Poroelastic and Adsorptive Properties of Activated Carbon



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ABSTRACT: The characterization of petrophysical and geomechanical properties of source rocks presents inherent challenges due to lithology heterogeneity, lamination, distribution of organic matter, and presence of fractures. Organic-rich shales also present some distinctive features that make hydrocarbon production and CO_2 geological storage unique in these rocks. The objective of this paper is to quantify and model the deformational behavior of carbon-based compounds due to changes of stress and pressure that happen simultaneously with gas adsorption and desorption processes. We designed an experimental procedure that consists of: (1) compaction of organic-rich grains/powder under oedometric conditions, (2) measurement of poromechanical properties in the absence of adsorption effects using helium in a triaxial cell through independent changes of confining pressure and pore pressure, (3) measurement of the adsorption strain, and stress for methane (CH₄). An adsorptive-poromechanical model permits explaining the experimental data, discriminating between the strain/stress caused by poroelastic response from the adsorption-induced strain/stress, and measuring the poroelastic-sorption properties of the organic-rich compound. We applied this procedure to activated carbon and measured skeletal volumetric modulus ranging from 11.8 to 16.6 GPa and skeletal adsorption stress of ~100 MPa for CH₄ at 7 MPa of adsorbate pressure. The proposed procedure and model are useful to explain and predict the unique properties of carbon-based adsorbents which can be extended to kerogen, a critical component in source rocks.

1. INTRODUCTION

Reserves estimation and gas flow rate prediction are more challenging for organic-rich rocks than for conventional gas reservoirs. These challenges are not only limited to characterization of petrophysical and geomechanical properties (i.e., lithology heterogeneity, lamination, total organic content and, the presence of fractures) but also to capturing the physics that governs these processes. Gas adsorption heavily affects the estimation of the original gas in place (Moore et al., 2012). Organic-rich surfaces can adsorb various gas molecules (N₂, CH₄ and CO₂ among others) increasing vastly the storage capacity in organic-rich rocks (Busch and Gensterblum, 2011).

Changes in surface energy caused by gas adsorption can result in bulk solid strains and stresses (Ravikovitch and Neimark, 2006; Vandamme et al., 2010; Gor et al. 2017). This coupled mechanical-adsorptive response can also happen in organic-rich rocks (Espinoza et al., 2016). such as in coal beds, where it increases productivity of wells (Moore et al., 2012). This unusual behavior includes an exponential increase in permeability (up to 100) with decreasing reservoir pressure. Conversely, injection of gases such as CO_2 can produce a significant decrease of permeability (Espinoza et al., 2016). Fig. 1 illustrates the effect of adsorption–induced deformation (adapted from Gor et al. 2017). Fig. 1a shows reversible opening and closing of an adsorbent membrane caused by changes in air humidity. Fig. 1b exemplifies swelling of zeolite crystals due to adsorption, which leads to reduction of pore space.



Fig. 1. (a) Reversible closing and opening of a star-shaped membrane actuator 'flower' (after Zhao et al., 2014). (b) Schematic of adsorption-induced swelling in Zeolite crystals (after Yu et al., 2011).

The objective of this paper is to present a procedure to characterize the adsorptive-poromechanical properties of a granular or powder adsorbents. First, the paper describes the measurement of poromechanical response in the presence of helium and one adsorbate (methane CH₄). Second, we propose a model for data analysis and calculate the model parameters that fully explain the adsorptive-poromechanical response measured in the laboratory.

2. MATERIALS AND METHODS

2.1. Adsorbent Sample

We use medical grade activated carbon made from coconut shells provided by Envirosupply & Service. The coal particles have a total surface area $1150 - 1250 \text{ m}^2/\text{g}$, maximum ash content of 3% and apparent density $0.50 - 0.52 \text{ g/cm}^3$. The granular material passes sieve #20 (841 μ m) and is retained by sieve #80 (177 μ m). We precompacted the sample with an oedometer frame up to 7.6 MPa of axial stress (Fig. 2). Pre-compaction is required to improve the accuracy of adsorption stress measurement (Espinoza et al., 2016).

2.2. Compaction and Poromechanical Testing

The compaction procedure is conducted under oedometric conditions. Increasing effective axial stress decreases sample porosity. The macroporosity represents the volume outside activated carbon grains (ranging in size from 177 to 841 μ m), i.e., excludes mesoporosity and microporosity within activated carbon grains. The macroporosity reduces to 0.12 at the maximum compaction load (7.6 MPa). The (virgin) loading constrained modulus at the highest load is M = 45 MPa.

$$M = \left(\frac{\Delta \sigma'_{ZZ}}{\Delta \varepsilon_{ZZ}}\right)_{\varepsilon_{XX}, \varepsilon_{YY} = cst} \tag{1}$$

Where σ'_{zz} is Terzaghi effective vertical stresses, ε_{xx} , ε_{yy} are horizontal strains, and ε_{zz} is the vertical strain. For uniaxial strain tests, ε_{xx} , $\varepsilon_{yy} = 0$, and the volumetric strain reduces to $\varepsilon_{vol} = \varepsilon_{zz}$. The unloading process implies elastic recovery. The sample length after removing the entire load was 51.1 mm.



