Evaluation of relative permeability functions as inputs to multiphase flow models simulating supercritical
CO₂ behavior in deep geologic formations

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Abstract

Multiphase flow models that simulate flow and entrapment behavior of supercritical CO₂ (scCO₂) can be used to design and evaluate CO₂ sequestration strategies in deep geologic formations. The accuracy of model predictions depends on the constitutive models that relate capillary pressure (P_c) and relative permeability (k_r) to phase saturations (S_w). Any studies to evaluate various constitutive models remain a major challenge, as necessary data are not easy to obtain in field settings. As it is not feasible to create deep formation pressure conditions in the laboratory to keep CO₂ under supercritical conditions, surrogate fluids that mimic the behavior of scCO₂ and brine were used. The $k_r - S_w$ relationship for the surrogate fluid system was measured independently using long-column and hydrostatic methods. The measured $P_c - S_w$ data for the same surrogate fluid system was used to derive the $k_r - S_w$ relationships using the van Genuchten – Mualem model. The relative permeability relationships obtained independently from experiments and derived from measured $P_c - S_w$ data using the van Genuchten – Mualem constitutive model were then applied to a multiphase model to simulate an injection experiment in an intermediate scale test tank. The comparison demonstrated that the model simulation that used directly measured $k_r - S_w$ relationships was able to match the experimental observations slightly better than the simulation performed using the empirically derived relative permeability functions. Even though this was a limited study using a homogeneous packing configuration, the results demonstrate the importance of using the correct relative permeability functions in multiphase models used in carbon storage studies.

Keywords: Relative permeability; TOUGH2 T2VOC; Carbon sequestration

1. Introduction

Injection of supercritical CO₂ (scCO₂) into deep geological formations is under study as a long-term carbon storage project (IPCC, 2005). Deep saline aquifers are promising candidates because of their high potential storage capacity, which has been estimated to be between 1,700 and 20, 000 Gt in the United States (Elliot and Celia, 2012). However, such schemes pose potential risks due to possible leakage of CO₂ from the deep formation to shallow aquifer zones from the loss of integrity of caprock and defects in wellbore structures (Celia et al., 2004; Juanes et al., 2006; Sakaki et al., 2013a; Wolterbeek et al., 2013). Numerical models with the ability to simulate the migration and distribution of scCO₂ in geologic formations could play a useful role in designing injection schemes and to assess storage permanence to reduce leakage risks (Juanes et al., 2006).

Multiphase flow models such as the ones that simulate scCO₂ and brine flow use constitutive models that relate capillary pressure (P_c) and relative permeability (k_r) to phase saturations (S_w) (Juanes et al., 2006; Kuang and Jiao, 2011). Use of laboratory measured $P_c - S_w$ relationship to obtain relative permeability (k_r) to phase saturations (S_w) is quite common in soil physics applications (Brooks and Corey, 1964; Mualem, 1976; van Genuchten, 1980) and in early applications in reservoir engineering (Burdine 1953). Alternate constitutive models for $k_r - S_w$ relationships can be found in Chen et al. (1999) and Jang and Santamarina (2013). The use of these empirical constitutive models is advantageous in that they can be used to estimate $k_r - S_w$ relationships without direct experimental measurements that are difficult to perform. However, oversimplification of the pore geometries used in the development of these models often results in discrepancies between relationships derived from the constitutive models and experimental measurements (Fischer and Celia, 1999; Tuller and Or, 2002; Cihan et al., 2009). Furthermore, many constitutive models such as van Genuchten (1980) and Brooks and Corey (1964) were developed for agricultural soil physics applications and may not be applicable for types of geologic materials that are of relevance in CO₂ sequestration. Ruan and Illangasekare (1999) experimentally demonstrated the limitations of the empirically based van Genuchten – Mualem model for sandy soils and proposed a more physically realistic alternate model based on sheet flow within the pores.

