

Density-driven enhanced dissolution of injected CO₂ during long-term CO₂ geological storage

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Geological storage of CO₂ in deep saline formations is increasingly seen as a viable strategy to reduce the release of greenhouse gases into the atmosphere. However, possible leakage of injected CO₂ from the storage formation through vertical pathways such as fractures, faults and abandoned wells is a huge challenge for CO₂ geological storage projects. Thus, the density-driven fluid flow as a process that can accelerate the phase change of injected CO₂ from supercritical phase into aqueous phase is receiving more and more attention. In this paper, we performed higher-resolution reactive transport simulations to investigate the possible density-driven fluid flow process under the ‘real’ condition of CO₂ injection and storage. Simulation results indicated that during CO₂ injection and geological storage in deep saline formations, the higher-density CO₂-saturated aqueous phase within the lower CO₂ gas plume migrates downward and moves horizontally along the bottom of the formation, and the higher-density fingers within the upper gas plume propagate downward. These density-driven fluid flow processes can significantly enhance the phase transition of injected CO₂ from supercritical phase into aqueous phase, consequently enhancing the effective storage capacity and long-term storage security of injected CO₂ in saline formations.

1. Introduction

Global emissions of greenhouse gas (GHG) especially carbon dioxide (CO₂) have increased rapidly and led to global climate change and ocean acidification with severe potential consequences for ecosystems and for human society (Holloway 2001; West *et al.* 2005; Bachu 2008). CO₂ capture and geological storage (CCGS) into deep saline formations is one of the most promising ways for reducing anthropogenic CO₂ emissions into the atmosphere (Hitchon *et al.* 1999; Gunter *et al.* 2000; Allen *et al.* 2005; Benson and Cole 2008; Izgec *et al.* 2008).

During geological storage of CO₂, the dissolution of the free-phase CO₂ gas into the aqueous phase increases the water density (Pruess and Zhang 2008), which can result in gravitational instabilities. The downward propagation of CO₂-saturated water by gravity is accompanied with the upper migration of CO₂-unsaturated water. The density-driven convective activity accelerates the dissolution and spatial distribution of injected CO₂ gas compared to the diffusion process alone (Lu and Lichtner 2007), which is favourable for the effective storage and long-term storage security of the gas in geologic formation (Pau *et al.* 2010).

Keywords. Carbon dioxide; geological sequestration; reactive transport modelling; density-driven fluid flow; grid resolution.

Currently, studies on density-driven CO₂ enhanced-dissolution have been widely performed through four main aspects, including

- (1) analytical simulations for determining the onset of convection and the initial wavelength of convective instabilities (e.g., Ennis-King *et al.* 2005; Hassanzadeh *et al.* 2006; Riaz *et al.* 2006; Xu *et al.* 2006b; Javaheri *et al.* 2010);
- (2) laboratory experiments for visualizing and conceptual understanding of the dissolution–diffusion–convection (DDC) process (e.g., Kneafsey and Pruess 2010), and for measurement of enhanced mass transfer (e.g., Yang and Gu 2006; Farajzadeh *et al.* 2007a; Backhaus 2010; Neufeld *et al.* 2010; Moghaddam *et al.* 2012);
- (3) natural analogues for investigating and identifying the role of density-driven convection in the mobility of CO₂-rich aqueous phase in geologic media (e.g., Gilfillan *et al.* 2008, 2009); and
- (4) numerical simulations for evaluating the mixing behaviour after the occurrence of convective activity as the complement and partial confirmation of the analytical stability theory (e.g., Ennis-King and Paterson 2005, 2007; Hassanzadeh *et al.* 2005, 2006, 2007; Farajzadeh *et al.* 2007b, 2011; Lu and Lichtner 2007; Zhang *et al.* 2007, 2011; Pruess and Zhang 2008; Chen and Zhang 2010; Green and Ennis-King 2010; Neufeld *et al.* 2010; Pau *et al.* 2010; Yang *et al.* 2011).

Among these different research methods, numerical modelling has become an important tool for the investigation of multiphase fluid flow in geologic media (Dimri *et al.* 2012), such as the density-driven CO₂ enhanced-dissolution process.

Recently, many researchers (e.g., Audigane *et al.* 2007; Ennis-King and Paterson 2007; Andres and Cardoso 2011; Li 2011; Zhang *et al.* 2011) have paid more attention to the impact of geochemical reactions such as mineral dissolution and precipitation on the density-driven CO₂ enhanced-dissolution. Audigane *et al.* (2007) performed two-dimensional (2D) reactive transport modelling to investigate geochemical effects from the interplay between fluid flow and geochemical reactions. Their simulation results indicated that the downward migration of brines containing higher-concentration of dissolved CO₂ accelerates the CO₂ dissolution into water. In addition, the higher mesh refinement in horizontal direction enhances the gas dissolution. Ennis-King and Paterson (2007) investigated effects of CO₂ dissolution and geochemical reactions on density-driven convection using analytical and numerical methods. Their results showed that

