



## Thermodynamic model for swelling of unconfined coal due to adsorption of mixed gases

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Permeability evolution in coal reservoirs during CO<sub>2</sub>-Enhanced Coalbed Methane (ECBM) production is strongly influenced by swelling/shrinkage effects related to sorption and desorption of both CO<sub>2</sub> and CH<sub>4</sub>. Other gases, such as N<sub>2</sub>, may perhaps also be used in ECBM operations. Much work has been done on the sorption/swelling response of coal to the pure gases. However, there is a clear need for an improved understanding of swelling behaviour of coal matrix material as a result of mixed gas adsorption. We therefore constructed a thermodynamic model for swelling of unconfined coal due to mixed gases adsorption, considering the equilibrium state (swelling strain  $e_{ads}^{eq}$ ), focusing initially on a binary gas mixture. Following Hol et al (2012, IJCG, 93, 1-15), we started with the following basic assumptions: a) nanoporous coal matrix material only allows diffusion and adsorption, b) the matrix hosts  $n_s^i$  ( $i=\alpha, \beta$ ) localised adsorption sites for the two gas components  $\alpha$  and  $\beta$ , c) the material is homogeneous in structure and composition but may be anisotropic in properties as appropriate for natural coal, d) adsorption is allowed to proceed until equilibrium is reached, at which point the chemical potential of the adsorbed component  $i$  is equal to the potential of the free component phase  $i$ , and e) the volume change (strain) associated with adsorption of one molecule of component  $i$  is insensitive to the adsorbed concentration of either component. Three models were derived corresponding to three possible interactions:

- 1) Isolated adsorption sites model. This assumes that each component has its own specific adsorption sites. Adsorption of  $\alpha$  and  $\beta$  accordingly leads to independent swelling responses that sum to give total volumetric strain.
- 2) Shared adsorption sites model. This postulates that both gases have full access to all adsorption sites ( $n_s^\alpha = n_s^\beta = n_s$ ). This model is thermodynamically equivalent to the Extended Langmuir model. If the free fluids behave as ideal gases, the adsorbed concentrations predicted reduce to the Langmuir isotherm for mixed gases.
- 3) Preferential adsorption sites model. This assumes adsorption sites show selectivity towards one gas, i.e.  $n_s^\alpha$  adsorption sites can be occupied by both gases (*cf.* 2) while only  $(n_s^\alpha - n_s^\beta)$  adsorption sites can be occupied by gas  $\beta$  (*cf.* 1). This model can be treated as a combination of Models 1 and 2.

We compared these models to experimental measurements of swelling of an Australian sub-bituminous coal exposed to CH<sub>4</sub>, CO<sub>2</sub> and to their mixtures at pressures up to 15 MPa, performed by Day et al. (2012, IJCG, 93, 40-48). Compared to other two models, the preferential adsorption sites model describes the experimental results best. This finding complies with the conventional view that CH<sub>4</sub> is displaced by CO<sub>2</sub> due to both depletion of CH<sub>4</sub> partial pressure and preferential CO<sub>2</sub> adsorption. However, our findings contradict the proposal by Day et al., based on their experiments, that CH<sub>4</sub> and CO<sub>2</sub> have access to all adsorption sites and that swelling solely depends on partial pressures. Additional experiments on different rank coals and gas species are underway to evaluate our models further.