The use of empirically based constitutive models of relative permeability as inputs for multiphase codes may introduce errors as a result of oversimplification and/or improper assumptions that cannot be justified in CO₂ sequestration applications. Also, performing laboratory experiments for the direct measurement of these parameters presents major challenges. Many studies (Klute and Dirksen, 1986; Demond and Roberts, 1993; Dane et al., 1998) indicate that experimental methods to derive $k_r - S_w$ are not always easy due to constraints on controllable measurement ranges of pressure, temperature and scale. Additionally, maintaining CO₂ in a supercritical state can be experimentally challenging in many laboratory settings under ambient temperature and pressure conditions. To overcome this difficulty, the use of surrogates for brine and scCO₂ under ambient conditions has been proposed (Trevisan et al., 2014; Mori et al., 2015). In a companion paper, Mori et al. (2015) showed that these surrogate fluids were able to replicate the scCO₂ and brine $P_c - S_w$ relationships by comparing the results with actual scCO₂ and brine capillary pressure measurements for quartz sand presented by Tokunaga et al. (2013).

The aim of this research is to use surrogate fluids for scCO₂ and brine: 1) to experimentally obtain the $k_r - S_w$ relationship independently without deriving it from $P_c - S_w$ data, and 2) to investigate efficacy of using the directly measured $k_r - S_w$ relationships for the improvement of numerical model predictions of plume migration.

2. Test materials

2.1. Selection of surrogate fluids

Nordbotten et al. (2005) list the density and viscosity of scCO₂ and brine under various field conditions associated with scCO₂ injection into geologic formations (e.g. deep/shallow formations and cold/warm basin). To experimentally mimic flow and capillary trapping of scCO₂ in saline aquifers, Soltrol 220 (hereafter referred to as Soltrol) and an 80 % by weight solution of glycerol in water (hereafter referred to as 80 % glycerol) were used as surrogates for scCO₂ and brine, respectively. These fluids were chosen as to be within the range of dimensionless groups such as capillary number, bond number, viscosity ratio, and density ratio, relevant to that of scCO₂ and brine (Cinar et al., 2007; Pentland et al., 2010; Aminzadeh et al., 2012; Trevisan et al., 2014; Mori et al., 2015). These dimensionless

numbers are defined in Mori et al. (2015). The same surrogate fluid pairs were used in previous studies of experimental simulations of scCO₂ injection conducted in intermediate-scale tanks (Trevisan et al., 2014) and the evaluation of scaling methods for $P_c - S_w$ relationships (Mori et al., 2015). **Table 1** presents the properties of the scCO₂/brine and the surrogate fluid system reported in Mori et al. (2015).

Table 1 Significant properties of surrogate fluids of scCO₂ and brine (Mori et al., 2015)

	scCO ₂	Brine	Soltrol	80 % glycerol
Density ρ (g/cm ³)	0.270 – 0.730 ¹⁾	0.95 – 1.23 ¹⁾	0.79 ²⁾	1.21 ⁴⁾
Viscosity μ (mPa s)	0.023 – 0.061 ¹⁾	0.20 – 1.58 ¹⁾	3.90 ³⁾	60.9 ⁴⁾
μ_{nw}/μ_w (-)*	0.03 – 0.20		0.064	
ρ_{nw}/ρ_w (-)*	0.22 – 0.75		0.65	
Interfacial tension σ (dyne/cm)	20.0 – 60.0		17.3 – 21.0 ⁵⁾	
Capillary number(-)	$10^{-5} - 10^{-8}$		$10^{-6} - 10^{-7}$	
Bond number (-)	$10^{-7} - 10^{-8}$		$10^{-5} - 10^{-6}$	
Solubility property	0-1.2 mol/kg ⁶⁾		Negligible	

¹⁾ Nordbotten et al. (2005), ²⁾ Kechavarzi et al. (2005), ³⁾ Fisher and Morrow (2006), ⁴⁾ Cheng (2008), ⁵⁾ Mori et al. (2015), ⁶⁾ Eke et al. (2011). * ρ_w and μ_w are density and viscosity to wetting fluid, and ρ_{nw} and μ_{nw} are density and viscosity to non-wetting fluid.