the coupling of ion concentrations such as Ca²⁺ and Mg²⁺ to water density accelerates the CO₂ dissolution process. Our previous paper (Zhang *et al.* 2011) investigated the convection process using a simple 2D reactive transport model based on mineralogical composition in Songliao Basin of China. According to changes in CO₂ in gas and aqueous phases, we divided the process into four stages (i.e., dissolution-dominated, diffusion-dominated, early and late convection-dominated periods). Simulation results indicated that geochemical reactions and mineral compositions are important not only to the CO₂ dissolution, but also to the dissolution of other species from mineral dissolution, which can both increase the water density. In addition, we found that the formation factors have important impacts on the dissolution–diffusion–convection process. For example, the increasing brine salinity delays the development of convection, lower initial CO₂ gas saturation accumulated beneath the caprock enhances the onset and evolution of convective activity, the permeability variations caused by the mineral alteration in the low-pH zone have an influence on the onset of convection, the increase in vertical permeability has a strong effect on the convection process compared to the increasing horizontal permeability, and the increasing strength of permeability perturbations reduces the onset time for convective mixing. Simulation results also showed that changes in the model height have no significant effect on the onset and evolution of convective activity during early convection-dominated period. However, decrease in the model height suppresses the CO₂ dissolution during late convection-dominated period due to the accumulation of CO₂-saturated formation water on the lower boundary of the model. Decrease in the model width delays the convective dissolution. Li (2011) used a novel reactive diffusion–convection transport model to investigate the flow during different CO₂ trappings in deep saline formations. The novel, fully coupled reactive transport model can successfully capture the heat- and density-driven fingering flow of CO₂. They considered the effect of the precipitation of carbonate minerals on convective activity and found that the higher reaction (precipitation) rate will delay the downward flow of CO₂-rich aqueous phase. Similar to the study of Li (2011), Andres and Cardoso (2011) suggested that when CO₂ precipitation reactions are considered, the increasing reaction rate decreases the growth rate of the instability, increases the onset time of convection, and suppresses the finger interaction. We should note that they only considered the possible effect of CO₂ precipitation reactions on density-driven fluid flow, but the dissolution of

minerals and the subsequent increase of concentration of other dissolved species such as Ca²⁺, Mg²⁺, and Fe²⁺ except for the dissolved CO₂ may accelerate the onset of convective activity and the dissolution of CO₂ into water (Ennis-King and Paterson 2007; Zhang *et al.* 2011). For current reactive transport modelling studies on density-driven CO₂ enhanced-dissolution process, higher-resolution (in the order of one meter) simulations (e.g., Ennis-King and Paterson 2007; Zhang *et al.* 2011) considered this enhanced-dissolution process in smaller-scale models and assumed that the supercritical CO₂ has accumulated below the impermeable caprock, but did not identify the effect of spatial distribution of CO₂ gas on this

process, which should be very important for understanding the role of density-driven CO₂ enhanced-dissolution in long-term CO₂ geological storage process. However, other simulations (e.g., Audigane *et al.* 2007) studied the CO₂ enhanced-dissolution phenomenon during CO₂ injection and storage process in larger-scale models, the model resolution (in the order of tens of meters) is not high enough to accurately capture the density-driven CO₂ enhanced-dissolution process (Pruess and Zhang 2008; Pau *et al.* 2010).

Therefore, the purpose of this paper based on higher-resolution reactive transport modelling using TOUGHREACT includes: (1) investigating the possible density-driven fluid flow phenomenon during long-term CO₂ geological storage; and (2) identifying the effect of the density-driven fluid flow process on the enhanced-dissolution of injected CO₂ into water. Compared to most numerical modelling studies, those assumed that the injected supercritical CO₂ has accumulated below the caprock, the spatial distribution of injected CO₂ may increase the difficulty to understand and analyze mechanisms of density-driven CO₂ enhanced-dissolution process, but for the ‘real’ CO₂ geological storage, the spatial distribution could be affected by many factors such as permeability, porosity and residual gas saturation (Audigane *et al.* 2007; Zhang *et al.* 2009). Thus, it is necessary to simulate and discuss the density-driven CO₂

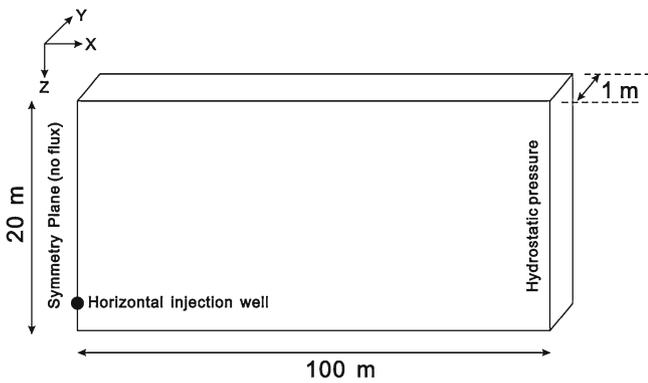


Figure 1. Schematic representation for CO₂ injection in a formation.