Fig. 2. Compaction results of granular activated carbon. The macroporosity represents the void space between particles. Total porosity includes intergranular and intragranular porosity.

After compacting the sample, we used a triaxial cell able to apply independently mean total stress (through confining pressure equal to $-\sigma_m$) and pore pressure *P*. A set of displacement transducers attached to the sample let measure strains. The device takes samples of approximately 2.5 cm diameter by 5 cm in length (1-in by 2-in). Fig. 2 shows the compaction results for Sample 7A. The initial dimensions are diameter = 24 mm, length = 61.4 mm, total porosity = 0.71 and macroporosity = 0.34. We used research grade Helium gas to perform the pore pressure loading without sorption and methane to apply pore pressure loading with an adsorbate. We initially applied vacuum to the sample to extract adsorbed gas and vapor molecules at ambient conditions.

2.3. Theoretical Framework

The relationship between mean total stress, volumetric strain, and fluid pressure for a poroelastic solid -in the absence of adsorption effects- is (Coussy, 2011):

$$\sigma_m = \varepsilon_{vol} K - \alpha P \tag{2}$$

Where σ_m is the mean total stress, ε_{vol} is the volumetric strain, *K* is the drained bulk modulus, *P* is the pore fluid pressure and α is the Biot coefficient. Parameters *K* and α are two basic poromechanical properties.

Alternatively, we can write this equation for a porous solid that generates adsorption-induced stresses and strains as follows:

$$\sigma_m = K\varepsilon_{vol} - s(P) \tag{3}$$

where s(P) represents a function of fluid pressure. Let us define the stress function s(P) as the summation of the "bulk adsorption stress" $s^{a}(P)$ and the response expected for a non-sorbing fluid, such that $s(P) = s^{a}(P) + aP$, where a is the Biot coefficient measured for helium (Eq. 2). A rigorous extension of Gibbs excess adsorption thermodynamics interprets $s^{a}(P)$ as the "derivative of the excess grand thermodynamic potential of the adsorbed phase" (Neimark, 2017). In the case of coal, exposed to CH₄, $s^{a}(P)$ is highly nonlinear, is linked to excess adsorption, and is greater than bulk fluid pressure $s^{a}(P) > P$.

We performed jacketed triaxial tests with alternating cycles of confining pressure $(-\sigma_m)$ and fluid pressure change *P* (Gueguen and Bouteca, 1999). The main variable to measure is volumetric strain, which in the context of Eq. 3 is

$$\varepsilon_{vol} = \frac{1}{K} [\sigma_m + s^a(P) + \alpha P] \tag{4}$$

We can re-write the Eq. (4) using the definition of the Biot coefficient as follows:

$$\varepsilon_{vol} = \frac{1}{K}(\sigma_m + \alpha P) + \frac{1}{K_s} \left[\frac{s^a(P)}{1 - \alpha} \right]$$
(5)

The first term on the right-hand-side quantifies the strain caused by poroelastic deformation and the second term quantifies the adsorption-induced strain. Additional details are available elsewhere (Espinoza et al., 2016; Espinoza, 2022).

3. RESULTS

3.1. Measurement of Poromechanical Properties with Helium

Fig. 3 shows the measured poroelastic response of precompacted granular activated carbon to helium, i.e., in the absence of adsorption effects. We performed two cycles of stress and pore pressure loading, first at a range of 250-500 psi of Terzaghi effective stress, and then at 500-750 psi of Terzaghi effective stress.



Fig. 3. (a) Stress and pore pressure path to measure Biot coefficient. The procedure was carried at two levels of Terzaghi effective stress: 250–500 psi and 500-750 psi with Helium. (b) Stress, pore pressure and volumetric strain as a function of time.

Plotting the experimental data as suggested by Eq. (5) permits solving for the Biot coefficient α and bulk drained modulus *K* (notice that $s^{a}(P)$ is zero for helium in the absence of adsorption). Fig. shows the best-fit results for sample 7A subjected to helium pore pressure loading.

The results indicate a Biot coefficient $\alpha = 0.99$ to 0.98 and K = 166 to 236 MPa. Such low bulk modulus makes difficult to accurately determine the Biot coefficient. In addition, the theory of poroelasticity permits calculating the skeletal bulk modulus K_s of activated carbon.

$$K_s = \frac{K}{1 - \alpha} \tag{6}$$



Fig. 4. Biot effective stress and volumetric strain relationship for best obtaining the Biot coefficient α . The results are different because of material non-linearity with mean effective stress.

The experiments indicate a value $K_s = 11.8$ to 16.6 GPa. The values are comparable to the bulk modulus of common rock-forming minerals (5 to 30 GPa, Mavko, 2020), slit-shaped carbide-derived activated carbon (7 GPa, Kowalczyk et al., 2008), and coal matrix (3.9 to 5 GPa, Espinoza et al. 2016). The uncertainty of the calculated values is high due to the proximity of the Biot coefficient to one.