Glycerol of 80 % volume fraction has high viscosity, resulting in slow fluid flow that will result in long experimental times to make measurements of relative permeability. Therefore, the feasibility of using a second wetting fluid consisting of 50 % by weight glycerol in water (hereafter referred to as 50 % glycerol) was tested with the goal of reducing the experimental time. By lowering the glycerol fraction to 50 % from 80 %, the viscosity of the mixture dropped by an order of magnitude as shown in **Table2**.

Table 2 Density (ρ) and viscosity (μ) of 80 % and 50 % by weight solutions of glycerol in water (Cheng, 2008)

	ρ (g/cm ³)	μ (mPa s)
80 % glycerol	1.21	60.9
50 % glycerol	1.13	6.0

It is expected that the changes in the properties of the wetting fluid will affect the $k_r - S_w$ relationship. Relative permeability of fluids in a given porous medium primarily depends on the phase saturations, temperature, interfacial tension, fluid viscosity, and capillary number (N_c) (Brooks and

Purcell, 1952; Fucher et al., 1985; Kumar et al., 1985; Shen et al., 2006). The dimensionless capillary number is defined as (Krevor et al., 2012):

$$N_c = \frac{v\mu}{\sigma} \quad (1)$$

in which v refers to Darcy velocity (LT^{-1}), μ is the viscosity of the wetting phase ($ML^{-1}T^{-1}$), and σ is the interfacial tension (ML^{-2}).

Assuming the use of same porous medium and non-wetting fluid, a change of the wetting fluid will affect the interfacial tension, viscosity, and N_c . The relative difference in interfacial tensions between 80 % glycerol – Soltrol and 50 % glycerol – Soltrol is only about 3 %. Therefore, changes in the N_c are primarily caused by the change in the viscosity and Darcy velocity.

The N_c values and Darcy velocities of test sand saturated with 80 % glycerol and 50 % glycerol are listed in **Table 3**. Details of the test sand are described in the Section 2.2. The Darcy velocity was measured at head gradient of 1.0 without external pressure applied to the system.

Table 3 Darcy velocity of the test sand for glycerol/water of 80 % and 50 % mixture and capillary number

$v[cm/s]$		$N_c [-]$	
80 % glycerol	50 % glycerol	80 % glycerol	50 % glycerol
2.11×10^{-3}	2.00×10^{-2}	7.42×10^{-8}	6.93×10^{-8}

The relative permeability is an intrinsic property of the porous medium. According to Krevor et al. (2012), the relative permeability is also impacted by changes in N_c when the N_c is greater than 10^{-6} . The N_c values for both 80 % glycerol and 50 % glycerol were significantly below 10^{-6} as shown in **Table 3**, suggesting that using 80 % glycerol and 50 % glycerol does not affect the measured relative permeability values. Hence, using 50 % glycerol/water facilitates the flow of the wetting fluid, and the test conditions reach steady state significantly faster than when using 80 % glycerol. **Table 3** shows the N_c values for the two fluid mixtures. The two N_c values are very close with only a 6 % relative difference. This suggests that the use of 50 % glycerol/water in place of the 80% mixture has no effect on the relative

permeability measurements. To verify that relative permeability would not significantly change with the fraction of glycerol in water, we also obtained wetting phase relative permeability data for both 80 % and 50 % glycerol from column experiments.

2.2. Test sands

Uniform silica sand, Accusand #30/40 manufactured by Unimin Corporation, was chosen as the test sand to measure the $k_r - S_w$ relationships and to be used in the tank experiment. Selected hydraulic properties of the test sand for surrogate fluids are given in **Table 4**. The van Genuchten parameters shown in the table were obtained by fitting to the capillary pressure measurements from the dielectric sensor method (Mori et al., 2015). The capillary pressure and saturation relationships were given in Mori et al. (2015).

Table 4 The principle hydraulic properties of test sands. The van Genuchten parameters and irreducible (S_i) and residual saturation (S_r) for surrogate fluids are from Mori et al. (2015).

