



Thermodynamic models for swelling of unconfined coal due to adsorption of mixed gases



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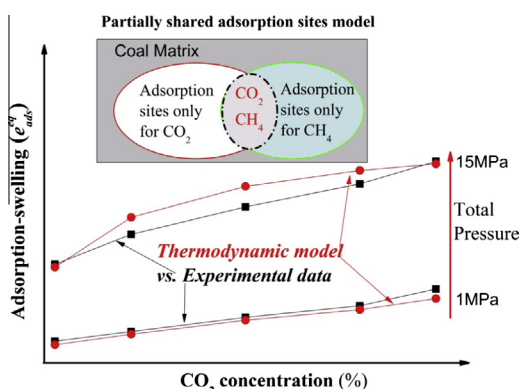
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HIGHLIGHTS

- Four swelling models derived for adsorption of binary gas mixture by coal.
- Sub-bituminous coal swelling best explained by partial pressure plus selective sorption model.
- Generalized model applicable to any coal and any binary gas mixture.
- Better basis for modeling coal seam permeability during ECBM.

GRAPHICAL ABSTRACT



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ABSTRACT

Permeability evolution in coal seams during CO₂-Enhanced Coalbed Methane (ECBM) production is strongly influenced by swelling/shrinkage effects related to sorption and desorption of both CO₂ and CH₄. Other gases, such as N₂, have also been proposed for injection in ECBM operations. In addition, water vapour will almost always be naturally present. Much work has been done on the sorption/swelling response of coal exposed to pure gases. However, to address in-situ coal-seam conditions realistically, an understanding of the swelling behaviour of coal matrix material due to multiple-species adsorption is needed. Here, we construct new thermodynamic models for swelling of unconfined coal due to adsorption of multiple gas/fluid species, addressing the equilibrium state and focusing on a binary gas mixture. Four models are derived, covering three possible end-member interactions, plus a generalized case. The end-member models considered correspond to adsorption of gases α and β at fully separate sites, at fully shared sites and at partially shared sites (Models 1–3, respectively). We compare our model predictions with literature data on the swelling behaviour of Bowen Basin coal exposed to CH₄/CO₂ mixtures at total pressures up to 15 MPa and at 55 °C. The results show that swelling of the Bowen Basin coal exposed to CO₂/CH₄ mixtures is best explained by Model 3, which in turn implies that adsorption and swelling is in this case determined by both partial pressure and selective adsorption (affinity) effects. Model 3 is easy to parameterize and its applicability to specific coals and gas mixtures is easily evaluated. Though more difficult to parameterize, our generalized swelling model (Model 4) can be applied to any coal rank, and to any binary gas mixture. It therefore offers an important tool for modeling swelling and permeability evolution during ECBM operations.

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1. Introduction

The laboratory finding that coal matrix material has higher sorption capacity for pure CO₂ than for pure CH₄ at given pressure and temperature (*PT*) conditions has led to the now well-known concept of enhanced coalbed methane (ECBM) production coupled with storage of CO₂ in underground coal seams [1]. In this concept, CO₂ injection into a coal seam displaces the coalbed methane, which is then recovered and used for energy production, while the CO₂ generated is, in effect, re-injected [2]. Several field tests (e.g. in Canada, U.S.A., Poland, Japan and China) have confirmed the potential of CO₂-ECBM production [3–5]. However, most sites investigated to date have shown reduced CO₂ injectivity with time due to permeability reduction in the coal seam [3,4,6]. These effects are generally recognized to be caused by sorption-induced swelling of the coal as a result of CO₂ injection and sorption, while CH₄ is desorbed [7–13]. This exchange, or preferential adsorption effect, is considered to be due to either the reduction of CH₄ partial pressure as CO₂ penetrates the system or to truly selective adsorption of CO₂ over CH₄ [2]. The resulting partial replacement of CH₄ by CO₂ leads to net swelling, reflecting equilibration with respect to the new composition of the gas/fluid mixture present in the coal seam [2,14].

However, most experimental measurements and theoretical models for adsorption and swelling of coal focus on a single, pure gas, and not on mixed gases. Much less is known about competitive adsorption between CH₄ and CO₂, and there is insufficient evidence to resolve whether the controlling factor is a partial pressure or a selective sorption effect. To avoid confusion about the meaning of these terms that has crept into the literature in recent years, in this paper we use the term “preferential adsorption” of species α to mean that the number of adsorption sites occupied by α , in a given coal mass at equilibrium with a gas/fluid mixture containing species α plus β , is greater than the number of sites occupied by β , regardless of the reason. We use the term “selective adsorption” of species α to mean that the number of adsorption sites occupied by α is greater than occupied by β , due to different site accessibilities (i.e. different affinities), even when α and β are present in the gas/fluid phase at equal activities (see Table 1 for definition of terms).

We return now to the lack of evidence on whether preferential adsorption of CH₄ and CO₂ in coal is controlled by partial pressure or selective sorption effects. To date, strongly conflicting experimental results have been reported. For example, in experiments on high volatile bituminous coal performed by using mixtures containing 25–75% CO₂ at 25 °C and 0.1–4 MPa total pressure, Majewska et al. [15] observed that CH₄ preferentially adsorbed

with respect to CO₂. Czerw [16] repeated the experiments of Majewska et al., using the same apparatus, similar coals and a 75:25 CO₂-CH₄ mixture at 25 °C and 4 MPa total pressure, but reported that CO₂ preferentially adsorbed with respect to CH₄. Similarly, Busch et al. [13,17] reported that whereas preferential adsorption of CO₂ and preferential desorption of CH₄ were observed in high rank coals at all total pressures investigated (1–23 MPa), low rank samples showed preferential adsorption of CH₄ at low pressures and preferential desorption of CO₂ at all pressures. These authors [17] further reported that preferential sorption is independent of CO₂-CH₄ mixture composition, (i.e. of partial pressure), and proposed that preferential sorption is determined purely by selective sorption. On the other hand, in experiments on the effect of moisture on the (otherwise) pure CO₂ and pure CH₄ sorption capacity of bituminous coals at 55 °C and total pressures up to 20 MPa, Day et al. [8] found that the heat of adsorption (i.e. hence K) for pure CO₂ and CH₄ are similar when drying, falling only slightly when water is present. Their calculations were done based on Dubinin–Radushkevich model applied for pure CO₂ and pure CH₄, ignoring potential effects of water in this model. They therefore proposed that CO₂ and CH₄ have about the same access to all adsorption sites, i.e. that selective adsorption effects are negligible. The important question thus remains as to whether sorption by coal of a given rank exposed to mixed gases is solely determined by partial pressure or also by selective adsorption. Understanding the relative importance of these effects, via a physically correct sorption model, clearly plays a crucial role in assessing whether CO₂-ECBM operations are feasible in practice.

Focusing on the swelling response to mixed gas sorption, Day et al. [14] recently reported measurements performed on four Australian coals, exposed to CO₂, methane and mixtures of the two. Measurements were made on laterally unconstrained (i.e. mechanically unconfined), monolithic samples (30 × 9 × 9 mm) at 55 °C, applying total gas pressures up to ~15 MPa. Volumetric swelling strain ranged from about 1.0% to 5.5%, depending on coal rank and the proportion of CO₂ in the CH₄-CO₂ mixture. These authors found that the swelling observed using mixed gases lay between the values obtained for the pure end members. They also performed experiments in which CO₂ was injected in an attempt to displace CH₄ from the same coals. In these runs, coal samples were first equilibrated with CH₄ at a pressure of 15 MPa at 55 °C. CO₂ was then injected, keeping the total pressure constant. It was found that CH₄ was completely displaced from the coal, causing it to swell to the same level as if exposed to pure CO₂ at the same *PT* conditions. Upon subsequent injection of helium, which does

Table 1

Definition of terms used in this paper for the case of adsorption of gas/fluid species α and β , i.e. for adsorption from a binary gas mixture. Note that $n_s^{\alpha\beta}$ is the number out of all adsorption sites fully accessible to α and β , C_s^i is the concentration of available adsorption sites accessible to component i in mole per kg coal, K^i is the equilibrium constant for the adsorption process of species i , a_g^i is the activity of the free gas/fluid species i .

