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Experimental and modeling investigations of adsorption-induced swelling and damage in microporous materials

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Abstract

The purpose of this work is to achieve a better understanding of the coupling between adsorption and swelling in microporous materials. This is typically of utmost importance in the enhancement of non-conventional reservoirs or in the valorization of CO_2 geological storage. We consider here the case of fully saturated porous solids with pores down to the nanometer size ($\leq$ 2nm). Hardened cement paste, tight rocks, activated carbon or coal are among those materials. Experimentally, different authors tried to combine gas adsorption results and volumetric swelling data, especially for bituminous coal. However, most results in the literature are not complete in a sense that the adsorption experiments and the swelling experiments were not performed on the exact same coal sample. Other authors present simultaneous in-situ adsorption and swelling results but the volumetric strain is extrapolated from a local measurement on the surface sample or by monitoring the two-dimensional silhouette expansion. Only elastic and reversible swellings are reported in the literature. Theoretically, most continuum approaches to swelling upon adsorption of gas rely on a coupling between the adsorption isotherms and the mechanical deformation. A new poromechanical framework has been recently proposed to express the swelling increment as a function of the increment of bulk pressure with constant porosity. However, this framework has to be extended to take into account the porosity evolution upon swelling. This paper aims at presenting a new experimental set-up where both adsorption and strain are measured in-situ and simultaneously and where the full-field swelling is monitored by digital image correlation. Permanent strain and damage are observed. On the other hand, we present an extended poromechanical framework where the porosity is variable upon swelling. A new incremental nonlinear scheme is proposed where the poromechanical properties are updated at each incremental pressure step, depending on the porosity changes. Interactions between swelling and the adsorption isotherms are examined and a correction to the classical Gibbs formalism is proposed. Predicted swellings are compared with results from the literature.

Keywords: Poromechanics; swelling; adsorption; microporous materials

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1. Introduction

The mechanical response of porous solids saturated with a fluid phase is investigated with the help of poromechanics. We consider here the case of fully saturated porous solids and focus on *nanoporous* (or *microporous* following the IUPAC[1] recommendation) materials, e.g. solids with pores down to the nanometer size ($\leq 2nm$). Hardened cement paste, tight rocks, activated carbon or coal are among those materials. For these materials, a deviation from standard poromechanics is expected. In very small pores, the molecules of fluid are confined. Interaction between molecules is modified. This effect, denoted as molecular packing, includes fluid-fluid and fluid-solid interactions. Furthermore, adsorption is important because the inner surface of the pore is very large compared to the volume of fluid contained inside the pore.

Experimentally, different authors tried to combine gas adsorption results and volumetric swelling data, especially for bituminous coal, because it is of utmost importance in the context of CO_2 geological sequestration and coal bed reservoirs exploitation. Indeed, in situ adsorption-induced coal swelling has been identified as the principal factor leading to a rapid decrease of CO_2 injectivity during enhanced coal bed methane production by CO_2 injection. The coal swelling may close the cleat system and reduce the global permeability. However, most results in the literature are not complete in a sense that the adsorption experiments and the swelling experiments were not performed on the exact same coal sample (Ottiger et al., 2008). Other authors present simultaneous in-situ adsorption and swelling results but the volumetric strain is extrapolated from a local measurement on the surface sample or by monitoring the two-dimensional silhouette expansion (Day et al., 2008). Only elastic and reversible swellings are reported in the literature.

