Relative Permeability for Multiphase Flow for Oven-Dry to Full Saturation Conditions

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Abstract

Numerical simulation of supercritical CO₂ (CO₂) injection into deep geologic reservoirs often requires the modeling of multifluid flow and transport. The classical capillary and relative permeability models assume that the residual water is immobile and irreducible. This assumption is not in agreement with the flow process for CO₂ injection into a saline aquifer. In this paper, the relative permeability (k_r) – saturation (S) relationships for both the aqueous and non-aqueous phases are derived for oven-dry (i.e., zero liquid saturation) to full saturation conditions by extending the classical k_r - S relationships. The extended relative permeability models reduce to the corresponding classical forms when the aqueous saturation is higher than the critical value, but deviates from the latter when the aqueous saturation is lower than the critical value. The implementation of the extended models in the STOMP multifluid flow and transport model is demonstrated by the simulation of dry CO₂ injection from a vertical well into a homogeneous reservoir. The extended models overcome the limitations of the classical models and can simulate the dry-out processes associated with the residual water. The extended models are expected to simulate CO₂ injection and the subsequent processes (e.g., the dry-out of brine and salt precipitation) more accurately than the classical models.

Key Words: Geologic Sequestration; Hydraulic Properties; Residual Saturation; Numerical Simulation; Dry-Out; Salt Precipitation

1. Introduction

Numerical simulation of super-critical CO₂ (CO₂) injection into deep geologic reservoirs often requires the modeling of multifluid flow and transport (e.g., USEPA, 2013). For convenience, the CO₂ in super-critical phase is referred to as the non-aqueous or gas phase hereafter. The calculation of relative permeability of the aqueous (wetting, brine) or the non-aqueous (non-wetting, CO₂) phase using classical models, such as those in Burdine (1953) and Mualem (1976), is based on the definition of the effective saturation, $\bar{S}_l$, defined as

$$\bar{S}_l = \frac{S_l - S_{lr}}{1 - S_{lr}} \quad (1)$$

where S_l and S_{lr} are the saturation and residual saturation of the aqueous phase, respectively.

Most, if not all, relative permeability models assume that the aqueous flow is negligibly small when a porous medium is at or less than S_{lr} . In other words, the residual water is considered immobile and irreducible. Practically, the reasons for finite value of S_{lr} are that the dominant historical wetting fluid content measurements were in the wet range and the typical fluid capillary data demonstrated an asymptotic behavior.

The hydraulic properties at very low water content, conceptualized as networks of surface capillary channels interspersed with thin films, have been measured and modeled (e.g., Pachepsky et al., 1984; Tokunaga and Wan, 1997; Tokunaga et al., 2000). Theoretically, the classical relative-permeability models are based only on capillary flow while any other flow types (e.g., film or corner flow) are not considered. Consequently, these models generally produce acceptable results at high and intermediate wetting fluid content and relatively poor results at low wetting fluid content. These models do not apply to conditions of $S_l \leq S_{lr}$, such as during CO₂ injection where the residual water can be evaporated by the injected dry CO₂ or water imbibition into the dry-out zone. During CO₂ injection, the evaporation of water can dry

out the residual water even when the water is immobile. However, when CO₂ injection stops, water will imbibe into the dry-out zone and the relative permeability at the very low water saturation must be quantified in order to simulate this imbibition process without imposing arbitrary k_{rl} .