3.2. Measurement of Adsorption-induced Strain and Stress in the Presence of Methane (CH₄)

We measured the adsorptive response of the granular activated carbon described in Section 3.1 in the presence of CH_4 at ambient temperature following the stress-pore pressure path shown in Fig. 5a.



Fig. 5. (a) Stress and pore pressure path to measure adsorption properties of granular activated carbon in the presence of CH₄. Notice that volumetric strain continues changing after pore pressure P stabilizes. The full experiment goes through adsorption and desorption cycles. (b) The volumetric strain is not a sole function of either Terzaghi or Biot effective stress. The deviation is caused by adsorption-induced strains.

Unlike the response to helium, the adsorptive-mechanical response to CH₄ causes a complex deformational response which depends on $s^a(P)$. Let us discriminate between pressure outside activated carbon matrix P_f (pressure of fluid in intergranular pore space, where f stands for fractures in the context of fractured porous media) and pressure within the activated carbon grains (or matrix) P_m . These two pressures are equal at thermodynamic equilibrium. The equilibration time depends on the grain size, grain permeability, fluid viscosity, and adsorption kinetics. Using this nomenclature in Eq. 5 results in

$$\varepsilon_{vol} = \frac{1}{K} \left(\sigma_m + \alpha P_f \right) + \frac{1}{K_s} \left[\frac{s^a(P_m)}{1 - \alpha} \right] \tag{7}$$

where the only unknown is $s^{a}(P_{m})$ as long as the other properties are known (from Section 3.1). The volumetric

strain observed in Fig. 5b permits a direct estimation of adsorption stress following this procedure:

- 1) Calculate expected poroelastic strain due to change in effective stress with K and α obtained for helium.
- Calculate the adsorption-induced volumetric strain by subtracting the poroelastic strain from the total strain.
- 3) Calculate the incremental change of adsorption stress for each pore pressure increase, solving for $s^{a}(P)$.

The adsorption stress s^a is a nonlinear function of pressure P_m . Previous work shows that the adsorption stress can be calculated from excess sorption amount and a coefficient that quantifies the magnitude of adsorption-strain coupling (Espinoza et al., 2016). Here, we adopt a simplified approach to estimate adsorption stress independently of sorption amount by assuming an empirical equation for adsorption stress:

$$\frac{s^a(P_m)}{1-\alpha} = P_m + s^a_{max} \frac{P_m}{P_L + P_m} \tag{9}$$

where $[s^{a}(P_{m})/(1-\alpha)]$ is the "skeletal" or "matrix" adsorption stress, and the two fitting parameters are the asymptotic maximum adsorption stress s_{max}^{a} and Langmuir pressure P_{L} . This equation is motivated by previous theoretical work (Espinoza et al., 2016).

Fig. 6a shows the skeletal adsorption stress measured from experiments (from incremental volumetric strain in Fig. 5a not explained by poroelastic expansion) and the fitted model with Eq. (9). Similar to the estimation of K_s with helium, the determination of skeletal adsorption stress for granular activated carbon has a high uncertainty because it is calculated involving a division by $(1 - \alpha)$. The measured values in the order of ~100 MPa for CH₄ pressures up to 7 MPa agree with previous calculations for sorption stress in coal (Espinoza et al., 2016).

With the complete poromechanical characterization (K, α , and $s^{a}(P)$), it is possible to predict the full response of granular activated carbon subjected to changes of mean stress and pore pressure. Furthermore, we break down the changes of pore pressure into changes of P_{f} and P_{m} to capture separately poroelastic and adsorption responses. Fig. 6b shows the prediction of the model on top of the experimental data, with the following parameters:

- K = 235.9 MPa and $\alpha = 0.98$ from the Helium experiment.
- $s_{max}^a = 171.3$ MPa and $P_L = 5.64$ MPa, determined from the CH₄ experiment.



Fig. 6. (a) Skeletal adsorption stress of activated carbon in the presence of CH₄: experimental data and model. P_m is the CH₄ pressure in the matrix of activated carbon. (b) Full model prediction (Eq. 7) including changes of mean total stress (confining pressure in triaxial system) and CH₄ pore pressure.

The analytical model has an offset of $\varepsilon_{vol} = +0.0319$ to accommodate for initial compression strains before the pore pressure loading at 250 psi. Poroelastic and adsorption responses happen simultaneously during pore pressure increases, so it is nearly impossible to calculate them independently without the adoption of a theoretical model. The difference between poroelastic and adsorption response is clearer in the experiment result for the fourth pressure increase (P_m increase from 750 to 1000 psi – loop in far left in Fig. 6b).

4. CONCLUSIONS

- The adsorptive-mechanical properties of porous media can be measured through an extension of the Biot coefficient experimental procedure.
- Such extension requires a modification in the equations of poroelasticity to account for adsorption stress.

- The applied method and theory gave the following results for pre-compacted granular activated carbon:
 - Drained modulus K = 235.9 MPa and Biot coefficient $\alpha = 0.98$ measured with helium with effective stress range of 3.45-5.17MPa.
 - Sorption stress parameters $s_{max}^a = 171.3$ MPa and $P_L = 5.64$ MPa, for CH₄ in the range of pressure 0 to 8 MPa.

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