Sand no.	¹ Intrinsic permeability k_i (cm ²)	¹ Particle diameter (mm)	S_r (-)	S_i (-)	van Genuchten parameters (drainage)		van Genuchten parameters (imbibition)	
					α (1/cm)	n (-)	α (1/cm)	n (-)
#30/40	1.1×10^{-6}	0.52	0.739	0.076	0.21	6.56	0.60	4.59

¹Sakaki et al. (2013b). Abbreviation: S_r : residual glycerol/water 80 wt% saturation (-); S_i : irreducible

glycerol/water 80 wt% saturation (-). Residual glycerol/water saturation refers to the saturation

when the glycerol/water trapped by the capillary force and becomes discontinuous in the pore.

While, irreducible glycerol/water saturation refers to the saturation of glycerol/water when the

Soltrol depleted in the pore and becomes a discontinuous phase.

3. Development of relative permeability model

In this section, methods for measuring wetting phase and non-wetting phase relative permeabilities are described. In multiphase flow applications dealing with air – water systems with air as the non-wetting phase with low viscosity, normally only the relative permeability of the wetting phase is

measured (Irmay 1954; Corey 1994). A low viscosity wetting phase fluid was used as a surrogate for brine to reduce experimental time. The two techniques that were used to measure the wetting phase and non-wetting phase relative permeabilities are presented next.

3.1. Wetting Phase Relative Permeability Measurement: Long-Column Method

The long-column method presented by Corey (1994) to measure the $k_r - S_w$ relationship of the wetting phase for an air-water system was modified for the surrogate fluid system used in this study. The left side of **Fig. 1** shows the setup of the long-column experiment. This setup consists of a 90 cm-long acrylic pipe oriented vertically, installed with two ECH₂O EC-5 soil moisture sensors and two tensiometers to measure the phase saturation and head gradient of the wetting phase. The EC-5 soil moisture sensors were located 35 cm and 75 cm from the bottom of the pipe, while tensiometers were placed 30 cm and 80 cm from the bottom. The top of the column was open to the atmosphere, and the bottom was connected to a constant-head reservoir that maintained the wetting fluid head level at the same elevation as the bottom of the column. The column was packed tightly and uniformly with sand except for the top and bottom 5 cm lengths, which contained gravel layers to distribute the fluids uniformly across the column section before entering and leaving the test sand. Both glycerol solution and Soltrol were injected from the top of the column using Mariotte's bottles and the injection rates were adjusted by changing the size of needles connected to the outlet of the bottles.

Intrinsic permeability (k_i) of the packed sand was measured using glycerol mixture and compared with the previously measured values listed in **Table 4** to examine consistency of the sand packing. Then, for each injection rate, the relative permeability was measured after the head gradient and the saturations stabilized, indicating that the flow had reached steady state.

3.2. Non-Wetting Phase Relative Permeability Measurement: Hydrostatic Method

The non-wetting phase relative permeability (k_{rnw}) was measured using the hydrostatic method first presented by Dane et al. (1998). The experimental setup shown on the right side of **Fig. 1** consisted of two concentric cylinders, the inner cylinder made of ceramic and the outer cylinder made of Teflon. The two cylinders were glued to two circular Teflon plates at each end. The length of the double walled

cylindrical annulus was 6.5 cm. The ceramic cylinder was hydrophilic and impermeable to Soltrol, the non-wetting fluid. The two cylinders and the end plates sealed with O-rings were assembled and tightened with threaded rods and wing nuts. The sample was contained between two 200 mm steel meshes to prevent the sand from clogging the fluid supply tubing. The annulus between the Teflon and ceramic cylinders was filled with the glycerol mixture. When the fluid level in the constant-head device is at the same elevation as the top of the Teflon cylinder, the saturation in the soil is 1.0 (fully saturated). Lowering the height of the constant-head device changes the saturation of the sample. The sand was wet packed inside the ceramic cylinder with glycerol solution to avoid air trapping in the sample. Under hydrostatic conditions, the capillary pressure (P_c) is constant everywhere within the sample.

