Contents lists available at ScienceDirect

Computers and Geosciences

journal homepage: www.elsevier.com/locate/cageo

Effect of brine composition on the onset of convection during CO₂ dissolution in brine

Saeed Mahmoodpour^a, Behzad Rostami^{a,*}, Mohamad Reza Soltanian^b, Mohammad Amin Amooie^c

^a Institute of Petroleum Engineering, School of Chemical Engineering, College of Engineering, University of Tehran, Iran

^b Departments of Geology and Chemical and Environmental Engineering, University of Cincinnati, Cincinnati, OH, USA

^c Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA

ARTICLE INFO

Keywords: CO₂ sequestration Onset of convection Saline aquifer Brine composition Salinity

ABSTRACT

We study the effect of brine composition on CO₂ dissolution in brine. In particular, we address the effect of brine composition on the onset of convection through experiments, numerical simulations, and theoretical analyses. We use two brine solutions-one containing sodium chloride (NaCl) and one containing mixtures of NaCl and in isothermal conditions (~50 C) with pressure range of 500-535 psi for different salinities and permeabilities (Rayleigh number of 2900 to 4900). Our experimental conditions and set-up design allow us to avoid problems associated with analogue fluids as well as with blind cells. We also conduct linear stability analysis (LSA) and high-resolution direct numerical simulations (DNS). We analyze pressure data and calculate other parameters such as diffusion coefficient, viscosity, and solubility. Specifically, we obtain the onset of convection from pressure decay curves and critical wave number from image analyses. We show that the onset of convection occurs earlier with higher wave number in brine solutions containing NaCl. Pressure results show that using mixture of NaCl and CaCl₂ results in a higher CO₂ diffusion coefficient, which in turn damps convective instabilities. Thus, the onset time of instabilities is later and finger growth rate is smaller for brines with NaCl and CaCl₂. Our DNS results show that deviation between the cumulative dissolved CO₂ as well as the dissolved CO₂ due to only diffusion process occurs earlier for NaCl solution. We found a dimensionless Rayleigh-dependent onset of instability with parameters that are close for two mixtures. However, differences in the CO₂ diffusivity result in smaller Rayleigh numbers for NaCl and CaCl2 containing mixtures. Our results have practical implications for CO₂ geological sequestration in saline aquifers.

1. Introduction

Extra CO₂ emission into atmosphere could deteriorate the environment (Zhang et al., 2018a; Li and Zhang, 2018). CO₂ sequestration in geological formations is now considered as a viable solution to reduce CO₂ concentration in the atmosphere (Holloway, 2005; Schrag, 2007; Gershenzon et al., 2014; Zhang et al., 2018b). Among geological formations, saline aquifers are main targets for CO₂ geological sequestration due to their chemistry, reasonable permeability and porosity, and, more importantly, widespread distribution (Riaz and Cinar, 2014; Mahmoodpour and Rostami, 2017; Soltanian et al., 2016a, 2018). However, one major concern is CO₂ leakage from the target formation because of the presence of open fractures or faults, as well as the potential presence of abandoned wells away from the injection locations (Kim and Song, 2017; Soltanian et al., 2018).

Structural trapping, capillary trapping, solubility trapping, and mineral trapping are trapping mechanisms associated with CO_2 sequestration in saline aquifers (Emami-Meybodi et al., 2015). CO_2 dissolution in brine is an important trapping mechanism towards permanent CO_2 storage (Javaheri et al., 2010; Szulczewski et al., 2013; Martinez and Hesse, 2016; Newell et al., 2018; Shi et al., 2018). Diffusion of CO_2 molecules into brine initiates the dissolution process (Soltanian et al., 2016b, 2017; Amooie et al., 2018). The resulting diffusive layer is more dense than the formation brine, leading to density-driven instabilities (Soltanian et al., 2017). As these instabilities grow, they migrate toward the formation bottom through convection. This accelerates the dissolved CO_2 to CO_2 -brine interface and sharpening CO_2 concentration gradient (Hassanzadeh et al., 2005, 2007; Farajzadeh et al., 2007a; Emami-Meybodi et al., 2015). Since convection plays an important role

https://doi.org/10.1016/j.cageo.2018.12.002 Received 26 August 2018; Received in revised form 19 November 2018; Accepted 14 December 2018 Available online 15 December 2018 0098-3004/ © 2018 Elsevier Ltd. All rights reserved.



Research paper





^{*} Corresponding author. *E-mail address:* brostami@ut.ac.ir (B. Rostami).

| Nomenclature | | | Critical time for onset of instability |
|------------------|----------------------------------------|------------------|-----------------------------------------------|
| | | v | Dimensionless Darcy velocity |
| С | Solute concentration | х | Mole fraction |
| с | Dimensionless solute concentration | y _{co2} | Mole fraction of CO ₂ in gas phase |
| Cs | Equilibrium concentration at interface | Z | Gas compressibility factor |
| D _{CO2} | Diffusion coefficient | Φ | Fugacity coefficient |
| g | Gravity acceleration | β | Densification coefficient |
| Н | Height of the saturated porous medium | ζ | Interaction coefficient |
| k | Permeability | κ | Wave number |
| L | Length of the system | λ | Interaction coefficient |
| Μ | Molecular weight | μ | Viscosity |
| n | Number of moles | ν | Partial molar volume |
| Р | Pressure | μCO2 | Chemical potential of CO ₂ |
| R | Gas constant | ρ | Density |
| Ra | Rayleigh number | τ | Dimensionless time |
| Т | Temperature | φ | Porosity |
| t | Time | ω | Growth rate |

in decreasing formation pressure in response to CO_2 injection, it can enhance cap rock integrity. Estimating when onset of convection occurs is essential in any CO_2 sequestration project. To provide such estimation is one goal of this paper.

There is an extensive body of literature on theoretical and experimental studies of the CO₂ dissolution in brine and the onset of convection. Rayleigh number ($Ra = \frac{k \Delta \rho g H}{\mu \varphi D_{CO2}}$; which shows the strength of the convective dissolution over the diffusive one) and dimensionless time $(t_c = \frac{tD_{CO2}}{H^2}$ or $t_c = \frac{k^2 g^2 \Delta \rho^2}{q \mu^2 D_{CO2}})$ are used to report findings in prior work, where D_{CO2} , H, g, μ , φ , $\Delta \rho$, and k are respectively diffusion coefficient, domain height, gravitational acceleration, viscosity, porosity, density difference, and permeability (Ennis-King et al., 2005; Riaz et al., 2006; Mahmoodpour et al., 2018a). It is also common to use correlations such as $t_c = c_1 R a^{c_2}$ between the Rayleigh number and the dimensionless time $(c_1 \text{ and } c_2 \text{ are constant values})$. Also, linear stability analysis (LSA) based on quasi steady-state approximation (QSSA) is a common approach to study onset of instabilities (Emami-Meybodi and Hassanzadeh, 2013; Emami-Meybodi, 2017). However, mass transfer increase due to convective flow is not captured by LSA. Therefore, direct numerical simulations (DNS) are used to examine nonlinear dynamics of convective instabilities (Farajzadeh et al., 2011; Soltanian et al., 2016a, 2017; Amooie et al., 2017a, 2017b).

To reach high-pressure conditions in laboratory experiments is not a straightforward task, especially in the context of convection in porous media. Analogue fluids (e.g., propylene glycol-water system) are usually considered, instead, to examine the dissolution process (Ennis-King et al., 2005; Neufeld and Jerome, 2010; Backhaus et al., 2011; MacMinn et al., 2012, 2013; Taheri et al., 2012; Slim et al., 2013; Tsai et al., 2013; Agartan et al., 2015). However, analogue fluids show differences in comparison with CO2-brine systems (Jafari-Raad and Hassanzadeh, 2015). There are few studies in high-pressure blind PVT cells, but they do not allow visual capturing of instabilities and the resulting convection (Yang and Gu, 2006; Farajzadeh et al., 2009; Nazari-Moghaddam et al. 2012, 2015; Seyyedi et al., 2014; Newell et al., 2018). Pressure decay data are analyzed in the latter experiments in order to quantitatively study the dissolution behavior. The simultaneous use of qualitative (visual examination) and quantitative (pressure decay) data provides an excellent means to better understand the dissolution processes. There are only a few studies that have utilized the combination of such data, but they are limited to atmospheric pressure conditions (Taheri et al., 2017, 2018). In this paper, we study the onset of convection using visual analyses as well as pressure decay data in high-pressure conditions that can better represent the in-situ conditions of saline aquifers as the main CO₂ sequestration target sites. To this end, we have specifically designed and constructed a high-pressure Hele-Shaw cell in order to both qualitatively and quantitatively elucidate the

underlying processes.

Most studies cited above were performed in systems with pure water (i.e., with no salinity). However, brine is typically composed of different salts (Aggelopoulos et al., 2011). Data on brine composition shows dominance of chloride (Cl⁻) and sodium (Na⁺) ions. Among other cations, calcium (Ca²⁺) is the most frequent one (Wellman et al., 2003; Gaus et al., 2005; Xu et al., 2006; Bacon et al., 2009; Azin et al., 2013; Mohamed et al., 2013; Wang et al., 2016; Vu et al., 2017; Shi et al., 2018). In this study, we consider the effects of salinity by using two brine solutions, one with only sodium chloride (NaCl) and one with NaCl and calcium chloride (CaCl₂).

