. 5–26.
- White, J.M. and Mazurkiewicz, M., 1989. Effect of moisture content on mechanical properties of Nemo coal, Moberly, Missouri, U.S.A. *Mining Science and Technology*, 9, 181–185.

- Wong, S., Law, F., Deng, X., Robinson, J., Kadatz, B., Gunter, W.D., Jianping, Y., Sanil, F. and Zhiqiang, F., 2007. Enhanced coalbed methane and CO₂ storage in anthracitic coals - micropilot test at South Qinshui, Shanxi, China. *International Journal* of Greenhouse gas Control, 1, 215–222.
- Yamaguchi, S., Ohga, K., Fujioka, M. and Masao, N., 2006. Field test and history matching of the CO₂ sequestration project in coal seams in Japan. *International Journal of Society of Material Engineering Resources*, 13 (2), 64–69.
- Yamazaki, T., Aso, K. and Chinju, J., 2006. Japanese potential of CO₂ sequestration in coal seams. *Applied Energy*, 83, 911–920.
- Yu, H., Zhou, L., Guo, W., Cheng, J. and Hu, Q., 2008. Predictions of the adsorption equilibrium of methane/carbon dioxide binary gas on coals using Langmuir and ideal adsorbed solution theory under feed gas conditions. *International Journal of Coal Geology*, 73, 115–129.