The influence of capillary pressure on the phase equilibrium of the CO_2–water system: Application to carbon sequestration combined with geothermal energy

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ABSTRACT

We quantify the capillary-pressure effect on the phase equilibrium of the CO_2–water system and subsequently on the CO_2 storage capacity and heat-energy recovery for CO_2–water injection into geothermal reservoirs. Our interest is in the capillary-pressure range between 0 and 100 bars for temperatures between 293 and 372 K and wetting-phase pressures between 25 and 255 bars. For this purpose, we have implemented capillary pressure in the PRSV equation of state.

The results show that capillary pressure promotes interfacial evaporation. Capillary pressure reduces the CO_2 solubility in water and the aqueous-phase density up to 64% and 1.3%, respectively, whereas it increases the water solubility in the CO_2-rich phase and the CO_2-rich-phase density up to 1172% ($1.0 + 11.7 = 12.7$ times) and 13%, respectively. If the CO_2-rich-phase properties were calculated as a function of the wetting-phase pressure, capillary pressure would shift the CO_2 liquid–vapor transition and consequently the upper critical point of the CO_2–water system to a lower pressure. Therefore, the CO_2-rich-phase properties must be calculated using the non-wetting-phase pressure to avoid this shift.

For mixed CO_2–water injection into a geothermal reservoir, the influence of capillary pressure on the phase equilibrium reduces both the heat recovery up to 37% and the CO_2-storage capacity up to 37%. We construct a plot of the recuperated heat energy versus the maximally stored CO_2 for a variety of conditions; we compare the results including and excluding the effect of capillary pressure in the phase-equilibrium calculations. We also provide a cursory evaluation of the energy and economics of mixed CO_2–water injection into a geothermal reservoir.

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1. Introduction

In the transition period from a fossil-fuel based society to a sustainable-energy society, it is expected that CO_2 capture and sequestration in geological formations plays a major role in reducing greenhouse gas emissions. An alternative way of reducing CO_2 emissions is to partly replace conventional-energy sources for heating buildings (e.g., cogeneration units) with geothermal energy. For CO_2 sequestration, the interaction between water and CO_2 (i.e., the mutual solubility of CO_2 and water in the CO_2-rich phase and in the aqueous phase) plays a crucial role to estimate the CO_2-storage capacity. As a result, many experimental data and thermodynamic models of vapor–liquid and liquid–liquid equilibrium (VLE and LLE) of a mixture of CO_2 and water/brine can be found in the literature (e.g., Duan et al., 1995; Duan and Sun, 2003; Spycher et al., 2003; Pruess and Spycher, 2007).

One of the characteristics of porous media that does not exist in bulk is capillary pressure. However, studies of the thermodynamic behavior of petroleum mixtures are usually performed in a laboratory PVT-cell in the absence of a porous medium. The assertion that the depletion behavior of the mixture in a PVT-cell is the same as in a petroleum reservoir is not always correct; it disregards the influence of capillary forces on thermodynamic equilibrium. Capillary pressure (interfacial phenomena) influences the phase equilibrium of fluid mixtures (e.g., shifts phase compositions and dew/bubble temperature/pressure points), particularly in less permeable media, since capillary pressure is inversely proportional to the square root of the permeability (Leverett, 1939). The magnitude of this shift in thermodynamic behavior with respect to bulk conditions depends on various factors, such as the texture, pore radius, phase contact angles, pore shape, and surface properties (Llamedo et al., 2004). The effect of interfacial phenomena on oil–gas systems has been studied for less-permeable gas condensate reservoirs (Brusilovsky, 1992; Bedrikovetsky, 1993; Guo et al., 1996; Shapiro et al., 2000; Zhang et al., 2001; Qi et al., 2007a, 2007b). Furthermore, the effects of capillary pressure on phase equilibria in shale-gas reservoirs and in very tight rocks are important because of very low permeabilities of shales and caprocks and consequently very high capillary pressure (Hildenbrand et al., 2002, 2004; Li et al., 2005; Tonnet et al., 2011; Skurtveit et al.,

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2012; Ishida et al., 2012). Recently, Liu and Flemings (2011) studied the three-phase (liquid + gas + hydrate) stability of the methane-hydrate system in marine sediments by considering the capillary effects on both hydrate and free gas phases. They concluded that capillary pressure exerts a key control on the methane solubility in liquid + hydrate and liquid + gas systems.

However, none of the existing experimental data and/or thermodynamic models includes the effect of capillary forces on the phase behavior of the CO_2–water system, since many experiments have been performed outside porous media or in highly permeable cores, for which capillary-pressure effects are negligible. Consequently, thermodynamic models have been optimized/tuned based on the available experimental data in bulk.

In this paper, we include the capillary-pressure effect in the phase-equilibrium calculation of the CO_2–water system. However, effects of salinity are not considered. Implementation of salt in the CO_2–water system is kept for future work. Our rationale to investigate the influence of capillary pressure on the phase equilibrium of the CO_2–water system is that the effect might substantially influence the CO_2-storage capacity and CO_2-trapping mechanism in less permeable zones of reservoirs. Our hypothesis is that inclusion of capillary pressure in VLE reduces the solubility of CO_2 in the aqueous phase and increases the solubility of water in the CO_2-rich (non-wetting) phase. We use thermodynamics to determine the range of capillary pressures for which discernable effects occur in the fluid-phase equilibrium compositions and densities.