Theoretically, most continuum approaches to swelling of microporous materials upon adsorption of gas rely on a coupling between the adsorption isotherms and the mechanical deformation. For saturated isotropic nano-porous solids, in reversible and isothermal conditions, Vermorel and Pijaudier-Cabot (2014) proposed an expression of the swelling volumetric deformation increment as a function of the increment of bulk pressure, and depending on a confinement coefficient which refers to the interstitial fluid high density compared to the bulk fluid. Vermorel and Pijaudier-Cabot (2014) show that the effective pore pressure and the swelling strains may be deduced from adsorption measurements. In the Gibbs adsorption framework, the Gibbs adsorption isotherm stands as a measurement of the number of adsorbate moles that exceeds the number of fluid moles at bulk conditions. Within this framework, they observed a fair agreement between the fit of the theoretical predictions and several sets of experimental data found in the literature. Particularly, it has been shown that the model parameters (porosity, apparent modulus and skeleton modulus) may be fitted to recover the swelling and adsorption measurement data obtained by Ottiger et al. (2008) on bituminous coal samples filled with pure CO_2 at $T = 45^oC$. At pressure up to $P_b = 7MPa$, a volumetric swelling strain of $\varepsilon \approx 3.5\%$ was observed. The fitted parameters did not match exactly the exact poromechanical properties of the coal tested by Ottiger et al. (2008) but were consistent with coal poromechanical properties reported in the literature. However, these properties were globally fitted on the whole swelling versus bulk pressure curve and thus they were supposed to be constant upon swelling. The porosity evolution may be evaluated within the same poromechanical framework and a relative increase of the porosity in the order of 30% (from 0.12 to ≈ 0.16) is predicted which is not negligible. In these conditions, the poromechanical properties should vary upon swelling and thus the poromechanical framework should be extended to take into account these variations.

This paper is organized as follows: in the first section, In the first section, we present an extension of the latter poromechanical framework where the porosity is variable upon swelling. A new incremental nonlinear scheme is proposed where the poromechanical properties (e.g. elastic properties and Biot coefficient) are updated at each incremental pressure step, depending on the porosity changes. The model is validated by comparing the predicted swelling with results obtained by Ottiger et al. (2008) on bituminous coal samples filled both with pure CO_2 and pure CH_4 at $T = 45^oC$. Comparisons with the experimental swelling do fairly agree even if the adsorption experiments and the swelling experiments were not performed simultaneously nor on the exact same coal sample. In order to have a better understanding on the coupling between adsorption and swelling on microporous material, we present in the second section a new experimental set-up where both adsorption and strain are measured in-situ and simultaneously and where the full-field swelling is monitored by digital image correlation.

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[1] International Union of Pure and Applied Chemistry

2. Extended poromechanical model with varying porosity

2.1. Poromechanical framework

Recently, Perrier et al. (2014) proposed a new poromechanical model for estimating swelling of nano-porous media fully saturated with a fluid phase. From the Gibbs adsorption isotherm, the effective pore pressure and the volumetric strain are estimated incrementally taking into account the variations of porosity upon swelling and therefore the variations of the poromechanical properties (apparent modulus, Biot coefficient, Biot modulus). Moreover the interaction between swelling and the adsorption isotherms are examined by proposing a correction to the Gibbs formalism by taking into account the pore volume variation upon swelling. Details may be found in Perrier et al. (2014) but the main results are presented here in order to illustrate how this new poromechanical model may be used to predict adsorption-induced swelling.

The poromechanical model proposed by Vermorel and Pijaudier-Cabot (2014) for constant porosity is rewritten in an incremental form to take into account the variation of the porosity upon swelling. At each bulk pressure step, a non-linear scheme is used to predict the porosity increment, the new poromechanical properties and the induced swelling strain increment depending on the adsorption measurements (see Eq. 1).

$$d\varepsilon = \left(\frac{b(\phi)}{1-\chi} - 1\right)\frac{dP_b}{K(\phi)} \quad ; \quad d\phi = \left(\frac{K(\phi)}{b(\phi)-(1-\chi)} + b(\phi)N(\phi)\right)\frac{d\varepsilon}{N(\phi)} \quad ; \quad b(\phi) = 1 - \frac{K(\phi)}{K_s} \quad ; \quad N(\phi) = \frac{K_s}{b(\phi)-\phi} \quad (1)$$

where ϕ is the varying porosity, ε is the swelling strain, $K(\phi)$ is the apparent modulus of incompressibility, $b(\phi)$ is the Biot coefficient, $N(\phi)$ is the Biot modulus, K_s the skeleton matrix modulus, P_b is the bulk pressure and $\chi = 1 - \frac{\rho_b}{\rho_f}$ is the confinement coefficient which refers to the confinement degree of the interstitial fluid at density ρ_f compared to the bulk fluid at density ρ_b.