This paper is organized as follows: We present our methodology in Section 2, which has three parts. Part 1 of Section 2 describes our experimental design and conditions. In part 2, we discuss governing equations for direct numerical simulation (DNS) and give information about input parameters. In part 3, we explain our linear stability analysis (LSA) method. In Section 3, we present our results. Finally, in Section 4 we highlight the concluding remarks of our work.

2. Methodology

CO₂ dissolution in brine starts with diffusion process that creates a diffusive boundary layer under the CO₂-brine interface. Since brine with dissolved CO₂ is more dense than the underlying brine, the system is gravitationally unstable. When the diffusive boundary layer is thick enough, gravitational instabilities occur in the system. At a sufficiently high *Ra* (> 55, Szulczewski et al., 2013), instabilities grow with time and manifest in convective fingers. To accurately capture the first appearance of convective fingers (the dimensionless time in DNS is $\hat{t}_{c,DNS}$) and corresponding wave number ($\kappa_{c,DNS}$ is wave number in DNS), high-resolution numerical simulations are required. In experiments, dissolved CO₂ concentration should reach a detectable pH so that the convective fingers are clear enough to see. Direct numerical simulations with input parameters from experiments can provide an approximation for $\hat{t}_{c,DNS}$.

At early times, convective fingers are not strong enough to significantly change the dissolution rate. As time increases, convective fingers interact with each other and create stronger fingers. These fingers bring the fresh brine with no dissolved CO_2 into the CO_2 -brine interface and sharpen the CO_2 concentration gradient. With higher concentration gradient at CO_2 -brine interface the dissolution rate increases and partial pressure of gas phase changes with higher rate than diffusion mechanism. If we consider only the diffusion mechanism, the dissolution flux and pressure reduction rate would decrease with time. Because, the concentration gradient which is the driving force for diffusion mechanism decreases. Activation of the density-driven convection increases the dissolution flux and pressure reduction rate. Therefore, the time at which pressure curve experiences a rapid decline after the diffusion mechanism shows the onset of convection. This time and the corresponding wavenumber are detected as the onset of convection (the dimensionless time in experiments is $\hat{t}_{c,EXP}$) and critical wavenumber for onset of convection ($\kappa_{c,EXP}$), respectively. Therefore, we face with three different phenomena and we have used three methods to capture them: 1) onset of instabilities (LSA), 2) first appearance of convective fingers and initial deviation of dissolved CO₂ concentration from the only diffusion dominated mechanism (DNS), and 3) rapid decline in pressure curves after the diffusion dominated regime (experimental tests, EXP). Our approach for calculating these values is explained below.

2.1. Experimental procedure

We designed and constructed a high-pressure Hele-Shaw cell for this study (see Fig. 1). This cell allows obtaining both qualitative (visual examination) and quantitative (pressure decay) data on CO₂ dissolution process. The cell has a 2.5 cm thickness with aluminum frame covered with a 5 cm thickness plexiglass enabling the visual examination. To prevent plexiglass expansion under high-pressure conditions, we attached a steel frame to the main frame. The main frame has an internal volume of 2700 cm^3 (36 $\text{cm} \times$ 30 cm x 2.5 cm). In comparison to cells used in prior work here we used a wider opening (2.5 cm) that allows adding porous structure into the cell. In bulk fluid experiments, onset of convection happens in early times and there is not sufficient data in diffusion-dominated regime to calculate diffusion coefficient. In the presence of porous media (system with lower permeability than bulk fluid), we have pressure data from diffusion-dominated regime, and we calculate diffusion coefficient from experimental data. In addition, this device has negligible boundary effects due to its size, as compared to Hele-Shaw cells used previously. We used this Hele-Shaw cell within our experimental setup in Fig. 2.

As mentioned in the introduction section, literature review about the brine composition revealed the dominance of chloride (Cl⁻) and sodium (Na⁺) ions. Among other cations, calcium (Ca²⁺) is the most frequent one. Therefore, we chose NaCl and CaCl₂ salts to understand the effect of brine composition. We tested reduction of NaCl amount to 80% of its initial value and for remaining 20%, we added CaCl₂. For example, in the corresponding solution of 1 Molal (M hereafter) NaCl, we used 0.8 M NaCl and 0.1 M CaCl₂. This way there is similar concentration of Cl⁻ in two solutions and for each divalent cation of Ca²⁺ there are two monovalent cations of Na⁺ in the corresponding solution. We selected two levels of salinity in a way that our experimental tests be a good representative of brine compositions based on the literature.

Initial pressures for the tests are in the range of 502.6–535.3 psi. We had restrictions about the higher pressures. However, the designed Hele-Shaw was tested for higher pressure; but for safety issues we used

this range of pressure. All tests are performed in an isothermal condition with temperature of 50 °C. We introduced brine into the cell by continuous mixing and gradually adding NaCl or mixture of NaCl and CaCl₂ into water. Bromocresol green is used as a pH indicator with 0.02% weight fraction in brine. The Hele-Shaw cell was packed with desired glass beads (representing permeability range of 400–550 Darcy) by shaking. We checked the smaller glass beads (for lower permeability values); but in this way, we missed the quality of pictures. With glass beads larger than the implemented ones (for higher permeability values), onset of convection happens earlier and there are limited pressure data in diffusive dominant regime. Therefore, calculation of the diffusion coefficient values will be difficult. Based on these explanations, we used the reported range of permeability for porous media. Note that porosity is ~0.36 for all cases described below.

The effect of capillary pressure is negligible due to high permeability values. However, in order to increase the accuracy, we packed the cell to the desired height of brine with glass beads (CO₂ is injected into the void upper section) to eliminate the capillary transition zone. This way, we obtain comparable results with those in prior work (DNS or LSA studies) where the potential effects of capillarity within the sharp CO₂-brine interface was neglected.

The cell is placed in the oven and vacuum pump is used to saturate it with brine and the pH indicator solution. Then, the transfer vessel cylinder is loaded with CO_2 gas phase. CO_2 -containing cell is pressurized, and all equipment in the oven is kept under the 50 °C for at least 12 h. Before inserting gas mixture into the cell, a pump vacuumizes the cell. A valve between gas cylinder and the cell is opened gradually to reduce possible disturbances. Once we obtain a desired pressure, we close the cylinder valve and open the pressure gauge valve. Since the tests are performed in constant volume conditions, dissolution of CO_2 into brine decreases the pressure of the cell. Thus, pressure data provide a quantitative measure for CO_2 dissolution. We continuously monitor pressure and temperature data. We also continuously take photos using a digital camera (see Fig. 2a).

Overall, we conducted four tests with NaCl (2 and 1 Molal) and four tests with mixture of NaCl and $CaCl_2$ (1.6 and 0.8 Molal NaCl) (see Table 1). The implemented approach in this study helps to reduce the possible errors in order to guarantee the reproducibility. Before each test, the Hele-Shaw was dismantled, washed and dried. Based on the previous explanations, the effect of capillary pressure is excluded through the sharp gas-liquid interface. Continuous mixing during the preparing of brine helps to have a homogeneous mixture in which all of the introduced salts was dissolved. Leakage tests have been done before each test. Also, the trend of pressure data is tracked during the test. Based on the visual capability of the system, a horizontal and smooth surface is implemented for gas-liquid interface and in this way, the possible errors from the slop and morphology of the interface is decreased. We have used thermocouple to track the temperature continuously and possible errors from the temperature fluctuation is



Fig. 1. Constructed high-pressure Hele-Shaw cell: a) dismantled structure; b) connected structure, and c) model domain with initial and boundary conditions for DNS (u, c, and c^s shows the velocity and concentrations of CO₂ within the domain and at CO₂-brine interface, respectively).



Fig. 2. Experimental set up. (a) High-pressure pump, (b) PVT cylinder, (c) Hele-Shaw cell, (d) Camera, (e) Thermocouple, (f) Pressure gauge, (g) Data acquisition system, and (h) a PC for data storage.

 Table 1

 Brine composition, permeability, and initial pressure condition for all cases.

| Case | Brine composition (Molal) | Permeability (D) | Initial pressure (psi) |
|------|---------------------------------------------------|------------------|------------------------|
| 1 | 2 NaCl | 550 | 523.1 |
| 2 | 2 NaCl | 400 | 511.2 |
| 3 | 1 NaCl | 550 | 535.3 |
| 4 | 1 NaCl | 400 | 510.6 |
| 5 | 1.6 NaCl + 0.2 CaCl ₂ | 550 | 512.7 |
| 6 | 1.6 NaCl + 0.2 CaCl ₂ | 400 | 514.7 |
| 7 | 0.8 NaCl + 0.1 CaCl ₂ | 550 | 502.6 |
| 8 | $0.8 \ \mathrm{NaCl} \ + \ 0.1 \ \mathrm{CaCl}_2$ | 400 | 505.5 |
| | | | |

obviated by introducing the temperature effect in calculation of CO_2 moles (PV = znRT). Also, we have exact values of the gas phase volume too. Since, the impurity along the CO_2 may affect the onset of convection (Mahmoodpour et al., 2018b); therefore, before introducing the CO_2 , we have used the vacuum pump to evacuate system from the air. We introduced the CO_2 gas gradually to the system in order to reduce the possible disturbances.

