Adsorption-induced swelling of porous media

Sahar Bakhshian, Muhammad Sahimi[*]

Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, CA 90089-1211, USA

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ABSTRACT

This paper studies deformation and swelling of porous media induced by sorption of fluids, and in particular carbon dioxide. The phenomena are significant, not only to the capacity of porous formations for storing CO_2, but also to the effect that they have on the mechanical properties of the formations and microseismic events that they might possibly trigger. To study the phenomena we formulate the problem by energy consideration in which the Hamiltonian (total energy) of a porous medium and its fluid content is represented as the sum of the elastic energy of the system, and the energies associated with the interactions between the adsorbates and between them and the medium's solid matrix. The gas phase is described by a density functional theory, while the solid matrix can be either linearly or nonlinearly elastic. The model provides predictions for the sorption isotherms, the dependence of the strain on the bulk pressure, and the change in the porosity. The change in the strain is anisotropic due to the deformation of the solid, as well as the difference between the stiffness of the matrix and the fluid phase. During desorption the strain is also released and, similar to the sorption isotherms, exhibits hysteresis. This opens up the possibility of using mechanical measurements during sorption experiments to gain insight into the structure of a porous medium. When the model was applied to sorption of CO_2 in clay particles, all the reported experimental features of the phenomena were reproduced.

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1. Introduction

Swelling of porous materials due to their liquid content, or by storage of gases in their pore space, is a widespread phenomenon. Print papers swell when they come into contact with water, or even by the coating fluid that makes high quality surface (Ghassemzadeh et al., 2001). In biomedical science the interactions between ions and charged proteoglycans govern the deformation of cartilaginous soft-hydrated tissues. Swelling of polymers and biopolymers have numerous applications, ranging from size-exclusion chromatography, to efficient materials for drug delivery, gel electrophoresis during filtration processes, contact lenses, and food stuff.

An important class of porous media to which swelling is important is that of natural geomaterials. For example, porous formations that contain charged molecules and brine may swell if penetrated by fresh water. Moreover, swelling of smectite clays by water has been studied for decades. Clay swelling is of critical importance to geotechnical and geoenvironmental fields, as it may cause damage to the foundations of buildings, giving rise to cracks and displacements of footings. These are irreversible phenomena with considerable economic implications. Bentonitic-based compacted

clays have low hydraulic conductivity, plasticity (Benson et al., 1994), swelling and adsorptive capacity for contaminants, which is why they are used as sealing materials to prevent leaking of contaminants to the environment. Storage of radioactive nuclear wastes in geological formations is perhaps the only viable solution to problem of safeguarding such materials, and compacted clays may be used for sealing the storage area. Yet another example is provided by gas-bearing shales that represent unconventional sources of energy that have attracted wide attention. Their swelling is a major negative factor during drilling, as it can cause significant problems for wellbore stability.

A more recent problem in which swelling of porous media is important is sequestration of carbon dioxide in geological formations, such as depleted oil and gas reservoirs, and unminable coal seams (Michels et al., 2015; de Jong et al., 2014; Hemmen et al., 2012; Loring et al., 2012; Tsotsis et al., 2004; Yang et al., 2011; Billemont et al., 2013; McDonald et al., 2015; Cho et al., 2015; Dadwhal et al., 2008), as well as in metal-organic frameworks and other types of adsorbents that have been fabricated for capturing CO_2 (Sumida et al., 2012). The main characteristics of the geological formations for long-term CO_2 geo-sequestration include high storage capacity and effective sealing of the caprocks that are composed frequently of shale and, thus, clay minerals. The low permeability of the clay formations reduces the possibility of upward migration of CO_2 in the formations and its penetration into the neighboring natural resources (Shukla et al., 2010).

Clay minerals are typically composed of smectite, kaolinite, chlorite and illite (Loring et al., 2014; Gasparik et al., 2014), among which smectite has the highest sorption capacity due to their high internal surface area (Ji et al., 2012). Busch et al. (2008) studied CO_2 sorption in a shale sample and various clay minerals in order to investigate the storage capacity and sealing integrity of such formations. They reported that clay minerals, especially montmorillonite, have significant sorption and storage capacity for CO_2.

More generally, numerous experimental studies have been carried out to understand adsorption of CO_2 in porous media. For example, a study by Ravikovitch et al. (2005) on adsorption of CO_2 in soil samples containing various organic matters at 273 K and low pressures indicated that CO_2 tends to adsorb onto the domain of soil that is rich in organic matter. In another experimental study of CO_2 storage in organic-rich shale samples, it was found that even such formations that are nearly impermeable and have low porosity are capable of storing a remarkable amount of CO_2, which was attributed to the finely-distributed organic nanopores (Kang et al., 2011). Many careful and precise experiments, as well as theoretical studies have also been reported on the effect of CO_2 sorption in coal (Vandamme et al., 2010; Hol et al., 2011, 2012; Hol and Spiers, 2012).

Theoretical and computational studies of fluid sorption in porous media have also been carried out, including lattice density functional theory (DFT) (Pan and Connell, 2007; Ottiger et al., 2008; Woo et al., 2001), quenched solid DFT (Yang et al., 2011; Gor and Neimark, 2011), nonlocal DFT (Ravikovitch and Neimark, 2006), thermodynamic models (Grosman and Ortega, 2008; Kulasinski et al., 2015b; Liu et al., 2015), and molecular dynamics (MD) (Ghassemzadeh et al., 2000; Xu et al., 2001; Ghassemzadeh and Sahimi, 2004; Kim et al., 2005, 2007; Liu and Bhatia, 2013; Rao and Leng, 2016) and Monte Carlo simulations (Valiullin et al., 2006).

