

Capillary Pressure and Relative Permeability Model Uncertainties in Simulations of Geological CO₂ Sequestration

LU Chuan*, LI Long, LIU Yan-guang, WANG Gui-ling

The Institute of Hydrogeology and Environmental Geology, CAGS, Shijiazhuang, China.

Abstract: Precise descriptions of saturation, capillary pressure and relative permeability s - p_c - k_r relations are essential for predictions and simulations on multiphase flow system. The primary object of this work is to investigate their influence on geological CO₂ sequestration processes. Five types of commonly used s - p_c - k_r relations are examined in this study. Simulation results show significant influences of s - p_c - k_r relations on 1) the location and saturation of displacement fronts, 2) buoyancy driven migration speed, 3) horizontal spreading distance and the rate of dissolution of supercritical CO₂. The effects of capillary pressure on the horizontal spreading of supercritical CO₂ plume and its dissolution rate was resolved in this study for the 1st time in literatures. Simulation results of subsurface CO₂ storage suggest that that careful selection of s - p_c - k_r relations and calibration methods are essential for accurate predictions.

Keywords: CO₂ storage; Relative permeability; Capillary pressure; Hysteresis

Introduction

CO₂ sequestration (capture, separation, and long term storage) in various geologic media (such as depleted oil reservoirs, saline aquifers, oceanic sediments at different depths) is being considered as a possible solution to reduce green house gas emissions. This approach has been widely discussed in literatures during the last decade (Holt Jensen, Lindeburg, 1995). Field-scale experiments are currently being conducted in various locations around the globe. For example, large scale CO₂ disposal in deep saline aquifers has been practiced in the Norwegian sector of the North Sea (Sleipner) since 1996 (Karbol, Kaddour, 1995).

It is widely accepted that the mechanisms to keep sequestered CO₂ from escaping to the surface strongly rely on four mechanisms: hydrodynamic (mobile), residual, solubility and mineral trapping (S Bachu, Gunter, Perkins, 1994; Hitchon, Eds, 1996; Orr Jr, 2004). First, supercritical (SC) CO₂ can be stored as a mobile phase below a low

permeable formation or cap rock. This trapping mechanism is called “hydrodynamic trapping”. Second, SC CO₂ can be trapped in pores as immobile phase due to capillary pressure that immobilizes CO₂, called residual trapping. The time scale of both hydrodynamic and residual trapping is generally considered to be on the order of hundreds of years. Third, both mobile (free-flowing) and immobile (residual) CO₂ can subsequently dissolve into reservoir fluids, i.e. solubility trapping. The time scale of solubility trapping is generally considered as between a hundred and a thousand years. Finally, the dissolution of SC CO₂ into formation waters will decrease the pH of the reservoir fluid and induce corresponding dissolution of the primary minerals in the host rock and lead to subsequent precipitation of carbonate minerals. This mechanism is referred to as mineral trapping. The time scale of mineral trapping is generally considered as greater than a thousand years because of the slow rates of relevant reactions.

Accurate simulation and prediction of these trapping mechanisms are essential to forecast the

*Corresponding author. E-mail: luchuancn@163.com

fate of sequestered CO₂. Traditional multiphase modeling approaches simultaneously solve mass conservation equations for every primary component based on a continuum formulation wherein an extended Darcy's law is adopted to calculate fluid flow rates in multiphase systems. Models describing constitutive relations between saturation-capillary pressure-relative permeability (s - p_c - k_r) are necessary for equation enclosure. Many forms of constitutive relations of s - p_c - k_r have been proposed. Among them, the van Genuchten--Mualem (Van Genuchten, 1980) model and Brooks and Corey--Burdine (Brooks, Corey, 1964) model are the most commonly used relations. Many hysteretic models based on these models have also been developed (Lenhard, Parker, 1987; White, Oostrom, 1998). However model validations have been limited by lack of experimental data, especially for the SC CO₂--brine and SC CO₂--brine--oil systems. Although CO₂ flooding has been studied for decades as one of important methods for enhanced oil recovery, the emphasis of the petroleum industry is on oil--CO₂ phase interactions, whereas the water--CO₂ system is treated using rather rough approximations. In addition, many brine formations considered as candidate sequestration sites are quite deep, where pressure, temperature and other conditions generally exceed the applicable range of these relations as typically encountered in the petroleum industry. Similarly, experiences gained from studies of air-water systems may not be applicable either, since these experiments are usually conducted under atmospheric pressure and the non-wetting phase behavior in these systems are significantly different from that in a deep SC CO₂/saline system. Even though experimental data are available in some cases, a closed form formula is still greatly desired, as it makes application easier, especially for hysteretic models, since experiments cannot provide scanning curves with all possible turning points. A pre-determined form for s - p_c - k_r relations is strongly desirable.

In many cases, the regressed residual does not give useful information for model selection, especially when data are sparse or do not covers the whole drainage--imbibitions range, or the estimated experimental error associated with the data exceeds the difference between models. Moreover, the information about the capillary

pressure and relative permeability may not exist for candidate sites under investigation, especially on the early site screening stage. Numerical simulations have to be based on assumptions. It is necessary to understand how different s - p_c - k_r relations lead to different simulation results. This aspect has been studied for LNAPL (e.g. Oostrom, Hofstee, Dane, 1997), DNAPL (e.g. Rathfelder, Abriola, 1998) and two phase steam/water systems (e.g. Doughty, Pruess, 1998) and in variably saturated or saturated media, although with divisive conclusions. For the SC CO₂ system, this topic has not been widely discussed according to authors' knowledge.

Although hysteretic characteristic curves are routinely employed by the petroleum industry, they are less commonly used in studies of the vadose zone, geologic isolation of nuclear waste, and many other research areas where multiphase flow does happen (Doughty, 2007). This is mainly because the aqueous phase behavior is important in applications of these field and hysteresis effects are usually weak for the wetting phase relative permeability (Kaluarachchi, Parker, 1992). However, simulations regarding geological CO₂ storage require emphasis on the non-wetting SC CO₂ phase instead of the aqueous phase. Meanwhile, the CO₂/saline system does have some new features. For instance, the interfacial tension (IFT) and consequentially the capillary pressure, relative permeability are dependent on the system pressure, temperature and salinity (Stefan Bachu, Bennion, 2007). The wettability alteration caused by the dissolution of CO₂ in aqueous phase was observed experimentally as well (Chalraud *et al.* 2009). How these phenomena affecting the s - p_c - k_r relations and the simulation results consequently should be investigated. Another example is the formation dryout behavior during SC CO₂ injection, caused by the evaporation of water in SC phase. Though the solubility of H₂O in SC CO₂ phase is low, it can cause the formation near wellbore dry out (Pruess, Muller, 2009). This behavior generally does not exist in contaminant hydrology studies. During the drying out and rewetting processes, how to determine or predict the s - p_c - k_r relation and how these relations affecting simulation results remain subjects of debate. Studies and discussions around these issues beyond the scope of this work, study results on

some topics of them will be reported in a separate publication, future studies should attempt to resolve these mysteries.

The goal of this study is to investigate the influence of different saturation--capillary pressure--relative permeability models on simulation results for geological CO₂ storage modeling. Most investigations will focus on migration, redistribution, hydrodynamic and residual trapping of the SC CO₂ phase. The influence of saturation--capillary pressure--relative permeability relations on the solubility trapping mechanism is investigated in this work as well. Simulations are conducted with 5 types of non-

hysteretic s - p_c - k_r relations to examine the sensitivity of results to model selection.