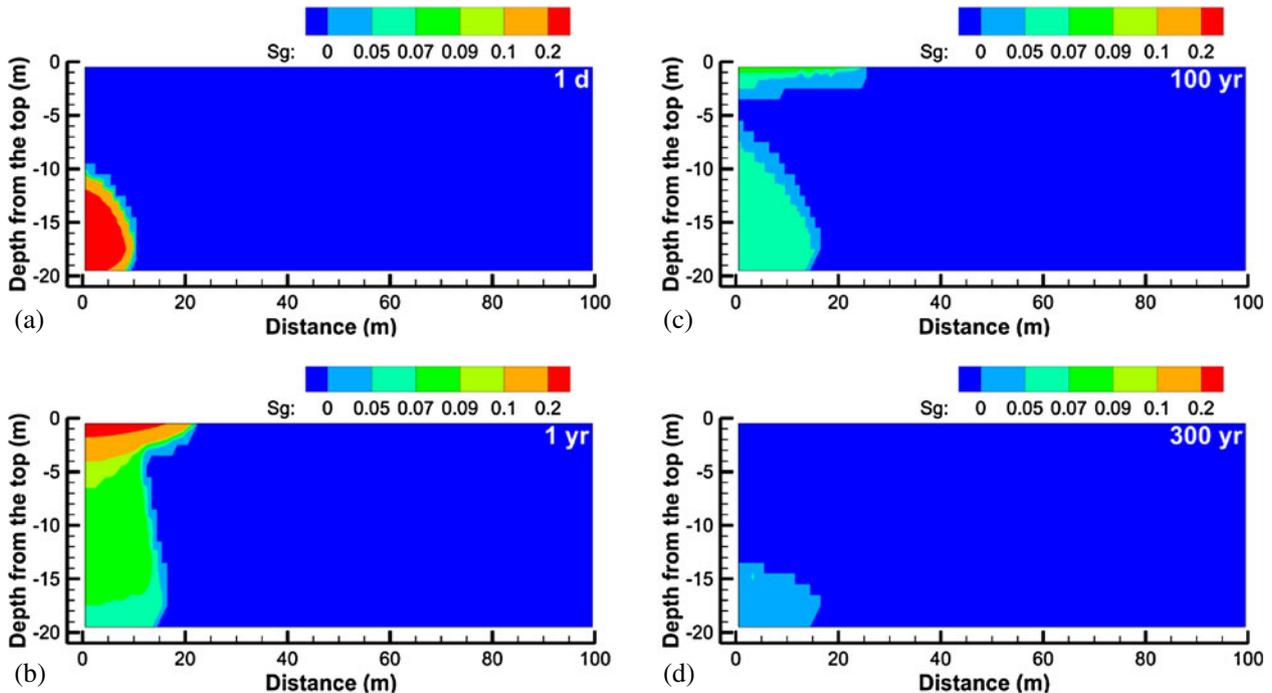


Figure 2. Spatial distribution of injected CO₂ gas obtained from the base-case after different times (S_g is CO₂ gas saturation in pore space).

enhanced-dissolution process under the consideration of the spatial distribution of injected CO_2 in deep saline formations (IEA GHG 2008).

2. Model setup

A simple 2D-model was used to study the temporal evolution and spatial distribution of injected CO_2 and subsequent geochemical changes and density-driven fluid flow process. The modelling based on a 3D model should be more accurate (Pau *et al.* 2010). However, due to constraints of computational capacity of the modelling code used in our studies, we did not consider the 3D modelling here. Our previous paper (Zhang *et al.* 2011) has discussed the difference between 2D and 3D models.

The 2D model was a sandstone formation of 20 m thickness as shown in figure 1. In the

vertical direction, 20 model layers were used with a constant spacing of 1 m. In the horizontal direction, a distance of 100 m was modelled with a constant spacing of 1 m that is the same with the vertical resolution of this model. The number of grid blocks is 2000. The volume of the outer grid element is specified at a large value of 10^{30} m^3 , representing an infinite lateral boundary. CO_2 injection was applied at the bottom portion of the well using a constant rate of 0.05 kg/s per meter (per meter normal to the 2D model) that is the same with the study of Rutqvist and Tsang (2002) for a period of 2 days. The fluid flow and geochemical transport simulation was run for a period of 300 years. The upper and lower boundaries of this model were assumed as impermeable caprock and bedrock, respectively. A hydrostatic pressure distribution over the depth was specified initially. Change in temperature with depth was not considered. The porous medium was assumed