Term	Definition	Controlling factors	Model developed in this study
Preferential adsorption	The number of adsorption sites occupied by one component is greater than that occupied by the other component, regardless of the reason	C_s^i , K^i , ϕ , a_g^i	
Selective adsorption	The number of adsorption sites occupied by one component is greater than that occupied by the other component even when each gas component has equal activity, due to different site accessibilities	C_s^i , K^i , ϕ	
Site-sharing factor ϕ	The fraction of the total adsorption sites n_s^{total} present in the coal matrix material that is accessible to gas α and to gas β . $\phi = n_s^{\alpha\beta} / n_s^{total}$, $0 \leq \phi \leq n_s^\alpha / n_s^\beta \leq 1$	K^i	
Independent adsorption sites	The adsorption sites accessible to each gas component (α , β) are fully separate and independent, such that $\phi = 0$	K^i	Model 1
Fully shared adsorption sites	All adsorption sites are fully accessible to (i.e. can take up) both gas components (α , β), so that $\phi = 1$	K^i	Model 2
Partially shared adsorption sites: Type I	All adsorption sites accessible to gas α are also accessible to gas β , while all remaining adsorption sites are accessible only to gas β . ($\phi = n_s^\alpha / n_s^\beta < 1$)	K^i	Model 3
Partially shared adsorption sites: Type II	$n_s^{\alpha\beta} = \phi n_s^{total}$ sites are accessible to both gases (cf. Model 2). The remaining adsorption sites can only take up one component (cf. Model 1), such that $(n_s^\alpha - \phi n_s^{total})$ adsorption sites are accessible only to gas α , while $(n_s^\beta - \phi n_s^{total})$ adsorption sites are accessible only to gas β	K^i	Model 4

not adsorb, the CO₂ was completely displaced by helium, causing the coal to shrink to its original dimensions. On this basis, Day et al. [14] proposed that CH₄ and CO₂ have similar access to all adsorption sites, and that the swelling behaviour of the coal studied is determined solely by the partial pressures of the sorbing gases, with no selective sorption effects. In these experiments, the swelling strains developed upon exposure to CH₄–CO₂ mixtures were linearly dependent on CO₂ mole percentage. Assuming that this partial pressure relationship holds for nitrogen and that swelling due to nitrogen adsorption is about half that due to methane, Day et al. [14] proposed that a mixture of 30% CO₂ and 70% N₂ would induce the same swelling effect as pure methane at 15 MPa total pressure. They accordingly suggested that a 30:70 CO₂–N₂ mixture might be suitable for injecting in ECBM operations, as there would then be no net swelling of the coal when methane is displaced. Similarly, Fujioka et al. [3] showed that N₂ flooding temporarily improved the daily CO₂ injection rate in CO₂–ECBM field tests in the Ishikari coal basin of Japan, and proposed that N₂ flooding may help reverse the permeability reduction caused by CO₂ injection, due to the smaller swelling caused by N₂ sorption. To evaluate such shrinkages, however, a reliable, physically based model describing the sorption and swelling behaviour of coal exposed to mixed gases is pre-requisite.

Aside from recent developments in molecular dynamics modeling [18], current models for mixed gas adsorption and swelling in coal are based on the extended Langmuir model (ELM) [10,19,20]. The best known of these is the model developed by Pan and Connell [10]. However, the ELM is only applicable to mixed gases when adsorption sites are the same for each component, and when the gas phase behaves as an ideal gas [20,21]. These represent highly restrictive assumptions. An alternative, more general approach lies in extending the thermodynamic model developed by Hol et al. [9] for the equilibrium concentration of a pure gas/fluid (CO₂) adsorbed by unconfined coal matrix material (or indeed any material exhibiting monolayer adsorption, i.e. any Langmuir type sorbent). This model describes the change in adsorbed concentration as a combined effect of the changing chemical activity of the fluid and the changing availability (i.e. occupancy) of adsorption sites, and for an ideal gas reduces to the Langmuir model for a single gas/fluid species. Hol et al. [9,22] applied this model to the swelling of coal matrix material due to CO₂ adsorption, assuming that swelling is linearly proportional to adsorbed concentration. The result obtained successfully described the swelling behaviour of high volatile bituminous coal matrix exposed to CO₂ at pressures up to 100 MPa at 40 °C.

In present paper, based on the work of Hol et al. [9], we construct a new thermodynamic framework for modeling adsorption-induced swelling of unconfined coal matrix material exposed to a binary gas/fluid mixture. Three models are derived to address three possible end-member interactions. These are also cast in a single generalized model. We evaluate the four models by comparing their predictions with the experimental measurements on mixed gas sorption and swelling of coal reported by Day et al. [14]. In contrast to Day et al.'s conclusion that only partial pressure is important in causing coal swelling due to mixed gas sorption, we find that selective adsorption also plays a significant role.

2. Modeling

2.1. Hol and Spiers model for swelling due to adsorption of a single, pure gas or fluid

This forms the basis for the mixed gas sorption/swelling model developed in this paper. The key result derived by Hol et al. [9] is the following expression for the occupied fraction θ of adsorption

sites present in a stress-free coal particle immersed in an adsorbing gas or fluid at fixed PT conditions:

$$\theta = \frac{\exp\left(\frac{\mu_{g0} - \mu_s}{kT}\right) a_g}{1 + \exp\left(\frac{\mu_{g0} - \mu_s}{kT}\right) a_g} \quad (1a)$$

or

$$\theta = \frac{K a_g}{1 + K a_g} \quad (1b)$$

Here $K = \exp\left(\frac{\mu_{g0} - \mu_s}{kT}\right)$ is the equilibrium constant for the adsorption process, μ_s is the chemical potential of a single adsorbed molecule located in the potential well associated with the adsorption sites present [23], a_g is the chemical activity of the free gas or fluid at pressure P , and μ_{g0} is the potential of the free gas or fluid in the reference state defined by the fluid activity $a_g = 1$.

In Eq. (1), the site occupancy θ is seen to depend on (a) the activity, hence pressure or chemical potential of the free fluid phase, and (b) the equilibrium constant K , which is expressed statistically through the gas activity independent potential $\mu_s = \mu_s(T)$. For an ideal gas, the activity becomes equal to the gas pressure and the model reduces to the Langmuir model [19]. The equivalent relation for the equilibrium concentration of gas or fluid molecules adsorbed by stress-free coal matrix material at fixed pressure and temperature is

$$C = C_s \theta = \frac{C_s K a_g}{1 + K a_g} \quad (2)$$

where C_s (mol/kg) is the concentration of available localized adsorption sites present in the coal (i.e. sites capable of adsorbing a given gas/fluid species). Assuming that each adsorbed molecule contributes a fixed amount of swelling to the host sorbent, the swelling exhibited by unconfined coal matrix due to adsorption of a single pure fluid is accordingly given by Hol et al. [9] as

$$e_{ads}^{eq} = \frac{C_s K a_g}{1 + K a_g} V_0 \rho \quad (3)$$

where ρ is the density of the coal, and where V_0 is the absolute change in coal volume when one mole of the gas/fluid species is adsorbed (assumed to be insensitive to adsorbed concentration). At low gas pressures where site occupancies are low, i.e. when $\theta^i \ll 1$, Eq. (3) can be simplified to

$$e_{ads}^{eq} = C_s K a_g V_0 \rho \quad (4)$$

which is easily seen from Eqs. (1b) and (2) that the denominator term in Eq. (3) approaches 1. For practical application, note that all parameters in this model can be obtained from basic, Langmuir-type, isothermal laboratory experiments on adsorption and swelling [9].

2.2. Present model development: starting assumptions and cases considered

We now proceed to address swelling of unconfined coal induced by adsorption from a binary gas/fluid mixture. For simplicity, we henceforth use the term “gas”, to cover both gas and supercritical fluid components. We assume there is no chemical or physical interaction between the two gases. Following Hol et al. [9,24], we begin by considering a small cube of nano-porous coal matrix material of mass m and side l ($l \leq 1$ mm), which hosts n_s^i ($i = \alpha, \beta \dots$) localized adsorption sites for the two gas components α and β . The cube is assumed to contain nano-pores only, so that there is no Darcian flow and negligible storage of free (unadsorbed) mixed gases. In other words, the coal particle is so

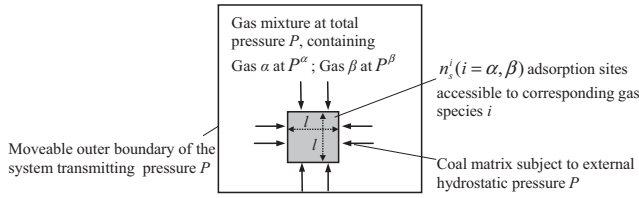


Fig. 1. Representative volume of coal matrix material used in the present analysis of adsorption under mechanically unconfined or stress-free conditions. The representative volume consists of a small cube of coal matrix material of mass m and side l ($l \leq 1$ mm), containing n_s^i ($i = \alpha, \beta$) localized adsorption sites accessible to the corresponding gas species i . The cube is free of cleats and consists entirely of nanoporous coal matrix material. Once the coal particle is exposed to gas α and gas β at constant total pressure P and at constant temperature T , it is assumed to take up α and β only by diffusion and adsorption.

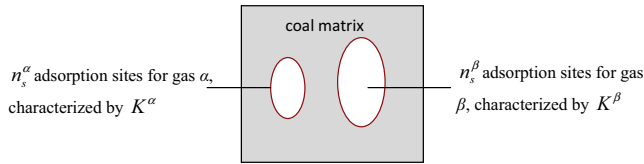


Fig. 2. Schematic illustration of the independent adsorption sites distribution. The model is characterized by n_s^α adsorption sites for gas α and n_s^β adsorption sites for gas β . These two categories of site represent completely separate adsorption sites for α and β in the coal sorbent phase. The number of total adsorption sites n_s^{total} present in the coal is therefore equal to the sum of n_s^α and n_s^β . Note that the different sites are drawn schematically in different special domains but are actually distributed throughout the coal particle considered.

small that it is cleat free and can take up gases only by diffusion and adsorption. The material is assumed homogeneous in structure and composition at the length scale l , but may be anisotropic in properties. The coal is now exposed to gases α and β at constant total pressure P and at constant temperature T (Fig. 1).