1. Model description and Numerical Solution

1.1 Governing equations and numerical solution approach

For multiphase subsurface flow, the conventional governing equations are adopted in this study, read as:

$$\frac{\partial}{\partial t} \sum_{\alpha} (\phi s_{\alpha} \rho_{\alpha} X_i^{\alpha}) + \nabla \cdot \sum_{\alpha} [q_{\alpha} \rho_{\alpha} X_i^{\alpha} - \phi s_{\alpha} D_i^{\alpha} \rho_{\alpha} \nabla X_i^{\alpha}] = Q_i \quad (1)$$

for mass conservation, and

$$\frac{\partial}{\partial t} \left[\phi \sum_{\alpha} s_{\alpha} \rho_{\alpha} U_{\alpha} + (1 - \phi) \rho_r c_r T \right] + \nabla \cdot \left[\sum_{\alpha} q_{\alpha} \rho_{\alpha} H_{\alpha} - \kappa \nabla T \right] = Q_e \quad (2)$$

For energy conservation, where α denotes the phase index (aqueous and SC CO₂), and i refers to a component index ($i=1$ for the saline component, 2 for CO₂). The Q_i and Q_e are the source/sink term of component i and energy. The quantities ρ , s , D , U , H are the density, saturation, diffusion coefficient, internal energy and enthalpy of each phase, respectively. The quantities X_i^{α} are the molar fraction of component i in phase α . The quantity T stands for temperature. ϕ denotes porosity, τ is tortuosity of the porous media. The quantities c_r , and λ are rock heat capacity, and conductivity, respectively. The summation are conducted over all phases, giving the total mass of component i or energy. The Darcy velocity q is given by an extended form of Darcy's law,

$$q_{\alpha} = - \frac{k k_{\alpha}}{\mu_{\alpha}} \nabla p_{\alpha} - W_{\alpha} \rho_{\alpha} g Z \quad (3)$$

with permeability k , relative permeability k_{ra} , fluid viscosity μ_{α} and pressure p_{α} of Phase α . The difference of pressure between the pressures of two phases p_{α} and p_{β} satisfies the relation:

$$p_{\alpha} = p_{\beta} - p_{c,\alpha\beta} \quad (4)$$

Where $p_{c,\alpha\beta}$ is the capillary pressure. Both p_c and k_{ra} are functions of saturations, they can be calculated by correlation formulas, as shown in the next section.

Equations of state (EOS) are used to calculate the phase density, internal energy and enthalpy. EOSs are generally functions of the concentrations of species in addition to the pressure and temperature, *i.e.* $\rho/U/H = f_1/f_2 f_3(p, T, X_i)$. The most recently published EOS was adopted to ensure accuracy (*e.g.* Span-Wagner EOS for SC CO₂ phase (Span, Wagner, 1996), IAPWS97 for water).

For a mixture of dissolved CO₂ and brine, the mixture density is calculated using a relation developed by (Carcia, 2003). From thermodynamic relations, the mixture density ρ_{mix} can be expressed in the form:

$$\rho_{\text{mix}} = \rho_{\text{saline}} + (W_{\text{CO}_2} - \rho_{\text{saline}} V_{\phi}) C_{\text{CO}_2} \quad (5)$$

Where ρ_{saline} denotes the brine density without CO₂, C_{CO_2} denotes the molar concentration of CO₂ in the brine, W_{CO_2} denotes the formula weight of CO₂. V_{ϕ} denotes the apparent molar volume of dissolved CO₂, indicates the non-ideal effects of mixing, given by an empirical relation:

$$V_{\phi} = a + bT + cT^2 + dT^3 \quad (6)$$

With coefficients $a=37.51$, $b=-9.585 \times 10^{-2}$, $c=8.740 \times 10^{-4}$, and $d=-5.044 \times 10^{-7}$ (all in SI units). The solubility of CO₂ at certain p , T and brine concentration is calculated using the (Duan, Sun, 2003) correlation, which is valid for pure water

and NaCl brines with temperatures ranging from 273 to 533 K, pressures from 0 to 2 000 bar, and ionic strength from 0 to 4.3 mol/kg H₂O.

Numerical simulations are performed using PFLOTTRAN, a parallel multiphase, multi-component reactive flow and transport code. It originated from the serial FLOTTRAN code developed at Los Alamos National Laboratory (Lichtner, 2001). PFLOTTRAN is based on the SciDAC TOPS-funded PETSc parallel library (Balay *et al.* 2004) using domain decomposition for parallelization. Its scalability has been demonstrated for up to 10 000 processors. The code has been applied to containment migration in the vadose zone (*e.g.* Hanford 300 area (Hammond, Lichtner, Lu, 2007)), and storage of CO₂ in deep geological formations (*e.g.* Lu, Lichtner, 2006)).

1.2 Five sets of s - p_c - k_r models

Five types of s - p_c - k_r relations are chosen to conduct a sensitivity analysis. The Brooks and Corey capillary pressure function (Brooks, Corey, 1964), combined with Burdine's (Burdine, 1953) permeability model is widely used in petroleum reservoir engineering and contaminant hydrology problems, read as:

$$p_c = P_D s_e^{-1/\lambda} \quad (7)$$

$$k_{rw} = s_e^{\frac{2+3\lambda}{\lambda}} \quad (8)$$

$$k_{rg} = (1-s_e)^2 (1-s_e^{\frac{2+\lambda}{\lambda}}) \quad (9)$$

where

$$s_e = \frac{s_w - s_{w,ir}}{1 - s_{w,ir}} \quad (10)$$

Is the effective water saturation, and p_c is the capillary pressure between the gas and liquid phases. This capillary pressure formula is referred as BC model, and together with the relatively permeability model are referred as BCB model in following discussions. The BCB model has a non-zero entry pressure P_D for the non-wetting phase, which gives non-zero values for p_c when the non-wetting phase is absent.

Some reported modifications can provide continuously differentiable functions over the full range of $p_c(s_w)$. Among them the van-Genuchten capillary model (van Genuchten, 1980) combined

with Mualem's (Mualem, 1976) permeability model has been widely used in soil science studies, given by:

$$p_c = \frac{1}{\alpha} (s_e^{-1/m} - 1)^{1/n} \quad (11)$$

$$k_{rw} = s_e^{1/2} [1 - (1 - s_e^{1/m})^m]^2 \quad (12)$$

and

$$k_{rg} = (1 - s_e)^{1/2} \left[1 - \left(1 - s_e^{1/m} \right)^m \right]^2 \quad (13)$$

With $m = 1 - \frac{1}{n}$. These two models are the most commonly used s - p_c - k_r relations in simulations involving lab--scale core experiments and field--scale modeling. This capillary pressure formula is referred as VG model, and together with the relatively permeability model are referred as VGM model in following discussion. Both BCB and VGM models are geometry-based, the s - k_r relations are derived from s - p_c data by assuming certain relations of pore size and the length of their interconnection, etc. For example, (Mualem, 1976) proposed a model to estimate the hydraulic conductivity function of unsaturated porous media, based on the assumptions that (1) the interconnected pores have a length proportional to their radii, (2) Poiseuille's law is valid for each individual pore, and (3) the tortuosity and correlation factors are power functions of s_e , solely depending on the pore radius R . With these assumptions the following equation for wetting phase relative permeability is obtained:

$$k_r(s_e) = s_e^\tau \frac{\left[\int_{R_{\min}}^R r f(r) dr \right]^2}{\left[\int_{R_{\min}}^{R_{\max}} r f(r) dr \right]^2} \quad (14)$$

where $f(r)$ is a distribution function of r (See (Mualem, 1976)). Noting that the capillary head $h = \frac{2\sigma_w}{r}$, the following relation is obtained

$$k_r(s_e) = s_e^\tau \frac{\left[\int_0^{s_e} h^{-1}(s) ds \right]^2}{\left[\int_0^1 h^{-1}(s) ds \right]^2} \quad (15)$$

Then by inserting VG capillary pressure model, the VGM s - p_c - k_r model was derived.

Experimental data, however, do not always testify these assumptions (e.g. Bennion, Bachu, 2006). So in this study, we also investigate a set of experimental s - p_c - k_r relations given by (Cole, 2000), obtained from core experimental data for supercritical CO₂ in a 1.2 m core of Bentheimer sandstone measured at 355.15 K and 20 MPa. The

$$k_{rg} = (s_t^* - s_e)^{1/2} [(1 - (1 - s_t^{*1/m})^m) - (1 - (1 - s_e^{1/m})^m)]^7 \quad (18)$$

Within this model, the capillary pressure and wetting phase relative permeability relation are regressed according to the VGM model with satisfactory accuracy; the relative permeability of the non-wetting SC phase is rather lower than VGM model at the same s_e . This model is referred as EXP model.

