

## Review

Temporal variations in near-wellbore pressures during CO<sub>2</sub> injection in saline aquifersRoland T. Okwen<sup>a,\*</sup>, Mark T. Stewart<sup>b</sup>, Jeffrey A. Cunningham<sup>c</sup><sup>a</sup> Schlumberger Cambridge Research, High Cross, Madingley Road, Cambridge CB3 0EL, United Kingdom<sup>b</sup> Department of Geology, University of South Florida, 4202 East Fowler Ave., Tampa, FL 33620, USA<sup>c</sup> Department of Civil and Environmental Engineering, University of South Florida, 4202 East Fowler Ave., Tampa, FL 33620, USA

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## ABSTRACT

Numerical simulations of carbon dioxide injection, via a fully penetrating well, into a homogeneous confined saline aquifer were conducted using TOUGH2 to study temporal variations in near-wellbore pressures. The effect of contrasts in fluid properties on near-wellbore pressure was studied by comparing the predicted pressure histories of carbon dioxide injection to that of water injection into a confined saline aquifer. Simulation results predict an initial jump followed by subsequent decline in near-wellbore pressure over time under isotropic and weakly anisotropic conditions due to phase separation between the less dense and highly compressible carbon dioxide-rich (gas) phase and weakly compressible brine. Conversely, near-wellbore pressure increased monotonically during water injection because the differences between the viscosities, densities, and compressibilities of resident brine and water are relatively small. Sensitivity studies on the effects of the compressibility and viscosity of carbon dioxide and permeability anisotropy suggest that temporal variations in near-wellbore pressures depend strongly on the contrast in density between carbon dioxide and brine, and on the ratio between vertical and horizontal permeabilities of the aquifer (permeability anisotropy). These results suggest that the monitoring near-wellbore pressures during carbon dioxide injection is crucial for maintaining the integrity of the caprock and thereby warrants geomechanical studies.

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## 1. Introduction

During carbon dioxide (CO<sub>2</sub>) injection in confined formations, the integrity of the seals or caprocks, especially the upper confining bed, is pivotal in minimizing risk of potential leakage into overlying environmentally sensitive formations, potable water aquifers for example, and subsequent discharge into the atmosphere. CO<sub>2</sub> leakage from target storage formations during the injection phase could be from pre-existing fractures and faults, leakages at the wellbore

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## Nomenclature

### Dimensionless parameters and constants

$\Gamma_L$	fractional length of pore bodies
$\lambda$	pore geometry parameter
$\phi$	fraction of original porosity
$P_0$	strength coefficient
$S_{lr}$	irreducible saturation of liquid phase
$S_{gr}$	irreducible saturation of gas phase
$S_l$	saturation of liquid phase
$S_{ls}$	liquid phase saturation at which capillary pressure vanishes
$k_{vh}$	permeability anisotropy ratio, $k_{vh} = k_v/k_h$

### Variables

$t$	time (years)
$\sigma$	effective stress (bar)
$\sigma_3$	minimum principal stress (bar)
$\sigma'_3$	minimum effective principal stress (bar)
$\sigma_v$	vertical or overburden stress (bar)
$k$	intrinsic permeability (m <sup>2</sup> )
$k_v$	permeability in vertical direction (m <sup>2</sup> )
$k_h$	permeability in horizontal direction (m <sup>2</sup> )
$P_w(t)$	near-wellbore pressure (bar)
$P_{init}$	initial pressure (bar)
$P_{cap}$	brine capillary pressure (bar)
$Q$	mass injection rate (kg/s)
$r$	radial distance from injection well (m)

due to improper installation, abandoned wells, or induced fracturing (Nordbotten et al., 2004). Induced fracturing refers to formation fracturing caused by an excessive increase in pore pressure via fluid injection (Martinez et al., 1992). This paper focuses on the temporal variations in maximum pore pressure as a parameter or metric for evaluating the likelihood of fracturing to occur. Since formation pressures are highest at the wellbore during injection, the study of temporal variations in pressure near injection wells is warranted.

Simulations of continuous CO<sub>2</sub> injection into a homogeneous and isotropic confined saline aquifer via vertical wells using a 1-D radial geometry predict monotonic increases in near-wellbore pressures over time ( $P_w(t)$ ) (Pruess et al., 2004). However, a similar simulation using 2D radial geometry ( $r, z$ ) predicts a decline in  $P_w(t)$  at early times (in years). The major difference between the above-mentioned simulations is that the former neglects flow in the vertical direction (vertical flow) as a result of the differences in fluid properties (density and viscosity) between brine and CO<sub>2</sub> while the latter does not. As a result, one may be tempted to conclude that the differences in the near-wellbore pressure histories between the two simulations is due to phase separation. A previous study involving underground waste water injection into deep confined saline aquifer predicted monotonic pressure build-up (Hickey and Vecchioli, 1986). Therefore, an investigation or study of why simulations of continuous injection of CO<sub>2</sub> into a confined aquifer do not predict monotonic pressure build-up over time is needed.

This paper investigates temporal variations in near-wellbore pressures during CO<sub>2</sub> injection in a confined aquifer of radial extent much greater than its thickness. A series of numerical experiments were conducted to investigate the following:

1. test the hypothesis that the decline in near-wellbore pressures during CO<sub>2</sub> injection in isotropic confined aquifers is mostly due to the contrast in density between CO<sub>2</sub>-rich (gas) and resident brine, referred to as gravity segregation (phase separation or buoyancy) and

2. study the effects of vertical permeability on changes in near-wellbore pressures over time.

## 2. Background

Injecting fluids into a porous formation results in net increases in pressures around injection wells. If the pressure increases above a threshold value, fracturing may occur. Previous studies have indicated that formation fracturing is caused by pore pressure exceeding the least principal compressive stress ( $\sigma_3$ ) of the formation (Fjær et al., 1992; Zoback, 2007).  $\sigma_3$  is the sum of pore pressure,  $P_p$ , and effective least principal stress ( $\sigma'_3$ ) i.e.,

$$\sigma_3 = P_p + \sigma'_3 \quad (1)$$

Generally, the effective stress ( $\sigma'$ ) of a formation is the pressure acting between rock grains within a formation (Dake, 1978; Fjær et al., 1992; Zoback, 2007). As  $P_p$  increases,  $\sigma'$  decreases and vice versa. When the  $\sigma'_3$  vanishes to zero,  $P_p$  becomes equivalent to the least principal stress  $\sigma_3$  and a slight increase in  $P_p$  will initiate formation fracturing in the direction perpendicular to  $\sigma_3$  (Fjær et al., 1992; Zoback, 2007).

Injection of CO<sub>2</sub> into a confined formation will cause a net increase in  $P_p$ . A rule of thumb generally employed is that the maximum fluid pressure should not exceed 90% of the overburden pressure ( $\sigma_v$ ) to avoid risk of formation fracturing in the vertical direction (Bachu and Adams, 2003), especially if  $\sigma_v = \sigma_3$ , which is usually the case at shallow depths.

The tendency of injected CO<sub>2</sub> to override resident brine under deep geologic conditions has been attributed to the contrasts in density and viscosity between CO<sub>2</sub>-rich (gas) phase and formation brine (Arts et al., 2004; Torp and Dale, 2004; Nordbotten et al., 2005). A schematic representation of CO<sub>2</sub> injection via a vertical well into a homogeneous confined aquifer is shown in Fig. 1. The effects of phase separation or buoyancy on CO<sub>2</sub> sweep efficiency, storage capacity, solubility in brine and fluid flow dynamics within a confined aquifer have been extensively addressed in the technical literature (van der Meer, 1995, 1996; Ennis-King and Paterson, 2002; Bachu and Adams, 2003; Nordbotten et al., 2005; IPCC, 2005; Ozah et al., 2005; Nordbotten and Celia, 2006; Doughty, 2007; Friedmann, 2007; Bachu, 2008; Okwen et al., 2010). However, the effects of phase separation on temporal variations of formation pressure near injection wells have not been fully addressed.