In this experiment, we fixed the elevation of the outlet Soltrol reservoir (indicated as drainage on **Fig.1**) at 1.5 cm from the top of the cylinder. The elevation of the Soltrol reservoir was determined to be $x = 4.3$ cm (equation 2) to provide the appropriate injection pressure to allow the Soltrol to flow into the sample and making the capillary pressure to be constant within the sample (Dane et al., 1998).

$$P_c(inlet) = (6.5 + x) \times \rho_{nw}g - 6.5 \times \rho_wg = \rho_{nw}g \times 1.5 = P_c(outlet) \quad (2)$$

where g is acceleration of gravity (M/L^2).

The Soltrol outflow rate (q_{nw}) was measured as a function of time and the effective permeability of the sand was calculated using the following equation derived by applying Darcy's law for two-phase flow (Dane et al., 1998):

$$k_{nw} = -\frac{q_{nw} \times \mu_{nw}}{(\rho_{nw} - \rho_w)g} \quad (3)$$

where k_{nw} is non-wetting phase effective permeability (L^2).

Fig. 1. Experimental setup for the long-column method (left), and for the hydrostatic method (right)

3.3. Verification of using 50 % glycerol for the wetting phase relative permeability measurement

In section 2.1, we showed that it was able to expedite the relative permeability measurement using the 50 % glycerol as the wetting phase instead of 80 % glycerol. To verify this approach, the relative permeabilities for both glycerol/water mixtures were measured for Accusand #30/40 and shown in **Fig. 2**. As the plots show, there are no distinct differences observed between the relative permeabilities of 80 % and 50 % glycerol. Once this assumption was verified with the long-column experiment, the hydrostatic relative permeability experiment was conducted only with 50 % glycerol.

Fig. 2. Comparison between the wetting phase relative permeability of 80 % and 50 % glycerol for Accusand #30/40.

3.4. Comparison between the constitutive model and the experimentally obtained relative permeability data

Fig.3 compares the relative permeability derived from the van Genuchten – Mualem model using $P_c - S_w$ measurements and the directly measured relative permeability data for Accusand #30/40. The van Genuchten – Mualem model used the van Genuchten parameters given in **Table 1**. No noticeable hysteresis was observed in either the wetting or non-wetting phase relative permeability when comparing the drainage and imbibition data as suggested by Corey (1994). The measured relative permeability values differed greatly from those derived using the van Genuchten – Mualem model. The difference between van Genuchten derived permeability values and the measured values was greatest for the non-wetting phase. This difference suggests that for the tested sand, the van Genuchten – Mualem model is not suitable. This result is not completely unexpected because the van Genuchten – Mualem model was originally developed for agricultural field soils, not for relatively uniform pore-sizes sand grains such as the ones used in this study (Irmay, 1954; Hausenberger and Zaslavsky, 1963; Ruan and Illangasekare, 1999).

Fig. 3. Comparison between experimental data and the constitutive model (van Genuchten – Mualem model) of $k_r - S_w$ relationships. Drainage and imbibition process of relative permeability experimental data for glycerol/water 50 % (Left). Drainage and imbibition process of relative permeability experiments data for Soltrol (Right).

3.5. Relative permeability model

The data presented in **Fig. 3** was used to develop the following relative permeability models:

$$k_r = 0.6436 \times S_w^2 + 0.48416 \times S_w - 0.12353 \quad (4)$$

$$k_{rn} = \frac{\left(\frac{1 - S_w}{1 - 0.076}\right)^{5.3}}{1.6} \quad (5)$$

The values for k_r and k_m were constrained so that they would not produce physically unrealistic negative values. While, to evaluate our relative permeability model, the constitutive models based on the van Genuchten – Maulem fitted parameter was used. These constitutive models are given as:

$$k_{rw} = S_{ew}^{1/2} \left[1 - \left(1 - S_{ew}^{\frac{1}{m}} \right)^m \right]^2 \quad (6)$$

$$k_{rn} = (1 - S_{ew})^{1/2} \left[1 - S_{ew}^{\frac{1}{m}} \right]^{2m} \quad (7)$$

Abbreviation: S_{ew} refers the effective saturation [-] and m is the van Genuchten parameter, which is equal to $1-1/n$ [-], which shown in **Table 4**

To evaluate the performance of the relative permeability based on the constitutive model and the one measured directly, they were used in a multiphase code to simulate the propagation of a plume observed in a two-dimensional tank.