While information about relative permeability is very limited in some scenarios, researchers usually use simple hypothetical functions to represent the relations to reduce the computational cost and eliminate some complexities for better insight and understanding of other factor, or try to get analytical solutions. A simple hypothetical model (Riaz, Tchelepi, 2006) adopted in this work for comparison, read as:

$$k_{rw} = s_e^2 \quad (19)$$

and

$$k_{rg} = s_{e,g}^2 \quad (20)$$

In this model, the relative permeability is the square of the effective saturation of each phase, with the wetting phase effective saturation s_e defined in Equation (10) and $s_{e,g}$ is the non-wetting phase effective saturation defined in Equation (21),

$$s_{e,g} = \frac{s_g - s_{g,ir}}{1 - s_{g,ir}} \quad (21)$$

Where $s_{g,ir}$ is the irreducible non-wetting saturation. No capillary pressure effects was considered in (Riaz, Tchelepi, 2006). This model is referred as SF model in following discussions.

There are many subsurface multiphase simulators available, ranging from commercial

data regression results in the following constitutive relations:

$$p_c = \frac{1}{\alpha} (s_e^{-1/m} - 1)^{1/n} \quad (16)$$

$$k_{rw} = s_e^{1/2} [1 - (1 - s_e^{1/m})^m]^2 \quad (17)$$

and

software (e.g. CMG-GHG, ECLIPS *etc.*) to research codes (e.g. TOUGH family, PFLTRAN, UTCHEM, *etc.*). All of them have to contain s - p_c - k_r constitutive relations. Users may directly choose from several options for easy implementation. One of such relation in the popular simulator TOUGH2 is used by (Doughty, 2007),

$$p_c = \frac{1}{\alpha} (s_e^{-1/m} - 1)^{1/n} \quad (22)$$

$$k_{rw} = s_e^{1/2} [1 - (1 - s_e^{1/m})^m]^2 \quad (23)$$

and

$$k_{rg} = (1 - s_e)^{1/3} \left[1 - \left(1 - s_e^{1/m} \right)^m \right]^2 \quad (24)$$

This model is referred as T2E model.

In sum, the above introductions present 5 sets of s - p_c - k_r relations, BCB and VGM model are derived from theoretical analysis; SF model is purely hypothetical assumption for simplicity; EXP model is obtained from experimental data; T2E model is chosen from a simulator. These 5 types of s - p_c - k_r relations are in quite different forms. Here we assume that there is no information available to determine the s - p_c - k_r relation. The numerical simulations can adopt any arbitrarily selected model and the corresponding parameters. However to make easier comparison, the parameters assigned to every model is based on the matching of the 2 s - p_c relations (shown in Fig. 1(a)). The parameters assigned to the different relations are summarized in Table 1. The corresponding s - p_c - k_r relations are shown in Fig. 1. Note that the wetting phase relative permeability for VGM, EXP and T2E models are identical.

Table 1 Parameters assigned to five constitutive relations considered

Index	Type	Eqn. Index	Parameters			
			α	$S_{w,ir}$	$S_{g,ir}$	m
1	VGM	9	1.5×10^{-3}	0.3		0.75
2	BCB	7	1/460	0.3		1.667*
3	Simple function(SF)	13		0.3		
4	Experiment(EXP)	12	1.5×10^{-3}	0.3		0.75
5	TOUGH2 Example (T2E)	15	1.5×10^{-3}	0.3		0.75

* λ in BCB model

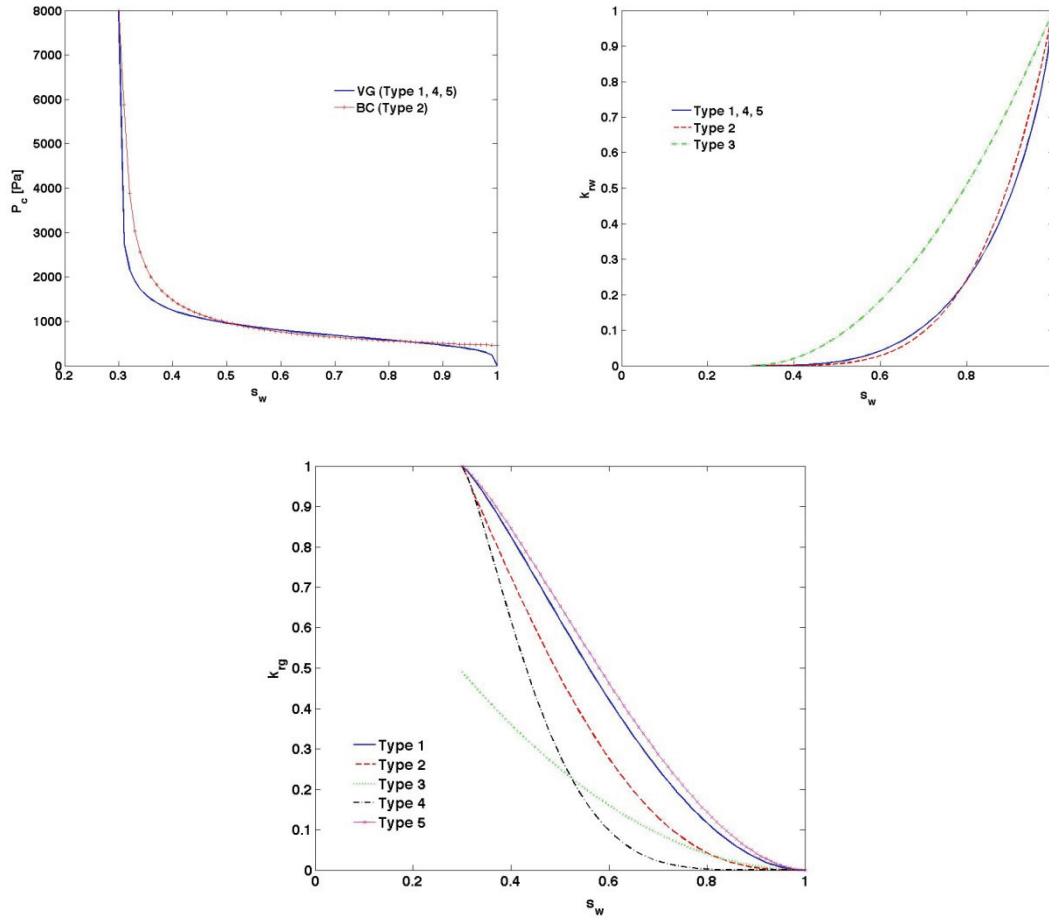


Fig. 1 Five types of s - p_c - k_r constitutive relations showing: (a) capillary pressure p_c ; (b) water relative permeability $k_{r,w}$; and (c) SC CO₂ relative permeability $k_{r,g}$, plotted as a function of liquid saturation s_w . Type 1-5 are corresponding to VGM, BCB, SF, EXP, T2E models respectively.

2. Simulation results and discussion

2.1 1D immiscible approximation: Estimation of the size of SC CO₂ plume during injection

Confined structures exist widely in many geological formations, making horizontal flow an important behavior when gas is injected into a confined layer, especially during the early stages of injection. Investigation of the migration of phase boundaries, i.e. the size of the supercritical (SC) plume, within a confined layer provides essential information for estimation and monitor of sequestration processes. This problem can be simplified as a 1D system in cylindrical coordinates, so Buckley-Leverett theory is applicable to such systems (Buckley, Leverett, 1942). Buckley-Leverett theory assumes that the physical properties of each phase are constant,

and the porosity and intrinsic permeability are also uniform. Neglecting dissolution, evaporation and capillary pressure, the mass conservation equations for brine and CO₂ can be lead to:

$$\frac{\partial s_g}{\partial t} + w \frac{\partial}{\partial a} f(s_g) = 0 \quad (25)$$

where

$a = \pi r^2$ is the area of the hypothetical SC plume with radio r , and

$$w = \frac{\dot{m}}{\phi \rho_g Z}, \rho_g \text{ and } s_g \text{ are SC phase density}$$

and saturation. (27)

The fractional flux function:

$$f(s_g) = \frac{\frac{k_{rg}}{\mu_g}}{\frac{k_{rg}}{\mu_g} + \frac{k_{rw}}{\mu_w}} \quad (28)$$

Since f is only a function of s_g , we may write $\frac{\partial f}{\partial a} = \frac{df}{ds_g} \frac{\partial s_g}{\partial a}$, then Equation (25) becomes

$$\frac{\partial s_g}{\partial t} + w \frac{df}{ds} \frac{\partial s_g}{\partial a} = 0 \quad (29)$$

This is a hyperbolic wave equation, its analytical solution defines a characteristic $a(t)$ with the interstitial velocity v by:

$$\frac{da}{dt} = v(a, t) = w \frac{df}{ds_g} \quad (30)$$

Let $s_{g,f}$ be the SC CO₂ saturation at the displacement front, Equation(31) has to be satisfied at the front:

$$\left. \frac{df}{ds} \right|_{s_{g,f}} = \frac{f(s_{g,f})}{s_{g,f}}, \quad (31)$$

and the location of the displacement front r_f is at

$$r_f(t) = \sqrt{\frac{wt}{\pi} \left. \frac{df}{ds} \right|_{s_{g,f}}} \quad (32)$$

Namely, the front saturation and velocity depend solely on the relative permeability functions and viscosity for a given constant injection rate and certain formation thickness and porosity.