Webb (2000) extended the classical capillary functions (e.g., Brooks and Corey, 1966; van Genuchten, 1980) to oven-dry condition applying the adsorption-based model of Campbell and Shiozawa (1992). Following Ross et al. (1991) and consistent with Webb (2000), the term oven dry is equivalent to zero liquid saturation conditions. However, the Webb (2000) model did not address the calculation of relative permeability at low water content. For numerical expedience, modelers hence often introduce arbitrary assumptions (e.g., by imposing the relative permeability being zero or other values) that are often not explicitly stated in the model descriptions. A discussion of some of these arbitrary methods, making capillary and relative permeability functions inconsistent, is discussed by Oostrom et al. (2016). To solve this problem, Zhang (2011) assumed that the classical capillary function definition applies to the full range of saturation and defined a state-dependent S_{lr} for the condition of $S_l < S_l^m$, where S_l^m is the critical wetting-phase saturation. In this way, the original capillary function definition and corresponding compatible relative permeability can be used without additional change. The Zhang (2011) model produces a small, but non-zero, aqueous saturation at the oven-dry condition. Physically this is possible because not all the water molecules are driven out from a formation or rock sample at the standard oven temperature (i.e., 105°C). An inconvenience of the Zhang (2011) model is that no explicit algebraic relationship is available to express capillary pressure, P_c , as a function of S_l when $S_l < S_l^m$. Hence, an iterative process would be needed to find P_c values corresponding to S_l

1 $< S_l^m$. The algorithm can be readily implemented but requires slightly more computational effort
2 than the classical models.

3 Peters (2013) described the full range capillary function as the summation of two curves, one
4 for the capillary water and the other for the adsorbed water. The resulting total $P_c(S_l)$ relationship
5 is equivalent to the Webb (2000) model except that Peters (2013) introduced an empirical weight
6 to separate the two components, while Webb (2000) used a tangent line method. Peters (2013)
7 further calculates the relative permeability using the commonly used models for capillary flow
8 for each of the two capillary function components. As the residual saturation is not a constitutive
9 parameter in the adsorption capillary model, actual water saturation, instead of the required
10 effective saturation, was imposed in Peters (2013) for the calculation of aqueous relative
11 permeability, k_{rl} , due to the adsorbed water.

12 In this paper, a formulation of the residual water content is derived for the adsorbed water
13 such that compatible $P_c(S_l)$ and $k_r(S_l)$ relationships can be obtained for the full range of water
14 content using the classical Burdine (1953) or Mualem (1976) models. Furthermore, $k_r(S_l)$
15 relationships compatible with the extended $P_c(S_l)$ relationship for the non-aqueous phase are
16 derived. The extended models were incorporated in a numerical simulator and demonstrated for
17 injection of CO₂ into three types of sandstone reservoirs.

18 **2. Theory**

19 In this section, after briefly summarizing the classical hydraulic functions and the Webb
20 (2000) extension of the capillary function, the formulation of the relative permeability for the
21 wetting and non-wetting phases compatible with the Webb (2000) model is presented.

2.1. Classical Hydraulic Functions and the Webb Extension

The non-hysteretic Brooks and Corey (1966) and van Genuchten (1980) models (referred to as the BC and VG models, respectively, hereafter) are two commonly used capillary functions for the aqueous phase:

$$\text{BC model:} \quad \bar{S}_l^I(P_c) = \begin{cases} (P_c^e / \beta P_c)^\lambda & \text{if } P_c > P_c^e \\ 1 & \text{if } P_c \leq P_c^e \end{cases} \quad (2a)$$

$$\text{VG model:} \quad \bar{S}_l^I(P_c) = [1 + (\alpha \beta P_c)^n]^{1/n-1} \quad (2b)$$

where the superscript I denotes the classical capillary models, β [-] is an interfacial-tension dependent scaling factor, P_c^e [Pa] is the air-entry capillary pressure, and α [Pa⁻¹] is a fitting parameter that is inversely proportional to the air-entry pressure; λ [-] and n [-] are fitting parameters related to particle-size distribution. Assuming that formation pores can be represented as a bundle of cylindrical capillaries, Burdine (1953) and Mualem (1976) developed similar but slightly different expressions for the relative permeability due to capillary flow. Their expressions can be written in a general form as

$$k_{rl}(\bar{S}_l) = \bar{S}_l^L \frac{\Gamma(0, \bar{S}_l)}{\Gamma(0,1)} \quad (3a)$$

$$k_{rg}(\bar{S}_l) = (1 - \bar{S}_l)^L \frac{\Gamma(\bar{S}_l, 1)}{\Gamma(0,1)} \quad (3b)$$

where

$$\Gamma(a, b) = \left[\int_a^b \left(\frac{d\bar{S}_l}{P_c(\bar{S}_l)^\omega} \right) \right]^\gamma \quad (4)$$