## 3. Approach

Radial 2-D simulations of CO<sub>2</sub> and water injection, via a fully penetrating well, into a confined saline aquifer were conducted to achieve the objectives of this study. As shown in Table 2, we considered an aquifer with a radius and thickness of 100 km and 100 m, respectively, or an area of about  $3.14 \times 10^{10}$  m<sup>2</sup>. The aquifer was discretized into 435 grids in the radial direction and 20 grids in the vertical, making a total of 8700 grid blocks. Grid sizes in the radial direction were logarithmically distributed, with the finest grid closest to the wellbore and coarsest at the lateral boundaries of the model. As a result, majority of the grid blocks are located within a 15 km radius of the injection well. Because the radial extent of the aquifer is most likely to be significantly greater than CO<sub>2</sub> plume extent, boundary effects are considered negligible. To ensure that boundary effects are minimized, grid blocks along the model's boundary were assigned a volume factor of  $10^{30}$ , thereby imposing constant pressures at the lateral boundaries of the aquifer. The aquifer was also considered to be bounded by two impermeable layers at its top and bottom. The temperature of the injected CO<sub>2</sub> in the simulations is assumed close enough to the temperature of the aquifer that the system may be considered isothermal. In practice,

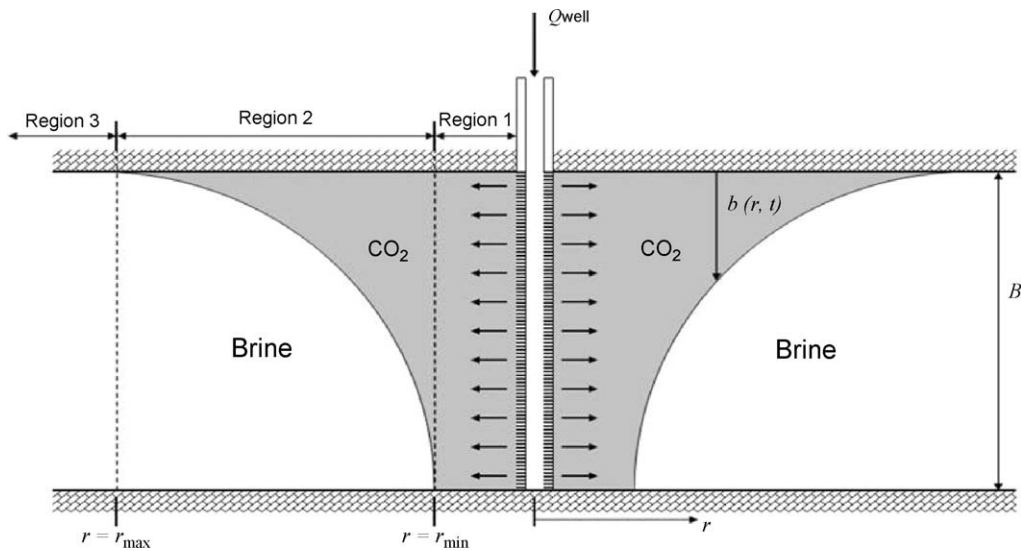


Fig. 1. Schematic representation of CO<sub>2</sub> injection into a confined aquifer via a single vertical injection well. Adapted from Nordbotten et al. (2005).

the difference in temperature between the injected CO<sub>2</sub> and the aquifer could be significant and may also have significant effects on wellbore stability, but those effects are not considered here.

A total of 16 numerical simulations were conducted to test the hypothesis and achieve the objectives stated in Section 1 (see Table 1). These simulations involve CO<sub>2</sub> injection at 100 kg/s at different values of vertical and horizontal permeability. A mass injection of 100 kg/s, for example, is equivalent to the CO<sub>2</sub> emissions from a 288 MWe coal-fired power plant (Hitchon, 1996). Vertical permeabilities ranging from 0.1 to 100 mD and horizontal permeabilities ranging from 10 to 1000 mD were used. Simulations with horizontal permeability less than 10 mD were not considered because formation pressure at or near the injection well exceeded 600 bar, which is the upper limit for the equation of state for CO<sub>2</sub> available in the technical literature (Spycher and Pruess, 2005). Nonetheless, the permeability range considered herein falls within the range of permeability values generally encountered in many sedimentary formations.

The hydrogeologic parameters used in the simulations are listed in Table 2. In Table 2, the symbols  $S_{lr}$ ,  $S_{gr}$ ,  $S_l$ ,  $\lambda$ ,  $P_o$ , and  $S_{ls}$  denote the residual liquid saturation, residual gas saturation, liquid phase saturation, pore geometry parameter, strength coefficient (van Genuchten, 1980), and liquid phase saturation at which  $P_{cap}$  vanishes (Pruess and García, 2002). The value of  $S_{lr}$  in estimation of capillary pressure ( $P_{cap}$ ) was set to 0.0 to avoid unrealistic behavior of the van Genuchten (1980) function in which as  $k_{lr} \rightarrow 0$ ,

Table 1  
Simulations conducted to achieve objectives.

$k_v$ (mD)	$k_h$ (mD)		
	1000	100	10
100	*	*	–
10	*	*	*
1.0	*	*	x
0.1	*	*	x <sup>a</sup>

$k_v > k_h$  is assumed not feasible. Six additional control simulations were also conducted. They include: (1) water injection, (2) viscous-CO<sub>2</sub> injection, (3) CO<sub>2</sub> injection into a gas-saturated formation, (4) 1-D CO<sub>2</sub> injection, (5) incompressible CO<sub>2</sub> injection, (6) CO<sub>2</sub> injection with permeability and porosity reductions for  $k_v = 0.1$  mD, and (7) CO<sub>2</sub> injection with permeability and porosity reductions for  $k_v = 100$  mD.  $Q = 100$  kg/s.

<sup>a</sup> Maximum pressure in simulation surpassed 600 bar (above pressure limit for CO<sub>2</sub> equation of state used).

$P_{cap} \rightarrow -\infty$  (Pruess, 1997; Pruess and García, 2002; Müller et al., 2009). The tubes-in-series model developed by Verma and Pruess (1988) was used to account for permeability reduction due to salt (NaCl) precipitation.  $\Gamma_L$  and  $\phi_r$  were both assigned a value of 0.8 in all simulations, similar to what was employed in Code Intercomparison Problem 3 (Pruess et al., 2004).  $\Gamma_L$  represents fractional length of pore bodies and  $\phi_r$  is the fraction of the original porosity at which permeability is reduced to zero (Verma and Pruess, 1988; Pruess and Müller, 2009).

The hypothesis that the decline in near-wellbore pressures during CO<sub>2</sub> injection in isotropic confined aquifers is principally due to contrast in density between CO<sub>2</sub>-rich (gas) and resident brine was tested by conducting three numerical simulations with similar aquifer dimensions and input conditions but with different injectants and displaced fluids under isotropic conditions. CO<sub>2</sub>, water, and a hypothetical high-viscosity CO<sub>2</sub> (viscous-CO<sub>2</sub>) were separately used in each simulation and their temporal changes in

Table 2  
Input parameters applied in all simulations ( $S_{lr} < S_l < 1.0$ , and  $S_{ls} \approx 1.0$ ).

Parameter	Value
Dimension ( $R \times H$ ) m	$10^5 \times 100$
Grid blocks ( $X:Z$ )	$435 \times 20$
Wellbore radius (m)	$r_w = 0.3$
Depth (top - bottom) (m)	$D = 1200-1300$
Pore compressibility ( $\text{Pa}^{-1}$ )	$c = 4.5 \times 10^{-10}$
Initial pressure (top-bottom (bar))	$P_{init} \approx 120-131$
Temperature ( $^{\circ}\text{C}$ )	$T = 45.0$
Average porosity	$\phi = 0.12$
Average horizontal permeability (mD)	$k = 0.1-1000$
Permeability anisotropy ratio	$k_{vh} = 0.001-1.0$
Simulation time (years)	$t = 150$
Relative permeability	
Brine: van Genuchten (1980)	
$k_{rl} = \sqrt{S^*} \{1 - (1 - [S^*]^{\frac{1}{\lambda}})^{\lambda}\}^2$	$S^* = \frac{S_l - S_{lr}}{1 - S_{lr}}$
Residual brine saturation	$S_{lr} = 0.3$
Exponent	$\lambda = 0.457$
Gas (CO <sub>2</sub> ): Corey (1954)	
$k_{rg} = (1 - \hat{S})^2 (1 - \hat{S}^2)$	$\hat{S} = \frac{S_l - S_{lr}}{1 - S_{lr} - S_{gr}}$
Residual gas saturation	$S_{gr} = 0.05$
Capillary pressure: van Genuchten (1980)	
$P_{cap} = -P_o ([S^*]^{\frac{1}{\lambda}} - 1)^{1-\lambda}$	$S^* = \frac{S_l - S_{lr}}{1 - S_{lr}}$
Residual brine saturation	$S_{lr} = 0.0$
Strength coefficient (Pa)	$P_o = 1.96 \times 10^4$
Exponent	$\lambda = 0.457$