Consider a formation with pressure $P=20$ MPa, temperature $T=50$ °C, applying Equation (31) to the five relative permeability functions with parameters listed in Table 1, the resulting front saturations are summarized in Table 2.

Table 2 Front saturation and flow fraction in 1D vertical system

Type	Sg,f	B	$\left. \frac{dB}{ds} \right _{s_{g,f}}$	$v_z \times 10^7$ (m/s) *	Time to reach the top (Years)**
1	0.1042	304.6524	2 923.77	1.2175	25.00
2	0.1739	237.4685	1 365.30	0.5685	53.55
3	0.1928	345.3696	1 790.88	0.7457	40.82
4	0.2899	121.3581	418.6707	0.1743	174.65
5	0.08725	316.5170	3 627.5945	1.5106	20.15

- * according to parameters in , and $\rho_w=996.53$ kg/m³, $\rho_{CO_2}=784.29$ kg/m³
- ** migrating from injection point at the depth of 96 m.

Analytical solutions are obtained for a 1D system with cylindrical coordinates, representing a thin aquifer with a thickness of 25 m. The injection rate assigned is 10 Kg/s, i.e. $\omega=2.0405 \times 10^{-3}$. At $t=20$ years, the simulated displacement front should be located at 1 296; 1 147; 970; 1 000; and 1 354 m according to Buckley-Leverett theory, for the five types of s - k_r relations (Table 1), respectively. The longest traveling distance is 40% farther than the shortest one, and the highest front saturation is over 1.6 times higher than the lowest one. The difference in front velocity and saturation is -13% and 52% between the BCB and VGM models.

Fig. 2 shows the SC phase saturation profile at 20 years obtained from numerical simulations. To be consistent with the assumptions used in the analytical solution, the capillary pressure is assigned as zero, the solubility is limited by setting a large value to Henry's coefficient, SC CO₂ phase density is set to the constant value 17.821 mol/L, the same value used in the analytical solutions. Front propagation distances gained from numerical simulations are 1 320, 1 150, 955, 1 000, 1 390 m, respectively. The maximum difference in distance is less than 3%, compared to the analytical solution. The saturation front is slightly smeared because of numerical dispersion, although the relative magnitude is consistent with the analytical solution.

Similar results can also be obtained for a 1D system in spherical coordinates, with simple modifications of $a = \frac{4}{3}\pi r^3$ and $\omega = \frac{\dot{m}}{\phi \rho_g}$.

2.2 2D simulations without hysteresis effects

2.2.1 Effects of s - k_r relations

This section presents results of numerical experiments investigating the influence of relative permeability relations on the migration, redistribution, trapping and dissolution of injected SC CO₂. These processes are simulated on a 2D homogeneous x - z coordinate system. The length

scale of this domain is 256 x 128 m, discretized with a 2x2 m uniform rectangular grid spacing. Parameters for this system are listed in Table 2. The top pressure of the domain are assigned as 20 MPa, hydrostatic pressure is assigned to initial, west and east boundary conditions with pure water's density. No flow condition is assigned to top and bottom boundary. The initial temperature is set at 50 °C uniformly. SC CO₂ is injected in the middle of the domain at the depth of 96 m with a flux of 10⁻⁴ Kg/s for 10 years. Simulations with five sets of s - p_c - k_r relations (summarized in Table 1) are conducted to analyze the influence of the choice of relative permeability constitutive relations to simulation results. No capillary pressure is considered in these simulations.

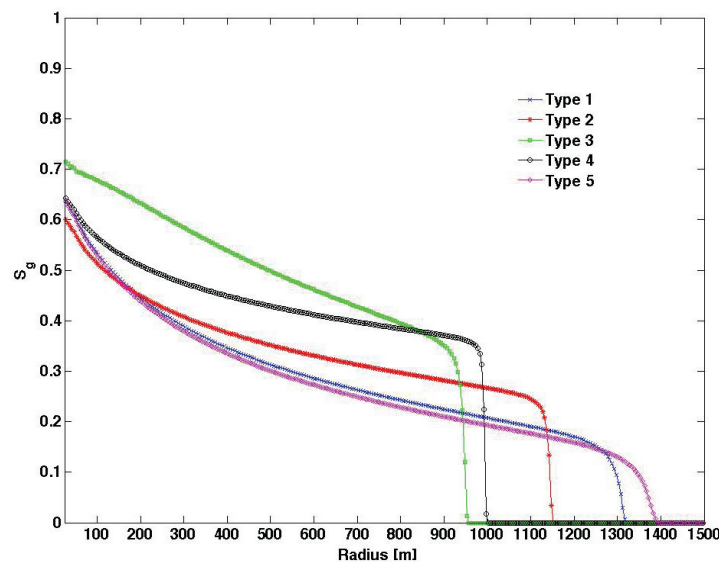
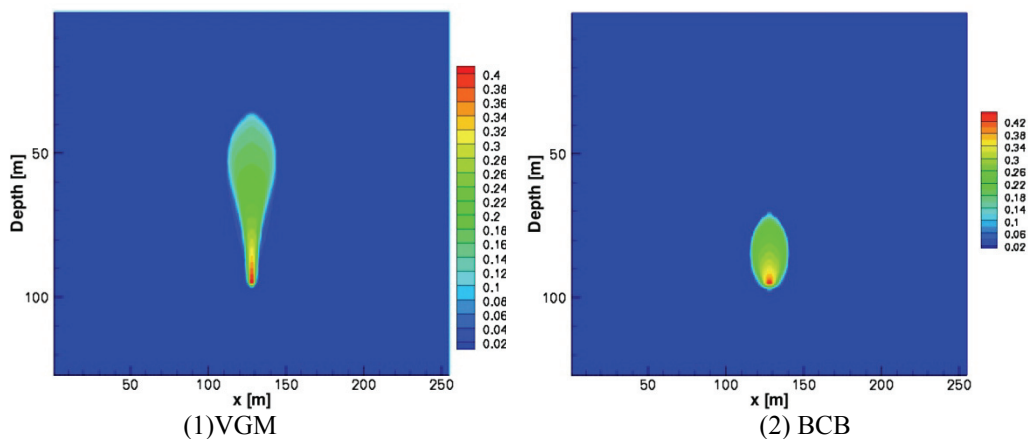


Fig. 2 Saturation profiles at 20 years of 1D horizontal simulation with 5 types of s - k_r relations. Type 1-5 is corresponding to VGM, BCB, SF, EXP, T2E models respectively.