L [-] is the connectivity-tortuosity coefficient, and ω [-] and γ [-] are constants; k_{rg} [-] is the relative permeability for the gas (CO₂) phase. Equation (3a) is equivalent to the Mualem (1976)

relationship when $\omega = 1$ and $\gamma = 2$ and the Burdine (1953) relationship when $\omega = 2$ and $\gamma = 1$ for the aqueous phase relative permeability. Substituting the Brooks and Corey (1966) relation (Eq. 2a) or the van Genuchten (1980) relation (Eq. 2b) into (3) produces the relative permeability models. The relative permeability model based on the Brooks and Corey (1966) and the Burdine (1953) relationships is referred to as the BC-B model and the model based on the van Genuchten (1980) and Mualem (1976) relationships is referred to as the VG-M model hereafter.

To describe the $P_c(S_l)$ relationships for the full-range of saturation, the aqueous phase is conceptualized as a combination of capillary water and absorbed water (Webb, 2000; Zhang, 2011). The $P_c(S_l)$ relationships are divided into two segments (Figure 1), separated by the critical capillary pressure, P_c^m , a point at which the tangent line passes the point corresponding to the oven-dry condition, P_c^d , which is typically assumed to be about 10^9 Pa (Groenevelt and Grant, 2004; Rossi and Nimmo, 1994). Segment I, valid for $P_c < P_c^m$, can be described by the classical models (e.g., BC and VG functions in Eq. 2), while an extension, e.g., using the method of Webb (2000), which was based on the log-linear adsorption model proposed in Campbell and Shiozawa (1992), is used for segment II:

$$S_l^H(P_c) = \begin{cases} 0 & \text{if } P_c \geq P_c^d \\ S_l^m \ln(P_c^d / P_c) / \ln(P_c^d / P_c^m) & \text{if } P_c^m < P_c < P_c^d \end{cases} \quad (5)$$

The log-linear capillary model has been verified against experiment data in the water-air system by many researchers (e.g., Campbell and Shiozawa, 1992; Fayer and Simmons, 1995; Rossi and Nimmo, 1994; Webb, 2000). The method to determine S_l^m for the van Genuchten (1980) function can be found in Webb (2000) and Zhang (2011), while the method for the Brooks and Corey function is described by Zhang (2011). Briefly, at the critical point, the slope of the $\ln(P_c)$ - S_l

1 curve for segment I is equal to that for segment II. Then P_c^m can be solved equating the two slope
 2 expressions using a numerical solver (e.g., the root function in MathCad, Parametric Technology
 3 Corporation, Needham, MA) and S_l^m can be obtained using the corresponding $P_c(S_l)$ relationship
 4 (Eq. 2).

5 **Figure 1.** Schematic of the classical and extended models of (a) capillary pressure, (b) aqueous
 6 relative permeability, and (c) the non-aqueous relative permeability. S_{lr} is a constant for the
 7 classical model and follows Eq. (6) for the extended model (green lines).
 8
 9

2.2. Relative Permeability at Low Water Content

The residual aqueous saturation S_{lr} is not a parameter in the adsorption-based model (Eq. 5), which is not compatible with the commonly used relative permeability models (Eq. 3) unless a zero value of S_{lr} is enforced as in Fayer and Simmons (1995). However, the use of zero S_{lr} makes the capillary function different from the classical version (Eq. 2), even for segment I.

The derivation below assumes that the same relative permeability, k_{rl} , model (e.g., Burdine, 1953; Mualem, 1976) for the capillary water can be extended to the full range of water content.