**Table 3**Initial values of density and viscosity for CO<sub>2</sub>, viscous-CO<sub>2</sub>, water, and brine.

Fluid	Density (kg/m <sup>3</sup> )	Viscosity (Pa s)
CO <sub>2</sub>	700	$5.6 \times 10^{-5}$
Viscous-CO <sub>2</sub> <sup>a</sup>	701	$8.4 \times 10^{-4}$
Water	1000	$6.0 \times 10^{-5}$
Brine	1100	$8.3 \times 10^{-4}$

<sup>a</sup> Hypothetical CO<sub>2</sub>.

near-wellbore pressures ( $P_w(t)$ ) for periods up to 150 years were compared. Water was chosen as an alternate injectant because the difference between the fluid properties of water and brine is small. Viscous-CO<sub>2</sub> is an unrealistic CO<sub>2</sub> used to test the contribution of viscosity to changes in  $P_w(t)$ . Viscous-CO<sub>2</sub> is assigned a density and viscosity of 701 kg/m<sup>3</sup> and  $8.4 \times 10^{-4}$  Pa s, respectively. The initial density and viscosity of the resident brine used in all simulations is 1100 kg/m<sup>3</sup> and  $8.3 \times 10^{-4}$  Pa s, respectively. It is worth noting that viscous-CO<sub>2</sub> and resident brine have similar viscosities but significantly different densities. The simulation using CO<sub>2</sub> as the injectant under isotropic conditions is considered as the base case simulation. The mass injection rate and intrinsic permeability (isotropic) applied in the above-mentioned simulations are 100 kg/s and 100 mD, respectively.

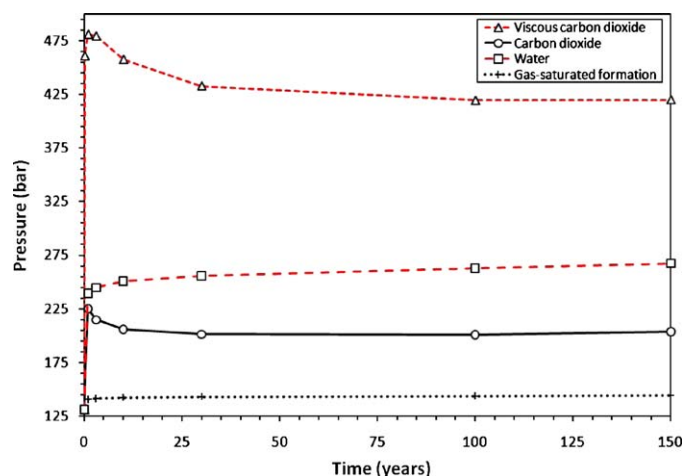
A hypothetical simulation of CO<sub>2</sub> injection into a gas (CO<sub>2</sub>) saturated formation with initial conditions (temperature and pressure) similar to those of the base case simulation, was conducted as a control experiment. This simulation represents a scenario in which fluid properties of the injected and displaced fluid are similar, like it is the case with water injection into a saline aquifer. Results from this simulation are compared to those of CO<sub>2</sub> and water injection into a saline aquifer to study how differences between the properties of the displacing and displaced fluids impact changes in  $P_w(t)$  over time.

The effect of CO<sub>2</sub> compressibility on near-wellbore pressure was studied by conducting a simulation with similar input conditions as the base case simulation, except that the physical properties of CO<sub>2</sub> were kept constant. Constant density and viscosity at initial temperature and pressure (45 °C and 120 bar) conditions, which correspond to about 700 kg/m<sup>3</sup> and  $5.57 \times 10^{-5}$  Pa s, respectively, were applied. Results achieved from this simulation are compared to those of the base case simulation to evaluate the contribution of CO<sub>2</sub> compressibility to changes in pressure around the wellbore.

The physical properties of CO<sub>2</sub> for control simulations, i.e., viscosity and density, were adjusted by editing the "CO2TAB" file in TOUGH2. This file contains tabular data of CO<sub>2</sub> density, viscosity and specific heat enthalpy at different temperatures and pressures (Altunin, 1975; Pruess, 2005). The control simulations conducted herein include injection of viscous-CO<sub>2</sub> and incompressible CO<sub>2</sub>.

Effects of vertical permeability on  $P_w(t)$  during CO<sub>2</sub> injection were investigated by conducting numerical simulations with anisotropic permeabilities. In the simulations used to investigate the contribution of permeability anisotropy, the vertical permeability ( $k_v$ ) was varied from 0.1 to 100 mD for a given value of horizontal permeability ( $k_h$ ) and constant CO<sub>2</sub> mass injection rate ( $Q$ ). The  $k_h$  values of 10, 100, and 1000 mD were employed. Simulations in which  $k_v > k_h$  are assumed to be unphysical. We define a permeability anisotropy parameter ( $k_{vh}$ ) herein as the ratio of the vertical to the horizontal permeability of an aquifer. In Cartesian coordinates ( $X, Y, Z$ ) vertical  $k_v$  is equivalent to permeability along the  $Z$ -axis while  $k_h$  represent permeabilities along both  $X$ - and  $Y$ -axes of a grid block. This infers that the permeabilities in the  $X$ - and  $Y$ -axes are assumed equal. The  $k_{vh}$  values considered in this study range from 0.0001 to 1.0.

The TOUGH2 general purpose numerical simulator with the ECO2N fluid property module was utilized to conduct numer-



**Fig. 2.** Effect of density on near-wellbore pressure history at the bottom of the aquifer. Similar trends were observed at the top of the aquifer ( $Q = 100$  kg/s and  $k_h = k_v = 100$  mD). Initial pressure at the bottom = 131 bar. The values of density and viscosity of viscous-CO<sub>2</sub> are 701 kg/m<sup>3</sup> and  $8.4 \times 10^{-4}$  Pa s, respectively. Viscous-CO<sub>2</sub> has viscosity equivalent to that of brine (high viscosity) and a density of supercritical CO<sub>2</sub>.

ical experiments. ECO2N gives accurate fluid properties for water-CO<sub>2</sub>-NaCl systems for temperatures ranging between 10 and 110 °C and pressures up to 600 bar (Pruess et al., 1999; Pruess and García, 2002; Pruess, 2004; Pruess and Spycher, 2006, 2007). TOUGH2 was selected because of its widespread usage by many research groups worldwide to solve CO<sub>2</sub> geological sequestration problems (Weir et al., 1995; McPherson and Lichtner, 2001; Ennis-King and Paterson, 2002; Pruess et al., 2003).

## 4. Results

### 4.1. Density and viscosity effects

The effect of differences in the physical properties between CO<sub>2</sub> and brine on temporal variations in pore pressure close to the injection well ( $P_w(t)$ ) was investigated by comparing results of CO<sub>2</sub>, viscous-CO<sub>2</sub>, and water injection into a homogeneous and isotropic confined saline aquifer. Table 3 shows the initial densities and viscosities of CO<sub>2</sub>, viscous-CO<sub>2</sub>, water, and brine. It can be seen from Table 3 that viscous-CO<sub>2</sub> is as dense as CO<sub>2</sub> and as viscous as brine. A mass injection rate of 100 kg/s and an isotropic intrinsic permeability of 100 mD were applied in the simulations. In the simulation involving injection of viscous-CO<sub>2</sub> into a confined saline aquifer, the density and viscosity of the injectant were kept constant.