2.2. Numerical simulation

We developed a two-dimensional (2D) direct numerical simulation (DNS) model for this work. The initial and boundary conditions are shown in Fig. 1C. We performed DNS for all cases in Table 1 with homogeneous permeability and porosity values. We examined the behavior of system in the aqueous phase. Water is almost incompressible in our experiments; we used Boussinesq approximation in order to write our governing equations below:

$$\nabla . V = 0 \tag{1}$$

$$\varphi \nabla. (D_{CO2} \nabla C_{CO2}) - V. \nabla C_{CO2} = \varphi \frac{\partial C_{CO2}}{\partial t}$$
(2)

where Darcy's law is used to describe fluid flow:

$$V = -\frac{K}{\mu}(\nabla P - \rho g).$$
⁽³⁾

where V, φ , D_{CO2}, C_{CO2}, k, μ , P, ρ and g show the Darcy velocity, porosity, diffusion coefficient of CO₂, concentration of CO₂, permeability, viscosity, pressure, density and gravity acceleration constant respectively. Density of NaCl solution is calculated based on the Potter and Brown's model (Potter and Brown, 1977). In order to obtain density of NaCl and CaCl₂ solution mixture, we used the proposed model by Ghafri et al. (2012), which considers relative density of NaCl and CaCl₂ mixture to NaCl solution (see Appendix A). The density difference between CO_2 -rich brine and fresh brine is the driving force for the convection. To calculate the density of CO_2 -rich brine, we used the approach by Garcia (2001):

$$\frac{M_{aq}}{\rho_{aq}} = \frac{x_w M_w + x_{s1} M_{s1} + x_{s2} M_{s2}}{\rho_b} + \sum_{i=1}^{NCG} x_i \nu_i$$
(4)

where subscripts *aq*, *w*, *s*, *b*, and *i* are used for the resulting solution, water, dissolved salts, brine, and dissolved gases, respectively. Also, NCG, x and ν represent the number of components in gas phase (here NCG = 1), solubility values and the partial molar volume. CO₂ solubility in brine was calculated by the proposed model of Duan et al. (2006). Partial molar volumes are obtained following Garcia (2001). Detailed information is provided in the Appendix Section.

Initially, there is no dissolved CO₂ in brine (i.e., C(t = 0, x, z) = 0). Lateral boundaries are no-flow and no-flux (U = 0 and $\frac{\partial C}{\partial x} = 0$) following our experimental set up. This is also true for the bottom boundary. At the top boundary, the brine is in equilibrium with the CO₂. Equilibrium concentration of CO₂ is calculated based on the described solubility model and the imposed boundary condition of $C(t, x, 0) = C_{CO2}^{eq}$. For each time step in our simulations, we integrate the amount of dissolved CO₂ concentration over the model domain and convert it to the mole of dissolved gas through real gas equation-of-state (EOS). All parameters are updated for each time step including density, viscosity, solubility, and diffusion coefficient based on the new pressure obtained by EOS:

$$p = \left(\frac{p_{int}^{CO2} v}{z_{int}^{CO2} RT} - n_{diss}^{CO2}\right) \frac{z^{CO2} RT}{v}$$
(5)

where $p_{int.}^{CO2}$, $z_{int.}^{CO2}$ and $n_{diss.}^{CO2}$ represent the initial pressure of CO₂, compressibility factor of CO₂ in the initial condition and amount of dissolved CO₂ in each time respectively. Volume changes of water due to CO₂ dissolution is considered negligible. Therefore, the height of water is remained constant.

To impose initial instabilities numerically, we use a sinusoidal perturbation of $c_{top} = 1 + 0.01 \sin\left(40 \frac{x}{2L}\right)$ on the top boundary in which we impose perturbation on the concentration field over the gas-liquid interface (see Farajzadeh et al., 2007b). The equations described above are coupled and solved using a Finite Element Method with 51,332 triangular elements (with maximum element size of 2 mm) in COMSOL 5.2.

2.3. Linear stability analysis (LSA)

We also study the onset of instabilities using linear stability analysis

(LSA). This will complement our experimental and numerical simulation results. We believe that our results, especially our experimental data, provide base cases for future tests on theoretical and numerical simulation analyses.

We considered a 2D homogeneous media with a length of 36 cm and a height of 23 cm. We assume a sharp CO₂-brine interface given negligible capillary effects explained in the previous section. For the top boundary, we used a constant concentration for CO₂ (*C*^{int}.). Density is a linear function of CO₂ concentration in brine with $\rho = \rho_b (1 + C_{CO2}\beta_{CO2})$, where ρ_b and β_{CO2} represent the density of brine and densification coefficient due to the CO₂ dissolution respectively. To perform LSA, we converted governing equations (Eqs. (1)–(3)) to their non-dimensional forms. Natural velocity of the system $(\frac{k g \ \nabla \rho}{\mu \varphi})$ is selected to scale velocities, following Slim (2014). At early times, the thickness of diffusive layer $(\frac{\varphi \ \mu \ D_{CO2}}{k g \ \nabla \rho})$ provides a natural scale for the

length (Riaz et al., 2006; Wen et al., 2018). With $\frac{\varphi \ \mu^2 \ D_{CO2}}{k^2 \ g^2 \ \nabla \rho^2}$, $\frac{\varphi \ \mu \ D_{CO2}}{k}$, C_{CO2}^s and $\nabla \rho = \rho_b \beta_{CO2} C_{CO2}^s$ as scales for the time, pressure, concentration and density, the governing equations are obtained in their dimensionless forms as (also see Kim and Song, 2017):

$$\nabla \cdot v = 0 \tag{6}$$

$$v = -\nabla p + k\hat{\rho} \tag{7}$$

$$\frac{\partial c_{CO2}}{\partial \tau} + \nu. \quad \nabla c_{CO2} = \nabla^2 c_{CO2} \tag{8}$$

where v, p, $\hat{\rho}$, c_{CO2} , and τ represent the dimensionless format of Darcy velocity, pressure, density, CO₂ concentration, and time respectively. Initially, diffusion is dominated mechanism for dissolution, and the diffusive transport is represented by:

$$\frac{\partial c_{CO2}^0}{\partial \tau} = \frac{\partial^2 c_{CO2}^0}{\partial z^2} \tag{9}$$

where the initial and boundary conditions are:

$$c_{\rm CO2}^0(z,\,\tau) = 0\tag{10}$$

$$c_{CO2}^{0}(0,\tau) = 1 \& \frac{\partial c_{CO2}^{0}}{\partial z}(Ra, \tau) = 0$$
(11)

An analytical solution to Eq. (9) is thus obtained as:

$$c_{CO2}^{0} = 1 - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{2}{(2n-1)} \sin\left(\frac{2n-1}{n}\pi z\right) \exp\left(-\left(\frac{2n-1}{n}\right)^{2} \pi^{2} \tau\right)$$
(12)

Since the penetration depth of the diffusive boundary layer is smaller than the domain size, our domain behaves semi-infinitely and the initial concentration is described as:

$$c_{CO2}^{0} = erfc\left(\frac{z}{\sqrt{4\,\tau}}\right) \tag{13}$$

In order to implement the LSA, small perturbations in velocity (v^*) and concentration (c^*_{CO2}) are introduced to our governing equations above. Ignoring higher-order terms results in the perturbed equations as:

$$\nabla_{xz}^2 \nu^* = Ra \ \nabla_x^2 c_{CO2}^* \tag{14}$$

$$\nabla_{xz}^2 c_{CO2}^* - \nu^* \frac{\partial c_{CO2}^0}{\partial Z} = \frac{\partial c_{CO2}^*}{\partial t}$$
(15)

where boundary conditions are:

$$c_{CO2}^{*}(z=0) = v^{*}(z=0) = c_{CO2}^{*}(z \to \infty) = v^{*}(z \to \infty) = 0$$
(16)

Perturbed quantities are described by Fourier analysis as:

$$\begin{bmatrix} v^*(x, z, t) \\ c^*_{CO2}(x, z, t) \end{bmatrix} = \begin{bmatrix} v^{**}(z, t) \\ c^{**}_{CO2}(z, t) \end{bmatrix} \exp(-i\kappa x + \omega t)$$
(17)

where κ and ω are wave number and growth rate of perturbations. Substituting Eq. (17) into Eqs. (14) and (15) yields the following equations:

$$\frac{\partial^2 v^{**}}{\partial z^2} - \kappa^2 v^{**} = Ra(-\kappa^2) c_{CO2}^{**}$$
(18)

$$\frac{\partial^2 c_{CO2}^{**}}{\partial z^2} - \kappa^2 c_{CO2}^{**} - \nu^{**} \frac{\partial c_{CO2}^0}{\partial z} = \omega c_{CO2}^{**}$$
(19)

The $\frac{\partial^2 v^{**}}{\partial z^2}$, $\frac{\partial^2 c^{**}_{CO2}}{\partial z^2}$, and $\frac{\partial c^0_{CO2}}{\partial z}$ terms are discretized with the three-point centered Lagrange polynomial approximation (Singh and Bhadauria, 2009). With this approximation, Eqs. (18) and (19) leads to an algebraic Eigenvalue problem below:

$$[(D_{\nu} - \kappa^2 I)][\nu^{**}] = -Ra * \kappa^2 c_{CO2}^{**}$$
⁽²⁰⁾

$$[(D_c - \kappa^2 I)][c_{CO2}^{**}] - [\nu^{**}] \frac{\partial c_{CO2}^0}{\partial z} = [\omega][c_{CO2}^{**}]$$
(21)

where we calculated D_{ν} and D_c are coefficient matrices which are obtained by Finite Differences (FD) discretization of the second derivatives of $\frac{\partial^2 v^{**}}{\partial z^2}$ and $\frac{\partial^2 c^{**}_{CO2}}{\partial z^2}$ (see Mahmoodpour et al., 2018b). The V^{**} is obtained from Eq. (20) and substituted into Eq. (21):

$$[(D_{c} - \kappa^{2}I)][c_{CO2}^{**}] - (-Ra * \kappa^{2}[(D_{v} - \kappa^{2}I)]^{-1}c_{CO2}^{**}] \left[\frac{\partial c_{CO2}^{0}}{\partial z}\right] = [\omega][c_{CO2}^{**}]$$
(22)

 CO_2 properties are incorporated into Eq. (22). The resulting eigenvalue problem is solved numerically. The maximum value of the coefficient matrix in the real part of the eigenvalue is considered as the growth rate in the values of *Ra*, *t* and κ . The time at which ω becomes positive for the first time is selected as *onset of instability*. The related wavenumber is defined as the critical wavenumber for a given set of *Ra* and *t*.