To examine for which values of the injected CO_2 concentrations inclusion of capillary pressure in the phase-equilibrium calculations shows an influence on the displacement process of the CO_2–water system, we simulate mixed CO_2–water injection into a geothermal reservoir. In this way, synergy is established between geothermal-energy production and subsurface CO_2 storage. We apply the non-isothermal negative-saturation (NegSat) solution approach (Salimi et al., 2011b, 2012a, 2012b) to solve efficiently non-isothermal compositional CO_2–water flow that involves phase appearance, phase disappearance, and phase transitions. The advantage of this solution approach is that it circumvents using different equations for single-phase and two-phase regions and the ensuing unstable switching procedure. In this paper, we use the simulation results of mixed CO_2–water injection for various injected CO_2 concentrations to give a complete overview of optimal heat recovery and maximally stored CO_2 for a selected heterogeneity structure derived from the Delft Sandstone Member (Gilding, 2010; Salimi et al., 2011a).

The objectives of this paper are (1) to construct a thermodynamic model in which the influence of capillary pressure on the phase equilibrium of the CO_2–water system is included; (2) to quantify conditions for which inclusion of capillary pressure can substantially shift the thermodynamic properties of the CO_2–water system; and (3) to assess inclusion of capillary pressure in the phase equilibrium on the efficiency of CO_2 sequestration and heat-energy recovery for mixed CO_2–water injection into a geothermal reservoir.

The paper is organized as follows. First, we develop a thermodynamic model in which the effect of capillary pressure on phase equilibria is included. Then, we briefly explain our novel NegSat solution approach for non-isothermal compositional flow to deal with problems that involve phase transitions. After that, we discuss the thermodynamic results that show for which values of capillary pressure the mutual solubilities of CO_2 and water and phase densities change. Subsequently, we give a set of simulation results that includes the effect of capillary pressure in the phase-equilibrium calculations of cold mixed CO_2–water injection into the geothermal reservoir. Next, we estimate the total amount of energy invested for

mixed CO_2–water injection into the geothermal reservoir for a variety of conditions. Afterward, we also provide a cursory evaluation of the economics of the proposed project. A plot of the recuperated heat energy versus the maximally stored CO_2 for a variety of conditions is discussed in detail; we compare the results including and excluding the effect of capillary pressure in the phase-equilibrium calculations. Finally, we summarize our findings in the conclusion section.

2. Thermodynamic model

The phase equilibrium of the CO_2–water system plays an important role in CO_2-sequestration processes. Cubic equations of state are reasonably fast in the numerical-multicomponent-phase-equilibrium (flash) calculations. To use an equation of state for the nonideal CO_2–water system, an appropriate mixing rule must be implemented. In this work, we include capillary pressure in the Peng–Robinson–Stryjek–Vera (PRSV) equation of state with the Modified Huron–Vidal second order (MHV2) mixing rule that uses the Non-Random Two-Liquid (NRTL) activity-coefficient model. The reason that we selected PRSV with MHV2 was that these EOS and mixing rule give the best fit to experimental data of CO_2 and water in the pressure and temperature range of our interest (Eftekhari et al., 2011). This thermodynamic model has been extended to include salt in the CO_2–water system (Eftekhari et al., 2011). The predicted liquid density by the PRSV equation has been adjusted using a volume-shift parameter (Péneloux et al., 1982). The general form of the PR equation of state (Peng and Robinson, 1976) is

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)}, \tag{1}$$

where T is the absolute temperature in Kelvin, P is the absolute pressure, v is the specific volume (m^3/mol) of the fluid mixture, and $R = 8.314\ Pa\ m^3$/(mol K) is the gas constant. The effects of the interactions between molecules and the volume of individual molecules are represented by the force parameter a and by the volume parameter b, respectively. The expressions for calculating parameters a and b for each component are given in Appendix A. The MHV2 (Dahl and Michelsen, 1990) is a modification of Huron and Vidal (HV) mixing rule (Huron and Vidal, 1979). For parameter b in Eq. (1), one uses

$$b = \sum_{i=1}^{N_c} x_i b_i, \tag{2}$$

where N_c denotes the number of components and x_i is the mole fraction of component i in the mixture. To find the force parameter a for the mixture, the following quadratic equation is solved for the variable ε

$$q_2 \varepsilon^2 + q_1 \varepsilon + \left(-q_1 \sum_{i=1}^{N} x_i \varepsilon_i - q_2 \sum_{i=1}^{N} x_i \varepsilon_i^2 - \frac{g^E}{RT} - \sum_{i=1}^{N} x_i \ln \frac{b}{b_i} \right) = 0. \tag{3}$$

In the summations of the above equation, $\varepsilon_i = a_i/(b_i RT)$ and g^E (J/mol/K) are functions of T and x_i. The mole fraction x_i belongs to the two-component CO_2–water system. The excess free energy g^E is calculated using the NRTL activity-coefficient model (see Eq. (B-1)). For the PRSV equation of state, the MHV2-model parameters q_1 and q_2 are -0.4347 and -0.003654, respectively (Huang and Sandler, 1993), independently of the system considered. Eq. (3) has a positive and a negative root. We choose the positive root for ε. Parameter a in Eq. (1) can then be calculated using the