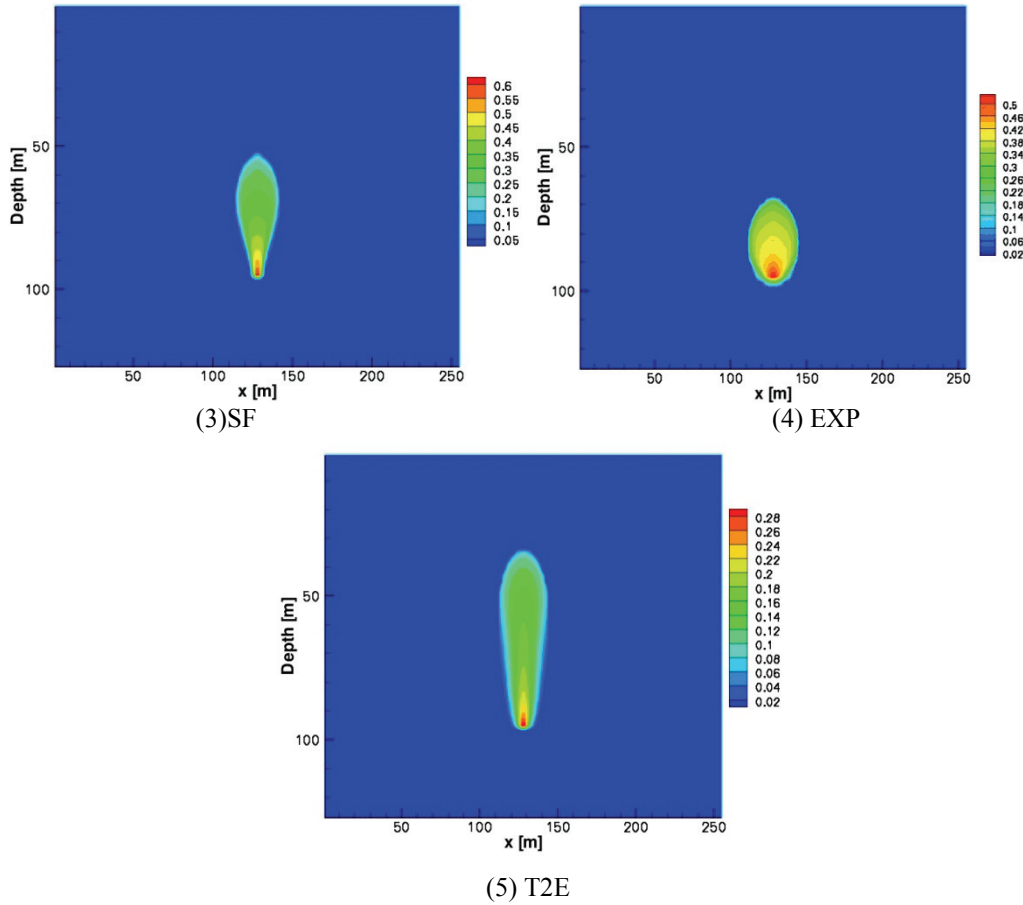


Fig. 3 Saturation profiles of SC CO₂ after an elapsed time of 10 years for the five different s - k_r curves discussed in the text.

Table 3 Formation properties simulated

Permeability (mD)		Porosity
x	Z	
10	5	0.25

Spatial moments are commonly used metrics to describe the saturation distribution quantitatively (Christ, Lemke, Abriola, 2005; Kueper, Gerhard, 1995). In two spatial dimensions they can be defined as:

$$M_{ij} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \phi_{CO_2} \rho_{CO_2} x^i z^j dx dz \quad (33)$$

Then the center of mass in the horizontal and vertical directions are X_{cm} and Z_{cm} , respectively, given as:

$$X_{cm} = \frac{M_{10}}{M_{00}}, \quad Z_{cm} = \frac{M_{01}}{M_{00}} \quad (34)$$

and the second spatial moments about the center of mass are

$$\sigma_{xx}^2 = \frac{M_{20}}{M_{00}} - X_{cm}^2, \quad \sigma_{zz}^2 = \frac{M_{02}}{M_{00}} - Z_{cm}^2 \quad (35)$$

Fig. 3 shows the saturation profiles of the SC CO₂ phase at 10 years when injection just ceases. As can be seen from the figure, VGM and T2E (Type 1 and 5 in Table 1) give the highest mobility of the SC CO₂ plume, and produce similar shaped plumes, although the SC CO₂ plume predicted by T2E spreads slightly more horizontally. The simulation results for the three other types of capillary relations give much smaller plumes with higher saturations. This is behavior can be explained by the analysis conducted in last section for 1D horizontal cylinder system, where the migration is pressure driven dominated.

After injections stops, buoyancy becomes the dominant driving force. The time evolution of Z_{cm} reflects the upward migration velocity. 4 shows the saturation profiles when the SC CO₂ phase reaches the impermeable caprock. The SC CO₂ plumes for VGM and T2E reach the top of the domain at approximately 20 years. For the simple function relation (SF in Table 1, Type 3), the plume reaches

the caprock at around 30 years, slightly earlier than for BCB relation (Type 2 in Table 1), which reaches the caprock at around 40 years. Similar to the analysis shown in last section, solving the Buckley-Leverett equation with gravity can be applied to a simplified 1D vertical system in order to estimate the vertical migration velocity as well. We follow here the method proposed by (Hayek, Mouche, Mugler, 2009).

$$\frac{\partial s}{\partial t} + \frac{\partial}{\partial z} F(s) = \frac{q_g}{\phi} \quad (36)$$

Where the q_g is the sink/source term of the gaseous SC phase, and $F(s)$ is the global flux function,

$$F(s) = \frac{1}{\phi} f(s) \left[v + \frac{k(\rho_w - \rho_g)}{\mu_w} k_{rw}(s) \right] \quad (37)$$

Where v is the total velocity, in terms of the original notation in Equation (16) and (17) of (Hayek *et al.* 2009). The $f(s)$ is the fractional flux function as defined in Equation (28)

Considering the 1D vertical migration of SC CO₂ plume after the termination of injection, q_g and v are equal to zero. Then Equation (36) and (37) become:

$$\frac{\partial s}{\partial t} + \frac{\partial}{\partial z} F(s) = 0 \quad (38)$$

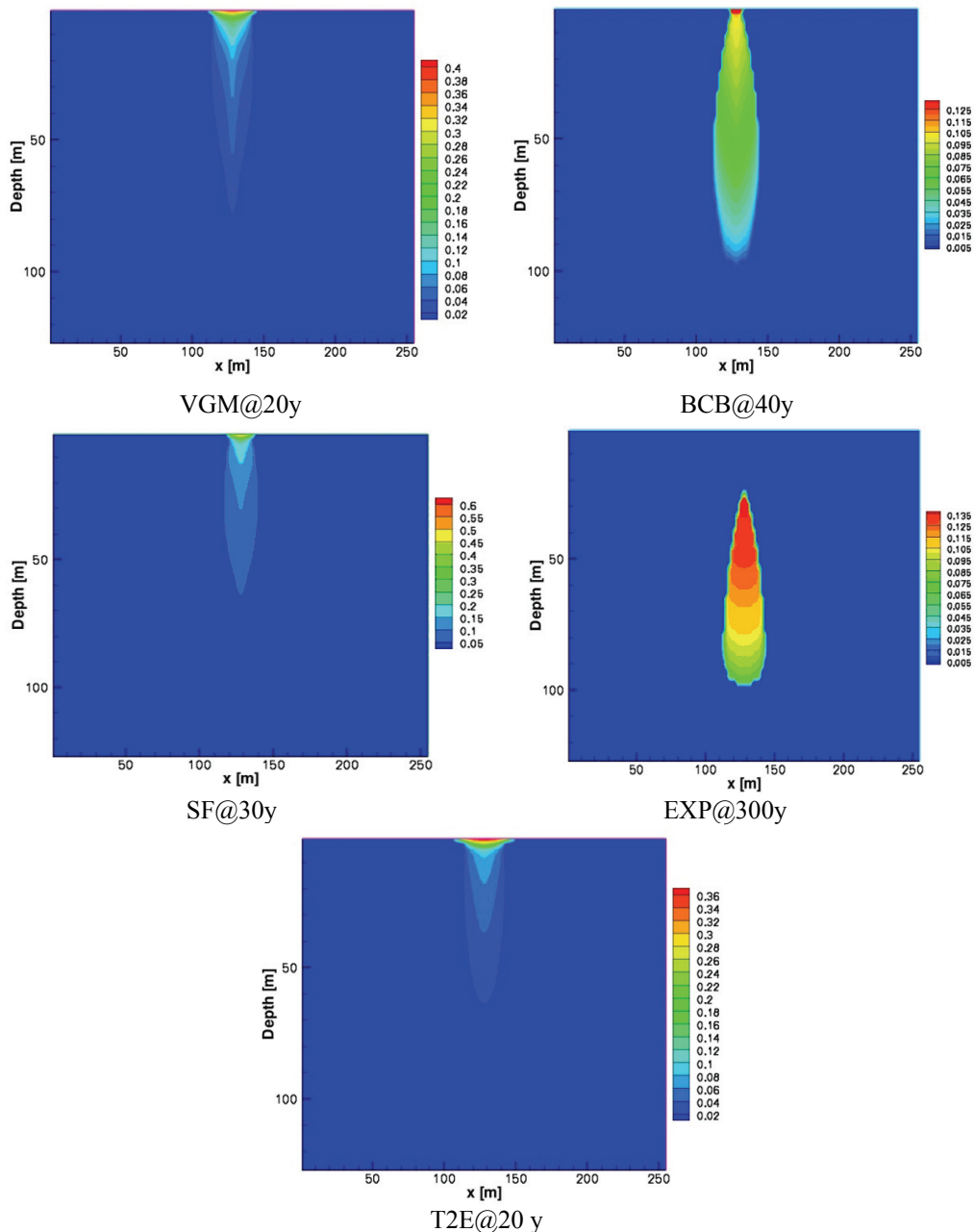


Fig. 4 Saturation profiles for SC CO₂ when plume reaches the caprock with the exception of Type 4 which does not reach the caprock