Fig. 3. Pressure curve for all cases in Table 1. Corresponding cases in two mixtures are represented with similar markers. In Case 1 to Case 4, the brine salinity is only by NaCl, and in Case 5 to Case 8, the brine salinity is by NaCl and CaCl₂. Arrows and mentioned times show the onset of convection for each Case.

FD is used to discretize nonlinear terms in Eqs. (20) and (21) $\left(\frac{\partial^2 v^{**}}{\partial z^2}\right)$, $\frac{\partial^2 c_{CO2}^{**}}{\partial z^2}$, and $\frac{\partial c_{O2}^0}{\partial z}$). To reach convergence we performed mesh refinement on the upper part of the numerical domain where the changes in concentration gradient are rapid (Emami-Meybodi and Hassanzadeh, 2013; Jafari-Raad and Hassanzadeh, 2016, 2017). We used the equation below for mesh refinement:

$$\Delta z_i = \frac{z_i}{\sum_{i=1}^N z_i} \tag{23}$$

where z_i and N refer to the depth of the *i*th grid cell and number of grid cells, respectively.

3. Results and discussions

In this section, we present our experimental results as well as results of our DNS and LSA. Our results below help to better understand how brine composition may affect the onset of convection during CO_2 geological sequestration.

Pressure decay curves for NaCl solutions (Case 1 to 4) as well as their corresponding experiments with NaCl and CaCl₂ mixtures (Case 5 to Case 8) are shown in Fig. 3 (with accuracy of \pm 0.1 psi). Qualitative data for some of these pressure curves are presented in the Supplementary videos. At early times, diffusion process is dominated, and the pressure decay has a small decline. There is also no evidence of fingering instabilities. Even though corresponding cases in two mixtures have the same permeability, the pressure decay rate in early times is smaller for NaCl solutions. CO₂ solubility is close for both mixtures with that for NaCl solutions being slightly higher (~2%). Details of the model for the solubility calculation is provided in Appendix A. Since, involving parameters in Rayleigh number formulation (permeability, density difference, height of saturated porous media, viscosity and porosity) except the diffusion coefficient of CO2 are almost the same for corresponding cases in two mixtures; therefore, the diffusion coefficient of CO₂ causes these differences in pressure curves of corresponding cases in two mixtures. Higher pressure reduction rate during diffusion dominated regimes in NaCl and CaCl₂ mixture than corresponding cases in NaCl mixture shows that CO₂ diffusivity in NaCl and CaCl₂ mixture is higher. Reasons for this observation could be related to lower molality for NaCl and CaCl₂ mixture as well as different molecular interactions in different salt solutions. We used Eqs. (1) and (2) to calculate CO₂ diffusivity in brine by matching simulation results with experimental data. Since, we can neglect the convective term during the diffusive dominated regime; therefore, direct numerical simulation of this period is a simple task. We have used direct numerical simulation to obtain diffusion coefficient by matching between numerical and experimental results (details of numerical simulation methodology is available in our previous study (Mahmoodpour and Rostami, 2017). Results are reported in Table 2 revealing that the NaCl and mixture of NaCl and CaCl₂ mainly change the diffusion coefficients. Consider that Case 1 and Case 3, Case 2 and Case 4, Case 5 and Case 7, and Case 6 and Case 8 which have similar properties except their salinity (Table 1).

At early times, the dissolution process is controlled by diffusion mechanism. Since, concentration gradient is the driving force for diffusion mechanism and it decrease with time; therefore, the dissolution flux decreases. This reduction in dissolution flux and corresponding decline in pressure curves continue until the convection mechanism is activated and brings fresh brine (brine without dissolved CO₂ gas) into CO₂-brine interface and sharpens the concentration gradient. Therefore, with onset of convection, dissolution flux increases and we see a rapid decline in pressure curves after the diffusion dominated regime. This time is detected visually from pressure curves and represented in Fig. 3 for all cases. Based on this explanation, onset of convection corresponds to the minimum of dissolution flux too. To check the detected times from the pressure curves, we compare these points with dissolution flux curves and this confirmed the represented times for onset of convection. Details of the dissolution flux calculation is provided in our previous work (Mahmoodpour et al., 2018b).

Fig. 4 shows some snapshots from the experimental tests. Images from the process progressing are important from some points: 1) we can calculate the critical wave number (number of the convective fingers divided by gas-liquid interface length at onset of convection); 2) we can obtain the exact height of the saturated porous media (which is important for Ra) and volume of gas phase (which is important for dissolution flux calculation); 3) it is possible to track the interaction between convective fingers (especially from the supplementary videos); 4) by imposing almost smooth and horizontal gas-liquid interface, possible errors from the morphology and slope of the interface is decreased; 5) capillary pressure effect is decreased through implementing a sharp gasliquid interface; 6) these figures give some insights from the dissolution process too. They show that rapid decline in the pressure curves happens later than appearance of the convective fingers. Actually, convective fingers need time to interact with each other to create stronger fingers. These stronger fingers can change the trend of pressure curves (dissolution flux) considerably. Therefore, there is a time difference between appearance of the convective fingers and the rapid decline in pressure curves.

How are our results applicable to real reservoir conditions? To answer this question, we found scalable correlations. We followed an approach in prior work in which key parameters are presented based on dimensionless numbers (Riaz et al., 2006; Hassanzadeh et al., 2007; Kim and Song, 2017; Taheri et al., 2017). We converted our experimentally obtained onset of convection (*t*) to a non-dimensional form using $\hat{t}_{c,EXP} = \frac{tD_{CO2}}{H^2}$ (H is the height of the saturated porous media). Dimensionless times are presented in Table 2. The NaCl and CaCl₂ mixtures result in delays in the onset of convection for cases with the

Table 2

Summarized results of experimental tests; DNS and LSA including diffusion coefficient (D_{CO2}), density difference ($\Delta \rho$), viscosity (μ), dimensionless onset of instability ($\hat{t}_{c,LSA}$) and convection (from experiments: $\hat{c}_{c,EXP}$ and from DNS: $\hat{t}_{c,DNS}$) with the corresponding wave number (from experiment: $\kappa_{c,EXP}$; from LSA: $\kappa_{c,LSA}$ and from DNS: $\kappa_{c,DNS}$); Reported values for *Ra* are based on initial pressures for each case.

| | - | | | | | | | | | |
|------|--------------------------------------------------------|----------------------|-------|------------------------------------------------------|-------------------|-------------------------------------------------------------------------------------------------------|------------------|-----------------------------------------|------------------|------|
| Case | Experiment | | | | | LSA DNS | | | | Ra |
| | D _{CO2} x10 ⁹ m ² /s | $\Delta \rho kg/m^3$ | μ ср | $\frac{\hat{t}_{c,EXP} \times 10^4}{\frac{tD}{H^2}}$ | $\kappa_{c, EXP}$ | $\hat{t}_{c,LSA} \mathrm{x10^6} t \left(\frac{k^2 g^2 \Delta \rho^2}{\varphi \mu^2 D_{CO2}} \right)$ | $\kappa_{c,LSA}$ | $\hat{t}_{c,DNS} x 10^5 \frac{tD}{H^2}$ | $\kappa_{c,DNS}$ | |
| 1 | 3.8 | 3.37 | 0.679 | 6.88 | 50 | 2.80 | 254 | 8.19 | 119.4 | 4444 |
| 2 | 3.7 | 3.32 | 0.679 | 13.01 | 37.5 | 5.18 | 186 | 13.43 | 88.9 | 3272 |
| 3 | 5 | 4.32 | 0.608 | 5.67 | 59.4 | 2.36 | 270 | 5.67 | 138.9 | 4841 |
| 4 | 4.9 | 4.23 | 0.608 | 10.23 | 46.9 | 4.49 | 202 | 12.23 | 102.8 | 3514 |
| 5 | 4.2 | 3.29 | 0.685 | 9.05 | 36.1 | 3.66 | 220 | 10.00 | 108.3 | 3893 |
| 6 | 4.1 | 3.31 | 0.685 | 16.04 | 30.6 | 6.51 | 166 | 17.67 | 80.6 | 2919 |
| 7 | 5.3 | 4.10 | 0.614 | 7.21 | 55.6 | 3.02 | 238 | 7.81 | 116.7 | 4283 |
| 8 | 5.2 | 4.19 | 0.614 | 12.50 | 44.4 | 5.28 | 182 | 14.16 | 88.9 | 3242 |
| | | | | | | | | | | |