In considering mixed gases, it is important to recognize that the properties of the available adsorption sites in the coal matrix are likely to be different for each gas [25,26]. For example some adsorption sites can perhaps adsorb several gas species, while other adsorption sites can take up only a specific gas species. In other words, different sorption sites may be characterized by either similar or very different K^i values, for the various gases present. On this basis, we now focus on three physically possible end-member cases (1–3), and then consider a generalized case (4).

Case 1: Independent adsorption of each gas. In this case, the adsorption sites present full with two categories characterized by widely different K^i values for α and β (Fig. 2). In other words, n_s^α adsorption sites can in effect only take up gas α , while n_s^β adsorption sites can only take up gas β . The total number of adsorption sites n_s^{total} present in the coal matrix is therefore equal to the sum of adsorption sites for each component, i.e. $n_s^{total} = n_s^\alpha + n_s^\beta$.

Case 2: Fully shared adsorption sites. In this case, all adsorption sites are characterized by different, but not widely different, equilibrium constants K^α and K^β . In other words, all the available adsorption sites are accessible to gas α and to gas β (Fig. 3). This means the number of available adsorption sites for each component is identical ($n_s^\alpha = n_s^\beta = n_s^{2\beta}$) [8,14], and that the total number of adsorption sites present in the coal matrix material is given as $n_s^{total} = n_s^{2\beta}$.

Case 3: Partially shared adsorption sites: Type I. In this case, only a sub-set of the population of adsorption sites is shared by α and β (c.f. case 2). In other words, n_s^α sites present in the coal matrix material are accessible to both gases α and β , while $(n_s^\beta - n_s^\alpha)$ adsorption sites, which are a different type of site compared to the n_s^α adsorption sites, can only be occupied by gas β

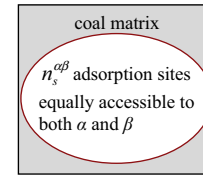


Fig. 3. Schematic illustration of the fully shared adsorption sites distribution. The model is characterized by $n_s^{2\beta}$ adsorption sites for α and for β . These sites are characterized by similar (though different) equilibrium constants for α and β .

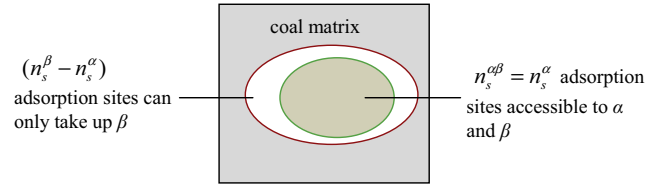


Fig. 4. Schematic illustration of the site population distribution corresponding to the Type I partially shared adsorption sites case. Here n_s^α adsorption sites are shared by both gases α and β , and $(n_s^\beta - n_s^\alpha)$ adsorption sites are accessible only to gas β , i.e. $n_s^{2\beta} = n_s^\alpha$ and $n_s^\alpha < n_s^{total} = n_s^\beta$.

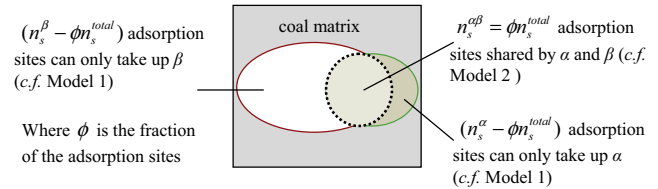


Fig. 5. Schematic illustration of the site population distribution corresponding to Type II partial sharing of adsorption sites. $n_s^{2\beta} = φ n_s^{total}$ adsorption sites are accessible to both gases α and β , while $(n_s^\beta - φ n_s^{total})$ adsorption sites are accessible only to gas β and $(n_s^\alpha - φ n_s^{total})$ adsorption sites are accessible only to gas α .

(Fig. 4). This means that $n_s^{2\beta} = n_s^\alpha$ and $n_s^\alpha < n_s^{total} = n_s^\beta$. The adsorption sites that are accessible to α and β are characterized by broadly similar site potential for these species, while these accessible only to gas β are characterized by a highly unfavorable site potential for gas α .

Case 4: Partially shared adsorption sites: Type II. In this fully general case (Fig. 5), a fraction $φ$ ($0 \leq φ \leq n_s^\alpha/n_s^\beta \leq 1$) of the total number of adsorption sites n_s^{total} is accessible to gas α and to gas β , i.e. $n_s^{2\beta} = φ n_s^{total}$ sites are accessible to both gases (c.f. case 2). The other adsorption sites can only take up one component so that a population of $(n_s^\alpha - φ n_s^{total})$ adsorption sites is accessible only to gas α , while $(n_s^\beta - φ n_s^{total})$ adsorption sites can only take up gas β . Here, $n_s^{total} = \frac{n_s^\alpha + n_s^\beta}{1 + φ}$. When $φ = 0$, this case reduces to end member case 1. When $φ = 1$, it reduces to case 2. When $φ = n_s^\alpha/n_s^\beta$, it reduces to case 3.

With respect to the above four cases, four models for swelling of unconfined coal exposed to gases α and β are now derived.

2.3. Model 1: Independent adsorption sites

This model corresponds to case 1. Here fully independent sorption of α and β , determined by a_g , C_s and K for each gas (see Eq. (2)), leads to independent swelling responses, further determined by V_0 for α and for β (see Eq. (3)) [9]. These swelling responses sum to give total volumetric strain. Model 1 can accordingly be derived from the Hol and Spiers model for single-gas adsorption-induced swelling [9], i.e. from Eqs. (2) and (3), by applying these equations

to the adsorption sites accessed by α and β independently. This yields

$$e_{ads}^{eq} = \frac{C_s^\alpha a_g^\alpha K^\alpha}{1 + a_g^\alpha K^\alpha} V_0^\alpha \rho + \frac{C_s^\beta a_g^\beta K^\beta}{1 + a_g^\beta K^\beta} V_0^\beta \rho \quad (5)$$

where C_s^i is the concentration of the adsorption sites accessible to component i in mol/kg, K^i is the equilibrium constant for gas species i , a_g^i is the activity of the free gas species i , and V_0^i is the absolute change in coal volume due to adsorption of one mole of the component i . Note here that V_0^i is assumed to be insensitive to the concentration of the species i , following Hol et al. [9]. It is also important to note here that while the equilibrium constant K^i for each species is independent of the partial pressure of the species i , it is sensitive to coal rank, fluid species and temperature.

2.4. Model 2: Fully shared adsorption sites

To obtain an expression for Model 2, which corresponds to case 2 (see Fig. 3), we consider the thermodynamic potential changes associated with reversible adsorption first of a single molecule and then of a population of n^i ($i = \alpha, \beta$) molecules of gas species i . We then derive an expression for swelling, assuming that the volume change associated with a single adsorbed molecule is insensitive to adsorbed concentration of either component, and that the total volume change is the sum of the contribution due to each component (α, β) weighted according to sorbent concentration [9].

2.4.1. Attachment energy for adsorption of a single molecule of species i

When a single molecule of species i (α or β) is adsorbed by the small, representative matrix cube specified above, the internal energy change of the solid phase (subscript s) is given by the Gibbs equation [9],

$$\Delta U_s^i = -P\Omega_0^i + T\Delta S_s^i + \mu_s^i \quad (6)$$

In this relation, Ω_0^i is volume change exhibited by the matrix particle, ΔS_s^i is the corresponding entropy change, and μ_s^i is the chemical potential of the adsorbed molecule within the potential well associated with the sorption site.

For each component i in the gas phase (subscript g), the internal energy change that occurs when a single molecule is removed from the gas mixture by adsorption is given, via an analogous Gibbs equation [9], as

$$\Delta U_g^i = P\Omega_g^i + T\Delta S_g^i - \mu_g^i \quad (7)$$

In this case, Ω_g^i is the partial molecular volume of the gaseous species i in the mixture at total pressure P , μ_g^i is the chemical potential of gaseous species i at partial pressure P^i , and ΔS_g^i is the entropy change associated with removing one molecule of species i from the gas mixture.

For the combined solid–gas system (subscript a), we hence get, adding (5) and (6),

$$\Delta \mu_a^i = \mu_s^i - \mu_g^i = \Delta U_a^i + P(\Omega_0^i - \Omega_g^i) - T\Delta S_a^i \quad (8a)$$

or

$$\Delta \mu_a^i = \mu_s^i - \mu_g^i = \Delta F_a^i + P\Delta V_a^i \quad (8b)$$

for each species i . Here, $\Delta \mu_a^i$ is simultaneously the change in potential associated with the adsorbed molecule i and the change in the energy of the system due to the attachment of the adsorbed molecule i . The term $\Delta V_a^i = \Omega_0^i - \Omega_g^i$ is the associated volume change of the system, while ΔF_a^i is the corresponding change in Helmholtz

free energy. The term ΔS_a^i is the entropy change of the system. By definition, under the present hydrostatic conditions, where both P and T are constant, the corresponding change in Gibbs potential of component i is

$$\Delta G_a^i = \Delta F_a^i + P\Delta V_a^i \quad (9)$$

where now we can identify $\Delta G_a^i = \Delta \mu_a^i$ as the partial Gibbs energy change associated with attachment of a single adsorbed molecule of component i . Physically, this ΔG_a^i represents the Gibbs energy of component i that must be supplied to remove an adsorbed molecule of species i from an adsorption site into the free gas phase.