In other words, the $k_{rl}(\bar{S}_l)$ and $k_{rg}(\bar{S}_l)$ relationships apply to the full range of water content without any change in formulation. This requires that the effective saturation for segment II,

$\bar{S}_l''(P_c)$, has the same form as $\bar{S}_l'(P_c)$ (Eq. 2), i.e., $\bar{S}_l''(P_c) = \bar{S}_l'(P_c)$. This way, the same

formulations for the aqueous and non-aqueous phase relative permeability can be used from full saturation to the oven-dry condition P_c^d . As a result, the matching S_{lr}'' for segment II is given as

$$S_{lr}''(P_c) = \begin{cases} 1 - \frac{1 - S_l''(P_c)}{1 - \bar{S}_l'(P_c)} & \text{if } P_c^m < P_c \leq P_c^{d*} \\ 0 & \text{if } P_c > P_c^{d*} \end{cases} \quad (6a)$$

where P_c^{d*} is the capillary pressure at which $S_{lr}'' = 0$ using Eq. (6a). P_c^{d*} is approximately equal to P_c^d . For most formations, P_c^{d*} ranges between $0.95 P_c^d$ and P_c^d except for very fine formations.

An exact value of P_c^{d*} can be found by setting $S_l''(P_c^{d*}) = \bar{S}_l'(P_c^{d*})$. Using Eqs. (5) and (6), the

modified effective aqueous saturation, $\bar{S}_l^*$, is then defined as

$$\bar{S}_l^*(P_c) = \begin{cases} \frac{S_l(P_c) - S_{lr}}{1 - S_{lr}} & \text{if } P_c \leq P_c^m \end{cases} \quad (7a)$$

$$\bar{S}_l^*(P_c) = \begin{cases} \frac{S_l(P_c) - S_{lr}^{II}(P_c)}{1 - S_{lr}^{II}(P_c)} & \text{if } P_c^m < P_c < P_c^d \end{cases} \quad (7b)$$

1 If S_{lr}^{II} for segment II (Eq. 6) is substituted into Eq. (7), it will produce the effective saturation
 2 for segment II being equal to the effective saturation for Segment I, namely, $\bar{S}_l^*(P_c) = \bar{S}_l^I(P_c)$.
 3 With the modified definition of effective saturation in Eq. (7), the relative permeability models
 4 (Eq. 3) are now compatible with the capillary functions for both segments I (Eq. 2) and II (Eq. 5)
 5 and apply to the full range of wetness after replacing $\bar{S}_l$ with $\bar{S}_l^*$ in Eq. (3). The extended BC-B
 6 and VG-M hydraulic conductivity models as a function of $\bar{S}_l^*$ are given as

$$k_{rl} = \bar{S}_l^{*L_b+1+2/\lambda} \quad (8a)$$

Extended BC-B model:

$$k_{rg} = (1 - \bar{S}_l^*)^{L_b} \bar{S}_l^{*(L+\lambda)/\lambda} \quad (8b)$$

$$k_{rl} = \bar{S}_l^{*L_m} \left[1 - \left(1 - \bar{S}_l^{*1/m} \right)^m \right]^2 \quad (9a)$$

Extended VG-M model:

$$k_{rg} = \left(1 - \bar{S}_l^* \right)^{L_m} \left[1 - \bar{S}_l^{*1/m} \right]^{2m} \quad (9b)$$

7 where L_b and L_m are constant with typical values of 2 and 0.5, respectively. The above
 8 formulation can be readily incorporated into a numerical simulator. Researchers (e.g., Tokunaga,
 9 2009; Zhang, 2011) have found that film flow may become relatively important over capillary
 10 flow at low fluid content. In a fractured rock, water film at fracture surfaces becomes important
 11 only at near-zero capillary pressure (Tokunaga and Wan, 1997). If film flow is to be considered,
 12 the total permeability is the sum of the contributions due to both flow mechanisms (Zhang, 2011).

2.3. Water Evaporation

In a multi-phase system (e.g., CO₂ gas phase and brine), the aqueous phase may be evaporated into the non-aqueous phase. The partial aqueous vapor pressure in the gas phase is related to the capillary pressure by the Kelvin equation (Nitao, 1988):