Fig. 4. Snapshots from the dissolution process for all cases. Same times are used for all cases to compare the convective fingers positions and distributions in all cases.

same permeability. We plot the onset times versus Rayleigh number on logarithmic scale in Fig. 5 demonstrating t_c scales with Ra as $t_c \sim Ra^{-2}$. Dimension format of this relationship $(\frac{lonset D_{CO2}}{H^2} \propto \frac{D_{CO2}^2 \varphi^2 \mu^2}{k^2 \Delta_{\rho} \rho_g^2 H^2} \rightarrow t_{onset} \propto \frac{D_{CO2} \varphi^2 \mu^2}{k^2 \Delta_{\rho} \rho_g^2 r^2})$ reveals the independency of the onset of convention from the length scale (i.e., height of system). Also, it shows

that the onset of convection is directly related to the diffusion coefficient ($t_{onset} \propto D_{CO2}$), and in this way the NaCl and CaCl₂ mixture shows later onset of convection while other parameters are close to those of the NaCl mixture (comparison between Case 1 and Case 5, Case 2 and Case 6, Case 3 and Case 7, and Case 4 and Case 8). To choose an appropriate aquifer, the onset of convection is an important factor.



Fig. 5. Left panel) Dimensionless onset time versus *Ra* on logarithmic scales. Linear relationships are clear for all cases; Right panel) Critical wave number for instability and convection onset versus *Ra* on logarithmic scale. Results of linear stability analysis, direct numerical simulation and experimental tests are represented by legends of LSA, DNS and EXP in the marker section respectively. Results are reported based on their Ra values; therefore, it is possible to find each case in these plots based on Ra values in Table 2.

Therefore, the resulting relations here can be used to rank different aquifers with different permeability and brine composition. We found the corresponding wavenumber for the onset of convection by counting the number of convective fingers over the domain width and dividing it by the length of the system (at $t = t_{onset}$). Results are reported in Table 2.

The t_c and k_c are plotted versus Ra on logarithmic scale in Fig. 5, showing k_c scales with Ra as $k_c \sim Ra^1$. The critical wavenumber for the onset of convection versus Ra shows similar trends for both NaCl and CaCl₂ mixture and NaCl solution (Fig. 5). Also, this trend of the wavenumber versus Ra number shows that to better capture the convective flow in numerical simulations we need to reduce the grid block size based on the provided relation. In particular, it is required to use grid block with a size smaller than wavenumber for robustly capturing the system behavior (see Soltanian et al., 2016b). We implemented the grid blocks smaller than wavenumber in our direct numerical simulations. Also, we suggest to use grid blocks size based on this trend to study the similar process in a wide range of Ra.

Fig. 5 also shows the obtained t_c and κ versus Ra for LSA. The results confirm linear relations in logarithmic plot. An important observation is

that the onset of convection in experimental data show the same trend as in LSA ($\hat{t}_{c,EXP} \propto Ra^{-2}$ and $\hat{t}_{c,LSA} \propto Ra^{-2}$). To compare different cases theoretically, we calculated growth rate of instabilities based on wave numbers (Eq. (22)) in Fig. 6. It is clear that the growth rates are higher in brine with NaCl than the brine with NaC and CaCl₂, emphasizing the higher damping of instabilities in NaCl and CaCl₂ solution. As shown, diffusion coefficient is higher in NaCl and CaCl₂. Therefore, this higher diffusion coefficient reduces the downward movement of convective fingers. Comparing convective fingers and their position in the Supplementary videos clearly shows this effect in our experiments.

Our results demonstrate that salinity could delay the onset fingering and intensify the potential influence of diffusion process as restoring force during gravitational fingering of CO₂-rich brine (comparing the results for Case 1 and Case 3, Case 2 and Case 4, Case 5 and Case 7, and Case 6 and Case 8). Our results are consistent with results of numerical simulations (e.g., by Soltanian et al. (2016a,b, 2017)) suggesting diffusion as the damping factor. Therefore, our suggestion is to incorporate the potential effects of salt solution on brine properties when studying convection processes.



Fig. 6. Comparison of growth rate versus wave number for cases in Table 1 times of $t_{c,1} = 3x10^{-6}$; $t_{c,2} = 6x10^{-6}$ and $t_{c,3} = 9x10^{-6}$: a) Case 1 and 5, b) Case 2 and 6, c) Case 3 and 7, and d) Case 4 and 8.



Fig. 7. Cumulative dissolved CO_2 concentration (in dimensionless format) based on the dimensionless time from the DNS results. Deviation time from the pure diffusion mechanism is represented by vertical lines and data are reported in Table 2.

As described in Section 2 and Fig. 5 shows (linear trends for onset of instability and onset of convection in logarithmic scale), there is a time difference between onset of instability and onset of convection. We should emphasize that it takes some time until the dissolved CO₂ reaches the point at which the solution color is detectably changed (pH reaches to detectable levels with pH indicator) and one can detect the convective fingers by visual examination (see Supplementary videos). Also, dissolution process requires some time until the convective fingers get stronger and can change the pressure curve in a meaningful way. The nonlinear behavior of system after the onset of instability is not detectable with LSA. To capture the system behavior in the range of the time from onset of instability to onset of convection from experimental data, we use DNS with input parameters extracted from our experimental data. The time at which the dissolved CO₂ concentration from DNS (which considers cumulative effects of the diffusion and convection regimes) deviates from the diffusive regime for the first time can be obtained with a high temporal resolution. We found this time for all cases and represented in Fig. 7. The deviation time between dissolved CO2 amount from pure diffusion regime and overall dissolution is reported based on the $(\hat{t}_{c,DNS} = \frac{tD}{H^2})$. Dimensionless time for the onset of convection and critical wave number from DNS are plotted in Fig. 5. Linear curves with similar trends of the experimental data and LSA results fit the DNS results. This trend confirms that during the time from onset of instability to detectable time in pressure curves from experimental tests, the interaction between convective fingers (merging to creating stronger fingers) are well scaled with Ra.

4. Conclusions

We have conducted series of experiments at high-pressure conditions to examine the potential effects of brine composition on the onset of convection during CO₂ sequestration in saline aquifers. Instead of using analogue fluids to perform our experiments, we built a real CO₂brine system that does not pose the problems associated with using analogue fluids (e.g., a non-monotonic density profile). Thus, we provided original insights from the dissolution of CO₂ in brine at highpressure conditions in laboratory. Our set-up also reduces the boundary effects on convective fingers. Additionally, using set-up with high-permeability values in previous work results in a quick initiation of fingering; consequently, there are not enough data on the diffusiondominated regime. Here, our experimental set-up allowed for using a wider opening in our Hele-Shaw cell. This enabled us to use glass beads to represent porous media. In this way, we obtained data during the diffusion-dominated regime to calculate diffusion coefficient of CO₂ from the pressure decay curve. The onset of convection was also detectable from pressure decay curves. We also performed direct numerical simulations and linear stability analyses to make comparisons with our experiments.

Four tests with NaCl brine at different salinity and permeability values were performed and compared with four NaCl and CaCl₂ solutions with the same overall salinity and permeability. We combined quantitative (pressure data) and qualitative (image) results to reduce possible errors. Our results reveal that CO_2 diffusion is the most important factor for the onset of convection between corresponding cases in two mixtures and is significantly different in two mixtures; CO_2 solubility and brine viscosity are similar in two mixtures. Also, porosity and permeability are the same for corresponding cases. Therefore, the CO_2 diffusion coefficient needs to be measured or calculated accurately in brines with different salinity.

Comparison between visual data and pressure data shows that the faster decline in pressure curve after the diffusion dominated regime, occurs later than the convective fingers appear. This is because smaller convective fingers need to interact and merge in order to create stronger fingers until they are able to alter the trend of pressure curve. Therefore, we used linear stability analyses to examine system behavior. Results indicate that the higher diffusion coefficient in brine solutions containing NaCl and CaCl₂ mixture damps the instabilities. Therefore, there is delay in the onset of instabilities for NaCl and CaCl₂ mixture, and instabilities grow with a lower rate compared to brine with only NaCl. The critical wave number of instability for NaCl and CaCl₂ mixture is lower than that of NaCl. To examine the nonlinear behavior of system after the onset of instabilities, we used high-resolution direct numerical simulations. Our numerical simulation results detect the initial deviation of dissolved CO2 concentration from the diffusion regime.

Our scaling analyses on the onset of instability and onset of convection can be explained by a relation of $t_c = aRa^b$ with $b \sim -2$ in all our analyses. Higher diffusion coefficient in NaCl and CaCl₂ mixture (lower Ra) results in delays of onset of instability and convection. Critical wave number could be explained by a relation of $\kappa_c = cRa^d$. Comparison of the scaling relationships shows that $d \sim 1$ for all cases. These trends reveal that density-difference instabilities are created, grow, and eventuate in the convective fingers corresponding to their Rayleigh number.