2.4.2. Adsorption energy associated with uptake of n^i molecules of species $i = \alpha, \beta$

For a total population of shared adsorption sites $n^{\alpha\beta}$, and assuming that each adsorption site remains empty or else takes up one gas molecule, then n^i molecules of gas species i , (i.e. n^α molecules of α and n^β molecules of β), can only be distributed over $(n^{\alpha\beta} - n^i)$ adsorption sites, where n^i represents n^β and n^α ($j \neq i$) respectively. From combination theory, the number of different ways that n^i molecules can be distributed over these available sites can be written as $W^i = \frac{(n^{\alpha\beta} - n^i)!}{n^i!(n_s^{\alpha\beta} - \sum_{l=\alpha, \beta} n^l)!}$. This contributes a configurational entropy term $\Delta S^i = -k \ln W^i$ to the overall change in Gibbs potential that occurs when n^i molecules of species i are adsorbed. The adsorption energy for n^i molecules of species i is accordingly given as

$$\Delta G^i = n^i \Delta G_a^i - kT \ln \frac{(n_s^{\alpha\beta} - n^i)!}{n^i!(n_s^{\alpha\beta} - \sum_{l=\alpha, \beta} n^l)!} \quad (10)$$

Because we assume that there is no interaction between gases α and β , the total change in Gibbs energy for the whole system, when n^α and n^β molecules of α and β are adsorbed, can thus be written as

$$\Delta G = \sum \Delta G^i \quad (11a)$$

or

$$\Delta G = n^\alpha \Delta G_a^\alpha + n^\beta \Delta G_a^\beta - kT \ln \frac{(n_s^{\alpha\beta} - n^\alpha)!}{n^\alpha!(n_s^{\alpha\beta} - \sum_{l=\alpha, \beta} n^l)!} - kT \ln \frac{(n_s^{\alpha\beta} - n^\beta)!}{n^\beta!(n_s^{\alpha\beta} - \sum_{l=\alpha, \beta} n^l)!} \quad (11b)$$

where $\sum_{l=\alpha, \beta} n^l = n^\alpha + n^\beta$

2.4.3. Equilibrium concentration of components adsorbed from a mixture of gases α and β

For mixed gases, we assume that the adsorption of each gas proceeds until equilibrium is reached, subject to the condition that there is zero interaction between components. At that point, the total Gibbs energy must be minimum and its partial derivatives equal to zero, i.e. $\left(\frac{\partial \Delta G}{\partial n^i}\right)_{P, T} = 0$. Applying Stirling's approximation $\ln x! \approx x(\ln x - 1)$ for large x to the above expression for ΔG (Eq. (11)) and differentiating now gives

$$\left(\frac{\partial \Delta G}{\partial n^i}\right)_{P, T} = \Delta G_a^i + kT \ln \left(\frac{\theta^i}{1 - \sum_{l=\alpha, \beta} \theta^l} \right) = 0 \quad (12)$$

where $\theta^i = n^i/n_s^{\alpha\beta}$ is the concentration of adsorbed species i amongst the total number of adsorption sites $n_s^{\alpha\beta}$. This in turn means that at equilibrium

$$\theta^i = \frac{\exp\left(\frac{-\Delta G_a^i}{kT}\right)}{1 + \exp\left(\frac{-\Delta G_a^i}{kT}\right) + \frac{\theta^j}{\theta^i} \exp\left(\frac{-\Delta G_a^j}{kT}\right)}, \quad (j \neq i) \quad (13a)$$

or

$$\frac{\theta^i}{1 - \theta^j} = \frac{\exp\left(\frac{-\Delta G_a^i}{kT}\right)}{1 + \exp\left(\frac{-\Delta G_a^j}{kT}\right)}, \quad (j \neq i) \quad (13b)$$

which on further manipulation, putting $i = \alpha, \beta$ and simultaneously putting $j = \beta, \alpha$, yields

$$\theta^i = \frac{\exp\left(\frac{-\Delta G_a^i}{kT}\right)}{1 + \sum_{l=\alpha, \beta} \exp\left(\frac{-\Delta G_a^l}{kT}\right)} \quad (14)$$

Now from the thermodynamics of fluid systems, the potential of the free species i is given by

$$\mu_g^i = \mu_{g0}^i + kT \ln a_g^i \quad (15)$$

where $a_g^i = a_g^i(P^i, T)$ is the chemical activity of the free gaseous species i at partial pressure P^i and temperature T in the gas mixture, and where μ_{g0}^i is the potential of each gas in the reference state $a_g^i = 1$. Recalling that $\Delta G_a^i = \Delta \mu_a^i = (\mu_s^i - \mu_g^i)$ from Eqs. (8) and (9), and combining Eqs. (14) and (15), we hence obtain the following expressions for the concentration of adsorbed molecules per available site $n_s^{z\beta}$, for each component α and β in the gas mixture, namely

$$\theta^i = \frac{a_g^i \exp\left(\frac{\mu_{g0}^i - \mu_s^i}{kT}\right)}{1 + \sum_{l=\alpha, \beta} a_g^l \exp\left(\frac{\mu_{g0}^l - \mu_s^l}{kT}\right)} \quad (16a)$$

or

$$\theta^i = \frac{a_g^i K^i}{1 + \sum_{l=\alpha, \beta} a_g^l K^l} \quad (16b)$$

where $K^i = \exp\left(\frac{\mu_{g0}^i - \mu_s^i}{kT}\right)$ is the equilibrium constant for adsorption of species i , which depends only on temperature T for a given coal and gas species i . In these relations, if the free gas components outside the coal particle behave as ideal gases, then, for reference states defined by the partial pressures $P_0^i = 1$ and $a_g^i = P^i$, the adsorption model reduces to the well-known Langmuir isotherm for mixed gases [19].

2.4.4. Swelling strain development

Finally, using the relation for swelling strain $e_{ads}^{eq} = C_s \theta V_0 \rho$ given by Hol and Spiers [22], we can obtain an expression for the swelling strain predicted by Model 2, i.e. for case 2. This is given

$$e_{ads}^{eq} = C_s^{\alpha\beta} (\theta^\alpha V_0^\alpha + \theta^\beta V_0^\beta) \rho \quad (17a)$$

or

$$e_{ads}^{eq} = C_s^{\alpha\beta} \left(\frac{a_g^\alpha K^\alpha}{1 + a_g^\alpha K^\alpha + a_g^\beta K^\beta} V_0^\alpha + \frac{a_g^\beta K^\beta}{1 + a_g^\alpha K^\alpha + a_g^\beta K^\beta} V_0^\beta \right) \rho \quad (17b)$$

where $C_s^{\alpha\beta} = n_s^{\alpha\beta} / (N_A \cdot m)$ is the (constant) number of potential adsorption sites in moles per kg of coal and $V_0^i (i = \alpha, \beta) = N_A \Omega_0^i = 1 / \rho (\partial e_{ads}^i / \partial C^i)$ is the absolute change in coal volume when one mole of gas species i is adsorbed, which is assumed to be insensitive to the concentration of the species i , and where N_A is Avogadro constant.

2.5. Model 3: Partially shared adsorption sites, Type I

This model corresponds to case 3 (see Fig. 4), which assumes that a selective sorption effect between α and β plays a role in

swelling behaviour. Here adsorption of α and β into the n_s^z shared sites leads to a swelling response described by Model 2 (Eqs. (17a) and (17b)). At the same time, adsorption of β into the $(n_s^\beta - n_s^\alpha)$ β -only sites leads to a swelling response described by Hol and Spiers Model for β (see Eq. (3)), but replacing C_s in Eq. (3) by $(C_s^\beta - C_s^\alpha)$. The total swelling strain due to adsorption of mixed gases predicted by Model 3 can therefore be written as

$$e_{ads}^{eq} = C_s^\alpha \left(\frac{a_g^\alpha K^\alpha}{1 + a_g^\alpha K^\alpha + a_g^\beta K^\beta} V_0^\alpha + \frac{a_g^\beta K^\beta}{1 + a_g^\alpha K^\alpha + a_g^\beta K^\beta} V_0^\beta \right) \rho + (C_s^\beta - C_s^\alpha) \frac{a_g^\beta K^\beta}{1 + a_g^\beta K^\beta} V_0^\beta \rho \quad (18)$$

where $C_s^\alpha = C_s^{\alpha\beta}$ and $C_s^\alpha < C_s^{total} = C_s^\beta$.