Fig. 2 shows changes in  $P_w(t)$  over time at the bottom of the aquifer. All the simulations predict an instantaneous pressure jump at the beginning of injection (see Fig. 2). For example, results in Fig. 2 show the  $P_w(t)$  for CO<sub>2</sub>, viscous-CO<sub>2</sub>, and water to increase from 131 bar to about 225 bar, 480 bar, and 240 bar, respectively, after 1 year. These results are in agreement with the findings of Vilarrasa et al. (1988), which suggest that the most likely moment for caprock failure to occur is at the beginning of injection.  $P_w(t)$  increases monotonically over time in the simulation that used water as injectant. On the other hand, the CO<sub>2</sub> injection simulation predicts an initial jump in  $P_w(t)$  followed by a decline for up to 30 years after which it stabilizes and increases thereafter ( $t > 100$  years). Since the only difference in the input conditions of both simulations is the injectant used, it may be deduced that the difference in the  $P_w(t)$  history depicted in Fig. 2 is due to differences between the physical properties of CO<sub>2</sub>, water, and brine. However, the differences in the physical properties of water and brine (viscosity and density) are negligible compared to that between CO<sub>2</sub> and brine.



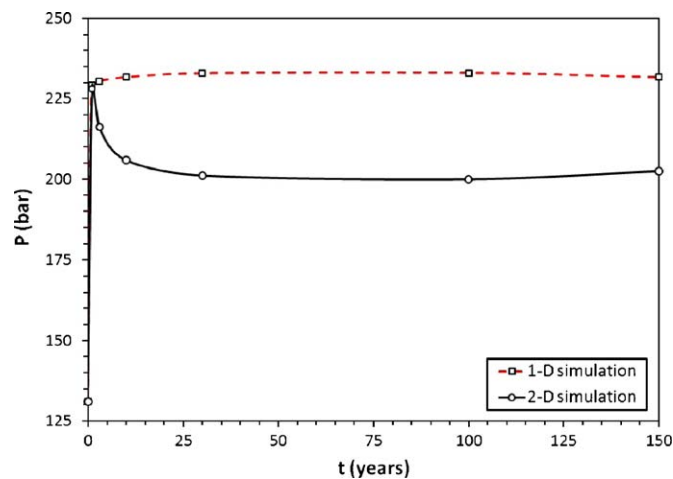


Fig. 3. Near-wellbore pressure (bottom of aquifer) for 1-D and 2-D simulations of  $\text{CO}_2$  injection into a confined aquifer ( $Q = 100 \text{ kg/s}$  and  $k_h = k_v = 100 \text{ mD}$ ).

Results in Fig. 2 also show  $P_w(t)$  for the viscous- $\text{CO}_2$  simulation to increase at early times (for at least 10 years) after which it declines and stabilizes after 100 years of injection. Since viscous- $\text{CO}_2$  and resident brine have equivalent viscosities and different densities, it can be deduced that the decline in  $P_w(t)$  between 3 years and 100 years is due to the difference in density between the former and the latter (buoyancy). The minimum difference in density between resident brine and viscous- $\text{CO}_2$  is about  $400 \text{ kg/m}^3$ . This is because the density of brine would increase during injection, especially at the  $\text{CO}_2$ –brine interface where  $\text{CO}_2$  dissolves into brine and also due to increase in pressure as more fluid is injected into the aquifer. The  $P_w(t)$  for viscous- $\text{CO}_2$  is significantly greater than those of  $\text{CO}_2$  and water because it has a very high viscosity. A comparison of the  $P_w(t)$  histories for  $\text{CO}_2$ , viscous- $\text{CO}_2$ , and water suggest that  $P_w(t)$  increases with the viscosity of the displacing fluid, and a decline in  $P_w(t)$  over time is influenced by the density difference between the displacing fluid ( $\text{CO}_2$ , viscous- $\text{CO}_2$ , or water) and the displaced fluid (brine).

The  $P_w(t)$  history of the simulation of  $\text{CO}_2$  injection into a hypothetical gas-saturated formation (Fig. 2) increases monotonically over time. This is because the injected  $\text{CO}_2$  has fluid properties similar to the resident gas ( $\text{CO}_2$ ) in the formation. This hypothetical simulation is analogous to water injection into a confined saline aquifer in which both water and brine have similar fluid properties. A comparison of the results in Fig. 2 suggest that  $P_w(t)$  increases monotonically when the displacing and displaced fluids have similar densities and viscosities (under isothermal conditions).

A similar study of  $\text{CO}_2$  injection into a confined aquifer of infinite radial extent in which vertical flow (buoyancy) is considered negligible (1D radial mesh) predict  $P_w(t)$  to increase at early times (Pruess and García, 2002; Pruess et al., 2004) (see Fig. 3). This is because in the 1-D simulation, vertical flow is considered negligible. However, the 2-D simulation results, in which vertical flow (buoyancy driven flow) is taken into account, presented in Fig. 3 depict reduction in  $P_w(t)$  at early times, as it is the case with the simulation results present in Fig. 2.

The effect of vertical flow (buoyancy) observed at early times during  $\text{CO}_2$  injection into an isotropic and homogeneous saline aquifer can be conceptually described as follows. At the beginning of the injection phase in a  $\text{CO}_2$  sequestration project,  $\text{CO}_2$  cannot override the resident brine because it has to first displace the brine. As a result, a certain threshold pressure is required to displace the resident brine (Vilarrasa et al., 1988; Müller, 2011). At this stage, lateral viscous flow is dominant while vertical flow (buoyancy) is negligible. As the brine is displaced a separate gas-like

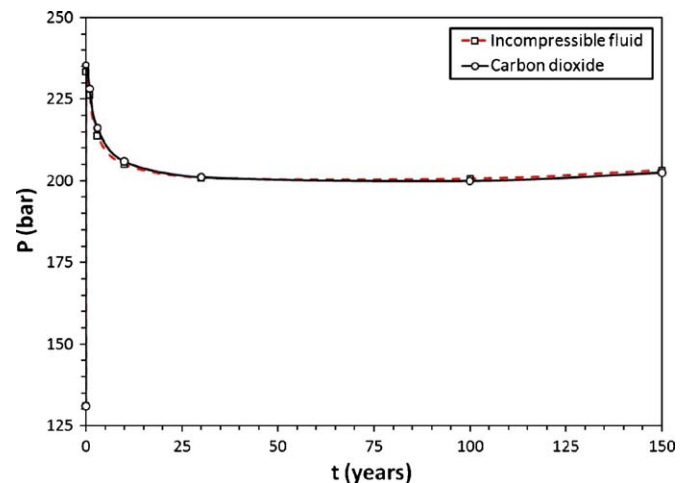


Fig. 4. Effect of  $\text{CO}_2$  compressibility on near-wellbore pressure history at the bottom of the aquifer. Similar trends were observed at the top of the aquifer ( $Q = 100 \text{ kg/s}$  and  $k_h = k_v = 100 \text{ mD}$ ). Initial pressure at the bottom = 131 bar.

phase ( $\text{CO}_2$  plume) would occupy the space between the injection well and the  $\text{CO}_2$ –brine interface. Vertical flow or buoyancy would become important at this point in time because there is room for the gas plume to migrate upwards. As more  $\text{CO}_2$  is injected, some of the gas or  $\text{CO}_2$  plume would migrate upwards because  $\text{CO}_2$  is less dense compared to brine. When a significant volume of the plume accumulates at the bottom of the caprock, the  $\text{CO}_2$  plume would override the brine because the former is less viscous. Therefore, the pressure required for a specified flow rate decreases as vertical flow becomes important. In other words, it is easier to push the  $\text{CO}_2$  into the aquifer when there is already some compressible and buoyant  $\text{CO}_2$  present, versus when there is only brine.