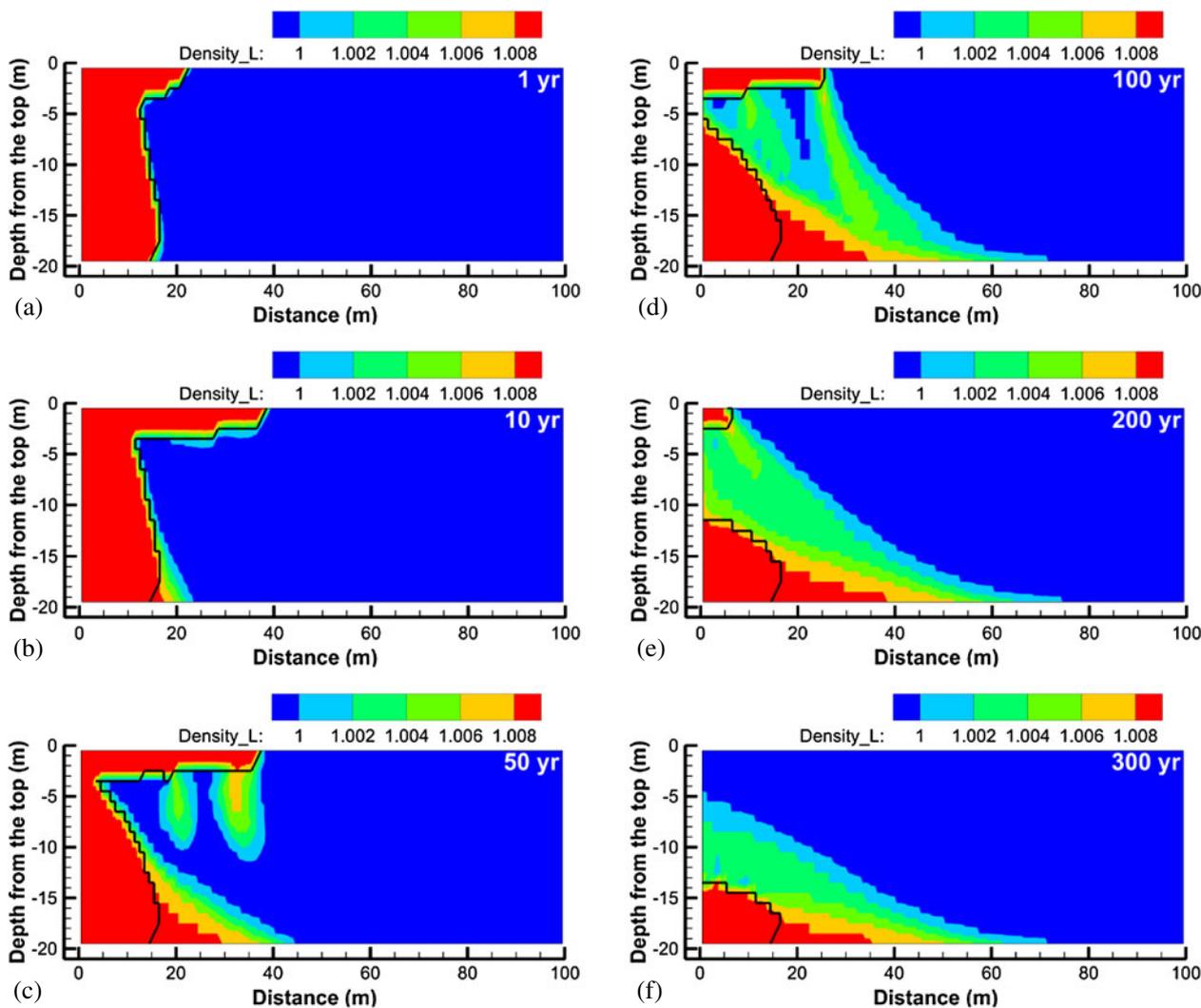


Figure 3. Spatial distribution of aqueous phase density (in kg L^{-1}) obtained from the base-case after different times (the black line represents the zero contour line of gas saturation).

as homogeneous, but a small random permeability modification (0.99–1.01) was applied to promote the onset of density-driven convective activity. However, the above condition is rare, because natural geological formations are usually highly heterogeneous. And it is well known that permeability heterogeneity significantly affects the transport processes in CO₂ geological sequestration (Simmons *et al.* 2010; Chen *et al.* 2013).

We used the same hydrogeological parameters as those used in the research in Songliao Basin of China (Zhang *et al.* 2009). Initial mineralogical composition and aqueous solution composition were used from Zhang *et al.* (2009). Dissolution and precipitation of minerals are considered under kinetic conditions. The kinetic parameters used here were taken from Xu *et al.* (2007). A temperature of 50°C was used, which may represent the temperature at a depth of about 1200 m, given a

land surface temperature of 15°C and a geothermal gradient of 30°C/km.

Numerical simulations were performed using the nonisothermal reactive transport code TOUGHREACT (Xu and Pruess 2001; Xu *et al.* 2006a). This code introduces reactive chemistry into the multiphase fluid and heat flow code TOUGH2 (Pruess 2004). A new fluid property module, ECO2N, based on Pruess' work was used (Pruess and Spycher 2007). This module provides an accurate description of the thermo-physical properties of mixtures of water and CO₂ under conditions typically encountered in saline formations of interest for CO₂ sequestration (31°C ≤ *T* ≤ 110°C; 73.8 bars < *P* ≤ 600 bars). The numerical method for solving fluid flow and chemical transport is based on an integral finite difference (IFD) method for space-discretization. The IFD method provides flexible discretization of

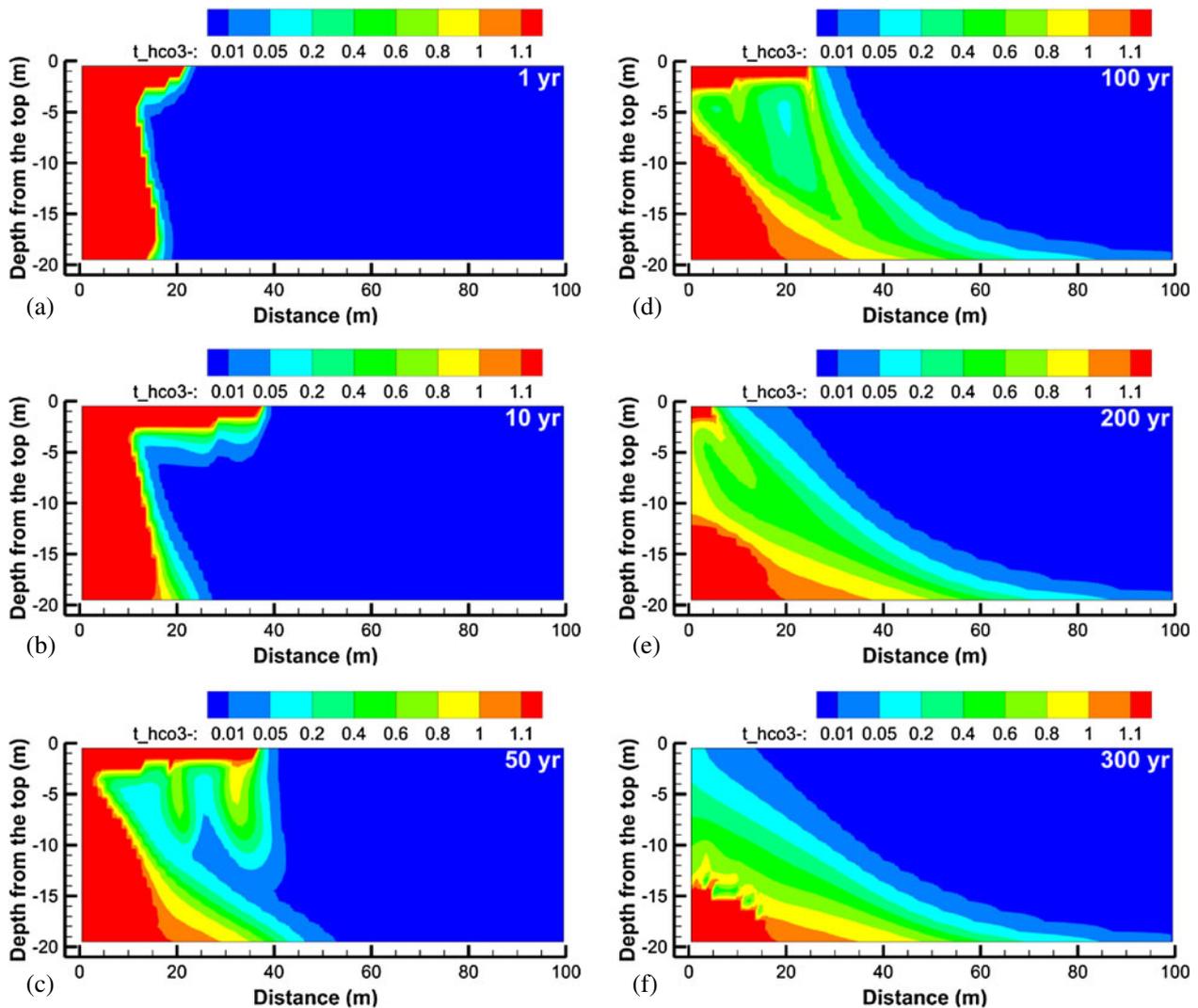


Figure 4. Spatial distribution of concentration (in mol kg⁻¹ H₂O) of total dissolved carbon obtained from the base-case after different times.