Where

$$F(s) = \frac{1}{\phi} f(s) \left[\frac{k(\rho_w - \rho_g)}{\mu_w} k_{rw}(s) \right] = \frac{k(\rho_w - \rho_g)}{\phi} \left[\frac{k_{rw}}{\mu_w} f(s) \right] = \frac{k(\rho_w - \rho_g)}{\phi} B \quad (39)$$

Table 4 Front saturation and flow fraction

Type	S _{g,f}	f	df/ds
1: VGM	0.1642	0.6732	4.0995
2: BCB	0.2502	0.8031	3.2103
3: SF	0.3153	0.7252	2.3000
4: EXP	0.3626	0.8845	2.4395
5: T2E	0.1415	0.6335	4.4755

with $B = \left[\frac{k_{rw}}{\mu_w} f(s) \right]$

Compare Equation (38) with Equation (25), similar solution can be derived for the front saturation as:

$$\left. \frac{dF}{ds} \right|_{s_{g,f}} = \frac{F(s_{g,f})}{s_{g,f}} \quad (40)$$

and velocity

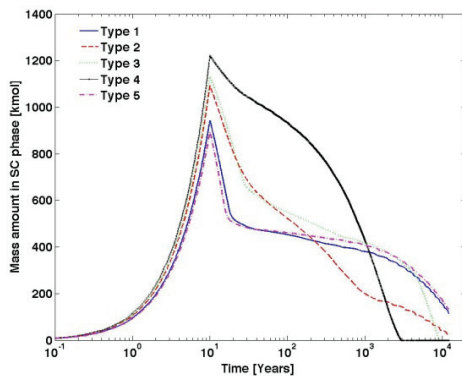
$$v_z = \left. \frac{dF}{ds} \right|_{s_{g,f}} = \frac{k(\rho_w - \rho_g)}{\phi} \left. \frac{dB}{ds} \right|_{s_{g,f}} \quad (41)$$

i.e. the front velocity is proportional to $\left. \frac{dB}{ds} \right|_{s_{g,f}}$.

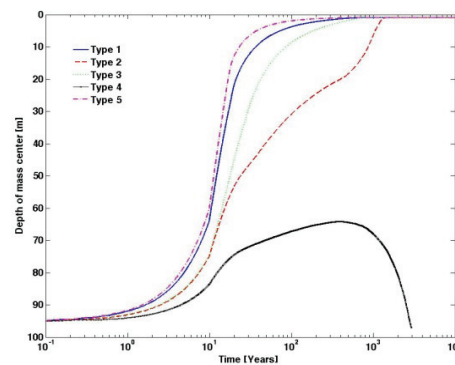
lists the front saturation and corresponding values of B and its derivatives. This estimation can roughly predict the upward front velocity of the simulated 2D systems. The time needed for the SC plume to migrate from the injection point (at the depth of 96 m) to the formation top are approximately 25, 54, 41, 175 and 20 years for VGM, BCB, SF, EXP and T2E s - k_r relations. The shortest and longest times are differed more than 8 times. Numerical simulations show that the time needed for the SC phase plumes reach to formation top are roughly 20, 40, 30, and 20 years for

corresponding s - k_r relations, which are comparable with but slightly shorter than the 1D analytical predictions, because of the pressure build up during the injection period. The numerical simulation shows that the SC phase plume of EXP model does not reach the formation top, because of the horizontal spreading and CO₂ dissolution into formation fluid during the relatively long migration period.

It also should be noticed that BCB and SF relations give quite low $k_{r,g}$ while $s_g < 0.15$ as shown in Fig. 1, where the relative permeability is less than 10^{-3} when $s_g < 0.07$ for the BCB relation. This feature makes the SC CO₂ phase actually immobile when its saturation becomes sufficiently low, causing quite long trailing saturation profiles as shown in Fig. 4. The magnitude of σ_{zz} (Fig. 5) indicates the length of SC CO₂ plume "tail". On the contrast, the σ_{zz} value decrease for VGM, SF and T2E relations, while the SC CO₂ remaining in the lower formation keeps migrating upward and accumulates under the top boundary. This behavior does not happen for the BCB relation in which the decrease in saturation happens very late and is actually caused by dissolution of the SC plume. Similar behavior also exists for the EXP relation as shown in Fig. 5(C).



A) SC CO₂ phase mass



B) depth of SC phase mass center

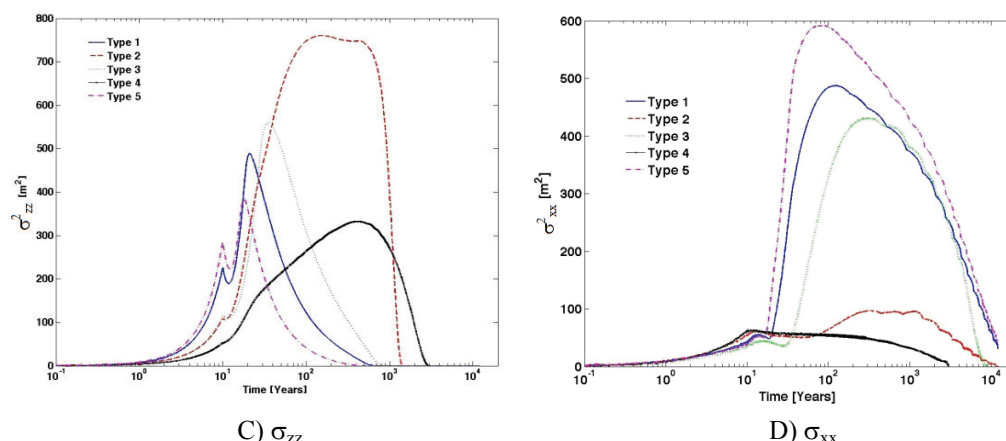


Fig. 5 Effects of $s-k_r$ relations on the behaviors of SC phase plume without capillary pressure. Type 1-5 are corresponding to VGM, BCB, SF, EXP, T2E models respectively.

Because the CO_2 enriched water under the P, T condition has higher mass density than native formation fluid, the dissolution of CO_2 in water can cause natural convection in aqueous phase, which can greatly enhance the dissolution process. After natural convection has developed, most “fresh” formation water/brine flows through the plume from top to bottom (but does not flow through the top boundary). It becomes saturated with CO_2 when it reaches the lower part of the plume. So it is observed that during the dissolution process, the upper part of the SC plume dissolves earlier than the lower part, if the plume does not reach the top boundary. However, the dissolution process cannot be enhanced in this manner if the SC CO_2 plume is covered by caprock or trapped below some kinds of no-flow boundary, since “fresh” water/brine cannot move into the two phase region from the top. Generally, the “tailing” behavior of SC phase plume can enhance the dissolution process. As shown in Fig. 5, the SC CO_2 phase for EXP model firstly completely dissolve of the five models, because its slow migration caused all of the SC CO_2 to stay in the lower formation, forming a quite long trailing profile. On the contrast, most SC CO_2 of VGM and T2E models move up to the formation top and covered by non-permeable top boundary, their dissolution are of the slowest, the SC phase exist at the end time (12 000 years) of our simulations. The SC phase plume of BCB and SF relations have greater tailing behavior than these of the VGM and T2E relations, SC phase dissolutions take thousands of years, respectively. Though the σ_{zz} shows that the tailing behavior of BCB relation is

more obvious than that of the SF relation, the dissolution time of SF relation is shorter. These phenomena may be caused by the higher aqueous phase relative permeability of SF model (the highest wetting phase $s-k_r$ relations, as shown in Fig. 1(B), which results in stronger natural convection. More detailed analysis will be conducted on this aspect in the future.