It has been shown by Vermorel and Pijaudier-Cabot (2014) that the confinement coefficient may be deduced from adsorption measurements. In the Gibbs adsorption framework, the Gibbs adsorption isotherm stands as a measurement of the number n_{ex} of adsorbate moles that exceeds the number of fluid moles at bulk conditions. If n_{tot} denotes the total number of moles of interstitial fluid, the confinement coefficient may be expressed as:

$$\chi = \frac{n_{ex}}{n_{tot}} \quad (2)$$

In the classical Gibbs formalism, the porosity is considered to be constant and n_{tot} is given by:

$$n_{tot} \approx n_{ex} + \frac{\rho_b V_\phi^0}{M} = n_{ex} + \left(\frac{\phi_0}{1-\phi_0}\right)\frac{m_s}{M}\frac{\rho_b}{\rho_s} \quad (3)$$

where V_ϕ^0 is the initial connected porous volume of the material, M the molar mass of the adsorbed gas, m_s the adsorbent sample mass and ρ_s the density of material composing the solid matrix of the porous adsorbent.

However, if the volumetric swelling of the material reaches tenths of percent or even several percents, as respectively observed in coal by Meehan (1927); Bangham and Fakhoury (1928); Levine (1996) and by Ottiger et al. (2008); Day et al. (2008), the increase of pore surface may be also significative. Therefore the latter expression has to be corrected in order to take into account the pore volume variation:

$$n_{tot}(\phi) = n_{ex} + \frac{\rho_b V_\phi}{M} = n_{ex} + \left(\frac{\phi}{1-\phi}\right)\frac{m_s}{M}\frac{\rho_b}{\rho_s} \quad (4)$$

where V_ϕ is the current connected porous volume of the material upon swelling and ϕ the updated porosity through Eq 1. Note that under this corrected Gibbs formalism, the confinement coefficient (Eq. **??**) explicitly depends on the porosity and is thus incrementally estimated to predict the swelling strain through Eq. 1.

A change in the porosity leads to a change of the apparent modulus K upon swelling and therefore an homogenization model has to be adopted to relate the porosity, the apparent modulus and the skeleton matrix modulus depending on the pore size geometry. Assuming that the porosity is spherical, the homogenization model proposed by Mori and Tanaka is used to describe the variation of the apparent modulus with the porosity. Assuming that the porosity is

cylindrical, an homogenization model based on Halpin-Tsai equations is preferred. Note that, in most of cases, the actual porosity shape is in between the sphere and the cylinder so that the two models may be seen as upper and lower bounds. Note that it has been shown by Barboura (2007) that such homogenization scheme may lead to discrepancies for media presenting a high porosity. Therefore she proposed an iterative process of homogenization which able to recover a relevant homogenized behavior even for high porosity. The iterative process of homogenization is presented in (Perrier et al., 2014).

Spherical porosity.
Following the Mori-Tanaka homogenization technique Mori and Tanaka (1973), the expressions for the homogenized mechanical properties of a porous media with a spherical porosity depending on the skeleton materials properties are:

$$K^{MT}(\phi) = \frac{4K_s G_s (1-\phi)}{4G_s + 3K_s \phi} \ , \ G_s = \frac{3K_s(1-2\nu_s)}{2(1+\nu_s)} \tag{5}$$

where G_s and ν_s are respectively the shear modulus and the Poisson ratio of the skeleton matrix.

Cylindrical porosity.
For fiber-reinforced composites, Halpin and Kardos (1976) provide expression for the homogenized mechanical properties depending on both the matrix and the cylindrical fibers materials properties. For a porous medium with a cylindrical porosity, these expressions are adapted by considering cylindrical voids instead of cylindrical fibers:

$$K^{HT}(\phi) = \frac{K_s G_s (1-\phi)}{G_s + K_s \phi} \ , \ G_s = \frac{3K_s(1-2\nu_s)}{2(1+\nu_s)} \tag{6}$$

2.2. Results and comparisons with experimental results from the literature

From the experimental measurements of exceeding adsorbate quantities Ottiger et al. (2008), the swelling strain is estimated through Eq.1 for the Halpin-Tsai homogenization schemes (Eq. 6). Indeed, the Halpin-Tsai scheme based on a cylindrical porosity is a better representative of the actual porosity of the natural coal sample tested by Ottiger et al. (2008). Details on the poromechanical properties identification may be found in Perrier et al. (2014).