Contributions

S.M. designed and carried out the experiments and simulations, performed data analysis.

S.M. and B.R. wrote the draft manuscript. B.R. helped in experimental set-up design.

M.R.S. helped in data analysis. M.R.S. and M.A.A. helped in manuscript preparation.

Appendix A

A. 1. Solubility of CO_2 in brine

Here we present a well-known correlation below for calculating CO₂ solubility in brine (Duan and Sun, 2003; Duan et al., 2006):

$$\ln x_{CO2} = \ln(y_{CO2}\phi_{CO2}P) - \frac{\mu_{CO2}^{(10)}}{RT} - 2\lambda_{CO2-Na}(m_{Na} + m_K + 2m_{Ca} + 2m_{Mg}) - \zeta_{CO2-Na-Cl}m_{Cl}(m_{Na} + m_K + m_{Mg} + m_{Ca}) + 0.07m_{SO4}$$
(A1)

where *T* is in Kelvin and pressure is in bar. The $\mu_{CO2}^{1(0)}$, λ_{CO2-Na} , and $\zeta_{CO2-Na-Cl}m_{Cl}$ are standard chemical potential, interaction parameter between CO₂ and Na⁺, and interaction parameter between CO₂, Na⁺, and Cl⁻, respectively. Following equation is used to calculate these parameters:

$$Par(T, P) = c_1 + c_2T + \frac{c_3}{T} + c_4T^2 + \frac{c_5}{(630 - T)} + c_6P + c_7PlnT + c_8\frac{P}{T} + c_9\frac{P}{(630 - T)} + c_{10}\frac{P^2}{(630 - T)^2} + c_{11}TlnP$$
(A2)

The fugacity coefficient (ϕ_{CO2}) is calculated from the following non-iterative equation:

$$\phi_{CO2} = c_1 + \left[c_2 + c_3T + \frac{c_4}{T} + \frac{c_5}{T - 150}\right]P + \left[c_6 + c_7T + \frac{c_8}{T}\right]P^2 + \frac{\left[c_9 + c_{10}T + \frac{c_{11}}{T}\right]}{\ln P}$$
(A3)

Constants c_1 - c_{15} are presented in Table A1.

Table A1

Parameters of c_1 - c_{15} which are required in CO₂ solubility equations.

| Constant | $\frac{\mu_{CO2}^{1(0)}}{_{RT}}$ | λ_{CO2-Na} | $\zeta_{CO2-Na-Cl}m_{Cl}$ | ϕ_{CO2} |
|----------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------|------------------------------------------------------|--------------------------------------------------------------------------------------|
| C ₁ C ₂ C ₃ C ₄ C ₅ C ₆ | 28.9447706 - 0.0354581768 - 4770.67077 1.02782768E-5 33.8126098 9.04037140E-3 - 1.14934031E-3 | - 0.411370585 6.07632013E-4 97.5347708 - - - | 3.36389723E-4 - 1.98298980E-5 - - - - | 1.0 4.7586835E-3 - 3.3569963E-6 0.0 - 1.3179396 - 3.8389101E-6 0.0 |
| c ₈ c ₉ c ₁₀ c ₁₁ | - 0.307405726 - 0.0907301486 9.32713393E-4 - | - 0.0237622469 0.0170656236 - 1.41335834E-5 | 2.12220830E-3 - 5.24873303E-3 - - | 2.2815104E-3 0.0 0.0 0.0 |

A. 2. Viscosity of NaCl solution

We followed the approach by Mao and Duan (2009) to obtain viscosity of NaCl solution by:

| $\ln\left(\frac{\mu_{brine of CO2}}{\mu_{H2O}}\right) = Am + Bm^2 + Cm^3$ | (A4) |
|-----------------------------------------------------------------------------|------|
| where <i>A</i> , <i>B</i> and <i>C</i> are functions of temperature (in K): | |
| $A = c_1 + c_2 T + c_3 T^2$ | (A5) |
| $B = c_4 + c_5 T + c_6 T^2$ | (A6) |
| $C = c_7 + c_8 T$ | (A7) |

The c_1 - c_8 constants are obtained from experimental data and are presented in Table A2.

A. 3. Viscosity

To obtain the viscosity of the NaCl and CaCl₂ containing solution, a simple mixing rule is used (Zhang et al., 1997):

| $\Delta\mu_{mix.} = \Delta\mu_{CaCl2} + \Delta\mu_{NaCl}$ | (A8) |
|------------------------------------------------------------------------------------------------------------------------|-------|
| $\mu_{mix.} = \mu_{H2O}(1 + \Delta \mu_{mix.})$ | (A9) |
| $\Delta \mu_{NaCl} = c_1 m_{NaCl}^{0.5} + c_2 m_{NaCl} + c_3 m_{NaCl}^2 + c_4 m_{NaCl}^{3.5} + c_5 m_{NaCl}^7$ | (A10) |
| $\Delta\mu_{CaCl2} = c_6 m_{CaCl2}^{0.5} + c_7 m_{CaCl2} + c_8 m_{CaCl2}^2 + c_9 m_{CaCl2}^{3.5} + c_{10} m_{CaCl2}^7$ | (A11) |

where c_1 - c_{10} are calculated from experimental data on specific salt concentrations. In the required concentrations, parameters are interpolated. For 1 M. concentration of brine, these values are presented in Table A2.

| Table A2 |
|----------------------------------------------|
| Required parameters for the viscosity models |

| Constant | Mao & Duan's model | Zhang et al. model |
|-----------------|--------------------|--------------------|
| | | |
| c ₁ | -0.21319213 | 0.0061 |
| c ₂ | 0.13651589E-2 | - |
| c ₃ | -0.12191756E-5 | 0.01040 |
| c ₄ | 0.69161945E-1 | 0.000756 |
| c ₅ | -0.27292263E-3 | - |
| c ₆ | 0.20852448E-6 | 0.0157 |
| C7 | -0.25988855E-2 | 0.271 |
| c ₈ | 0.77989227E-5 | 0.04712 |
| C ₉ | - | 0.00941 |
| c ₁₀ | - | 0.00003 |

A. 4. Brine density

NaCl solution density is (Potter and Brown, 1977):

$$\rho_b = \frac{1000\rho_w + M_{NaCl}\rho_w}{1000 + A_0 m_{NaCl}\rho_w + B_0 m_{NaCl}^{1.5}\rho_w + C_0 m_{NaCl}^2\rho_w}$$
(A12)

To obtain the NaCl and CaCl₂ solution density, the relative density of the NaCl and CaCl₂ mixture to the NaCl solution is calculated by Al Ghafri et al. model (Al Ghafri et al., 2012).

$$\rho_b(T, P, m) = \rho_{ref}(T, m) \left[1 - C(m) x \ln \left\{ \frac{B(T, m) + P}{B(T, m) + P_{ref}(T)} \right\} \right]^{-1}$$
(A13)

$$\ln \frac{P_{ref}(T)}{P_c} = \left(\frac{T_c}{T}\right) \{\sigma_1 \varphi + \sigma_2 \varphi^{1.5} + \sigma_3 \varphi^3 + \sigma_4 \varphi^{3.5} + \sigma_5 \varphi^4 + \sigma_6 \varphi^{7.5}\}$$
(A14)

where T_c and P_c are critical values and $\varphi = \left(1 - \frac{T}{T_c}\right)$

$$\rho_{ref}(T, m) - \rho_0(T) = \sum_{i=1}^{i=3} \alpha_{i0} m^{(i+1)/2} + \sum_{i=1}^{i=3} \sum_{j=1}^{j=3} \alpha_{ij} m^{(i+1)/2} \left(\frac{T}{T_c}\right)^{(j+1)/2}$$
(A15)

$$B(T, m) = \sum_{i=0}^{j=1} \sum_{j=0}^{j=3} \beta_{ij} m^i \left(\frac{T}{T_c}\right)^j$$
(A16)

$$C(m) = \gamma_0 + \gamma_1 m + \gamma_2 m^{1.5}$$
(A17)

$$\frac{\rho_0(T)}{\rho_c} = 1 + c_1 \varphi_3^{\frac{1}{3}} + c_2 \varphi_3^{\frac{2}{3}} + c_3 \varphi_3^{\frac{5}{3}} + c_4 \varphi_3^{\frac{16}{3}} + c_5 \varphi_3^{\frac{43}{3}} + c_6 \varphi_3^{\frac{110}{3}}$$
(A18)

where $c_1 = 1.992741$; $c_2 = 1.099653$; $c_3 = -0.510839$; $c_4 = -1.754935$; $c_5 = -45.517035$; $c_6 = 674694.45$; $\beta_{00} = -1622.40$; $\beta_{01} = 9383.80$; $\beta_{02} = -14893.80$; $\beta_{03} = 7309.10$; $\gamma_0 = 0.11725$; $\sigma_1 = -7.859518$; $\sigma_2 = 1.844083$; $\sigma_3 = -11.786650$; $\sigma_4 = 22.680741$; $\sigma_5 = -15.961872$ and $\sigma_6 = 1.801225$. Required parameters for NaCl and CaCl₂ are presented in Table A3.