#### 4.2. Effect of $\text{CO}_2$ compressibility

A sensitivity study on the effect of  $\text{CO}_2$  compressibility on temporal variations in  $P_w(t)$  was achieved by comparing results obtained from incompressible and compressible  $\text{CO}_2$  injection simulations (Fig. 4). Results in Fig. 4 indicate that  $\text{CO}_2$  compressibility has a negligible effect. This is supported by the results presented in Fig. 5 which shows the changes in water and  $\text{CO}_2$  densities over time. It can be deduced from Fig. 5 that the water density

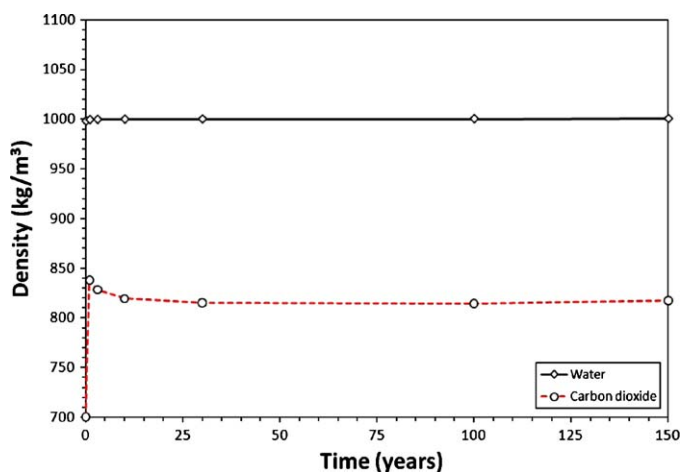


Fig. 5. Temporal variations in  $\text{CO}_2$  and water densities ( $Q = 100 \text{ kg/s}$  and  $k_h = k_v = 100 \text{ mD}$ ). Temporal changes in  $\text{CO}_2$  over time ( $\Delta \rho_{\text{CO}_2}(t)$ ,  $0 \leq \Delta \rho_{\text{CO}_2}(t) \leq 20 \text{ (kg/m}^3\text{)}$ ) is significantly lower than the difference between the densities of water and  $\text{CO}_2$  ( $\Delta \rho(t)$ ,  $170 \leq \Delta \rho(t) \leq 200 \text{ (kg/m}^3\text{)}$ ).

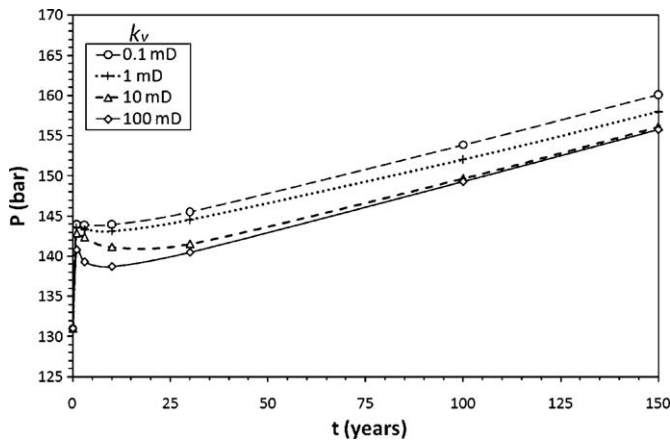


Fig. 6. Effect of  $k_v$  on near-wellbore pressure history at the bottom of the aquifer for high  $k_h$  values ( $Q = 100$  kg/s and  $k_h = 1000$  mD,  $10^{-4} \leq k_{vh} \leq 0.1$ ).

remains relatively constant over time while that of  $\text{CO}_2$  varies over time, especially at early times. However, the difference between the densities of water and  $\text{CO}_2$  is significantly greater than temporal changes in the densities of the individual fluids. The predicted  $P_w(t)$  of the  $\text{CO}_2$  injection case show a slight but noticeable increase after 100 years because as more and more  $\text{CO}_2$  is injected into the aquifer over time, it becomes less compressible and more dense near the wellbore.

The simulation results presented in Figs. 2–5 suggest that the decline in  $P_w(t)$  at early times ( $<30$  years) of  $\text{CO}_2$  injection into a homogeneous and isotropic confined saline aquifer is mostly due to the density difference between  $\text{CO}_2$  and brine. This is consistent with the hypothesis that the decline in near-wellbore pressures during  $\text{CO}_2$  injection in isotropic confined aquifers is due to contrast between the density of the  $\text{CO}_2$ -rich (gas) phase and that of resident brine (liquid phase).

#### 4.3. Effect of vertical permeability, $k_v$

The effect of vertical permeability on  $P_w(t)$  during  $\text{CO}_2$  injection was investigated by comparing  $P_w(t)$  histories obtained from simulations with different values of vertical permeability ( $k_v$ ). Values of  $k_v$  used in simulations ranged between 0.1–100 mD. When  $k_v$  is very small, fluids within the aquifer preferentially flow in the horizontal direction. This is because as  $k_v$  decreases the resistance to fluid flow in the vertical direction increases.

Results from different simulations with  $k_h$  values of 10 mD, 100 mD, and 1000 mD and  $k_v$  values of 0.1 mD, 1.0 mD, 10 mD, and 100 mD were compared to evaluate the effects of vertical permeability on  $P_w(t)$ . This makes up a set of numerical simulations conducted for a specified  $\text{CO}_2$  injection rate. As depicted in Table 1 the injection rate considered is 100 kg/s. Results from simulations with a  $k_h$  value of 1000 mD predict  $P_w(t)$  to generally increase monotonically over time as  $k_v$  is reduced from 100 mD ( $k_{vh} = 0.1$ ) to 0.1 mD ( $k_{vh} = 10^{-4}$ ) (see Fig. 6). Results in Fig. 6 suggest that both viscous flow and buoyancy are significant at early times ( $t < 10$  years) after which viscous flow is dominant (buoyancy negligible), in formations with  $k_h$  equal 1000 mD ( $k_{vh} = 0.1$ ).

On the other hand, results in Fig. 7 show vertical flow (buoyancy) effects to dissipate or become less important as  $k_h$  is reduced from 1000 mD to 100 mD, for the same values of  $k_v$  considered in Fig. 6, i.e.,  $k_{vh}$  ranging between  $10^{-3}$  and 1.0. It should be underscored that the main difference between Figs. 6 and 7 is that the minimum and maximum values of  $k_{vh}$  of the former is less than that of the latter by an order of magnitude. Results in Fig. 7 show  $P_w(t)$  to decrease at early times and subsequently increase at later stages of the simula-

tions, for  $k_v$  values greater than 1.0 mD ( $k_{vh} > 0.01$ ).  $P_w(t)$  increases monotonically over time at  $k_v$  equal to 0.1 mD ( $k_{vh} = 0.001$ ). For example, Fig. 7 shows  $P_w(t)$  to decrease over time for  $k_v$  values of 10 mD and 100 mD with gravity effect of the latter more pronounced than the former. However, the pressure history of the simulation with  $k_v$  equal 1 mD ( $k_{vh} = 0.01$ ) in Fig. 7 show an increase at early times with a slight decline over time. These results indicate under isotropic or weakly anisotropic conditions vertical flow is important and  $P_w(t)$  declines over time. However, vertical flow is prevented under anisotropic conditions and hence  $P_w(t)$  increases monotonically.

The  $\text{CO}_2$  plume evolution over time for the simulation with  $k_v$  equal to 1 mD ( $k_{vh}$  and  $Q$  equal 0.01 and 100 kg/s, respectively) and  $k_v$  equal 100 mD ( $k_{vh} = 1.0$ ) in Fig. 7 were closely studied to obtain a possible explanation to the behavior of the  $P_w(t)$  history for the former. Figs. 8 and 9 show  $\text{CO}_2$  plume distribution at selected times for up to 100 years. Fig. 8(a) and (b) depicts a piston-like flow at early times (1 and 10 years) during which vertical flow or buoyancy is less important and viscous flow is dominant. Vertical flow becomes important at large times (e.g.  $t \geq 30$  years), when the  $\text{CO}_2$ -brine interface is far from the injection well. This is marked by phase segregation (gravity or buoyancy) and formation of a “tongue” or thin layer of  $\text{CO}_2$  plume beneath the upper confining bed (see Fig. 8(c) and (d)). In addition, separation between  $\text{CO}_2$ -saturated brine and resident brine, at the  $\text{CO}_2$ -brine interface (van der Meer, 1996) is also dominant during this period. These findings are in agreement with those of Ennis-King and Paterson (2001) that buoyancy is significant far away from the  $\text{CO}_2$  injection well.