Fig. 1.a presents the exceeding adsorbate quantities measured by Ottiger et al. (2008) for both pure CH_4 and pure CO_2 at $T = 45^o C$ and the estimated total number of moles of interstitial fluid estimated through Eq. 7 for a variable porosity. It is found classically that the CO_2 adsorption capacity of coal are twice the CH_4 adsorption capacity.

Fig. 2.b presents the comparison between the volumetric strain measured by Ottiger et al. (2008) and the predicted swelling strain for both pure CH_4 and pure CO_2 at $T = 45^o C$. A swelling strain of $\approx 3.5\%$ is recovered for a CO_2 bulk pressure up to $7MPa$, whereas a swelling strain of $\approx 1.7\%$ is recovered for a CH_4 bulk pressure up to $12MPa$ and a fair agreement with the experimental measurements is observed.
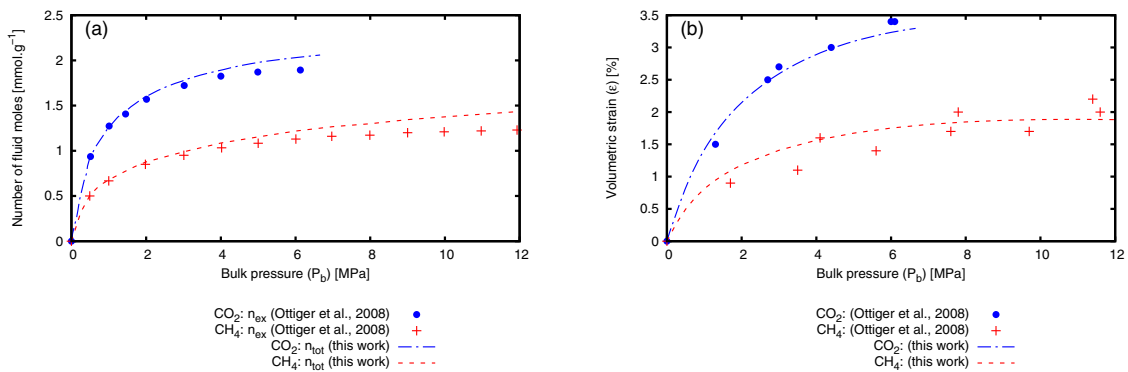

Fig. 1. (a) Evolution of the measured exceeding adsorbate quantities and the estimated total number of moles of interstitial fluid for a variable porosity; (b) Comparison between the volumetric strain measured by Ottiger et al. (2008) and the predicted swelling strain. Data reproduced from Perrier et al. (2014).

3. A new experimental set-up allowing the simultaneous in-situ measurements of both adsorption and swelling

As noted by Ottiger and co-workers, the adsorption experiments and the swelling experiments presented in Ottiger et al. (2008) were not performed on the exact same coal sample. Indeed, the coal samples were drilled in the same coal mine but not at the same time and the same precise location. Therefore the extrapolation of the results presented should be done cautiously. The fair agreement of the model with the experiments is encouraging but there is a need of additional experimental data of *simultaneous* gas adsorption and swelling for a complete validation. In this section, a new experimental set-up allowing the simultaneous in-situ measurements of both adsorption and swelling is presented.

The experimental set-up couples adsorption measurements of excess quantities by a manometric technique and full-field displacement measurements based on a digital image correlation technique (Figure 2).

Adsorption measurements.
The adsorption isotherm is drawn step by step by estimating the excess adsorbed quantities for imposed increasing incremental pressure at thermal equilibrium. All volumes are initially calibrated with helium which does not adsorb on the substrate. At the pressure step *i*, the excess adsorbed quantities are given by:

$$n_{ex}^{(i)} = n_{ex}^{(i-1)} + \Delta n_{ex}^{(i)} = n_{ex}^{(i-1)} + \frac{\rho_D^{(i)} V_D}{M} - \frac{\rho_{eq}^{(i)}(V_D + V_M)}{M} \tag{7}$$

where $\rho_D^{(i)}$ is the gas density in the dosing cell (when the measuring cell is isolated, see Figure 2) estimated through the gas state equation knowing the dosing volume V_D and the dosing pressure P_D at the thermal equilibrium T_D, $\rho_{eq}^{(i)}$ is the gas density in the total volume knowing the total volume $V_D + V_M$ and the total pressure P_{eq} at the thermal equilibrium T_{eq} and M the molar mass of the adsorbed gas.