$$P_l^g(P_c) = P_{l0}^g \exp\left(-\frac{M_l P_c}{RT}\right) \quad (10)$$

where P_l^g is the partial vapor pressure [Pa] of capillary water in the gas phase, P_{l0}^g is the P_l^g of free water ($P_c = 0$), R is gas constant [$\text{J mol}^{-1} \text{K}^{-1}$], T is temperature [K], and M_l is the molar mass of water [kg mol^{-1}]. As the formation approaches full aqueous saturation, P_c approaches zero and hence P_l^g approaches to P_{l0}^g . However, when S_l approaches S_{rl} , the P_c values may differ dramatically depending on whether the classical or the extended models are used. For the classical $P_c(S_l)$ models (Eq. 2), P_c approaches infinity in an unrealistically way as S_l approaches S_{rl} and hence P_l^g approaches zero. As a result, the residual aqueous water cannot be evaporated. For the extended $P_c(S_l)$ models (Eq.5), P_c will be finite and bounded by the oven-dry condition, which is about 10^9 Pa (Groenevelt and Grant, 2004; Rossi and Nimmo, 1994). Hence, the extended formulation allows all the water (including residual water) to be evaporated according the Kelvin's equation (Eq. 10). It is pointed out that vaporization and condensation are controlled by mass transfer between phases, while the relative permeability controls fluid flow.

3. Demonstration - Numerical Simulation of CO₂ Injection

3.1. The STOMP-CO2 Simulator and Simulation Scenarios

The simulations conducted for this investigation were executed using the STOMP-CO2 simulator (White et al., 2015) after incorporating the extended capillary and relative permeability

models for both the aqueous and non-aqueous phases. Thermodynamic properties for CO₂ are computed via interpolation from the property data table in Span and Wagner (1996). Phase equilibria calculations use the formulations of Spycher et al. (2003) and Spycher and Pruess (2010). The Kelvin equation (Eq. 10) relates the water vapor partial pressure to the capillary pressure. Aqueous density is computed from a series of calculations starting with the pure-water density, computed as a function of temperature and pressure using the American Society of Mechanical Engineers' steam table formulations (Meyer et al., 1993). Gas phase density is computed from the pure CO₂ and pure water vapor densities using mass fraction weighting. Precipitated salt density is computed as a function of temperature and pressure from the formulation of Battistelli et al. (1997). Additional details on the equations of state used in STOMP-CO₂ can be found in the user guide by White et al. (2012). A well model is defined as a type of source term that extends over multiple grid cells, where the well diameter is smaller than the grid cell. A fully coupled well model in STOMP-CO₂ was used to simulate the injection of CO₂ under a specified mass injection rate. The CO₂ injection rate is proportional to the pressure gradient between the well and surrounding formation in each grid cell.

To demonstrate the difference between the classical and extended hydraulic functions on the transport of injected CO₂ in the subsurface, a one-dimensional (1-D) constant-rate CO₂ injection into a homogeneous confined saline aquifer, as described in Section 3 of Mathias et al. (2013), was simulated for three sandstone types (i.e., Paaratte, Berea, and Mt. Simon; Table 1). The hydraulic properties of the sandstones were reported in Krevor et al. (2012). Dry CO₂ is injected via a 0.2-m-radius vertical well screened through the whole reservoir thickness into a 30-m-thick homogeneous reservoir at the rate of 15 kg s⁻¹ (0.47 million metric tonnes per year) for 10 years. The initial pressure was 100 bar, temperature was 40°C, and the salt mass fraction was 0.15. The

1 injection process was simulated with a 1-D radial flow in a 40,000-m (40-km) radius cylindrical
2 domain with the injection well at the center. The top and bottom boundaries were closed while
3 the pressures at the side boundary were kept constant at the same values for the initial conditions.
4 The grid spacing in the radial direction varied between 0.05 m and 100 m and the spacing
5 increased by a factor of 1.02 as the distance from the injection well increased. There were 734
6 cells in the simulation domain. Two sets of simulations were carried out, one with the classical
7 relationships and the other with the extended relationships considering the Webb extension of the
8 BC capillary function, and the compatible relative permeability relationships (Eq. 8). The critical
9 aqueous saturation and critical capillary pressure of the BC capillary functions for the three rocks
10 are calculated internally in STOMP-CO2 and are given in Table 1.

11

Table 1. Sandstone hydraulic parameter values (from Krevor et al., 2012), and computed critical aqueous and capillary pressures for the Brooks-Corey (1966) model.