2.2.2 Effects of $s-p_c$ relations

In last section, numerical simulations are conducted without considerations on the effects of $s-p_c$ relations. Studies by by (Rathfelder, Abriola, 1998) showed that different capillary pressure functions lead to diverged simulation results, In their investigations on the DNAPL migration in aquifers, the discrepancy in simulation results with van-Genuthon and Brooks-Coery $s-p_c$ relations are illustrated. In our study in this section, we compare the simulation results obtained by applying identical $s-k_r$ relations and $s-p_c$ formula with different magnitude. The $s-k_r$ relation adapted by all simulations in this section is assigned as Equation (23) and (24), i.e. T2E model, with parameters in Table 1. The $s-p_c$ relation takes the form of Equation (22) with an amplifier AMP, as shown in Equation (49). Five values of AMP: 0, 1, 2, 4, 8, are investigated, greater AMP value means stronger capillary pressure.

$$p_c = \frac{AMP}{\alpha} \left(s_e^{-1/m} - 1 \right)^{1/n} \quad (42)$$

During the pressure driven injection period and the gravity driven migration period, the effects of capillary pressure are relatively weak. As shown in

Fig. 6(A-C), the CO_2 amount in SC phase, the migration of mass center depth Z_{cm} and the second order momentum σ_{xx} of the five AMP values are close to each other within the first 20 years. Then after the plume hits the impermeable layer at the top, the rapid increase of σ_{xx} indicates the commencement of horizontal expansion as shown in Fig. 6(C). At early stages after the plume reach the top boundary, the expansion is still driven by buoyancy, and the SC CO_2 remaining in the lower formation continues to join the pool of non-wetting SC CO_2 phase located just beneath the caprock, increasing the SC CO_2 phase pressure, and invading the adjacent fully saturated grid nodes horizontally, same as shown in Fig. 4(C, D) and Fig. 5(C, D).

If capillary pressure is absent, after a major fraction of the SC CO_2 reaches the top, the horizontal expansion of the SC CO_2 phase ceases

and begins to shrink slowly because of dissolution (Fig. 6(C), the solid black line with AMP=0). However, if capillary pressure is present, it plays the dominating role in the migration of the SC CO_2 phase after then. If the caprock can be considered ideally horizontal and no more SC CO_2 comes from beneath, the capillary pressure is the only driving force for the SC CO_2 phase to spread horizontally, and its magnitude determines the rate of spreading. At the spreading front, SC CO_2 and the aqueous phase flow in opposite directions. Since the total amount of SC CO_2 phase is limited, the spreading behavior may reduce its pressure and finally stop its expansion if the aqueous phase recharge rate is slower than the SC CO_2 phase spreading rate. During this period, the horizontally spreading mechanism can be illustrated in Fig. 8 using a simplified 1D model.

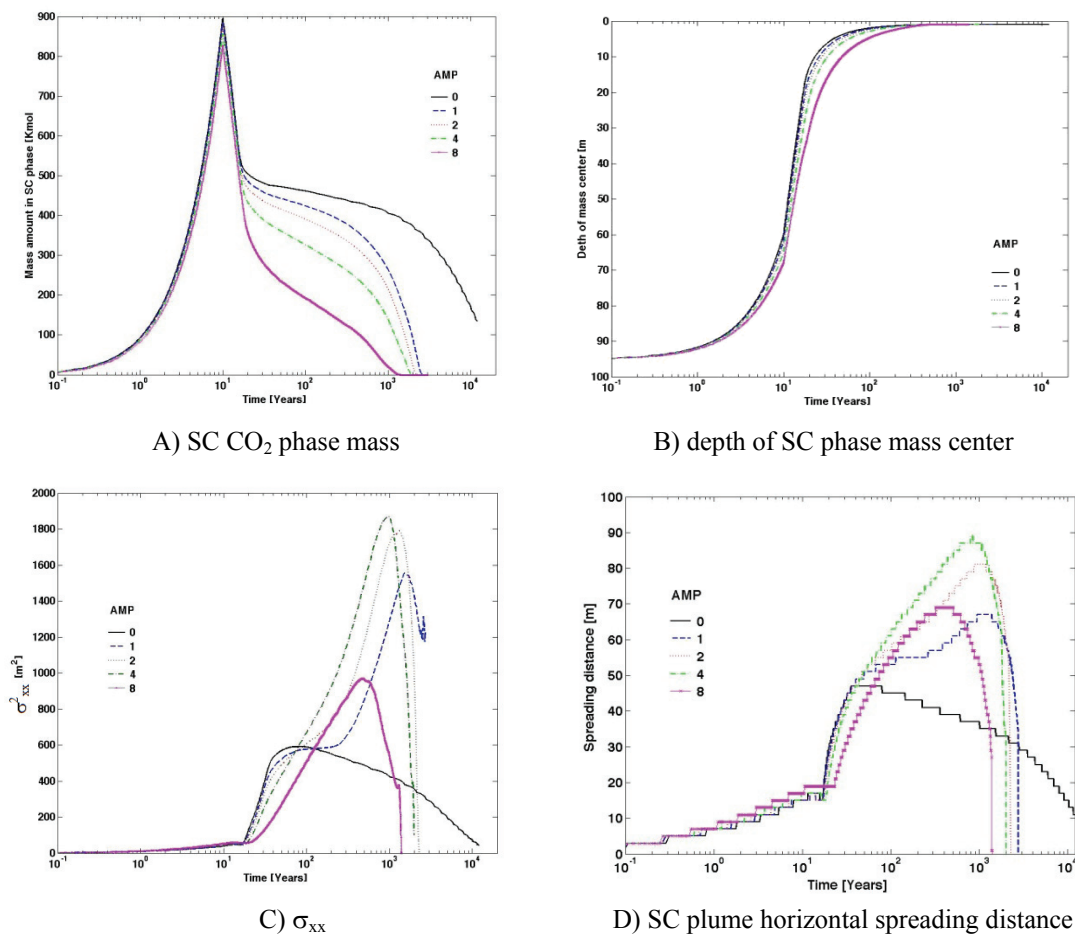


Fig. 6 Effects of Capillary pressure on the behaviors of SC phase plume. The value of AMP indicates the magnitude of capillary pressure.

The SC CO₂ phase (g) and aqueous phase (l) flow rates are equal to

$$V_g = -k \frac{k_{rg}}{\mu_g} \frac{\partial P}{\partial x} \quad (43)$$

and

$$V_l = -k \frac{k_{rl}}{\mu_l} \left(\frac{\partial P}{\partial x} - \frac{\partial P_c}{\partial x} \right) \quad (44)$$

It is then necessary that the following inequality be satisfied ($V_l > V_g$)

$$\frac{dP_c}{ds_w} \frac{\partial s_w}{\partial x} \geq \left(1 + \frac{k_{rg}}{k_{rl}} \frac{\mu_g}{\mu_l} \right) \frac{\partial P}{\partial x} \quad (45)$$

To maintain the SC CO₂ phase pressure for continue spreading.

In most cases, the SC CO₂ saturation at the capillary driven spreading front is low. Under such condition, the 1st order derivative of the s - p_c function near the wetting end is important in determining the spreading distance. Generally, a larger 1st order derivative of the s - p_c function near the wetting end leads to wider spreading, although it may be affected by other factors as well, such as the flow fraction. Fig. 6(C, D) shows the σ_{xx} and spreading distance with the AMP values varies from 0 to 8, in which the maximum distances are 41, 67, 81, 89 and 69 m. While AMP increases from 0 to 4, the distances increase with it. While AMP increases to 8, the spreading distance decreases because of the dissolution effect. Without the enhancement of convection, the mass transfer process by diffusion process is very slow. If the SC phase plume is located under a low permeable region, imbibition is a very important mechanism to bring surrounding water/brine into the 2--phase region, making SC phase spreading

and dissolving. Fig. 6(A) shows the mass amount in the SC phase, the total dissolution times are approximately 2 748, 2 284, 2 000 and 1 400 years while AMP are 1, 2, 4 and 8. For the zero capillary pressure case (AMP=0), SC phase keeps existing until the termination of simulation at 12 000 years.