Full-field swelling measurements.
The swelling is estimated by digital image correlation technique (DIC) using the icasoft software (Morestin et al., 1996; Mguil-Touchal et al., 1996). This software has already been applied in various research domain such as dynamic fracture (Grégoire et al., 2009) or damage identification in biomaterials (Grégoire et al., 2011). DIC is used here to quantify the volumetric swelling by measuring the full-field displacement of the bottom-face of the measuring cell (see Figure 2). Practically, different images corresponding to a reference and different deformed states are acquired by the camera and described by discrete functions representing the grey level of each pixel. Then each displacement field corresponding to each deformed states are estimated by minimizing a cross-correlation coefficient on a set of initial image pixels. Details about the technique may be found in (Grégoire et al., 2009) or (Grégoire et al., 2011).

Preliminary results on active carbon.
Figure 2 presents preliminary results on simultaneous in-situ measurements of swelling and adsorption on activated carbon filled with pure CO_2 and pure CH_4 at $T = 30^oC$. We can observe that the adsorption and desorption isotherms are purely reversible whereas permanent strain is observed on the swelling response.
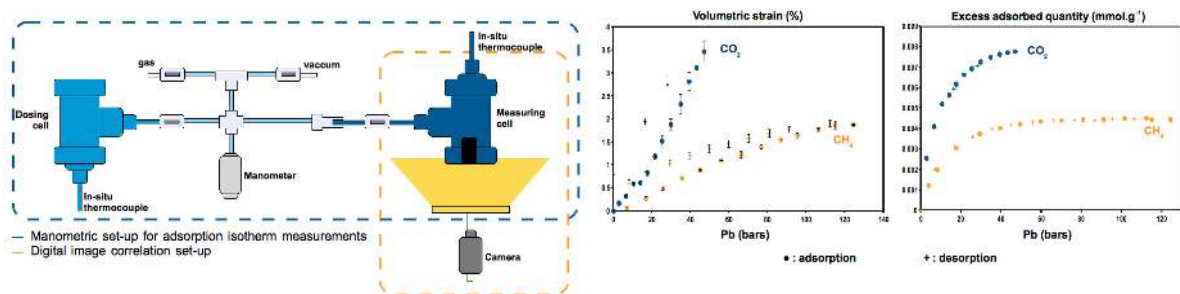

Fig. 2. Simultaneous in-situ measurements of swelling and adsorption on activated carbon filled with pure CO_2 and pure CH_4 at $T = 30^oC$.

4. Concluding remarks

- A new incremental poromechanical framework with varying porosity has been proposed allowing the prediction of the swelling induced by adsorption.
- The proposed model has been compared with experimental data obtained by Ottiger et al. (2008) on bituminous coal samples filled with pure CH_4 and pure CO_2 at $T = 45^oC$ and a fair agreement is observed. A swelling strain of $\approx 3.5\%$ is recovered for a CO_2 bulk pressure up to $7MPa$ and a swelling strain of $\approx 1.7\%$ is recovered for a CH_4 bulk pressure up to $12MPa$.
- A correction to the classical Gibbs formalism has been proposed to take into account the variations of porosity and to quantify the influence of the deformation of the porous structure on the adsorption isotherm. Upon swelling and assuming that the porous volume changes, the total number of interstitial fluid is corrected by taking into account the updated porosity.
- As noted by Ottiger and co-workers, the adsorption experiments and the swelling experiments presented in Ottiger et al. (2008) were not performed on the exact same coal sample. Indeed, the coal samples were drilled in the same coal mine but not at the same time and the same precise location. Therefore the extrapolation of the results presented should be done cautiously. Therefore a new experimental set-up allowing the simultaneous in-situ measurements of both adsorption and swelling has been developed.
- Preliminary results on simultaneous in-situ measurements of swelling and adsorption on activated carbon filled with pure CO_2 and pure CH_4 at $T = 30^oC$ have been presented. A swelling strain of $\approx 3.5\%$ is recovered for a CO_2 bulk pressure up to $5MPa$ and a swelling strain of $\approx 1.7\%$ is recovered for a CH_4 bulk pressure up to $12MPa$. Permanent strain and damage are observed.

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