Sandstone	Permeability (m ²)	Porosity (m ³ m ⁻³)	Residual Saturation, S_{lr} (-)	Entry Capillary Pressure, P_c^e (Pa)	λ Parameter (-)	Critical Saturation, S_l^m (-)	Critical Capillary Pressure, P_c^m (Pa)
Paaratte	1.14×10^{-12}	0.283	0.05	2097	0.90	0.058	4.03×10^5
Berea	9.02×10^{-13}	0.221	0.11	2499	0.67	0.137	4.68×10^5
Mt. Simon	7.4×10^{-15}	0.244	0.22	4596	0.55	0.287	4.01×10^5

For the range of temperature and pressure conditions present in deep saline reservoirs, three phases are possible: 1) water-rich liquid (aqueous phase), 2) CO₂-rich gas (non-aqueous phase), and 3) crystalline salt (precipitated salt). A fraction of CO₂ is allowed to dissolve in the brine and a fraction of water is allowed to evaporate in the injected CO₂. Salt is allowed to precipitate when salt concentration reaches its solubility limit because of the evaporation of water in the CO₂ gas phase.

3.2. Results and Discussion

Injection of dry CO₂ into saline aquifers may cause formation dry-out and salt precipitation near the injection well. The main physical mechanisms during the CO₂ transport process include displacement of brine away from the injection well by injected CO₂, evaporation of liquid water into the flowing CO₂ stream, and salt diffusion/precipitation.

3.2.1. Extended and Classical Hydraulic Properties

To demonstrate the difference between the classical and the extended models, the capillary pressure and aqueous and non-aqueous relative permeability relations of the three selected

1 sandstones (i.e., Paaratte, Berea, and Mt. Simon; Table 1) are compared and the Mt. Simon
2 results are shown in Figure 2 as an example. Per definition, when $S_l \geq S_l^m$, the extended models
3 reduce to the corresponding classical models; when $S_l < S_l^m$, the results using the extended
4 models deviate from those using the classical models. These comparisons indicate that the
5 classical models tend to underestimate k_{rl} but overestimate k_{rg} when $S_l < S_l^m$, relative to the
6 extended models. The extended models treat the residual water as mobile and therefore their use
7 would result in more available pore volume for the CO₂ phase and hence a smaller CO₂ plume
8 extent at a given time for a given CO₂ volume than those predicted by the classical models.

9 It is pointed out that in Figure 2, k_{rl} is plotted on a logarithmic scale and is very small when S_l
10 is low. However, it is difficult to determine at what level k_{rl} becomes negligible. During a short
11 period of time (e.g., minutes to days for many laboratory experiments), some small k_{rl} values
12 may not matter much in terms of generating meaningful volumes of aqueous flow. However,
13 over a long period (e.g., years, decades, or longer), the cumulative effects of these same small
14 values may not be negligible. The proposed k_{rl} model quantifies both the aqueous and non-
15 aqueous flow over any time period of interest.

Figure 2. Comparison between the classical and extended a) capillary function, b) aqueous relative permeability, and c) non-aqueous relative permeability models for the Mt. Simon sandstone.

3.2.2. Displacement of Brine

Figure 3 shows the simulated CO_2 gas saturation distribution using the classical and extended capillary pressure and relative permeability formulations. Early in the simulation (e.g., before

1 about 10^{-3} yr), the injected CO₂ gradually fills the pore space in the rock by displacing brine and
2 thus the gas saturation within the plume is less than the maximum value. It is noted that, in the
3 STOMP simulator, when salt precipitation starts to occur, S_g and S_l are defined relative to the
4 available void space excluding the volume of solid salt. However, the definition may be different
5 in other simulators. The maximum gas saturation hence is $1-S_{lr}$ for the classical models but is 1
6 for the extended models. As the injection continues, an inner zone, defined as the region without
7 mobile water, is formed around the injection well. Within the inner zone, the gas saturation
8 reaches the maximum values. The lateral extent of both the inner and outer zones increases with
9 time.

