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The Role of Water Activity and Capillarity in Partially Saturated Porous Media at Geologic CO_2 Storage Sites

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I. Introduction

The amount of water dissolved in supercritical CO_2 will evolve during and after injection operations at geologic CO_2 storage sites. Injection of dry CO_2 may lead to a region of water-free CO_2 or dry-out around the wellbore or along preferential flowpaths. Change in the activity or "effective concentration" of water will occur, which may affect performance metrics including: mineral precipitation and/or dissolution; CO_2 injectivity; residual trapping of CO_2; relative permeability and capillary pressure; and shrink-swell properties and sealing efficiency of clayey caprocks.

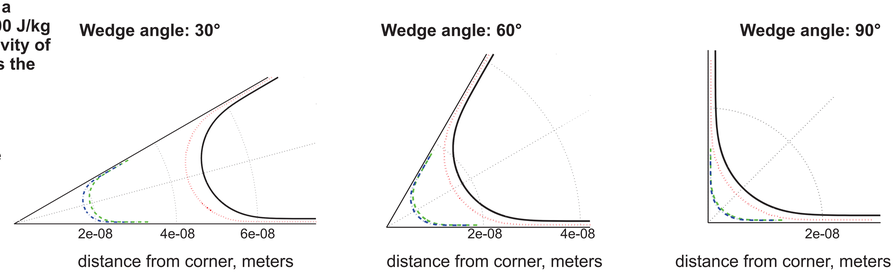
We present a pore-scale model of water film adsorption and capillary condensation as an explicit function of chemical potential and activity of water in supercritical CO_2. This model estimates water film configuration on flat and wedge-shaped pores to explore the importance of capillary condensation. With the model, we investigate water saturation and "snap off" (i.e., the spontaneous filling of a pore with water) in porous media in mineral-CO_2-water systems under different water activities. Maximum water activities in equilibrium with an aqueous phase are less than unity due to dissolution of CO_2 in water (i.e., the mole fraction of water in the aqueous phase is less than one), which may limit snap off in large pores.

II. Water films in corners of pores

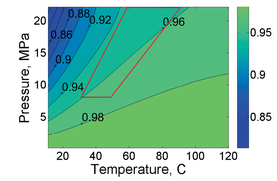
Water films determined at a chemical potential of -5,000 J/kg (may correspond with activity of water of 0.96) for quartz as the solid bounding phase

Legend

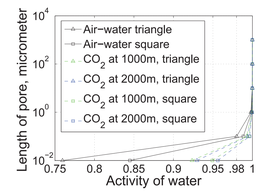
- Air-water in Vadoze Zone
- CO2 at depth of 0m
- CO2 at depth of 1000m
- CO2 at depth of 2000m



III. Acitivty of water and water films in triangular/square pores



Activity of water for the bulk CO_2-water system (not confined in pores) as calculated by program EQ3/6. The region enclosed by the red polygon is for P&T conditions of geologic CO_2 storage. *The standard state of pure water implies that dissolution of CO_2 in water may not allow activities of water of unity to be reached.*



Assuming that the chemical potential of the pore-scale model can be related to that of EQ3/6 through $\Delta\mu = RT\ln(a_{H2O})$, the plot of Part III is reproduced here. The possible conclusion is that snap off may not occur for large pores in the CO_2-water system since high activities of water may not be reached.

II. Theory

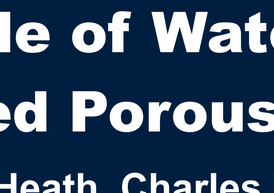
Goal: use thermodynamic concepts to estimate interfacial configurations of liquid water (i.e., film thicknesses) on flat pore surfaces and in corners as a function of the chemical potential and activity of water in supercritical CO_2. Our approach is similar to that of the Vadose Zone literature (e.g., see Tuller et al., 1999).

$$\Delta\mu_{H2O} = A(h) + C(\bar{c})$$

Water-CO_2 interface: surface of constant partial specific Gibbs free energy or chemical potential, which combines adsorption A and capillarity C, where h is water film thickness on flat surfaces and c is mean curvature of the fluid-fluid interface.

Assume pure liquid water has unit activity at standard state

Angular Pore



(modified from Tuller et al., 1999)

$$\Pi(h) = \Pi_{vdW}(h) + \Pi_e(h) + \Pi_s(h) + \Pi_a(h)$$

Van der Waals; Structural, due to sreric or hydration forces; Electrostatic, calculated from Poisson Boltzmann Equation; Adsorptive, important for nonionic solutions

Adsorptive component: For the moment, ignore C. If $\Delta\mu$ is expressed as energy per volume, we have the disjoining pressure Π. It is force per area that reflects the tendency of solid-water and water-CO_2 interfaces (i.e., the two Gibbs dividing surfaces) to repel or attract each other. For our model, we incorporate only the van der Waals and electrostatic terms.