geologic media by allowing the use of irregular grids, which is well suited for simulation of flow, transport, and fluid–rock interaction in heterogeneous and fracture rock systems with varying petrology. For regular grids, the IFD method is equivalent to the conventional finite difference method. An implicit time weighing scheme is used for the flow, transport and kinetic geochemical equations. A sequential non-iterative approach is used for the coupling between transport and geochemical reactions. The program can be applied to one-, two-, or three-dimensional porous and fractured media with physical and chemical heterogeneity. It can accommodate any number of chemical species present in the liquid, gas and solid phases. A wide range of subsurface thermo-physical-chemical processes are considered under various thermohydrological and geochemical conditions such as pressure, temperature, ionic strength, pH and Eh.

3. Results and discussions

Figure 2 shows that once CO₂ injection begins, the injected CO₂ gas migrates upward by buoyancy forces and moves horizontally along the impermeable caprock. This finding has been verified by many modelling studies (e.g., Carneiro 2009; Yamamoto *et al.* 2009; Zhang *et al.* 2009).

The emphasis of this paper is density-driven fluid flow process that may enhance the dissolution of injected CO₂ into water. The spatial distribution of water density (figure 3) indicates exciting simulation results (note that the black solid line represents the zero contour line of gas saturation, the left side of this contour line is the two-phase (gas and aqueous phases) zone, the right side is the single-phase aqueous phase zone), including the downward migration and horizontal movement of higher-density (concentration) CO₂-rich aqueous phase (figure 4) in the bottom of the CO₂ gas plume along the bottom of the formation, and the formation of ‘fingering’ phenomenon in the top of the gas plume. This is similar to the experimental result of MacMinn *et al.* (2012). They conducted laboratory experiments with water and solution of methanol and ethylene glycol (MEG) instead of with groundwater and supercritical CO₂ to investigate the effect of the interaction between buoyant spreading, convective dissolution, and the finite thickness of the aquifer on the maximum extent and lifetime of the buoyant current. Experimental results (please see figures 5 and 6 in MacMinn *et al.* 2012) showed that water with dissolved MEG accumulates and spreads at the bottom of the flow cell as a dense gravity current. This indicated that our higher-resolution reactive transport modelling can better capture the spatial spreading and distribution of CO₂-rich (higher-density) aqueous phase.

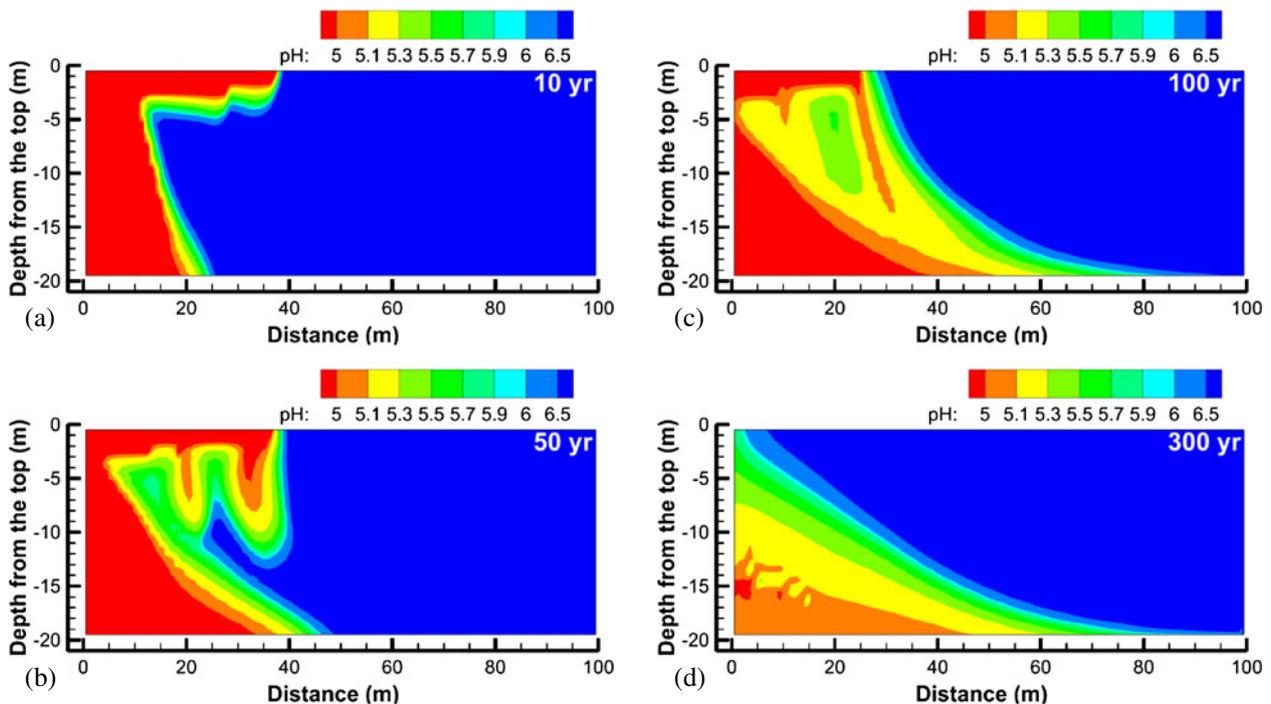


Figure 5. Spatial distribution of pH obtained from the base-case after different times.