A “tongue” of  $\text{CO}_2$  plume develops beneath the upper confining bed (phase segregation) at early times (1 year) for the simulation with  $k_v$  equal 100 mD ( $k_{vh} = 1.0$ ) (Fig. 9(a)). The distance between the tip of the plume and the injection well increases over time during which the  $\text{CO}_2$  plume “tongue” becomes more visible (Fig. 9(a)–(d)). A comparison of the results in Figs. 8 and 9 suggest that the  $\text{CO}_2$  plume is well spread across the thickness of the aquifer in Fig. 8 ( $k_v = 1$  mD) than in Fig. 9 ( $k_v = 100$  mD) due to high resistance to vertical flow in the former. On the other hand, the radial extent of the  $\text{CO}_2$  plume after 100 years in Fig. 9 ( $k_v = 100$  mD) is greater than that in Fig. 8 because former has a higher  $k_v$  value. As a result, vertical flow or buoyancy is enhanced as  $k_v$  is increased. The radial extent of the  $\text{CO}_2$  plume refers to the distance between the tip of the  $\text{CO}_2$  plume and the injection well. Overall, it can be seen from Figs. 8 and 9 that isotropic formations permit gravity segregation, while anisotropic formations suppress gravity segregation.

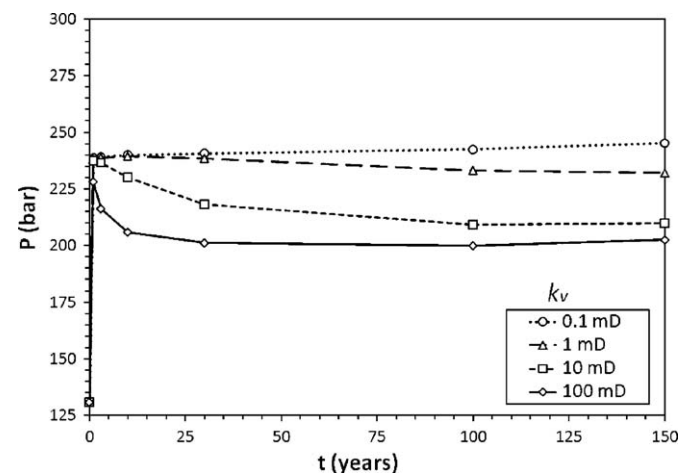
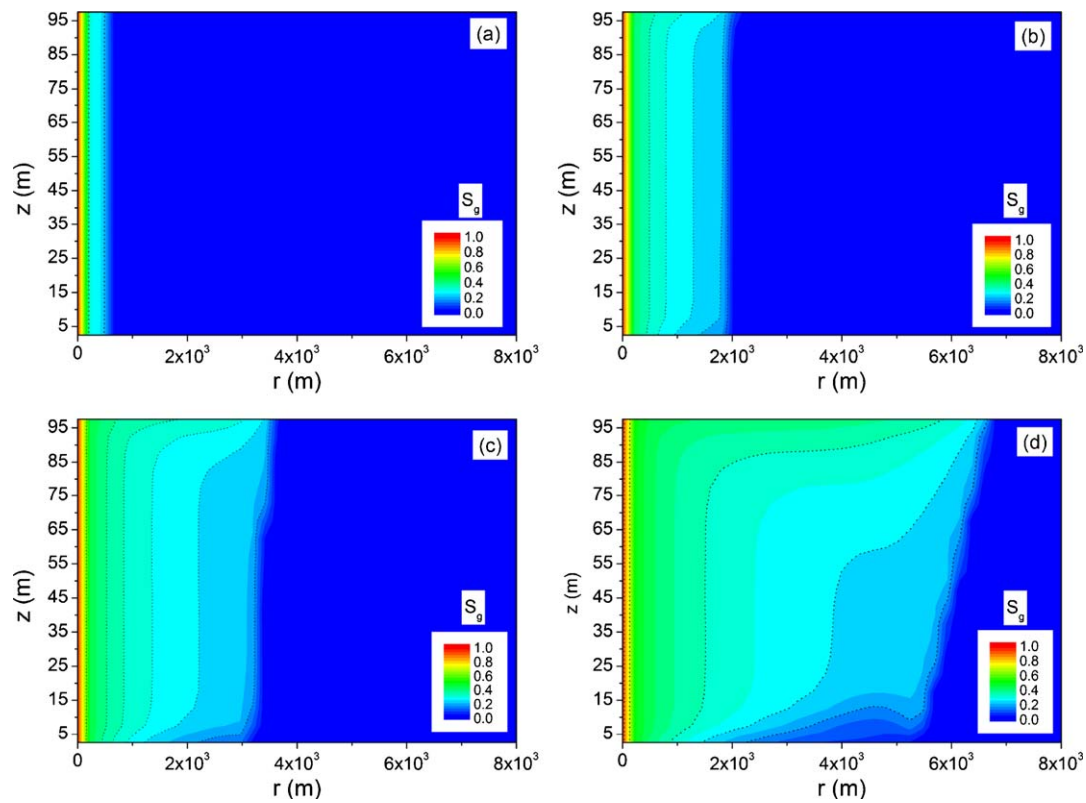
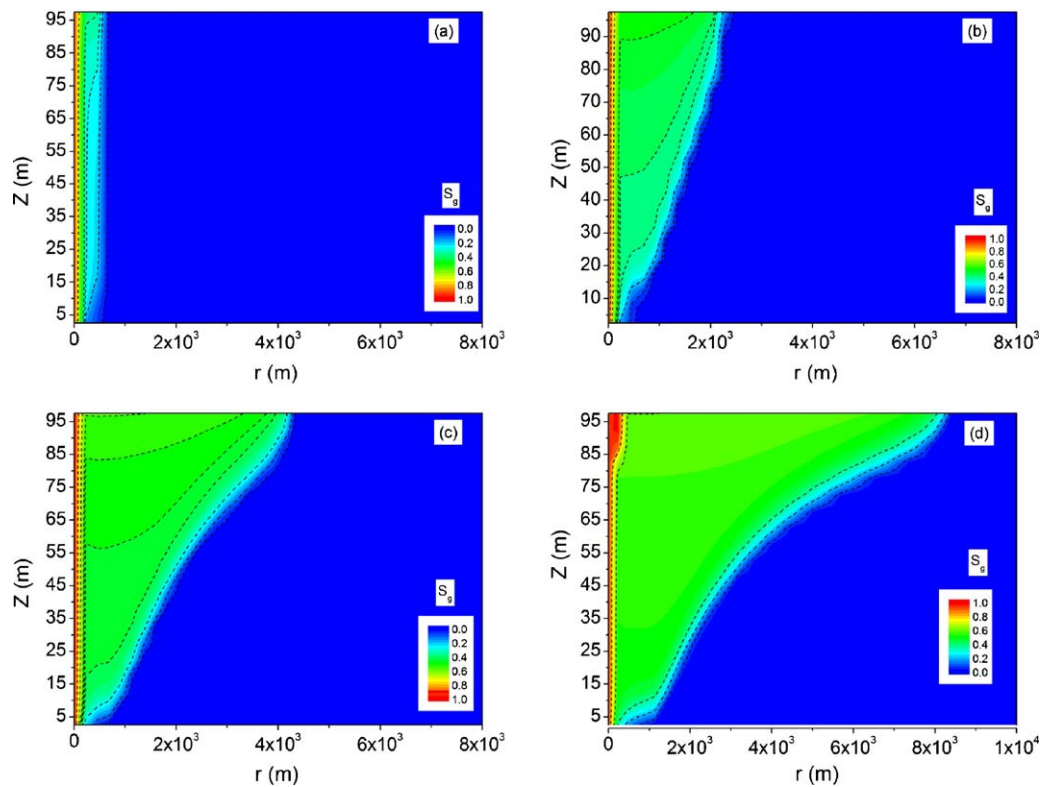


Fig. 7. Effect of  $k_v$  on near-wellbore pressures at the bottom of the aquifer as a function of time ( $Q = 100$  kg/s and  $k_h = 100$  mD,  $10^{-3} \leq k_{vh} \leq 1$ ).



**Fig. 8.** Gas saturation distribution over time at  $k_{vh}$  equal to 0.01 ( $k_v = 1$  mD and  $k_h = 100$  mD). (a) 1 year, (b) 10 years, (c) 30 years, and (d) 100 years. Vertical injection well is positioned at  $r = 0.0$  m.



**Fig. 9.** Gas saturation distribution over time at  $k_{vh}$  equal to 1 ( $k_v = 100$  mD and  $k_h = 100$  mD). (a) 1 year, (b) 10 years, (c) 30 years, and (d) 100 years. Vertical injection well is positioned at  $r = 0.0$  m.

**Table 4**

$\Delta P_w(t)$  (bar) as a function of permeability reduction ( $k_v = k_h = 100$  mD or  $k_{vh} = 1.0$ ), at the bottom of the formation ( $Q = 100$  kg/s).