2.6. Model 4: Partially shared adsorption sites, Type II

Following the same approach applied above to obtain Model 3, using the Hol and Spiers Model and our Model 2, a generalized model corresponding to case 4 (see Fig. 5) can be derived. This involves applying Model 2 to the fraction ϕ of the total number of sorption sites n_s^{total} that is accessible to α and to β . Model 1 is applied to the $(n_s^\alpha - \phi n_s^{total})$ sites that are accessible only to α , and the $(n_s^\beta - \phi n_s^{total})$ sites that are accessible only to β . The result is given by

$$e_{ads}^{eq} = \phi C_s^{total} \left(\frac{a_g^\alpha K^\alpha}{1 + a_g^\alpha K^\alpha + a_g^\beta K^\beta} V_0^\alpha + \frac{a_g^\beta K^\beta}{1 + a_g^\alpha K^\alpha + a_g^\beta K^\beta} V_0^\beta \right) \rho + (C_s^\beta - \phi C_s^{total}) \frac{a_g^\beta K^\beta}{1 + a_g^\beta K^\beta} V_0^\beta \rho + (C_s^\alpha - \phi C_s^{total}) \frac{a_g^\alpha K^\alpha}{1 + a_g^\alpha K^\alpha} V_0^\alpha \rho \quad (19)$$

where $C_s^{total} = \frac{C_s^\alpha + C_s^\beta}{1 + \phi}$ is the concentration of total adsorption sites present in the coal matrix material, and where ϕ ($0 \leq \phi \leq n_s^\alpha / n_s^\beta \leq 1$) is the site-sharing factor. Recall here that $C_s^i = n_s^i / (N_A \cdot m)$. This then gives $n_s^\alpha / n_s^\beta = C_s^\alpha / C_s^\beta$. When $0 < \phi < C_s^\alpha / C_s^\beta < 1$, this model represents the generalized model corresponding to Fig. 5 described above. When $\phi = 0$, the model reduces to Model 1. When $\phi = 1$, it reduces to Model 2. When $\phi = C_s^\alpha / C_s^\beta$, it reduces to Model 3.

Finally, at low gas pressures where site occupancies are low, i.e. when $\theta^i \ll 1$, it is easily seen from Eqs. (13) and (14) that the denominator terms in Eq. (19) all approach 1 [9,24]. The generalized model can then be simplified to

$$e_{ads}^{eq} = (C_s^\alpha a_g^\alpha K^\alpha V_0^\alpha + C_s^\beta a_g^\beta K^\beta V_0^\beta) \rho \quad (20)$$

in which ϕ no longer appears, as all terms in Eq. (19) containing ϕ now drop out. This simplified model can therefore be directly applied to the three end-member cases when gas pressures are low.

3. Comparison of model predictions with experimental data

We now compare the predictions of our models with available experimental data. This requires experimental data on both the sorption capacity and swelling behaviour of a given coal exposed to pure α and β (to obtain V_0^α , V_0^β , C_s^α , C_s^β , K^α , K^β), as well as swelling data obtained on the same coal exposed to mixed gases. The only data that we are aware of that are suitable for this purpose are those of Day et al. for two almost identical sub-bituminous coals from the Bowen Basin, Queensland, Australia (denoted as Coal N and Coal C by Day et al.) [14,27]. As Day et al. [14,27] do not quote the errors or give error bars for the data, had no choice but to assume that their experimental data are accurate enough

for our purpose. Since our three end-member models each have a clear physical meaning, we first compare the predictions of the three end-member models with Day et al.'s experimental data [14] to assess which model fits best. We then compare our Model 4 with Day's et al. data [14] by varying the site-sharing factor ϕ to evaluate whether Model 4 offers any improvement upon Models 1–3.

3.1. The data of Day et al.

We start by reviewing the data presented by Day et al. on the swelling response of Coal N versus gas composition [14]. These data consist of volumetric strain values measured as a function of CO₂ and CH₄ partial pressures, the latter being specified in terms of mixture composition. Note that sorption was not measured in these experiments, nor was bulk modulus or density. The experiments on Coal N were carried out at total pressures in the range 1–15 MPa at a temperature of 55 °C. The gas mixture composition (% CO₂), measured using Gas Chromatography, was systematically varied in the range 0–100%, thus including measurements for pure CH₄ and pure CO₂. The total volumetric strain e_v^{eq} measured by Day et al. [14] includes both (a) the elastic compression response e_{el}^{eq} of the coal sample due to imposed total gas pressure P , and (b) the adsorption-induced swelling strain e_{ads}^{eq} , [10,12,22] so that

$$e_v^{eq} = e_{ads}^{eq} + e_{el}^{eq} \quad (21)$$

Here we emphasize that the term e_{el}^{eq} represents an elastic response of the coal matrix, rather than a poro-elastic response. This is because our model assumes that the nanoporous matrix only allows penetration of the gas or fluid species by diffusion and adsorption, i.e. there is zero fluid pressure in the matrix, [10,12,22] so that

$$e_{el}^{eq} = P/K_s \quad (22)$$

where K_s is the bulk modulus of the coal matrix.

The swelling due to adsorption alone can thus be expressed as

$$e_{ads}^{eq} = e_v^{eq} - P/K_s \quad (23)$$

We applied this equation to obtain the true adsorption-induced swelling strain e_{ads}^{eq} of Coal N from total strain, using the bulk

modulus K_s presented by Day et al. for Coal C [14,27]. We plot the quantity e_{ads}^{eq} versus CO₂ concentration (mole percentage) in the CO₂–CH₄ mixture in Fig. 6.

We now review the data presented by Day et al. on swelling response versus sorption, but for Coal C [27]. These authors measured the volumetric strain of Coal C exposed to pure CO₂ and CH₄, using the same experimental methods for Coal N under the same PT conditions. In addition, they measured the concentrations of CO₂ and CH₄ adsorbed when crushed Coal C was independently exposed to pure CO₂ and pure CH₄, under the same PT conditions, using a gravimetric method. On the basis of these measurements, Day et al. plotted the quantity e_v^{eq} versus adsorbed concentration C for pure CO₂ and CH₄. We obtained the true adsorption-induced swelling strain e_{ads}^{eq} of Coal C versus adsorbed CO₂ and CH₄ concentration, using Eq. (23) to correct for elastic compression. This yielded a near-linear relationship with a best fit slope of 0.0232 kg/mol ($R^2 = 0.951$) for CO₂ and 0.0203 kg/mol ($R^2 = 0.959$) for CH₄.

3.2. End-member model parameters and calculation method

We now calculate the parameters V_0 , C_s and K for Coal N for pure CO₂ and pure CH₄, following the approach adopted by Hol and Spiers [22] for a pure single gas. Recall that these parameters are assumed to be insensitive to the adsorbed gas concentration. The values of $V_0^{CO_2}$ and $V_0^{CH_4}$ for Coal N were first calculated from the above-mentioned relationship between e_{ads}^{eq} versus C obtained. This was done for Coal C exposed to pure CO₂ and CH₄, using the relation $V_0 = 1/\rho(\partial e_{ads}^{eq}/\partial C)$ (see Eqs. (2) and (3)). The results obtained were $V_0^{CO_2} = 1.42 \times 10^{-5}$ and $V_0^{CH_4} = 1.24 \times 10^{-5}$. The parameters C_s and K for pure CO₂ and pure CH₄ were then derived from the data on volumetric strain of Coal N versus pure gas pressure (the 0% and 100% end member) measured by Day et al. [14]. We first calculated the value of $C_s \times K$, using the relationship between adsorption-induced swelling and gas activity at low gas pressure expressed in Eq. (4). Inserting the value $C_s \times K$ thus obtained into Eq. (3), we then calculated the value of K using Eq. (3) for adsorption-induced swelling versus gas activity at high pressures. However, due to the paucity of swelling data at low

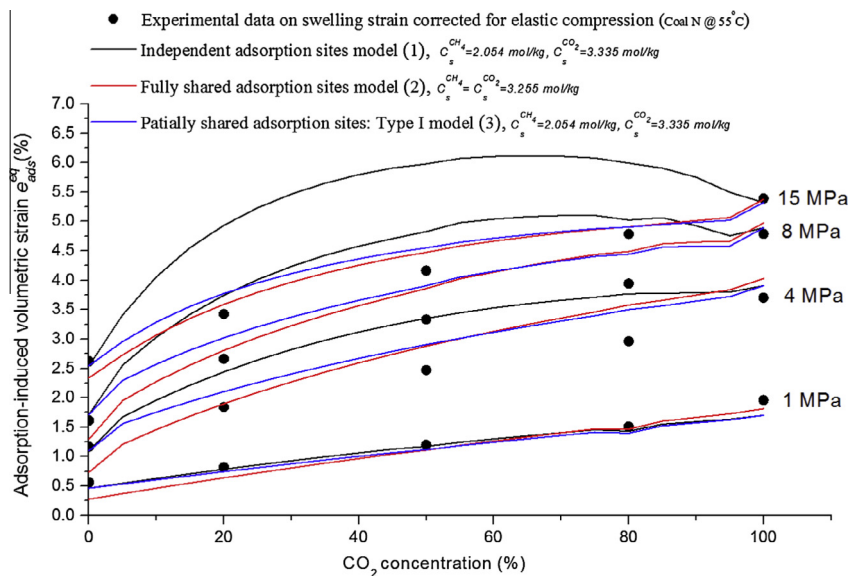


Fig. 6. Adsorption-induced swelling strains calculated from the experimental data of Day et al. [13] for Coal N (sub-bituminous coal from the Bowen Basin, Queensland) exposed to CH₄–CO₂ mixtures. The swelling data are plotted as a function of CO₂ concentration (mole percentage) in the CH₄–CO₂ mixture at the total pressures shown and at 55 °C. The predictions made using the present three end-member models (Models 1–3) are overlain for comparison.