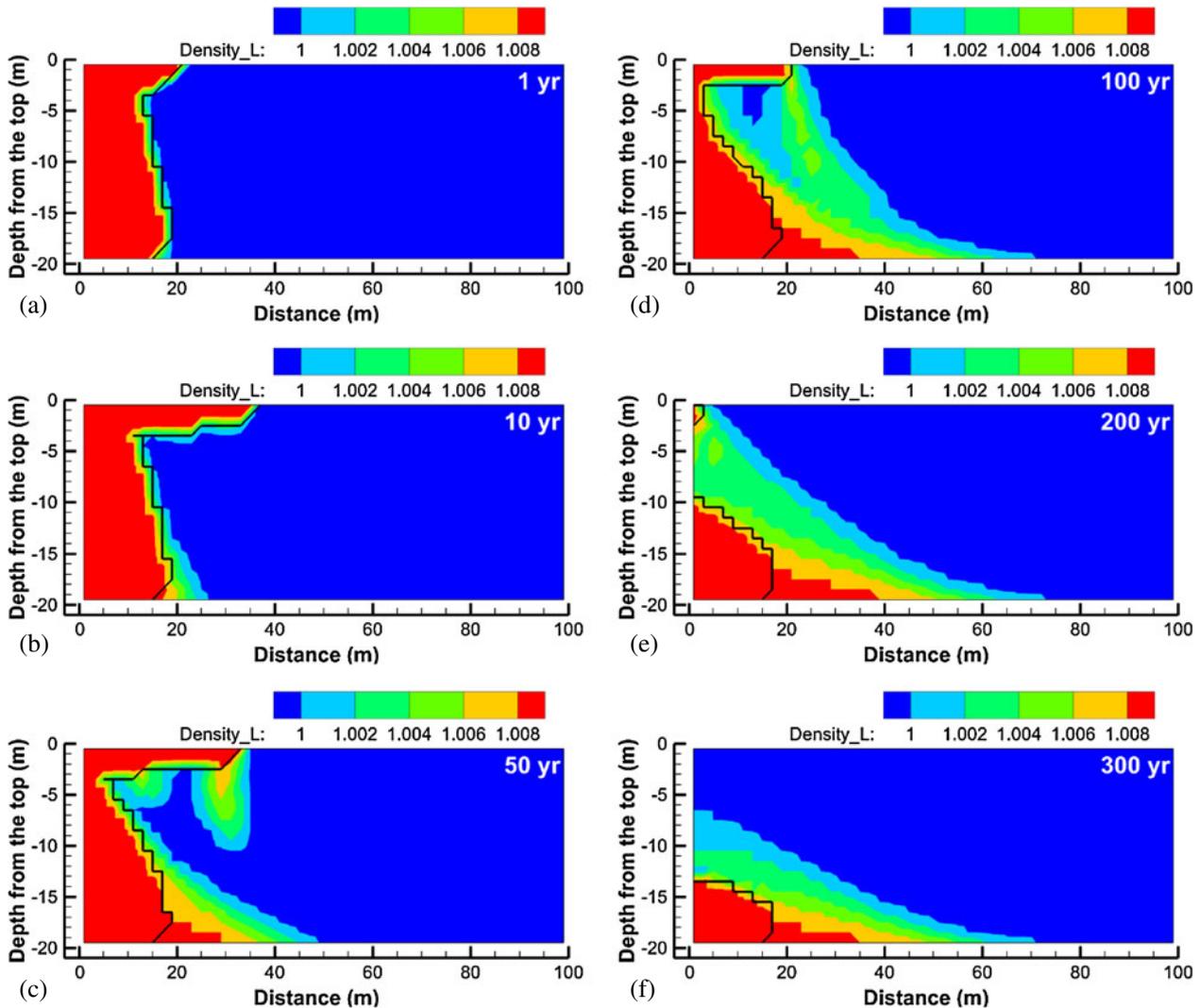


Figure 6. Spatial distribution of aqueous phase density (in kg L⁻¹) obtained from case 2 after different times.

Figures 3 and 4 show that the significant density-driven fluid flow process can increase the contact among CO₂ gas, formation water and minerals, which may promote their interreactions, further enhancing the transition of CO₂ from supercritical phase into aqueous and solid phases. It is well known that the mineral trapping of CO₂ is a slow process (e.g., Gaus *et al.* 2008; De Silva and Ranjith 2012), and our simulation results show that there is no significant increase in the amount of injected CO₂ in solid phase during current simulation time, so mineral alterations did not be shown in this paper. However, we still believe that the density-driven fluid flow can increase the contact between CO₂-rich brines with lower pH (figure 5) and minerals, further enhancing the dissolution of minerals such as carbonates and sulphates and the possible precipitation of other carbonates such as dawsonite and magnesite. The decrease of injected CO₂ gas in the storage formation can prevent the leakage

of CO₂ and its subsequent influence on environment (e.g., groundwater, ground surface and atmosphere) (Wilson *et al.* 2007; Zheng *et al.* 2009; Apps *et al.* 2010).

In order to identify the effect of density-driven fluid flow on the phase transition of CO₂, we conducted three sensitivity modelling in which the horizontal grid spacing is increased and decreased from 1.0 m to 2.0 m (case 2) and 0.5 m (case 3), respectively, and the density-independent multiphase fluid flow is considered (case 4). Because previous studies (e.g., Audigane *et al.* 2007; Lu and Lichtner 2007; Pruess and Zhang 2008; Pau *et al.* 2010) suggested that the density-driven CO₂ enhanced-dissolution is delayed and suppressed for the lower-resolution model. The comparison between the base-case and the sensitivity cases should be helpful for our understanding the role of density-driven fluid flow in enhancing CO₂ dissolution.