In order to illustrate the importance of the magnitude of the 1st order derivative furthermore, 2 numerical simulations are conducted with identical s - k_r relation (Equation (23) and (24)) and with different s - p_c relations, one of them uses VG model (Equation) and the other uses BC model (Equation). The model parameters are listed in Table 1. As shown in Fig. 1(A), the p_c values of these 2 relations are very close. Near the wetting end, the value given by BC relation is slightly higher than that given by VG relation, but the 1st order derivative of s - p_c relation given by BC is lower. Fig. 8(A-C) show the time evolution of the total CO₂ mass amount in SC phase, the depth of mass center and the spreading distance with the capillary pressures evaluated by VG, BC models and zero capillary pressure assumption. With the parameters adapted in our simulation, the s - p_c relations do not have obvious impacts on the vertical migration of SC phase mass center (Fig. 8(B)). But the maximal horizontal spreading distance of the VG, BC s - p_c relations and zero capillary pressure assumption are 67, 45 and 41 m, as shown in Fig. 8(C). Regarding the dissolution time, the SC phase last more than 12 000 years in the example with zero capillary pressure assumption. The dissolution rate predicted by VG relation is slight higher than that by BC relation, the final disappearance time given by the two relations are 2 714 years for VG relation and 2 811 years for BC relation (Fig. 8(A)), consistent with the analysis in Equation (45).

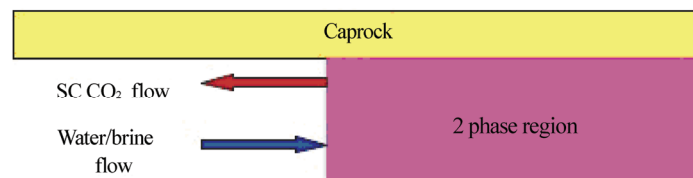


Fig. 7 Flow pattern below a horizontal caprock

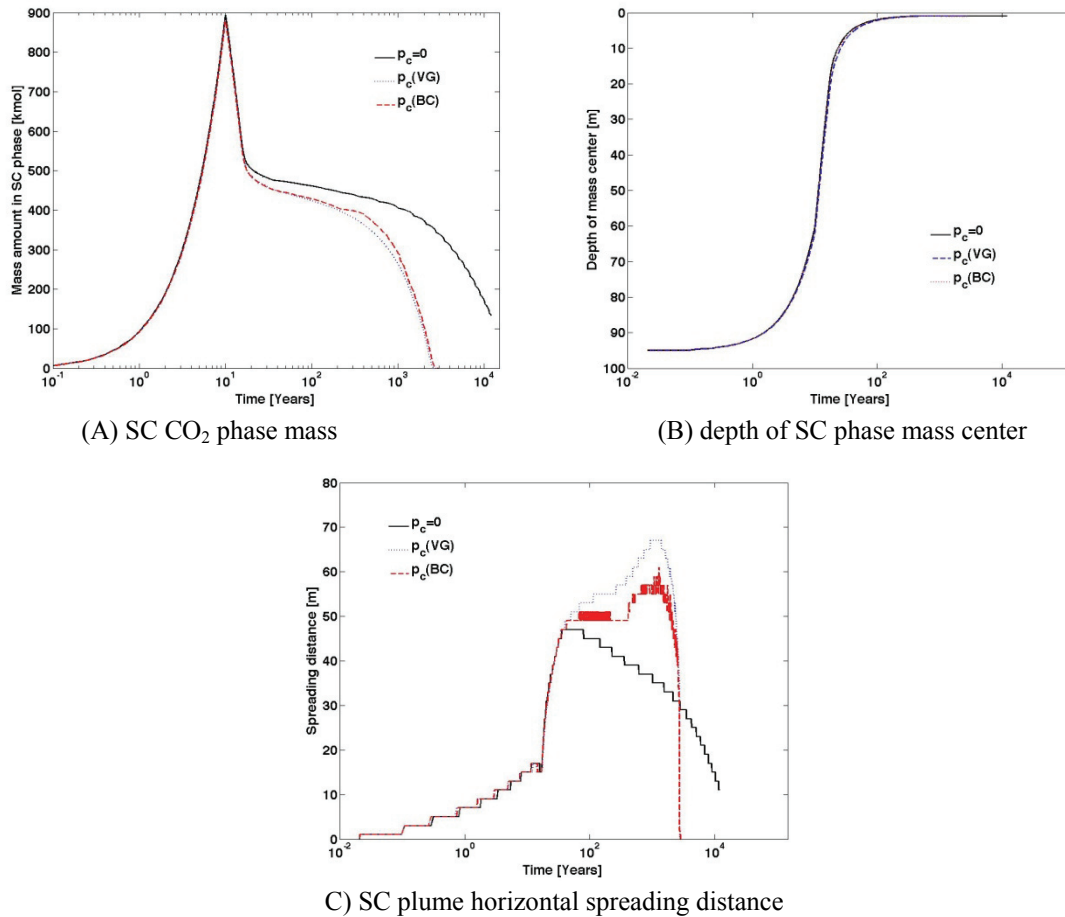


Fig. 8 Comparison of plume behaviors between VG and BC capillary pressure relation

In summary, the choice of s - p_c - k_r relations is critical. Analytical solutions for a simplified 1D system show that the front saturation velocities are strongly affected by the s - k_r relations. The significance of s - p_c - k_r relations varies during the system evolution. At the injection and buoyancy driven period, the relative permeability of the SC CO₂ phase is the most important factor, determines the migration rate and the profiles of the SC phase plume. If the plume reaches a low permeable caprock or non-permeable boundary and spreads beneath it, the s - p_c relations become important, since their values and values of the 1st order derivative have great effects on horizontal spreading and dissolution processes. This effect is resolved in this study for the 1st time in literatures. Aqueous phase relative permeability may affect the strength of natural convection induced by the density contrasts associated with dissolved CO₂ concentration, which can greatly enhance dissolution.

3. Summary and Concluding Remarks

In this work, the effects of relative permeability models on the simulation of geological CO₂ storage was investigated by numerical experiments on 2D homogeneous porous media with 5 types of relations. Different s - p_c - k_r relations give rise to quite different results for the migration and distribution of SC CO₂. Conclusions on this aspect are outlined as following:

1. Analytical solutions for a simplified 1D horizontal system show that the front saturation differed by more than 60% with different s - k_r relations, and the front velocities have similar discrepancies. Analytical prediction on vertical buoyancy velocity in 1D system can be differed by over 8 times with different s - k_r relations. Associated effects on residual and solubility trapping mechanisms are significant.

2. It is found that the magnitude of s - p_c - k_r relation effects varies during the system evolution.

Within the injection and buoyancy driven period, the relative permeability of the SC CO₂ phase is the most important factor, whose value determines the migration rate and the profiles of the SC phase plume. If the plume reaches a low permeable caprock or non-permeable boundary and spreads beneath it, the s - p_c relations become important, since their values and the values of their 1st order derivative have great effects on horizontal spreading and dissolution processes. This effect is resolved in this study for the 1st time in literatures.

3. Aqueous phase relative permeability affects the strength of natural convection induced by the density contrasts associated with CO₂ dissolution. Model selections and experiment arrangement should be performed carefully regarding the relative permeability and capillary pressure. It is also noticed that the preferred condition for quick solubility trapping is that the SC phase plume should spread widely, forming a big multiphase region with low SC phase saturation. SC phase plume gathering beneath a caprock or non-permeable boundary is not an ideal condition.

In sum, besides the numerous uncertainties related to geological CO₂ sequestration, such as the distribution of porosity and permeability, location of faults and fractures, types of rocks, etc., the uncertainty in relative permeability and capillary pressure evaluations make the modeling and simulations more complex and challenging. Results from these simulations suggest that careful selection of s - p_c - k_r relations and calibration methods are essential for accurate predictions. Neglects of this aspect will inevitably lead to erroneous results and affect the decisions on sitting, operating and monitoring procedures of geological CO₂ storage.

Acknowledgements

The work presented was partly supported by Research Fund Grant SK201413 provided by Institute of Hydrology and Environmental Geology, CAGS. The authors also appreciate suggestions from Dr. Peter Lichtner, which greatly improved this presentation.

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