Table 2
Summary of model parameters used in Models 1–3 for calculating swelling of the Bowen Basin sub-bituminous coal N, under the conditions of the mixed gas swelling experiments reported by Day et al. [13].

Models	Parameters and conditions for which they were determined							
	$V_0^{\text{CH}_4}$ (m ³ /mol) 55 °C pure CH ₄	$V_0^{\text{CO}_2}$ (m ³ /mol) 55 °C pure CO ₂	$C_s^{\text{CH}_4}$ (mol/kg) 55 °C pure CH ₄	$C_s^{\text{CO}_2}$ (mol/kg) 55 °C pure CO ₂	K^{CH_4} 55 °C pure CH ₄	K^{CO_2} 55 °C pure CO ₂	ρ (g/cm ³) 55 °C pure He	K_s (GPa) 55 °C pure He
1	1.24×10^{-5}	1.42×10^{-5}	2.054	3.335	0.0126	0.0288	1.637	9.41
2	1.24×10^{-5}	1.42×10^{-5}	3.255	3.255	0.0044	0.0323	1.637	9.41
3	1.24×10^{-5}	1.42×10^{-5}	2.054	3.335	0.0126	0.0288	1.637	9.41

pressures (<0.1 MPa), the uncertainty in calculating the value of $C_s \times K$ is large. To reduce this uncertainty, we optimized the value of K by varying the values of $C_s \times K$ to achieve the best fit of Eq. (3) to the full set of experimental data for pure CO₂ and pure CH₄ for Coal N. We conducted this process by the SOLVER function of Microsoft Excel (following Day et al. [8]). Finally, this procedure yielded $C_s^{\text{CO}_2} = 3.335$ mol/kg, $K^{\text{CO}_2} = 0.0288$ ($R^2 = 0.987$) and $C_s^{\text{CH}_4} = 2.054$ mol/kg, $K^{\text{CH}_4} = 0.0126$ ($R^2 = 0.986$). Note that throughout these calculations, the CO₂ activity was computed using the EoS for CO₂ developed by Span and Wagner [28], while the CH₄ activity was calculated according to the EoS for CH₄ developed by Setzmann and Wagner [29]. The density of Coal N needed to calculate swelling, via Eq. (3), was estimated from work on Coal C by Day et al. [27]. In the following, we now proceed to insert appropriate values for the key parameters V_0 , C_s and K for both CO₂ and CH₄ in Models 1–3. The values used for each model are summarized in Table 2.

3.2.1. The parameter values in Model 1

Model 1 assumes the adsorption sites and process for CO₂ are fully separate and independent compared with those for CH₄. We therefore took the above-mentioned values of C_s and K , which give the best fit for pure CO₂ and CH₄, as the parameter values appropriate for Model 1 (see Table 2).

3.2.2. The parameter values in Model 2

Model 2 assumes $C_s^{\alpha\beta} = C_s^{\text{CO}_2} = C_s^{\text{CH}_4}$. This means that the above best fit parameter values C_s (3.335, 2.054) and K (0.0288, 0.0126), obtained for pure CO₂ and CH₄, are not appropriate for Model 2. In exploring the applicability of Model 2 to describe swelling upon exposure to the mixed gases, we followed the same steps described above, but forced the requirement that $C_s^{\alpha\beta} = C_s^{\text{CO}_2} = C_s^{\text{CH}_4}$ as a constraint. Best fitting of Eq. (3) to the experimental data for pure CO₂ and pure CH₄ for Coal N then give $C_s^{\text{CO}_2} = 3.255$ mol/kg, $K^{\text{CO}_2} = 0.0318$ ($R^2 = 0.982$) and $C_s^{\text{CH}_4} = 3.255$ mol/kg, $K^{\text{CH}_4} = 0.0044$ ($R^2 = 0.824$) (see Table 2). Note here, however, that a significant difference exists between the values obtained for K^{CO_2} and K^{CH_4} , which is inconsistent with our assumption in Model 2 that all adsorption sites must be characterized by similar equilibrium constants K^α and K^β .

3.2.3. The parameter values in Model 3

Model 3 assumes $C_s^{\text{CO}_2} > C_s^{\text{CH}_4}$, which is consistent with the best fit values we obtained for C_s for pure CO₂ and CH₄ (Section 3.2). We therefore took the best fit values of parameters C_s and K , for pure CO₂ and CH₄, as the appropriate parameter values for Model 3 (see Table 2).

3.3. End-member models versus the experimental data

Using the parameter values mentioned above, we applied Models 1–3 to systematically calculate $e_{\text{ads}}^{\text{eq}}$ as a function of CO₂ concentration (mole percentage) in the gas mixture, for total

pressures in the range 1–15 MPa and a temperature 55 °C, as used in the experiments performed by Day et al. [14]. To do this, data on the activity of CO₂ and CH₄ in the mixed gas state are also needed. These were calculated using the EoS for CO₂ and CH₄ mixtures developed by Kunz et al. [30].

We now compare the predictions of the three end-member models with the data on $e_{\text{ads}}^{\text{eq}}$ versus CO₂ concentration in the CO₂–CH₄ mixture obtained from the data of Day et al. [14] for Coal N from the Bowen Basin at 55 °C (Fig. 6). The results show that Models 2 and 3 (for full and Type I partial sharing of sites) are in good agreement with the experimental data, whereas Model 1 (independent adsorption sites) fits poorly. Additionally, the predictions made by Model 1 were inconsistent with the trend observed by the authors that the swelling of coal increased with increasing CO₂ concentration and yielded the peak value when exposed to pure CO₂ (100%). This all suggests at least some degree of site sharing by CO₂ and CH₄. Day et al. [14] proposed that their results can be explained entirely in terms of CO₂ versus CH₄ concentration (or partial pressure) in the gas mixture, with negligible effect of selective adsorption, i.e. by our Model 2 for full site sharing. To assess if Model 2 or Model 3 best explains their results, the fit quality of Models 2 and 3 to the lab data has been investigated by calculating the coefficient of determination (R^2) in the fit of Models 2 and 3. The R^2 value obtained by fitting Model 2 to all experimental data shown in Fig. 6 is 0.949, while that obtained for Model 3 is 0.955. Model 3 accordingly fits Day et al. data best, though the values of R^2 for Models 2 and 3 are similar and the difference in R^2 is not necessarily statistically significant. At the same time, however, the ratio of K values ($K^{\text{CO}_2} : K^{\text{CH}_4}$) equals 7.34 for the Model 2 fit, indicating apparent selectivity to CO₂ with respect to CH₄. This is inconsistent with the assumptions underlying Model 2 whereby CO₂ and CH₄ are taken to have the same access to all adsorption sites. This means Model 2 is not physically acceptable for describing the swelling of sub-bituminous coal in the Bowen Basin due to adsorption of CO₂–CH₄ mixtures, and we reject it on this basis opting for Model 3 as the better description. This result implies that the swelling of sub-bituminous coal from the Bowen Basin due to sorption of mixed gases (CO₂ and CH₄) is not only determined by the partial pressures of the sorbing gases, as proposed by Day et al. [14], but is also sensitive to selective adsorption of CO₂ (i.e. to the ratio of the adsorption site concentrations $C_s^{\text{CO}_2} : C_s^{\text{CH}_4}$ and the ratio of the equilibrium constants $K^{\text{CO}_2} : K^{\text{CH}_4}$).

3.4. Model 4 versus Day et al.'s data

Model 4 (see Eq. (19)) represents the general condition corresponding to Fig. 5, when $0 < \phi < C_s^{\text{CH}_4}/C_s^{\text{CO}_2}$, but reduces to Model 1 (see Eq. (5)) when $\phi = 0$ and to Model 3 (see Eq. (18)) when $\phi = C_s^{\text{CH}_4}/C_s^{\text{CO}_2}$. To examine whether Model 4 (for the general case where $0 < \phi < C_s^{\text{CH}_4}/C_s^{\text{CO}_2}$) can work better for CO₂–CH₄ mixtures than Model 3, we inserted the values for the key parameters V_0 , C_s and K for CO₂ and CH₄ which were used in Model 3 (see Table 2). For Model 4, the site sharing factor ϕ was accordingly

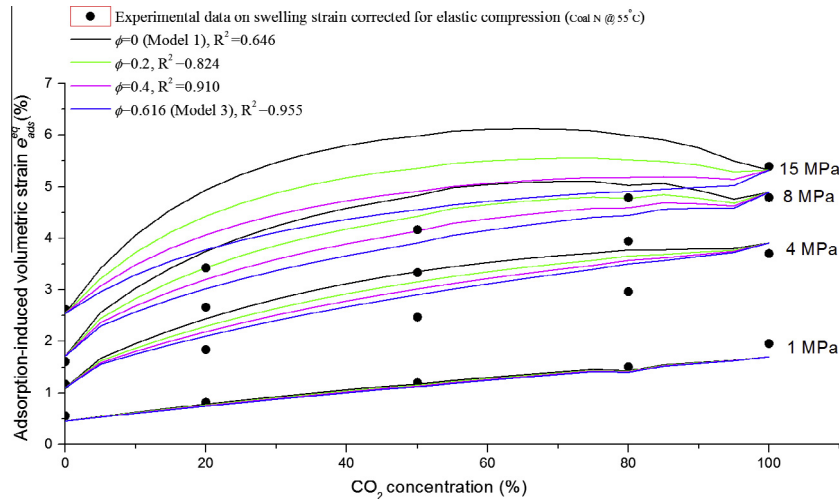


Fig. 7. Comparison of our generalized model (Model 4), applied by varying the site-sharing factor ϕ from 0 to 0.616, with the experimental data obtained from the paper by Day et al. [13] for Coal N from the Bowen Basin, Queensland, at 55 °C (cf. Fig. 6). The deviation of the model predictions from the experimental data are shown in terms of R^2 values.