10 When the classical models are used, the injected CO₂ never fills all the pore space because
11 the models assumed that the residual water is immobile and irreducible. Hence, there is always
12 residual water in the rock. Practically, residual water is unlikely to sustain in the inner zone. The
13 classical models, because of their limitation in the mathematical formulation, predict sustainable
14 irreducible water saturation in the inner dry-out zone. Conversely, the extended models
15 overcome this limitation and reasonably predict zero saturation in the inner zone (Figure 3).

16 The lateral extents of both the inner and outer zones obtained from the extended models for
17 the Paaratte (Figure 3a) and Berea (Figure 3b) scenarios are nearly the same as those from the
18 classical models, but slightly smaller for the Mt. Simon (Figure 3c) scenario. The difference
19 appears to be larger when the residual water saturation (Table 1) is higher.

Figure 3. Simulated CO₂ gas saturation distribution with the classical and extended models of capillary pressure and aqueous and non-aqueous phase relative permeability.

Figure 4 shows the gas pressure distribution. At a given time, gas pressure is the highest near the injection well (0.2 m) and decreases with distance as expected. The simulated gas pressure using the extended models is slightly larger than that using the classical models when $P_c > P_c^m$.

This can be explained by the slightly smaller gas relative permeability predicted by the extended models (Figure 2c) and more salt precipitation as discussed in a following section.

Figure 4. Simulated gas phase pressure for the classical and extended models of capillary pressure and aqueous and non-aqueous phase relative permeability.

3.2.3. Water Evaporation into the CO₂ Gas Phase

As dry CO₂ is injected into the saline aquifer, a fraction of the water in the brine is evaporated into the CO₂ stream following Kelvin's law. The STOMP-CO₂ simulator assumes that the evaporation happens instantaneously. Figure 5 shows the spatial distribution of the water vapor fraction in the gas phase simulated using the classical and extended models. Both models produce similar results for all cases. The water vapor mass fraction is about zero in the inner zone of the CO₂ plume because there is no water for the extended model or no mobile water for the classical model. Outside the inner zone, the water vapor fraction in the gas is nearly constant (i.e., about 0.0018) for the Paaratte and Berea scenarios and between 0.0018 and 0.0025 for the Mt. Simon simulation. The slightly higher water vapor fraction in the Mt. Simon reservoir is due to the much lower permeability of the rock and hence the much higher gas pressure, as shown in Figure 4. Because P_{l0}^g increases with P , the higher gas pressure causes a higher P_{l0}^g in the CO₂ plume for the Mt. Simon reservoir (Figure 5c). Note that there is no actual evaporation beyond the CO₂ plume (e.g., for radial distances greater than approximately 1000 m as shown in Figure 3). The water vapor mass fraction beyond the CO₂ plume in Figure 5 depicts the partial vapor pressure of free water in CO₂ gas phase. The transition from zero vapor fraction in the inner zone to the maximum value in the outer zone is more gradual for the extended models than for the classical models, because the change of P_c is more gradual when $P_c > P_c^m$, as shown in Figure 2a.

Figure 5. Water vapor mass fraction in the gas phase simulated with the classical and extended models of capillary pressure and aqueous and non-aqueous phase relative permeability.

3.2.4. Salt Precipitation

Several mechanisms may affect salt transport and precipitation/dissolution:

- i. *Brine convection due to pressure gradient.* The pressure gradient due to CO_2 injection drives brine away from the injection well.

1 ii. *Salt precipitation.* Evaporation of water in CO₂ gas first increases the salt concentration,
2 *C*, in brine. When *C* reaches the solubility limit, C^{max} , additional evaporation of water
3 will cause the precipitation of salt.

4 iii. *Brine convection due to capillary gradient.* Brine displacement by CO₂ gas creates a
5 capillary gradient in the opposite direction to the pressure gradient. The capillary gradient
6 causes slow brine movement toward the injection well when the capillary gradient is
7 larger than the pressure gradient.

8 iv. *Salt diffusion.* The diffusion of the dissolved salt from the region of higher *C* to the
9 region of lower *C* causes dissolution of precipitated salt.