Time (years)	Permeability reduction		
	Considered	Not considered	Difference
1	94.1	91.0	3.1
3	93.9	80.5	3.4
10	74.7	71.0	3.7
30	70.3	66.2	4.1
100	69.8	65.3	4.5

## 5. Discussions

Table 1 presents the simulations conducted to achieve the objectives stated in Section 1. The results presented in Figs. 2–5 demonstrate that the decline in  $P_w(t)$  at early times during CO<sub>2</sub> injection is mostly due to the difference in density between CO<sub>2</sub> and resident brine. This phenomenon is noticeable in isotropic confined formations where vertical flow or buoyancy effect is significant. Figs. 6 and 7 also demonstrate that  $P_w(t)$  strongly depend on  $k_v$ . The effect of buoyancy on  $P_w(t)$  diminishes as  $k_v$  decreases because strong anisotropy suppresses vertical flow.

Vertical flow (buoyancy) and permeability anisotropy can be viewed as competing over control of  $P_w(t)$  history during CO<sub>2</sub> injection. The length of time a CO<sub>2</sub> plume at the bottom of an aquifer could take to reach the top increases with decreasing vertical permeability and vice versa (Kumar et al., 2005). This suggests that phase separation between CO<sub>2</sub> and brine is impeded as vertical permeability decreases. Conversely, low vertical permeabilities also impede CO<sub>2</sub>-saturated brine at the CO<sub>2</sub>–brine interface from sinking by gravity towards the bottom of the aquifer (van der Meer, 1996; Kumar et al., 2005). However, buoyancy eventually predominates CO<sub>2</sub> plume migration far from the injection well (Ennis-King and Paterson, 2002), especially in aquifers having moderately low permeability anisotropy i.e. the  $k_{vh}$  value of 0.01 in this study.

To confirm that increases in near-wellbore pressures over time in highly anisotropic aquifers ( $k_v = 0.1$  mD) are due to a corresponding increase in the resistance to fluid flow in the vertical direction and not as a result of the salt precipitation (dry-out effect) (Pruess and García, 2002; García, 2003), we conducted control simulations in which permeability and porosity reductions due to salt precipitation are ignored. These simulations were conducted for  $k_v$  equal to 0.1 mD and 100 mD. Results of the near-wellbore pressures ( $P_w$ ) at the bottom of the aquifer for up to 100 years are presented in Tables 4 and 5.

Results in Tables 4 and 5 show pressures to be slightly greater in simulations that account for permeability reductions due to salt precipitation (dry-out effect) than those in which permeability reduction is ignored. These suggest that the effect of permeability reductions due to salt precipitation in the vicinity of the wellbore is significantly low compared to the effect of permeability anisotropy. The salinity used in the simulations conducted herein is 15%. Pressure increases due to salt precipitation may increase

at higher values of brine salinity as shown in Pruess and Müller (2009), where 25% brine salinity was employed.

The findings of this study suggest that changes in pressure histories ( $P_w(t)$ ), i.e. pressure decline, in the vicinity of fully completed vertical wells depend strongly on contrasts in density between CO<sub>2</sub> and resident brine during CO<sub>2</sub> injection into isotropic aquifers. However, the decline in  $P_w(t)$  diminishes as the aquifer becomes more anisotropic. The degree of formation anisotropy was measured using the formation anisotropy ratio ( $k_{vh}$ ). Based on the input conditions and parameters used in this study, both vertical flow and the rate at which  $P_w(t)$  declines strongly depend on  $k_{vh}$ . As  $k_{vh}$  decreases from 1.0 (isotropic) to 0.001 (highly anisotropic), both the rate at which  $P_w(t)$  declines and vertical flow vanish. Under isotropic conditions,  $P_w(t)$  initially jumps to a maximum and subsequently decline over time during CO<sub>2</sub> injection. On the other hand,  $P_w(t)$  initially jumps to a value greater than the background and subsequently increases over time at  $k_v$  equal to 0.1 mD. Results from this study suggest that the decline in  $P_w(t)$  under isotropic conditions may be due to vertical flow of CO<sub>2</sub> (buoyancy driven flow) while the increase in  $P_w(t)$  under anisotropic conditions is most probably due to increasing resistance to flow in the vertical direction especially at very small values of  $k_{vh}$ .

Results in Fig. 2 also suggest that the total near-wellbore pressure is highly sensitive to the difference in viscosity between the injectant and the displaced fluid. For example, the  $P_w(t)$  history of the viscous-CO<sub>2</sub> injection simulation is significantly greater than that of the CO<sub>2</sub> injection (base case) simulation because the former is much more viscous and has viscosity equivalent to that of the displaced fluid (resident brine).

Pressure histories could be used to estimate (1) the maximum pressure and (2) the time after which near-wellbore pressures begin to decline during CO<sub>2</sub> injection in weakly anisotropic aquifers i.e.  $k_{vh} > 0.001$ . The maximum pressure can then be compared to 90% of the overburden pressure (Bachu and Adams, 2003) to evaluate the risk of possible formation fracturing. The time after which  $P_w(t)$  begins to decline can be used as an indicator of the period during which close monitoring of pressure changes at the injection is critical. Pressure monitoring within this period could be pivotal in minimizing risk of undesired formation fracturing.

It should be underscored that variations in near-wellbore pressures may also depend on the absolute or intrinsic permeability, porosity and formation heterogeneity. However, the permeability values considered in this study span the range of permeability values generally encountered in deep geologic formations or reservoirs.

## 6. Conclusions

Numerical simulations of CO<sub>2</sub> injection into a homogeneous confined saline aquifer were conducted to investigate the root cause or causes of changes in near-wellbore pressures over time. The following conclusions can be made based on results obtained from the numerical simulations;

1. During CO<sub>2</sub> injection into isotropic aquifers, near-wellbore pressures initially increase sharply at the onset of injection, but then decrease slightly over a period of time ( $\approx 3$  years). The decrease is mostly due to contrast in density between CO<sub>2</sub> and resident brine.
2. Near-wellbore pressures are highly sensitive to viscosity of the injected fluid. Near-wellbore pressures increase as the viscosity of the injectant is increased.
3. In anisotropic formations, temporal changes in near-wellbore pressure histories are more strongly dependent on permeability

**Table 5**

$\Delta P_w(t)$  (bar) as a function permeability reduction ( $k_v = 0.1$  mD and  $k_h = 100$  mD or  $k_{vh} = 0.001$ ), at the bottom of the formation ( $Q = 100$  kg/s).

Time (years)	Permeability reduction		
	Considered	Not considered	Difference
1	103.3	100.2	3.1
3	104.3	100.8	3.5
10	105.3	101.4	3.9
30	106.3	102.1	4.2
100	108.5	103.8	4.7



anisotropy than on contrast in the properties of the injectant and displaced fluid, in anisotropic formations.

Results from this study indicate that close monitoring of near-wellbore pressure histories during the injection phase of deep geologic storage of CO<sub>2</sub> projects is pivotal. Furthermore, studies of the geomechanical effects on storage formations due to pressure build-up during CO<sub>2</sub> injection are warranted to assure containment.