varied in the range $0 < \phi < C_s^{\text{CH}_4} / C_s^{\text{CO}_2} = 2.054 / 3.335 = 0.616$. The predictions made by applying Model 4, for the site-sharing factor value ϕ between 0 and 0.616, are compared with the data on $e_{\text{ads}}^{\text{eq}}$ versus CO_2 – CH_4 mixture composition for Coal N in Fig. 7. The $e_{\text{ads}}^{\text{eq}}$ versus CO_2 concentration results, obtained by varying ϕ in the specified range, lie between those obtained using Models 1 ($\phi = 0$) and 3 ($\phi = 0.616$). The results further indicate that the greater the site-sharing value ϕ , the better Model 4 fits the data of Day et al. This was confirmed by evaluating the quality of the fit to the individual data points of Day et al. [14], yielding the R^2 values shown in Fig. 7 for each value of ϕ . The implication is that for Model 4, at least in this case, the greater the extent of site sharing assumed in the model, then the better the description of Day et al.'s data. This all suggests that Model 3 is a better option at least for swelling of Bowen Basin sub-bituminous coal due to adsorption of CO_2 – CH_4 mixtures.

4. Discussion

Overall, our results have demonstrated that the Type 1 partially shared adsorption sites model (Model 3) best describes the experimental data on Bowen Basin sub-bituminous coal presented by Day et al. [14]. This finding implies that coal swelling due to adsorption of CO_2 and CH_4 from the gas mixture is, at least in this case, determined by both partial pressure and selective adsorption effects, and not simply by partial pressure (as claimed by Day and co-workers) or by selective adsorption alone [17]. This finding is also supported by the study of Gensterblum et al. [26]. We explain this inference below by considering the physical meaning of the quantities appearing in the models.

4.1. Physical meaning of model parameters and implications for Bowen Basin coal

In our models for adsorption-induced swelling of coal due to exposure to a binary gas mixture (see Eqs. (5), (17)–(19)), swelling of the coal matrix is determined by the parameters C_s , K , V_0 , ϕ and by a_g for each gas component. All of these quantities have physical meaning and their values can be obtained from a basic study of the coal and/or gas components. Let us consider their roles systematically. First, selective adsorption of the two gases is controlled by the parameters C_s^α , C_s^β , K^α , K^β and ϕ . These all depend on coal

rank and gas species. Here C_s^α , C_s^β and ϕ , through the associated values of the site potentials μ_s^i , determine the total number of potential sites for adsorption and the degree of site sharing, and therefore play a key role in controlling coal selectivity to each component. In turn, $K^i = \exp\left(\frac{\mu_{g0}^i - \mu_s^i}{RT}\right)$ for species i , is determined by the

site potential μ_s^i , by the gas potential at a given reference state μ_{g0}^i , and by temperature. This together with a_g^i dictates the occupancy of sites by species i . In general, like K^i , V_0^i also depends on coal rank, gas species and temperature, linking adsorbed concentration to swelling behaviour (Eqs. (5), (17)–(19)). Finally, the activities of the gas species a_g^i , of course, depend on partial pressure (or concentration in the gas mixture) and temperature.

This all demonstrates that the swelling response of a given coal matrix material exposed to a binary gas mixture reflects the combined effects of four factors: (1) the composition of the binary mixture, i.e. the partial pressure, hence the activity and the chemical potential of the two components present in the free gas phase, (2) the equilibrium constant K for species i , expressed statistically through the gas activity independent chemical potential $\mu_g^i(T)$, (3) the adsorption site population for each component, expressed through the maximum adsorption site concentration per kg of coal C_s^i and the site-sharing fraction ϕ , and (4) the partial molar volume of each gas component in the adsorbed state, expressed by V_0 . Physically, the good fit between Model 3 and Day et al.'s data means, for the Bowen Basin coal, that injected CO_2 will displace CH_4 from coal due to both the reduction of CH_4 partial pressure and to truly selective sorption of CO_2 over CH_4 (refer Table 1). This is consistent with the conventional expectation, based on pure gas sorption experiments, that CO_2 can displace CH_4 not only due to partial pressure effects, as inferred by Day et al. [14], but also to selective adsorption effects [17]. The good fit of our Model 3 to the data of Day et al. also implies that swelling of coal due to sorption of a CO_2 – N_2 mixture will perhaps be more complicated than suggested by Day et al., who assumed a purely partial pressure effect [14]. This in turn means that to evaluate if a CO_2 – N_2 mixture is suitable for injecting in ECBM operations, our Model 3 should be preferred, being more physically proper, at least for the Bowen Basin sub-bituminous coal, which shows selectivity to CO_2 with respect to CH_4 . Another important advantage of Model 3 is that it is easy to parameterize, since the parameters appearing

in it are consistent with those obtained from swelling/sorption data for the corresponding pure components. This means Model 3 can be easily applied in practice to predict the swelling of coal due to adsorption of binary gas mixtures.

4.2. Application of the generalized model (Model 4) to other coals and gas mixtures

Application of our generalized model (Model 4) to the data of Day et al. [14] for the Bowen Basin sub-bituminous coal has shown that the end member model, Model 3 (for which $\phi = C_s^{\text{CH}_4} / C_s^{\text{CO}_2} = 0.616$), explains the observed swelling behaviour upon exposure to CO_2 – CH_4 mixture best. However, other coals and gas mixtures, characterized by different values of C_s^i , K^i , V^i and ϕ may show behaviour that is better described by Models 1 or 2, or by our generalized model applied for $0 < \phi < C_s^{\alpha} / C_s^{\beta}$. This may offer an explanation of why conflicting results have been reported in the literature on what controls swelling in mixed gas environments. Since the generalized model covers all possible distributions of adsorption sites that can be described in terms of single values for K^i , it can be widely applied to any coal rank, and to binary gas mixtures at any PT conditions, provided proper parameter values are available. The generalized model therefore offers an important tool for future reservoir modeling, as sorption-induced swelling of coal exposed to mixed gases strongly influences coal seam permeability and stress state, hence reservoir integrity and borehole stability. In reservoir modeling exercise, of this type, Model 4 can be applied for the two dominant gas species. Extending Model 4 from binary to multiple component gas mixtures is clearly desirable in this context. However, quantifying the combined effects of partial pressure and selective adsorption, using an approach analogous to Model 4, will become complicated for multiple component mixtures (≥ 3 gas species), because multiple possibilities in the sharing of adsorption sites for different components then arise. We therefore reserve these developments for a future paper.

4.3. Limitation of the present study

Our comparison of Models 1–4 with the swelling data of Day et al. shows that Model 3 ($R^2 = 0.955$) fits best. The fit is not especially good, but it is acceptable. The limited quality of fit could be due to four possible reasons: (1) insufficient data points lead to significant errors in the values of the fitting parameters C_s and K obtained using the method employed; (2) the V_0 values, which we obtained from sorption isotherm and swelling data for similar but nonetheless different Bowen Basin coal, might lead to errors; (3) the experimental swelling data presented by Day et al. [14] pertain to rather large samples ($30 \text{ mm} \times 9 \text{ mm} \times 9 \text{ mm}$) that might not have fully equilibrated with respect to changing gas mixture composition, leading to low measured swelling values; (4) interactions between CO_2 and CH_4 in the sorption process might be not negligible, though we assume them to be so in our modeling approach [18,31]. Under point 3 above, we do not wish to imply any shortcomings in the approach adopted by Day et al. in their truly excellent work, but note that numerous previous experiments show incomplete equilibrium effects caused by either long equilibration time [14–16] or the change of transport path due to swelling effect [31–33]. This means that more experimental data using samples of different sizes and longer equilibration times are required to evaluate our models thoroughly.

In addition, the present models focus on unconfined coal, without considering the effects of in-situ stress. However, both lithostatic stress and self-stressing due to laterally constrained swelling [9], under in situ conditions, reduce the adsorption

capacity of coal for pure CO_2 and pure CH_4 [9,24,34], thus influencing stress–strain development, cleat aperture evolution [35] and hence permeability change [36] during CO_2 –ECBM production. This means that a further constitutive model that fully couples stress–strain–sorption behaviour of coal exposed to mixed gases should be considered in future work. Moreover, building upon the studies by Nikoosokhan et al. [35] and Espinoza et al. [36], both experimental data and coupled models are needed, linking permeability to the stress–strain–sorption behaviour of stressed coal exposed to mixed gases.

5. Conclusions

This paper has constructed thermodynamic models for adsorption induced swelling of unconfined coal matrix material exposed to a binary gas/fluid mixture, based on the adsorption-induced swelling model for unconfined coal exposed to a single pure gas or fluid proposed by Hol et al. [9].