Table A3

| Parameters for de | ensity calculation | of NaCl and | CaCl ₂ brine |
|-------------------|--------------------|-------------|-------------------------|
|-------------------|--------------------|-------------|-------------------------|

| Con. | α_{10} | α_{11} | α_{12} | α_{13} | α_{14} | α_{20} | α_{21} |
|-----------------------------------|-----------------------------------------|-------------------------------------|------------------------------------------------------------------|-------------------------------------------------------------|--------------------------------------------------------------|--------------------------------|----------------------------------|
| NaCl | 2863.158 | - 46844.356 | 120760.118 | -116867.722 | 40285.426 | - 2000.028 | 34013.518 |
| CaCl ₂ | 2546.760 | - 39884.946 | 102056.957 | -98403.334 | 33976.048 | - 1362.157 | 22785.572 |
| Con. | $lpha_{22}$ | α ₂₃ | α ₂₄ | α ₃₀ | α ₃₁ | α ₃₂ | α ₃₃ |
| NaCl | - 88557.123 | 86351.784 | - 29910.216 | 413.046 | - 7125.857 | 18640.780 | 18244.074 |
| CaCl ₂ | - 59216.108 | 57894.824 | - 20222.898 | 217.778 | - 3770.645 | 9908.135 | 9793.484 |
| Con. NaCl CaCl ₂ | α ₃₄ 6335.275 3455.587 | β ₁₀ 241.57 307.24 | $egin{array}{c} \beta_{11} \ - 980.97 \ - 1259.10 \end{array}$ | $egin{array}{c} \beta_{12} \ 1482.31 \ 2034.03 \end{array}$ | $egin{array}{c} \beta_{13} \ -750.98 \ -1084.94 \end{array}$ | $\gamma_1 - 0.00134 - 0.00493$ | γ_2 0.00056 0.00231 |

A. 5. Partial molar volume

Partial molar volume of CO_2 in water is obtained by (Garcia, 2001):

$$V_{CO_2} = 37.51 - 9.585 \times 10^{-2} T + 8.740 \times 10^{-4} T^2 - 5.044 \times 10^{-7} T^3$$

where *T* is in degrees Celsius and V_{CO_2} is in cm³/mole.

(A19)

Appendix B. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.cageo.2018.12.002.

References

- Agartan, Elif, et al., 2015. Experimental study on effects of geologic heterogeneity in enhancing dissolution trapping of supercritical CO2. Water Resour. Res. 51 (3), 1635–1648.
- Aggelopoulos, C.A., Robin, M., Vizika, O., 2011. Interfacial tension between CO2 and brine (NaCl+ CaCl2) at elevated pressures and temperatures: the additive effect of different salts. Adv. Water Resour. 34 (4), 505–511.
- Amooie, M.A., Soltanian, M.R., Moortgat, J., 2017a. Hydrothermodynamic mixing of fluids across phases in porous media. Geophys. Res. Lett. 44 (8), 3624–3634.
- Amooie, M.A., Soltanian, M.R., Xiong, F., Dai, Z., Moortgat, J., 2017b. Mixing and spreading of multiphase fluids in heterogeneous bimodal porous media. Geomech. Geophys. Geo-Ener. Geo-Res. 3 (3), 225–244.
- Amooie, M.A., Soltanian, M.R., Moortgat, J., 2018. Solutal convection in porous media: comparison between boundary conditions of constant concentration and constant flux. Physical Rev. E 98 (3), 033118.
- Azin, Reza, Mahmoudy, Mohamad, Jafari Raad, Seyed Mostafa, Osfouri, Shahriar, 2013. Measurement and modeling of CO 2 diffusion coefficient in saline aquifer at reservoir conditions. Cent. Eur. J. Eng. 3 (4), 585–594.
- Backhaus, Scott, Turitsyn, Konstantin, Ecke, R.E., 2011. Convective instability and mass transport of diffusion layers in a hele-shaw geometry. Phys. Rev. Lett. 106 (10), 104501.
- Bacon, Diana H., Sass, Bruce M., Bhargava, Mohit, Joel Sminchak, Gupta, Neeraj, 2009. Reactive transport modeling of CO2 and SO2 injection into deep saline formations and their effect on the hydraulic properties of host rocks. Energy Procedia 1 (1), 3283–3290.

Duan, Zhenhao, Sun, Rui, 2003. An improved model calculating CO 2 solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. Chem. Geol. 193 (3), 257–271.

- Duan, Zhenhao, Sun, Rui, Zhu, Chen, Ming Chou, I., 2006. "An improved model for the calculation of CO2 solubility in aqueous solutions containing Na+, K+, Ca2+, Mg2+, Cl-, and SO42-. Mar. Chem. 98 (2–4), 131–139.
- Emami-Meybodi, Hamid, 2017. Dispersion-driven instability of mixed convective flow in porous media. Phys. Fluids 29 (9), 94102.
- Emami-Meybodi, Hamid, Hassan, Hassanzadeh, 2013. Stability analysis of two-phase buoyancy-driven flow in the presence of a capillary transition zone. Phys. Rev. 87 (3), 33009.
- Emami-Meybodi, Hamid, Hassan, Hassanzadeh, Green, Christopher P., Ennis-King, Jonathan, 2015. Convective dissolution of CO 2 in saline aquifers: progress in modeling and experiments. Int. J. Greenhouse Gas Contr. 40, 238–266.
- Ennis-King, Jonathan, Preston, Ian, Paterson, Lincoln, 2005. Onset of convection in anisotropic porous media subject to a rapid change in boundary conditions. Phys. Fluids 17 (8), 84107.
- Farajzadeh, Rouhollah, Ali, Barati, Delil, Harm A., Johannes, Bruining, Pacelli, L., Zitha, J., 2007a. Mass transfer of CO2 into water and surfactant solutions. Petrol. Sci. Technol. 25 (12), 1493–1511.
- Farajzadeh, Rouhollah, Salimi, Hamidreza, Pacelli, L., Zitha, J., Bruining, Hans, 2007b. Numerical simulation of density-driven natural convection in porous media with application for CO 2 injection projects. Int. J. Heat Mass Tran. 50 (25), 5054–5064.
- Farajzadeh, Rouhi, Zitha, Pacelli L.J., Johannes, Bruining, 2009. Enhanced mass transfer of CO2 into water: experiment and modeling. Ind. Eng. Chem. Res. 48 (13), 6423–6431.
- Farajzadeh, Rouhollah, Ranganathan, Panneer, Zitha, Pcelli Lidio Jose, Bruining, Johannes, 2011. The effect of heterogeneity on the character of density-driven natural convection of CO₂ overlying a brine layer. Adv. Water Resour. 34 (3), 327–339.
- Garcia, Julio E., 2001. Density of Aqueous Solutions of CO2. Lawrence Berkeley National Laboratory, LBNL-49023, Berekeley, CA.
 Gaus, Irina, Mohamed, Azaroual, Czernichowski-Lauriol, Isabelle, 2005. Reactive trans-
- Gaus, Irina, Monamed, Azarouai, Czerinchowski-Laurio, Isabene, 2005. Reactive transport modelling of the impact of CO2 injection on the clayey cap rock at sleipner (north sea). Chem. Geol. 217 (3–4), 319–337.
- Gershenzon, Naum I., Soltanian, Mohamadreza, Ritzi Jr., Robert W., Dominic, David F., 2014. Influence of small scale heterogeneity on CO2 trapping processes in deep saline aquifers. Energy Procedia 59, 166–173.
- Ghafri, Al., Saif, Maitland, Geoffrey C., Martin Trusler, J.P., 2012. "Densities of Aqueous MgCl2 (aq), CaCl2 (aq), KI (aq), NaCl (aq), KCl (aq), AlCl3 (aq), and (0.964 NaCl + 0.136 KCl)(aq) at Temperatures between (283 and 472) K, Pressures up to 68.5 MPa, and Molalities up to 6 Mol·kg–1. J. Chem. Eng. Data 57 (4), 1288–1304.
- Hassanzadeh, H., Pooladi-Darvish, M., Keith, D.W., 2005. Modelling of convective mixing in CO storage. J. Can. Petrol. Technol. 44 (10).
- Hassanzadeh, Hassan, Pooladi-Darvish, Mehran, Keith, David W., 2007. Scaling behavior of convective mixing, with application to geological storage of CO2. AIChE J. 53 (5), 1121–1131.
- Holloway, S., 2005. "Underground sequestration of carbon dioxide—a viable greenhouse gas mitigation option. Energy 30 (11–12), 2318–2333.
- Jafari-Raad, Mostafa, Seyed, Hassan, Hassanzadeh, 2016. Does impure CO 2 impede or accelerate the onset of convective mixing in geological storage? Int. J. Greenhouse Gas Contr. 54, 250–257.

Jafari-Raad, Mostafa, Seyed, Hassan, Hassanzadeh, 2017. "Prospect for storage of impure

carbon dioxide streams in deep saline aquifers—a convective dissolution perspective. Int. J. Greenhouse Gas Contr. 63, 350–355.