4. Results and Discussion

The goal of the modelling study was to test the ability of the relative permeability functions, obtained from direct measurements and based on a derived empirical model, to simulate the observed behaviour of a non-wetting fluid plume in a two-dimensional test tank. The multiphase simulation code TOUGH2 T2VOC (Falta et al., 1995) was used to simulate the migration of surrogate fluids of scCO₂ in brine. The non-wetting phase saturation data generated from one of the three two-dimensional tank experiments reported by Trevisan et al. (2014) was used to conduct this study.

4.1. Design and experimental procedures of two-dimensional tank experiment

The immiscible displacement experiment by Trevisan et al., (2014) was conducted in an intermediate scale tank packed homogeneously with #30/40 Accusand. A homogeneous packing setting was chosen to avoid data uncertainties resulting from soil heterogeneity. As shown in **Fig.4**, the tank has internal dimensions of 91.4 cm (length) by 5.6 cm (width) by 61.0 cm (height). An injection well made of a PVC pipe 2.3 cm diameter and an 11.0 cm height with a total screened area of 3.8 cm² was placed at the left boundary of the tank. The right side of the tank was connected to an external reservoir to control the boundary head.

The bottom right corner of the tank was raised to achieve a 2.0° angle of inclination of the cap rock. To create a synthetic reservoir, a 16 cm thick layer Accusand #30/40 was wet packed and a layer of very fine sand consisting of a 2:1 mixture of sieve sizes #110 and #250 was placed above the Accusand #30/40 to reproduce a capillary barrier for the Soltrol and a flow barrier for glycerol, acting as a confining cap rock. Separated from the Accusand #30/40 and fine sand layer by a screen, a vertical layer of coarse sand #8 (gravel) was packed at the right boundary of the tank connected to a constant head reservoir.

A Mariotte's bottle was used to supply Soltrol to the injection well at a constant pressure. The injection rate was continuously monitored through the weight of Mariotte's bottle containing Soltrol placed on an electronic scale. A total volume of 231 ml of Soltrol was injected at a rate of 0.7 ml/min for 5.5 hours. The spatial and temporal evolution of the plume saturation in the aquifer was measured non-destructively using X-ray attenuation (Trevisan et al., 2014). The X-ray source and a photon detector that move simultaneously along predefined scanning grids measured the volumetric fractions of the phases in the tank. The point measurements were interpolated to obtain two-dimensional maps of sand porosity and non-wetting phase saturation.

Fig. 4. Design of the two dimensional tank experiment (Trevisan et al., 2014)

4.2. Model structure and simulation outline

A finite difference multi-purpose simulation code, TOUGH2 T2VOC (Falta et al., 1995), was used to simulate two-phase flow in the two-dimensional tank. The model was setup for glycerol/water mixture as the wetting phase and Soltrol as the non-wetting phase. Separate simulations were performed employing either experimentally obtained $k_r - S_w$ relationships (Simulation 1) or $k_r - S_w$ relationships obtained from the van Genuchten – Mualem model (Simulation 2). Simulation 1 used the equation (4) and (5), and Simulation 2 employed the van Genuchten parameters obtained from Mori et al. (2015).

Since the fine sand that surrounded the synthetic aquifer acted as a flow barrier, the model domain was defined only to include #30/40 Accusand. A two-dimensional rectangular mesh with a constant width corresponding to the thickness of the sample in the tank was used to discretize the flow

domain. No-flow boundary conditions defined the cap rock interface. The grid mesh consisted of 1276 elements, and the element volume was about 1 cm³.