Three models were derived corresponding to three physical possible end-member interactions. These were also cast as a fourth, generalized model. Model 1 addresses the independent adsorption sites. Adsorption of gas/fluid species α and β accordingly leads to independent swelling responses that sum to give total volumetric strain. Model 2 describes the adsorption-induced swelling of coal exposed to a binary gas/fluid mixture when adsorption sites are fully shared by each component. This model is thermodynamically equivalent to the extended Langmuir model for ideal gases. When applied for ideal gases (low pressure), the adsorbed concentrations predicted reduce to the Langmuir isotherm for mixed gases. Model 3 addresses Type I partially shared adsorption sites for an end-member case. This model implies that the swelling of coal matrix material due to adsorption of a binary gas/fluid mixture is determined both by partial pressures of sorbing gases and by truly selective adsorption effects. Model 4 describes Type II partially shared adsorption sites for the general case. This model covers Models 1–3.

When compared with experimental data on the swelling behaviour of sub-bituminous coal from the Bowen Basin, exposed to CH_4 – CO_2 mixtures, Model 3 is preferred. This finding illustrates that CH_4 is displaced by CO_2 due to both the reduction of CH_4 partial pressure (dilution of CH_4) in the mixed gas phase and selective adsorption of CO_2 . Our results therefore differ from previous suggestions that CH_4 and CO_2 have access to all adsorption sites and that swelling solely depends on partial pressure [8,14], or that swelling solely depends on site accessibility [17]. Since Model 3 is easy to parameterize, it can be easily applied in practice to predict the swelling behaviour of coal exposed to CH_4 – CO_2 mixture during ECBM production, at least to sub-bituminous coals similar to those of the Bowen Basin. Our results further imply that Model 3 should be the most suitable for evaluating if CO_2 – N_2 mixtures will be effective in limiting coal swelling and permeability reduction in ECBM operations in sub-bituminous coals, such as those of the Bowen Basin. On the other hand, our generalized model, Model 4, can be widely applied to any coal rank, to any binary gas mixture and to any PT conditions, provided that proper parameter values are available. Model 4 therefore offers an important tool for modeling swelling and permeability evolution during ECBM operations, and through it, generality may prove to explain why sorption and swelling of some coals seem to be dominated by partial pressure effects and others by selective sorption effects.

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References

- [1] White CM, Smith DH, Jones KL, et al. Sequestration of carbon dioxide in coal with enhanced coalbed methane recovery a review. *Energy Fuels* 2005;19:659–724.
- [2] Busch A, Gensterblum Y. CBM and CO₂-ECBM related sorption processes in coal: a review. *Int J Coal Geol* 2011;87:49–71.
- [3] Fujioka M, Yamaguchi S, Nako M. CO₂-ECBM field tests in the Ishikari coal basin of Japan. *Int J Coal Geol* 2010;82:287–98.
- [4] van Bergen F, Krzysiolik P, van Wageningen N, et al. Production of gas from coal seams in the Upper Silesian Coal Basin in Poland in the post-injection period of an ECBM pilot site. *Int J Coal Geol* 2009;77:175–87.
- [5] Reeves SR. The coal-seq project: key results from field, laboratory and modeling studies; 2004. p. 1399–406.
- [6] van Bergen F, Pagnier H, Krzysiolik P. Field experiment of enhanced coalbed methane-CO₂ in the upper silesian basin of Poland. *Environ Geosci* 2006;13:201–24.
- [7] Day S, Fry R, Sakurovs R. Swelling of Australian coals in supercritical CO₂. *Int J Coal Geol* 2008;74:41–52.
- [8] Day S, Sakurovs R, Weir S. Supercritical gas sorption on moist coals. *Int J Coal Geol* 2008;74:203–14.
- [9] Hol S, Peach CJ, Spiers CJ. Effect of 3-D stress state on adsorption of CO₂ by coal. *Int J Coal Geol* 2012.
- [10] Pan Z, Connell LD. A theoretical model for gas adsorption-induced coal swelling. *Int J Coal Geol* 2007;69:243–52.
- [11] van Bergen F, Spiers C, Floor G, Bots P. Strain development in unconfined coals exposed to CO₂, CH₄ and Ar: effect of moisture. *Int J Coal Geol* 2009;77:43–53.
- [12] Vandamme M, Brochard L, Lecampion B, Coussy O. Adsorption and strain: the CO₂-induced swelling of coal. *J Mech Phys Solids* 2010;58:1489–505.
- [13] Busch A, Gensterblum Y, Krooss BM. Methane and CO₂ sorption and desorption measurements on dry Argonne premium coals: pure components and mixtures. *Int J Coal Geol* 2003;55:205–24.
- [14] Day S, Fry R, Sakurovs R. Swelling of coal in carbon dioxide, methane and their mixtures. *Int J Coal Geol* 2012.
- [15] Majewska Z, Ceglarska-Stefańska G, Majewski S, Ziętek J. Binary gas sorption/desorption experiments on a bituminous coal: simultaneous measurements on sorption kinetics, volumetric strain and acoustic emission. *Int J Coal Geol* 2009;77:90–102.
- [16] Czerw K. Methane and carbon dioxide sorption/desorption on bituminous coal – experiments on cubicoid sample cut from the primal coal lump. *Int J Coal Geol* 2011;85:72–7.
- [17] Busch A, Gensterblum Y, Krooss BM, Siemons N. Investigation of high-pressure selective adsorption/desorption behaviour of CO₂ and CH₄ on coals: an experimental study. *Int J Coal Geol* 2006;66:53–68.
- [18] Brochard L, Vandamme M, Pellenq RJ, Fen-Chong T. Adsorption-induced deformation of microporous materials: coal swelling induced by CO₂-CH₄ competitive adsorption. *Langmuir* 2012;28:2659–70.
- [19] Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J Am Chem Soc* 1918;40:1361–403.
- [20] Pan Z, Connell LD. Comparison of adsorption models in reservoir simulation of enhanced coalbed methane recovery and CO₂ sequestration in coal. *Int J Greenhouse Gas Control* 2009;3:77–89.
- [21] Do DD. Adsorption analysis: equilibria and kinetics. World Scientific; 1998.
- [22] Hol S, Spiers CJ. Competition between adsorption-induced swelling and elastic compression of coal at CO₂ pressures up to 100 MPa. *J Mech Phys Solids* 2012.
- [23] Tuin G, Stein H. The excess Gibbs free energy of adsorption of sodium dodecylbenzenesulfonate on polystyrene particles. *Langmuir* 1995;11:1284–90.
- [24] Hol S, Peach CJ, Spiers CJ. Applied stress reduces the CO₂ sorption capacity of coal. *Int J Coal Geol* 2011;85:128–42.
- [25] Ottiger S, Pini R, Storti G, Mazzotti M. Measuring and modeling the competitive adsorption of CO₂, CH₄, and N₂ on a dry coal. *Langmuir* 2008;24:9531–40.
- [26] Gensterblum Y, Busch A, Krooss BM. Molecular concept and experimental evidence of competitive adsorption of H₂O, CO₂ and CH₄ on organic material. *Fuel* 2014;115:581–8.
- [27] Day S, Fry R, Sakurovs R, Weir S. Swelling of coals by supercritical gases and its relationship to sorption. *Energy Fuels* 2010;24:2777–83.
- [28] Span R, Wagner W. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. *J Phys Chem Ref Data* 1996;25.
- [29] Setzmann U, Wagner W. A new equation of state and tables of thermodynamic properties for methane covering the range from the melting line to 625 K at pressures up to 1000 MPa. *J Phys Chem Ref Data* 1991;20:1061–155.
- [30] Kunz O, Klimeck R, Wagner W, Jaeschke M. The GERG-2004 wide-range reference equation of state for natural gases and other mixtures. *Fortschr. Ber.VDI: VDI-Verlag, Düsseldorf*; 2006. p. 1.
- [31] Kowalczyk P, Ciach A, Neimark AV. Adsorption-induced deformation of microporous carbons: pore size distribution effect. *Langmuir* 2008;24:6603–8.
- [32] Peng Y, Liu J, Wei M, Pan Z, Connell LD. Why coal permeability changes under free swellings: new insights. *Int J Coal Geol* 2014;133:35–46.
- [33] Hol S, Spiers CJ, Peach CJ. Microfracturing of coal due to interaction with CO₂ under unconfined conditions. *Fuel* 2012;97:569–84.
- [34] Pone JDN, Halleck PM, Mathews JP. Sorption capacity and sorption kinetic measurements of CO₂ and CH₄ in confined and unconfined bituminous coal. *Energy Fuels* 2009;23:4688–95.
- [35] Nikoosokhan S, Vandamme M, Dangla P. A poromechanical model for coal seams saturated with binary mixtures of CH₄ and CO₂. *J Mech Phys Solids* 2014;71:97–111.
- [36] Espinoza D, Vandamme M, Pereira J, Dangla P, Vidal-Gilbert S. Measurement and modeling of adsorptive-poromechanical properties of bituminous coal cores exposed to CO₂: adsorption, swelling strains, swelling stresses and impact on fracture permeability. *Int J Coal Geol* 2014;134:80–95.