- Javaheri, Mohammad, Abedi, Jalal, Hassan, Hassanzadeh, 2010. Linear stability analysis of double-diffusive convection in porous media, with application to geological storage of CO 2. Transport Porous Media 84 (2), 441–456.
- Kim, Min Chan, Song, Kwang Ho, 2017. Effect of impurities on the onset and growth of gravitational instabilities in a geological CO2 storage process: linear and nonlinear analyses. Chem. Eng. Sci. 174, 426–444.
- Li, H., Zhang, Z., 2018. Mining the intrinsic trends of CO₂ solubility in blended solutions. J. CO₂ Utilizat. 26, 496–502.
- MacMinn, Christopher W., Juanes, Ruben, 2013. Buoyant currents arrested by convective dissolution. Geophys. Res. Lett. 40 (10), 2017–2022.
- MacMinn, Christopher W., Jerome, A. Neufeld, Hesse, Marc A., Huppert, Herbert E., 2012. Spreading and convective dissolution of carbon dioxide in vertically confined, horizontal aquifers. Water Resour. Res. 48 (11).
- Mahmoodpour, Saeed, Rostami, Behzad, 2017. Design-of-Experiment-Based proxy models for the estimation of the amount of dissolved CO2 in brine: a tool for screening of candidate aquifers in geo-sequestration. Int. J. Greenhouse Gas Contr. 56, 261–277.
- Mahmoodpour, S., Rostami, B., Khoshkalam, Y., 2018a. Experimental investigation of the onset of convection during CO₂-N₂ mixture dissolution in brine. In: 80th EAGE Conference and Exhibition, Copenhagen, Denmark, https://doi.org/10.3997/2214-4609.201801149.
- Mahmoodpour, S., Rostami, B., Emami-Meybodi, H., 2018b. Onset of convection controlled by N₂ impurity during CO₂ storage in saline aquifers. Int. J. Greenhouse Gas Contr. 79, 234–247.
- Mao, Shide, Duan, Zhenhao, 2009. The viscosity of aqueous alkali-chloride solutions up to 623 K, 1,000 bar, and high ionic strength. Int. J. Thermophys. 30 (5), 1510–1523.
- Martinez, M.J., Hesse, M.A., 2016. Two-phase convective CO₂ dissolution in saline aquifers. Water Resour. Res. 52 (1), 585–599.
- Mohamed, Ibrahim, Jia, He, Hisham, A., Nasr-El-Din, 2013. Effect of brine composition on CO2/limestone rock interactions during CO2 sequestration. J. Petrol. Sci. Res. 2 (1), 14–26.
- Nazari-Moghaddam, Rasoul, Rostami, Behzad, Pourafshary, Peyman, Fallahzadeh, Yaser, 2012. Quantification of density-driven natural convection for dissolution mechanism in CO2 sequestration. Transport Porous Media 92 (2), 439–456.
- Nazari-Moghaddam, Rasoul, Rostami, Behzad, Pourafshary, Peyman, 2015. Scaling analysis of the convective mixing in porous media for geological storage of CO2: an experimental approach. Chem. Eng. Commun. 202 (6), 815–822.
- Neufeld, Jerome, A., et al., 2010. Convective dissolution of carbon dioxide in saline aquifers. Geophys. Res. Lett. 37 (22), L22404.
- Newell, D.L., Carey, J.W., Backhaus, S.N., Lichtner, P., 2018. Experimental study of gravitational mixing of supercritical CO₂. Int. J. Greenhouse Gas Contr. 71, 62–73.
- Potter, Robert W., Brown, David L., 1977. The Volumetric Properties of Aqueous Sodium Chloride Solutions from 0 to 500 C at Pressures up to 2000 Bars Based on a
- Regression of Available Data in the Literature. US Government Printing Office. Riaz, Amir, Cinar, Vildiray, 2014. "Carbon dioxide sequestration in saline formations: Part I—review of the modeling of solubility trapping. J. Petrol. Sci. Eng. 124, 367–380.
- Riaz, A., Hesse, M., Tchelepi, H.A., Orr, F.M., 2006. Onset of convection in a gravitationally unstable diffusive boundary layer in porous media. J. Fluid Mech. 548, 87–111.

Schrag, Daniel P., 2007. Preparing to capture carbon. Science 315 (5813), 812–813. Seyyedi, Mojtaba, Behzad, Rostami, Rasoul, Nazari Moghaddam, Mohammad, Rezai,

2014. Experimental study of density-driven convection effects on CO 2 dissolution rate in formation water for geological storage. J. Nat. Gas Sci. Eng. 21, 600–607.

- Shi, Z., Wen, B., Hesse, M.A., Tsotsis, T.T., Jessen, K., 2018. Measurment and modeling of CO₂ mass transfer in brine at reservoir conditions. Adv. Water Resour. 113, 100–111. Singh, Ashok K., Bhadauria, B.S., 2009. "Finite difference formulae for unequal sub-in-
- tervals using Lagrange's interpolation formula. Int. J. Math. Anal. 3 (17), 815.
- Slim, Anja C., 2014. Solutal-convection regimes in a two-dimensional porous medium. J. Fluid Mech. 741, 461–491.
- Slim, Anja C., Bandi, M.M., Miller, Joel C., Mahadevan, L., 2013. "Dissolution-Driven convection in a hele-shaw cell. Phys. Fluids 25 (2), 24101.
- Soltanian, Mohamad Reza, Amin Amooie, Mohammad, Cole, David R., et al., 2016a. Simulating the cranfield geological carbon sequestration project with high-resolution static models and an accurate equation of state. Int. J. Greenhouse Gas Contr. 54, 282–296.
- Soltanian, Mohamad Reza, Amin Amooie, Mohammad, Dai, Zhenxue, Cole, David, Moortgat, Joachim, 2016b. Critical dynamics of gravito-convective mixing in geological carbon sequestration. Sci. Rep. 6, 35921.
- Soltanian, Mohamad Reza, et al., 2017. Dissolution trapping of carbon dioxide in heterogeneous aquifers. Environ. Sci. Technol. 51 (13), 7732–7741.
- Soltanian, Mohamad R., et al., 2018. Impacts of methane on carbon dioxide storage in brine formations. Groundwater 56 (2), 176–186.
- Szulczewski, M.L., Hesse, M.A., Juanes, R., 2013. Carbon dioxide dissolution in structural and stratigraphic traps. J. Fluid Mech. 736, 287–315.
- Taheri, Amir, Torsaeter, Ole, Wessel-Berg, Dag, Soroush, Mansour, 2012. Experimental and simulation studies of density-driven-convection mixing in a hele-shaw geometry with application for CO2 sequestration in brine aquifers. In: SPE Europec/EAGE

S. Mahmoodpour et al.

Annual Conference. Society of Petroleum Engineers.

- Taheri, Amir, Lindeberg, Erik, Torsæter, Ole, Wessel-Berg, Dag, 2017. Qualitative and quantitative experimental study of convective mixing process during storage of CO 2 in homogeneous saline aquifers. Int. J. Greenhouse Gas Contr. 66, 159–176.
- Taheri, Amir, Torsæter, Ole, Lindeberg, Erik, Hadia, Nanji J., Wessel-Berg, Dag, 2018. Qualitative and quantitative experimental study of convective mixing process during storage of CO 2 in heterogeneous saline aquifers. Int. J. Greenhouse Gas Contr. 71, 212–226.
- Tsai, Peichun A., Riesing, Kathleen, Stone, Howard A., 2013. Density-driven convection enhanced by an inclined boundary: implications for geological CO 2 storage. Phys. Rev. 87 (1), 11003.
- Vu, Hong, Phuc, Black, Jay R., Haese, Ralf R., 2017. Changes in formation water composition during water storage at surface and post Re-injection. Energy Procedia 114, 5732–5741.
- Wang, Zhiyu, et al., 2016. A study on the impact of SO2 on CO2 injectivity for CO2 storage in a Canadian saline aquifer. Appl. Energy 184, 329–336.
- Wellman, Tristan P., Grigg, Reid B., McPherson, Brian J., Svec, Robert K., Lichtner, Peter C., 2003. Evaluation of CO2-brine-reservoir rock interaction with laboratory flow tests and reactive transport modeling. In: In International Symposium on Oilfield

Chemistry. Society of Petroleum Engineers.

- Wen, Baole, Ahkbari, Daria, Zhang, Li, Marc, A., Hesse, 2018. Dynamics of Convective Carbon Dioxide Dissolution in a Closed Porous Media System. arXiv preprint arXiv:1801.02537.
- Xu, Tianfu, Sonnenthal, Eric, Spycher, Nicolas, Pruess, Karsten, 2006. "TOUGHREACT—a simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media: applications to geothermal injectivity and CO2 geological sequestration. Comput. Geosci. 32 (2), 145–165.
- Yang, Chaodong, Gu, Yongan, 2006. Accelerated mass transfer of CO2 in reservoir brine due to density-driven natural convection at high pressures and elevated temperatures. Ind. Eng. Chem. Res. 45 (8), 2430–2436.
- Zhang, Hai-Lang, Chen, Geng-Hua, Han, Shi-Jun, 1997. Viscosity and density of H2O+ NaCl+ CaCl2 and H2O+ KCl+ CaCl2 at 298.15 K. J. Chem. Eng. Data 42 (3), 526–530.

Zhang, Z., Li, H., Chang, H., Pan, Z., Luo, X., 2018a. Machine learning predictive framework for CO₂ thermodynamic properties in solution. J. CO₂ Utilizat. 26, 152–159.

Zhang, Z., Li, Y., Zhang, W., Wang, J., Soltanian, M.R., Olabi, A.G., 2018b. Effectiveness of amino acid salt solutions in capturing CO₂: A review. Renew. Sustain. Energy Rev. 98, 179–188.