First, the model simulated the steady-state conditions for single phase 80% glycerol flow prior to Soltrol injection. After the steady-state condition that defines the initial conditions was reached, Soltrol was injected at 1.17×10^{-8} m³/s (0.7ml/min) for 5.5 hours. Because Soltrol is less dense than the 80% glycerol, Soltrol was observed to flow out only from the top of the well screen. Hence, defining a source in the grid at the top of the well screen best simulated the injection.

4.3. Application of relative permeability model to two-dimensional tank simulation

To verify the accuracy of the X-ray method, the total mass of injected Soltrol was compared with the mass estimated using the measured saturations. The total mass injected as measured by tracking the weight of the Mariotte's bottle using the precision electronic balance was 0.1825 kg. The total mass of Soltrol in the sand estimated using the saturation measured by the X-ray method was 0.1877 kg. This close match suggests that the X-ray saturation data can be used to give an accurate estimate of the mass of Soltrol within the plume.

Fig. 5 and **Fig. 6** compare the experimental observations with the model simulations using the two types of relative permeability functions that were developed. The plots in **Fig. 5** compare the observed saturations of Soltrol at 5 tank locations, (A, B, C, D, and E as labeled in the photograph; the photograph is taken at 24 hours since the start of the experiment) with the model predicted saturations incorporating the directly measured relative permeabilities (Simulation 1) and the van Genuchten model-derived relative permeabilities (Simulation 2). The tank observations do not match exactly for either simulation, but at points A and B, Simulation 1 shows better agreement with the observed saturations. Furthermore, Simulation 2 overestimates the saturation as time proceeded.

The saturation measurements from the X-ray system at selected points on the scanning grid was used to calculate the total Soltrol mass in vertical sections at 1.5 cm length intervals along the length of the plume. **Fig. 6** shows the observed mass distribution at the end of the injection period (5.5 hours). On the same figure, the model simulated mass is also plotted. Overall, neither of the two simulations

301 predicted the plume distribution accurately at the end of the injection period. In fact, while the computed
302 saturations in Simulation 1 better matched the mass of Soltrol observed close to the injection well, the
303 location of the front was underestimated. On the other hand, Simulation 2 showed the plume reaching the
304 right end of the tank at 5.5 hours matching the experimental observation. But, the simulation did not
305 predict the sharp change in Soltrol mass within the 30 cm length from the injection well.

Fig. 5. Saturation of Soltrol at Points A-E (labeled in the photograph) observed in the tank experiment using X-ray tomography and simulated using TOUGH T2VOC (Simulations 1 and 2). Simulation 1 uses experimentally obtained relative permeability, while Simulation 2 uses the van Genuchten- Mualem derived relative permeability

Fig. 6. Cumulative mass of Soltrol 220 from the simulation model and tank experiment conducted by Trevisan et al. (2014) at 5.5 hours from the start of the experiment

5. Conclusion

Empirically derived constitutive models of $k_r - S_w$ based on measured capillary pressure – saturation data and the experimentally determined $k_r - S_w$ were used as inputs to the multiphase code TOUGH2 T2VOC to simulate the scCO₂ displacing brine in an intermediate scale tank experiment. This tank experiment reported by Trevisan et al., (2014) used surrogate fluids in place of scCO₂ and brine. Our results indicate that the simulation, which used the directly measured relative permeability shows slightly better match to the observed plume propagation. Therefore, the empirical methods such as van Genuchten (1980) or Mualem (1976) that have been developed for soil physics applications for liquid-gas systems may not be suitable for fluid-fluid systems in CO₂ sequestration. However, based on the comparison with

the results from tank experiment, it is not possible to make a general conclusion on which of the relative permeability functions is to be used in numerical model simulations. The results suggest the use of correct relative permeability plays an important role in multiphase modeling and need for continued research to determine the relative permeability relationships in CO₂ sequestration modeling.

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