Figure 6 shows that for the lower-resolution case (case 2), the density-driven fluid flow process indeed be delayed and suppressed. As shown in figure 7, during CO₂ injection stage (the zone

labeled as (1) in figure 7), the decrease of mass fraction of CO₂ in gas phase for the base-case is slower than that in case 2, but after the end of CO₂ injection, the decrease of the injected CO₂

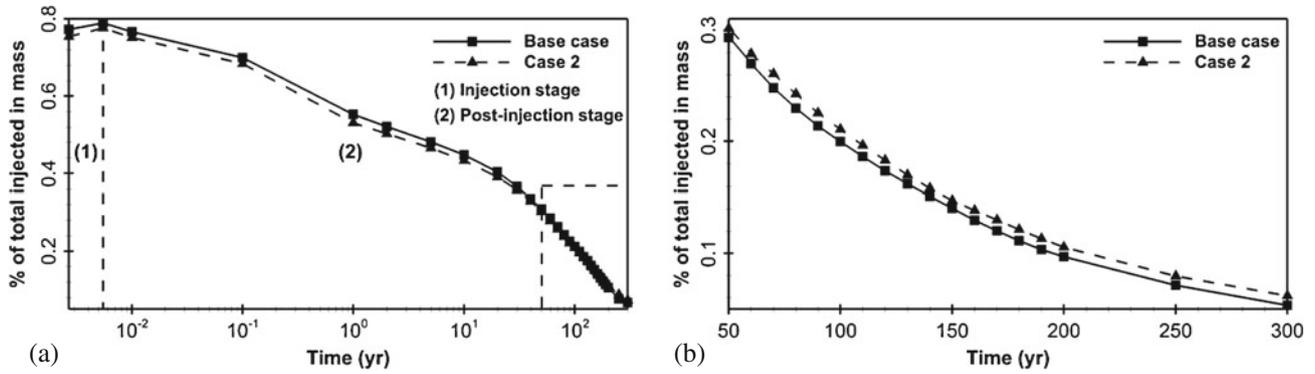


Figure 7. Time evolution of mass fraction of gas phase in the total injected CO₂ obtained from the base-case and case 2. Note that the right plot is the enlargement of 50–300 years in the left plot.

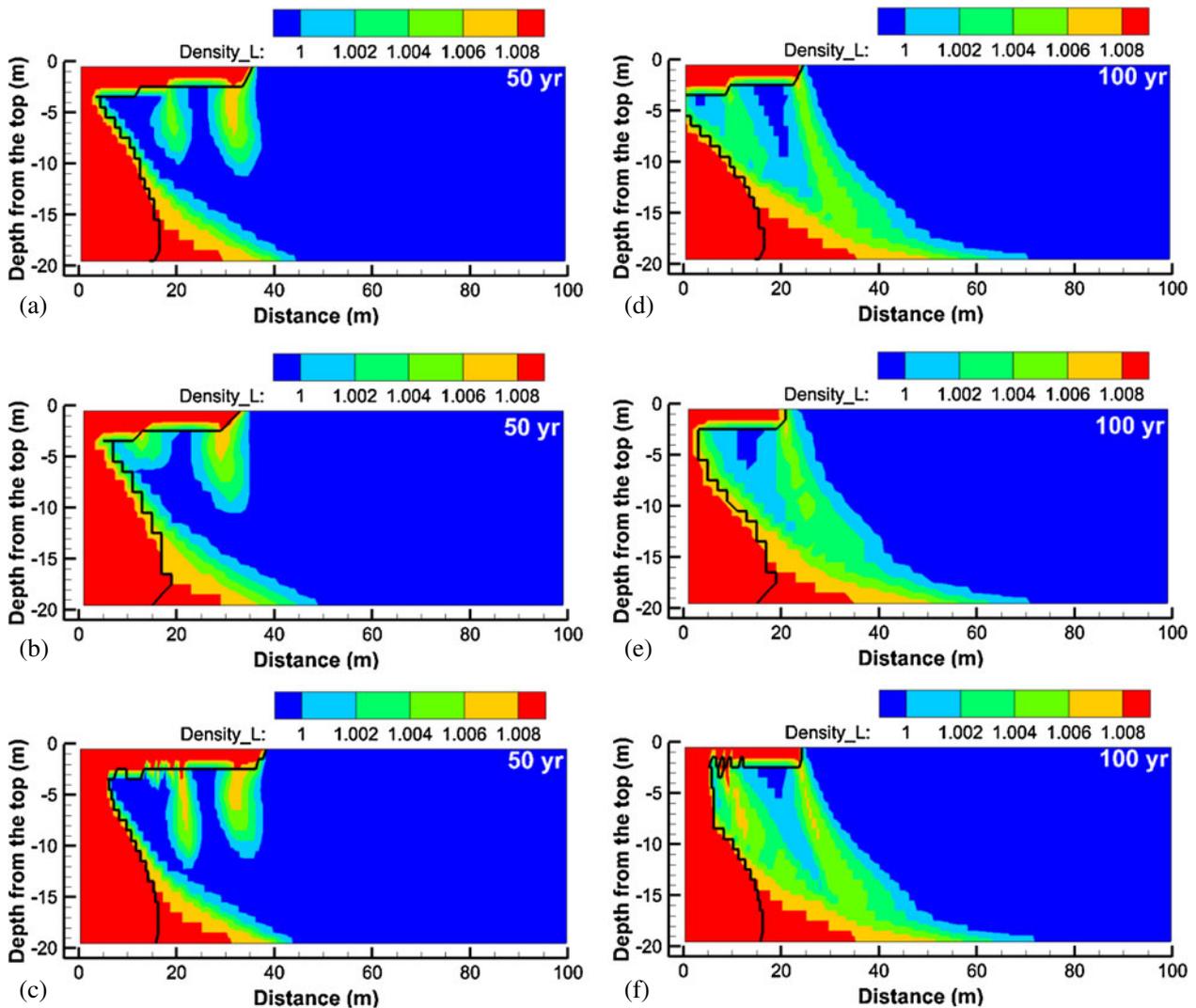


Figure 8. Spatial distribution of aqueous phase density (in kg L⁻¹) obtained from the base-case (top), case 2 (middle) and case 3 (bottom) after 50 and 100 years (the black line represents the zero contour line of gas saturation).