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## References

- Altunin, V., 1975. Thermophysical Properties of Carbon Dioxide. Publishing House of Standards, 551 pp.
- Arts, R., Eiken, O., Chadwick, A., Zweigel, P., van der Meer, L., Zniszner, B., 2004. Monitoring of CO<sub>2</sub> injected at Sleipner using time-lapse seismic data. *Energy* 29, 1383–1392.
- Bachu, S., 2008. CO<sub>2</sub> storage in geological media: Role, means, status, and barriers to deployment. *Progress in Energy and Combustion Science* 34, 254–273.
- Bachu, S., Adams, J.J., 2003. Sequestration of CO<sub>2</sub> in geological media in response to climate change: Capacity of deep saline aquifers to sequester CO<sub>2</sub> in solution. *Energy Conversion and Management* 44, 3151–3175.
- Corey, A., 1954. The interrelation between gas and oil relative permeabilities. *Producers Monthly*, 38–41.
- Dake, L., 1978. *Fundamentals of Reservoir Engineering*, vol. 8, 2nd ed. Elsevier Scientific Publishing, Amsterdam.
- Doughty, C., 2007. Modeling geologic storage of carbon dioxide: Comparison of non-hysteretic and hysteretic characteristic curves. *Energy Conversion & Management* 48.
- Ennis-King, J., Paterson, L., 2001. Reservoir engineering issues in the geological disposal of carbon dioxide. In: *Proceedings of the International Conference on Greenhouse Gas Control Technologies*, CSIRO, Melbourne, Australia, pp. 290–295.
- Ennis-King, J., Paterson, L., 2002. Engineering aspects of geological sequestration of carbon dioxide. Vol. SPE-77809, Asia Pacific Oil and Gas Conference and Exhibition, Melbourne, Australia, October 8–10, SPE and CSIRO Petroleum.
- Fjær, E., Holt, R., Horsrud, P., Raaen, A., Risnes, R., 1992. Petroleum related rock mechanics. In: *Development in Petroleum Sciences* 33, 1st ed. Elsevier.
- Friedmann, J., 2007. Geological carbon dioxide sequestration. *Elements* 3, pp. 197–184, Carbon Management Program, Lawrence Livermore National Laboratory.
- García, J.E., 2003. Fluid dynamics of carbon dioxide disposal in saline aquifers. Doctoral dissertation, University of California, Berkeley.
- Hickey, J., Vecchioli, J., 1986. Subsurface injection of liquid wastes with emphasis on injection practices in Florida, paper 2281. U.S. Geological Survey, U.S. Geological Survey Water-Supply.
- Hitchon, B., 1996. *Aquifer Disposal of Carbon Dioxide*. Geoscience Publishing Ltd., Sherwood Park, Alberta, Canada.
- IPCC, 2005. IPCC special report on carbon dioxide capture and storage. In: Metz, B., Davidson, O., de Coninck, H.C., Loos, M., Meyer, L.A. (Eds.), Prepared by Working Group III of the Intergovernmental Panel on Climate Change, Report, Intergovernmental Panel on Climate Change, Cambridge, United Kingdom and New York, NY, USA.
- Kumar, A., Ozah, R., Noh, M., Pope, G.A., Bryant, S., Sepehrnoori, K., Lake, L.W., 2005. Reservoir simulation of CO<sub>2</sub> storage in deep saline aquifers. *Society of Petroleum Engineering Journal* 9 (SPE89343), 336–348.
- Martinez, S., Steanson, R., Coulter, A., 1992. *Petroleum Engineering Handbook: Formation Fracturing*. Society of Petroleum Engineers, 12 pp. ISBN: 1-55-563-010-3 (chapter 55).
- McPherson, B., Lichtner, P., 2001. CO<sub>2</sub> sequestration in deep saline aquifers, Washington, D.C., U.S.A. First National Conference in Carbon Sequestration.
- Müller, N., 2011. Supercritical CO<sub>2</sub>–brine relative permeability experiments in reservoir rocks—literature review and recommendations. *Transport in Porous Media* 87, 367–383.
- Müller, N., Qi, R., Mackie, E., Pruess, K., Blunt, J., 2009. CO<sub>2</sub> injection impairment due to halite precipitation. *Energy Procedia* 1, 3507–3514, <http://dx.doi.org/10.1016/j.egypro.2009.02.143>.
- Nordbotten, J., Celia, M., 2006. Similarity solutions for fluid injection into confined aquifers. *Journal of Fluid Mechanics* 561, 307–327.
- Nordbotten, J., Celia, M., Bachu, S., 2005. Injection and storage of CO<sub>2</sub> in deep saline aquifers: Analytical solution for CO<sub>2</sub> plume evolution during injection. *Transport in Porous Media* 58, 339–360.
- Nordbotten, J.M., Celia, M.A., Bachu, S., 2004. Analytical solutions for leakage rates through abandoned wells. *Water Resources Research* 40, W04204.
- Okwen, R.T., Stewart, M., Cunningham, J., 2010. Analytical solution for estimating storage efficiency of geologic sequestration of CO<sub>2</sub>. *International Journal of Greenhouse Gas Control* 4 (1), 102–107.
- Ozah, R., Lakshminarasimhan, G., Sepehrnoori, K., Bryant, S., 2005. Numerical simulation of the storage of pure CO<sub>2</sub> and CO<sub>2</sub>–H<sub>2</sub>S gas mixture in deep saline aquifers. In: *SPE Annual Technical Conference and Exhibition*, SPE 97255, Society of Petroleum Engineers, Dallas, TX, USA, pp. 1–12.
- Pruess, K., 1997. On vaporizing water flow in hot sub-vertical rock fractures. *Transport in Porous Media* 28, 335–372.
- Pruess, K., 2004. The TOUGH2 code—a family of simulation tools for multiphase flow and transport processes in permeable media. *Vadose Zone Journal* 3, 738–746.
- Pruess, K., 2005. ECO2N: A TOUGH2 Fluid Property Module for Mixtures of Water, NaCl, and Carbon Dioxide. Lawrence Berkeley National Laboratory, Berkeley, CA.
- Pruess, K., García, J., 2002. Multiphase flow dynamics during CO<sub>2</sub> disposal into saline aquifers. *Environmental Geology* 42, 282–295.
- Pruess, K., García, J.E., Kovscek, T., Oldenburg, C., Rutqvist, J., Steefel, C., Xu, T., 2004. Code intercomparison builds confidence in numerical simulation models for geologic disposal of CO<sub>2</sub>. *Energy* 29 (9–10), 1431–1444.
- Pruess, K., Müller, N., 2009. Formation dry-out from CO<sub>2</sub> injection into saline aquifers: 1. Effects of solids precipitation and their mitigation. *Water Resources and Research* 45 (w03402), 1–11.
- Pruess, K., Oldenburg, C., Moridis, G., 1999. TOUGH2 users' guide, version 2.0, Manual LBNL-43134, Lawrence Berkeley National Laboratory, Berkeley, CA (accessed 10.06.07).
- Pruess, K., Spycher, N., 2006. ECO2N—a new TOUGH2 fluid property module for studies of CO<sub>2</sub> storage in saline aquifers. Lawrence Berkeley National Laboratory, Berkeley, CA.
- Pruess, K., Spycher, N., 2007. ECO2N - A fluid property module for the TOUGH2 code for studies of CO<sub>2</sub> storage in saline aquifers. *Energy Conversion and Management* 48 (6), 1761–1767.
- Pruess, K., Xu, T., Apps, J., García, J.E., 2003. Numerical modeling of aquifer disposal of CO<sub>2</sub>. *Society of Petroleum Engineering Journal* 8 (1), 49–60.
- Spycher, N., Pruess, K., 2005. CO<sub>2</sub>–H<sub>2</sub>O mixtures in the geological sequestration of CO<sub>2</sub>. II. Partitioning in chloride brines at 12 to 100 °C and up to 600 bar. *Geochimica et Cosmochimica Acta* 69, 3309–3320.
- Torp, T., Dale, J., 2004. Demonstrating storage of CO<sub>2</sub> in geological reservoirs: the Sleipner and SACS projects. *Energy* 29.
- van der Meer, L.G.H., 1995. The CO<sub>2</sub> storage efficiency of aquifers. *Energy Conversion and Management* 36 (6–9), 513–518.
- van der Meer, L.G.H., 1996. Computer modelling of underground CO<sub>2</sub> storage. *Energy Conversion and Management* 37 (6–8), 1155–1160.
- van Genuchten, M.T., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal* 44, 892–898.
- Verma, A., Pruess, K., 1988. Thermohydrologic conditions and silica redistribution near high-level nuclear wastes emplaced in saturated geological formations. *Journal of Geophysical Researches* 93 (B2), 1159–1173.
- Villarrasa, V., Bolster, D., Olivella, S., Carrera, J., 1988. Coupled hydrodynamical modeling of CO<sub>2</sub> sequestration in deep saline aquifers. *International Journal of Greenhouse Gas Control* 4, 910–919.
- Weir, G., White, S., Kissling, W., 1995. Reservoir storage and containment of greenhouse gases. *Energy Conversion and Management* 36 (6–9), 531–534.
- Zoback, M., 2007. *Reservoir Geomechanics*. Cambridge University Press, Cambridge, United Kingdom. ISBN: 978-0-521-77069-9.