10 These mechanisms occur at the locations containing the injected CO₂, but salt diffusion does
11 not take effect if there is no liquid water. Hence, the existence of residual water within the inner
12 dry-out zone of the CO₂ plume has a considerable impact on the salt precipitation.

13 Figure 6 shows the precipitated salt volume fraction of pore space (f_{sv}) near the injection well
14 over time. For all three cases, except at the early time, the predicted f_{sv} by the extended models
15 are substantially higher than the corresponding values predicted by the classical models. This
16 difference is possibly due to presence or lack of residual water (and dissolved salt) in the inner
17 zone of the CO₂ plume. When the extended models are used, there is no residual water and hence
18 no salt dissolution in the inner zone; namely, salt precipitation occurs to the residual water but
19 salt diffusion does not take effect due to the lack of water. As a result, the salt saturation is
20 relatively high and stable over time. When the classical models are used, some of the salt stays
21 dissolved in the residual water and hence there is less salt precipitation. Additionally, the
22 precipitated salt starts dissolving slowly at about 3 yr for the Berea (Figure 6b) scenario and at
23 about 0.2 yr for the Mt. Simon (Figure 6c) scenario, likely due to salt diffusion in the residual

water. This diffusion process is stronger in rock with higher S_{lr} (0.22 for Mt. Simon, Figure 6c) than in rock with a lower S_{lr} (0.05 for Paaratte, Figure 6a; 0.11 for Berea, Figure 6b).

Figure 6. Precipitated salt volume fraction of pore space in the first grid cell (radial distance of 0.225 m) near the injection well for the classical and extended models.

Because residual water is unlikely to sustain in the inner zone of the CO_2 plume, the above results indicate that the classical models tend to underestimate salt saturation. The precipitated

salt will reduce the porosity and permeability of rocks and thus the classical models are likely to underestimate the injection pressure. It is expected that the extended models can simulate CO₂ injection and the subsequent processes more accurately than the classical models.

4. Summary

The relative permeability – saturation relations for both the aqueous (wetting) and gas (non-wetting) phases are derived for oven-dry to full saturation conditions. This is achieved by defining the residual saturation for the segment of the capillary function that is described by the adsorption model. The definition of state-dependent S_{lr} extends the lower bound of k_{rl} and k_{rg} from the residual aqueous saturation to the oven-dry condition. The extended k_{rl} and k_{rg} models reduce to the corresponding classical forms when the aqueous saturation is higher than the critical value. However, extended and classical formulations deviate when the aqueous saturation is lower than the critical value. The formulation can be readily incorporated into a numerical multifluid simulator.

The primary difference between the extended and classical relative permeability models is that the former treats the residual water as being mobile while the latter treats it as immobile. The extended models and their impact on the development of a CO₂ plume, water evaporation in CO₂ gas phase, and salt precipitation were demonstrated by simulating these processes during an injection of dry CO₂ from a vertical well into a homogeneous reservoir. Soon after CO₂ injection begins, a region without mobile water within the CO₂ plume is developed. The classical models, which assume residual water is immobile, incorrectly predict the presence of an irreducible water saturation in the inner dry-out zone. The extended models overcome this limitation and reasonably predict zero saturation in the inner zone, as expected based on the physical processes.

1 The classical and extended models produce similar results for water vapor in the CO₂ phase,
2 but they predict substantially different results in salt precipitation and possible salt dissolution.
3 Except for early stages in the simulations, the precipitated salt volume fractions predicted by the
4 extended models are considerably higher than the corresponding values predicted by the classical
5 models. This difference is possibly due to presence or lack of residual water (with dissolved salt)
6 in the inner zone of the CO₂ plume. The extended models reasonably predict the process of salt
7 precipitation, while the classical models appear to underestimate salt saturation and hence the
8 injection pressure. It is expected that the extended models can simulate CO₂ injection and
9 associated processes more accurately than the classical models.

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Figure 1. Schematic of the classical and extended models of (a) capillary pressure, (b) aqueous relative permeability, and (c) the non-aqueous relative permeability. S_{lr} is a constant for the classical model and follows Eq. (6) for the extended model (green lines).

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Graphical Abstract