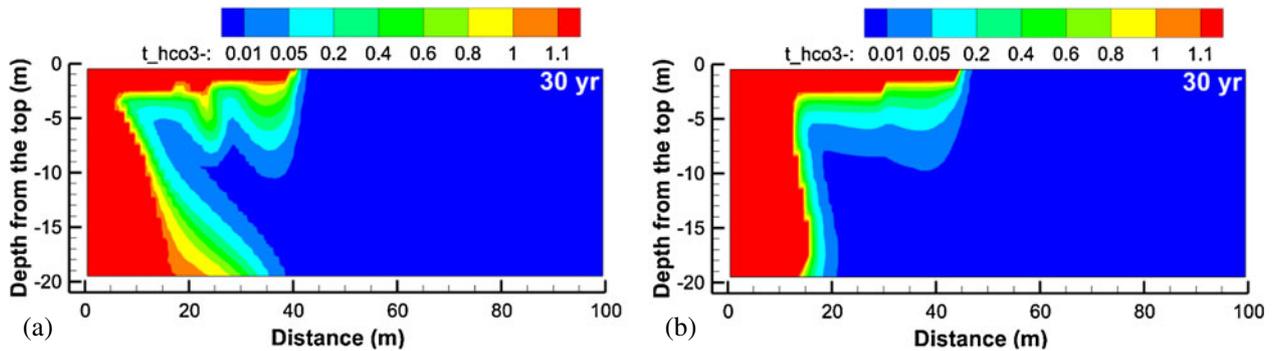


Figure 9. Spatial distribution of concentration (in mol kg⁻¹ H₂O) of total dissolved carbon obtained from the base-case (left) and case 4 (right) after 30 years.

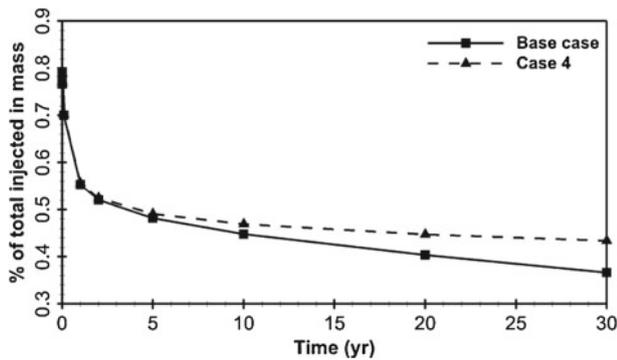


Figure 10. Time evolution of mass fraction of gas phase in the total injected CO₂ obtained from the base-case and case 4.

gas for the base-case is faster than that in case 2. This verifies that the lower-resolution modelling will underestimate the positive impact of density-driven fluid flow on the CO₂ dissolution. The rapid decrease of CO₂ gas in injection stage for the lower-resolution case is similar to the study of Audigane *et al.* (2007), which should be because that the coarser model overestimates the spatial distribution of injected CO₂ gas, consequently increasing the contact between CO₂ gas and formation water, further enhancing the CO₂ dissolution into water.

Due to constraints of computational capacity of modelling code and increase in grid resolution and number, the actual simulation time of the higher-resolution case (case 3) is only 100 years. However, the simulation result in case 3 still suggests that the higher-resolution model would be better to capture the density-driven fluid flow process, especially the fingering phenomenon (figure 8).

Figure 9 provides powerful evidence that the flow of CO₂-saturated brines in the upper and lower of the CO₂ gas plume for the base-case is indeed induced by the increasing density of the aqueous phase. Due to stronger fluid flow process in the base-case than that in case 4, the contact between CO₂ gas and CO₂-unsaturated aqueous phase is

enhanced, at the same time the dissolution rate of CO₂ gas into water is accelerated (figure 10).

4. Findings and conclusions

We have developed a 2D reactive transport model for density-driven fluid flow process during long-term geological storage, using mineralogical composition and water chemistry encountered in Songliao Basin of China. Major findings and conclusions from our simulations are summarized as follows:

- (1) During injection and geological storage of CO₂ in deep saline formations, there are significant density-driven fluid flow phenomena. Most studies which have been conducted focused on density-driven convective activity that mainly occurs below the CO₂ gas plume, especially the plume accumulated below the low-permeable caprock. However, we found that for the lower gas plume, higher-density CO₂-rich brines migrate downward and move horizontally along the bottom of the formation; for the upper gas plume, the higher-density ‘fingering’ phenomenon is formed, this means the occurrence of convective circulation between CO₂-saturated and CO₂-unsaturated brines.
- (2) Sensitivity test showed that due to the decrease of grid resolution, the density-driven fluid flow process is delayed and suppressed. Simulation results indicated that during CO₂ injection stage, the decrease of mass fraction of CO₂ in gas phase for the finer model is slower than that in the coarser model, but after the end of CO₂ injection, the decrease of injected CO₂ gas for the former is faster than that in the latter. The rapid decrease of CO₂ gas in injection stage for the lower-resolution case should be due to the coarser model overestimates the

spatial distribution of injected CO₂ gas, consequently increasing the contact between CO₂ gas and formation water, further enhancing the CO₂ dissolution into water. The comparison between simulation results of density-dependent and density-independent cases suggested that density-driven fluid flow process plays a great role in promoting the phase transition of injected CO₂ from supercritical phase into aqueous phase.

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