Adsorption of gases in a porous matrix leads to its swelling, which affects the porosity, permeability, diffusivity, and surface area of the pore space (Perera et al., 2011; Ozdemir and Schroeder, 2009), and has been studied both experimentally and theoretically (Ravikovitch and Neimark, 2006; Grosman and Ortega, 2008; Balzer et al., 2011). For example, a combined experimental and modeling study of adsorption of CO_2 and N_2 in coal samples has been reported, which demonstrated that volumetric strain caused by gas adsorption leads to reduction of the permeability (Pini et al., 2009). Another experimental study of coal swelling in response to CO_2 adsorption by Anggara et al. (2014) demonstrated that coal tends to swell anisotropically. The maximum volumetric swelling ranged from 1.60 to 2.35 percent. Recent molecular MD simulation of diffusion and adsorption of CO_2 in Montmorillonite structures as the model of clay minerals indicate that the basal spacing of the material changes (Dashtian et al., submitted). Pan and Connell (2007) developed a theoretical framework based on energy consideration to describe volumetric changes in coal due to gas adsorption. Their model was capable of predicting changes in the porosity and permeability of coalbeds as a result of swelling or shrinkage by gas adsorption. Vandamme et al. (2010) developed a model capable of calculating the macroscopic strains in response to adsorption in a porous medium. Using a thermodynamic framework, they developed the poromechanics of the process by considering the surface energy. The surface stress was modified by adsorption, a phenomenon that has also been studied by molecular dynamics simulation (see above). A thermodynamic framework was also developed by Hol et al. (2012) that modeled adsorption of CO_2 by unconfined and confined coal. They combined their model with poroelasticity and studied the competition between adsorption-induced strain and poroelastic strain in terms of the applied external stress, fluid pressure and concentration. In a study by Espinoza et al. (2013) a poromechanical model for adsorption and strain was developed. Their model predicted that strain anisotropy

is essentially due to anisotropy in the mechanical properties of porous solid.

Several studies of swelling induced by CO_2 sorption have been reported in coal samples (Yang et al., 2011; Kim et al., 2011; Kowalczyk et al., 2010), as well as in clay minerals and shales (Giesting et al., 2012; Rother et al., 2013; Kadoura et al., 2016; Rao and Leng, 2016). One such study was reported by Heller and Zoback (2014) who carried out experiments on the adsorption capacity of CO_2 and CH_4 of shale samples from four reservoirs, as well as pure illite and kaolinite. Their study indicated that gas adsorption causes a volumetric swelling strain on the order of 10^{-5} to 10^{-3}. In a more recent study swelling of shales as a result of CO_2 adsorption was investigated. All the samples studied exhibited anisotropic strain caused by CO_2 adsorption (Lu et al., 2016).

In terms of deforming rock – but not the mechanism by which the deformation is achieved – sorption-induced deformation of porous materials is somewhat similar to subsidence of oil and gas reservoirs (Doornhof et al., 2006). The mechanism of the two are, of course, different. Sorption-induced deformation is due to the chemical potential of the sorbing species, whereas subsidence is due to gas pressure reduction. Flow of oil or gas in some reservoirs causes deformation, compaction and subsidence in the reservoir. Thus, to model such phenomena one must couple the elastic or elasto-plastic equations governing the deformation to the equations of hydrodynamics governing fluid flow. In a similar spirit, any reasonable model of sorption-induced swelling of a porous medium must couple the elastic deformation of the solid to the thermodynamic state of the fluid in the pore space, the chemical potential of the sorbing species, and the interactions between the solid and the gas (Chin and Nagel, 2004; Guyer and Kim, 2015; see also Vandamme et al., 2010; Hol et al., 2012; Espinoza et al., 2013).

The goal of this paper is to present and use one such model by coupling the lattice gas DFT with the equation for elastic deformation and finite-element (FE) computations in order to study adsorption-induced swelling in a disordered porous medium, and in particular clay particles. We use the model to study sorption of CO_2 in clay minerals and its effect on their swelling.

The rest of this paper is organized as follows. In the next section we describe the details of the model for calculating the adsorption isotherms and the deformation strains. Next, the details of the numerical simulations are presented. The model is then applied to CO_2 sorption in clay and the resulting swelling and change in its porosity. The results are then presented and discussed. In particular, we study the effect of the model's parameters on sorption, strain and porosity. The extension of the model to changing the mechanical properties of porous media, as well as possible triggering microseismic events that have recently been reported, are discussed. We summarize the key conclusions in the last section.

2. The model

Let us first state clearly our assumptions. We assume, (i) a quasi-static system and (ii) a linearly-elastic solid matrix for the porous media (see also below). The coupling between the solid matrix and its deformation and the fluid, and the interactions between the two are formulated through the total energy E of the system (the porous media plus their fluid content). Thus,

$$E = E_f + E_s + E_{fs}, \qquad (1)$$

where E_f, E_s, and E_{fs} denote, respectively, the energy due to the fluid, the solid, and the interactions between the two. Various expressions can be used for each of the three terms on the right side of Eq. (1). One of the simplest of such expressions for E_f is given by a