Capillary component:

$$\Delta\mu = A(h) - \frac{\sigma}{\rho}\nabla\cdot\hat{n}$$

where σ is interfacial tension; ρ is density of water; and **n** is the unit normal vector of the curved fluid interface

Van der Waals Component of Π

$$\Pi_{vdW} = -\frac{A_{132}}{6\pi h^3}$$

$$A_{132} = \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{33}}\right)$$

Three phases for combining relations for Hamaker constant A_{132}
1 = Solid (Quartz for the examples herein)
2 = H_2O (with dissolved CO_2)
3 = C_2O (with dissolved H_2O)

$$\frac{(n_{mix}-1)^2}{(n_{mix}+2)^2} = \sum\frac{\phi_i(n_i-1)^2}{(n_i+2)^2}$$

Lorentz-Lorenz mixing rule for binary mixture of CO_2 in water or water in CO_2 (Meli et al., 2004)

$$\phi_i = \frac{x_i V_{m,i}}{\sum x_i V_{m,i}}$$

Lifshitz Theory for Hamaker constants

$$A_{ii} = \frac{3}{4}k_bT\left(\frac{\varepsilon_i - \varepsilon_{vacuum}}{\varepsilon_i + \varepsilon_{vacuum}}\right)^2 + \frac{3h\nu_e}{16\sqrt{2}}\frac{\left(n_i^2 - n_{vacuum}^2\right)^2}{\left(n_i^2 + n_{vacuum}^2\right)^{3/2}}$$

Electrostatic Component of Π

Unequal Double Layers Solution by Gregory (1975)

$$\Pi_e = n_\infty kT\left[2\left(\frac{1+\left(\frac{y_1+y_2}{4}\right)^2\csc h^2\left(\frac{\kappa h}{2}\right)}{1+\frac{1}{4}(y+y)^2\csc h^2\left(\frac{\kappa h}{2}\right)}\right) - \frac{(y_1-y_2)^2\exp(-\kappa h)}{1+\frac{1}{4}(y+y)^2\csc h^2\left(\frac{\kappa h}{2}\right)} - 2\right]$$

1/κ is the Debye Length

$$\kappa = \sqrt{\frac{2e^2 n_\infty z^2}{\varepsilon\varepsilon_0 kT}}$$

n_∞ is the number density or concentration of the bulk solution

y depends on electrostatic potential ψ of the solid-water and water-CO_2 interfaces (or Gibbs diving surfaces). ψ is -25 mV and 0 mV for the examples herein, for the quartz-water and water-CO2 interfaces, respectively.

$$y = \frac{ze\psi}{kT}$$

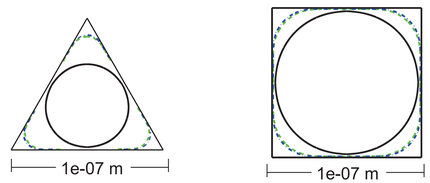
III. Water films in triangular/square pores

Legend

- Air-water in Vadoze Zone
- CO2 at depth of 1000m
- CO2 at depth of 2000m

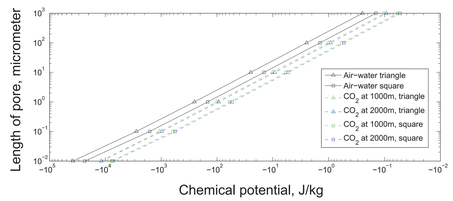
"Snap off" of the Vadose Zone air-water interface, compared to the CO_2-water interfaces at the same chemical potential (for the quartz-water-fluid system)

Assume "snap off" occurs when the fluid-fluid interface is an inscribed circles within the pore



Chemical potential for air-water "snap off" in triangular pore is -2,786 J/kg. The CO_2-water interfaces for the same chemical potential result in much reduced saturation (percent of pore space filled with water).

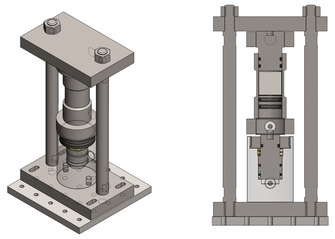
Chemical potential for air-water "snap off" in square pore is -1,602 J/kg, which is a smaller negative number than for the triangular pore. This shows that snap off in the square requires higher water content (less negative potentials).



"Snap off" for a given pore size vs. chemical potential: the figure to the left shows the chemical potential at snap off in a pore of a given size (the length of a side for a triangle or square pore) for the air-water and CO_2-water systems. The relationship is linear in log-log space. At a given pore size, snap off for the CO_2-water system requires less negative chemical potentials (e.g., greater water activity).

VI. Conclusions and ongoing work

- At the same given chemical potential, water adsorption and capillary condensation will be less for the CO_2-water system as compared to that of the air-water system for geologic CO_2 storage and vadose zone conditions, repsectively.
- Capillary water contributes much more greatly to pore saturation than adsorptive films, especially at pore sizes equal to or greater than 1e-07 m.
- The activity of water may limit pore "snap off" or spontaneous filling at a given chemical potential. If the standard state of acitivty of water of unity for pure phases is assumed, then the activity needed for snap off may not occur except for very small pores (less than .1 microns).



Ongoing work: capillary condensation will be tested at the neutron beam facility at LANL-LANSCE. The experiments to be performed in Feb. 2013 included measurement of pore structure of a swelling clay before and after wet scCO2 flows through a constant volume oedometer (unxial state of stress).

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