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Injection of CO$_2$-saturated brine in geological reservoir: A way to enhanced storage safety

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Running Title: Injection of CO$_2$-saturated brine in the geological reservoir
Key Points

- Injection of CO₂-saturated brine in a geological reservoir is modelled
- Intense dissolution of carbonate minerals is observed
- Significant ionic trapping of CO₂ is observed
- Injection of CO₂-saturated reduces leakage risk of free CO₂
Abstract: Injection of free-phase supercritical CO$_2$ into deep geological reservoirs is associated with risk of considerable return flows towards the land surface due to the buoyancy of CO$_2$, which is lighter than the resident brine in the reservoir. Such upward movements can be avoided if CO$_2$ is injected in the dissolved phase (CO$_2$$_{aq}$). In this work, injection of CO$_2$-saturated brine in a subsurface carbonate reservoir was modelled. Physical and geochemical interactions of injected low-pH CO$_2$-saturated brine with the carbonate minerals (calcite, dolomite and siderite) were investigated in the reactive transport modelling. CO$_2$-saturated brine, being low in pH, showed high reactivity with the reservoir minerals, resulting in a significant mineral dissolution and CO$_2$ conversion in reactions. Over the injection period of 10 years, up to 16% of the injected CO$_2$ was found consumed in geochemical reactions. Sorption included in the transport analysis resulted in additional quantities of CO$_2$ mass stored. However, for the considered carbonate minerals, the consumption of injected CO$_2$$_{aq}$ was found mainly in the form of ionic trapping.

Keywords: Injection of CO$_2$-saturated brine, geological storage, carbonate reservoir, carbonate mineral reactions, ionic trapping, enhanced storage safety
1. Introduction

Leakage of CO$_2$ from storage reservoirs is a main concern related to its geological sequestration (Haugan and Joos, 2004; Stone et al., 2009; Weir et al., 1996; Kopp et al., 2010). When CO$_2$ is injected in its supercritical phase (a state between gas and liquid), it is lighter than the resident formation brine and thus has a tendency to move upwards due to buoyancy (Audigane et al., 2007, Xu et al., (2003, 2007); Weir et al., 1996; García, 2001). Therefore, geological reservoirs overlain by low permeability caprock formations that physically hinder the upward movement of CO$_2$ are thought to be best candidates for CO$_2$ storage (García, 2003).

Injected CO$_2$ stays mainly as a separate free-phase over longer period of time and only small amount is dissolved in the resident brine. CO$_2$ injected in the reservoir react with in situ fluid with its conversion into carbonic acid (solubility trapping—dominates from tens to hundreds of years) followed by conversion into carbon-bearing ionic species (ionic trapping—dominates from hundreds to thousands of years) and then the precipitation of new carbonate minerals resulting in fixation of CO$_2$ that is the most secure form of sequestration (mineral trapping—dominates over thousands to millions of years) (IPCC, 2005). Audigane et al. (2007) observed only 30% of injected CO$_2$ converted into dissolved phase after 1000 years and complete dissolution of all the injected CO$_2$ after 10,000 years. They reported only 5% of injected mass consumed in minerals reaction after 10,000 years. Thus in the presence of highly permeable zones like poorly abandoned wells and fracture or conducting fault zones, CO$_2$ may leak towards the land surface (IPCC, 2005; Leonenko and Keith, 2007).
Brine resulting from dissolution of injected CO₂ gets denser than the resident brine and moves downward in the reservoir with reduced leakage risk (García, 2001; IPCC, 2005; Audigane et al., 2007). Dissolution of CO₂ in the formation brine also lowers its pH resulting in increased reactivity with the formation minerals (Xu et al., 2003, 2004; Audigane et al., 2007). Precipitation of carbonate minerals causes permanent consumption of CO₂, referred to as mineral trapping (Audigane et al., 2007). Minerals dissolution/precipitation caused by geochemical interaction with low-pH brine may also change the porosity and permeability of the porous media (Xu et al., 2003).

Nogues et al. (2013) have conducted a numerical study of porosity and permeability evolution at pore scale level driven by inflowing CO₂-saturated water and have suggested that to simplify the geochemical modelling it is appropriate to not include the minerals like kaolinite, anorthite, and albite in cases where carbonate minerals are abundant. Gherardi et al. (2007) have found porosity variations in the proximity of reservoir-caprock interface mainly due to calcite mineral reactivity with CO₂ brine. Gaus et al. (2005) have reported decrease in porosity of the caprock as a result of calcite and kaolinite precipitation resulting from dissolution of anorthite over a period of 500 years.

The leakage risk associated with injection of free-phase CO₂ in the subsurface reservoir motivates to inject CO₂ in dissolved phase in order to increase the safety of CO₂ geological storage (Aradóttir et al., 2012). Injection of CO₂ in its dissolved phase makes the resulting brine denser (nearly by 1% depending on pressure, temperature and salinity conditions) than the resident formation brine and thus may tend to move downwards being negatively buoyant after its injection in the reservoir. No cap rock above the
reservoir is needed if CO₂ is injected in dissolved form because CO₂-saturated brine is denser than the resident fluids (Gislason and Oelkers, 2014). Also solubility and ionic trapping can take place immediately if CO₂ is injected in dissolved phase in the reservoir (Gislason and Oelkers, 2014). Relatively fast mineral trapping can also be expected if CO₂ is injected in dissolved phase (Aradóttir et al., 2012). CO₂ injected in dissolved phase can only migrate out of the storage reservoir due to regional groundwater movement (IPCC, 2005). However, subsurface groundwater velocities can be expected on the order of millimetres to centimetres per year (Bachu et al., 1994). Thus, leakage rates of dissolved CO₂ can be expected as substantially lower than for free-phase CO₂ due to very small groundwater flow velocities in the subsurface (IPCC, 2005). Even if the leakage of dissolved CO₂ takes place from the storage reservoir, it will have less potential to reach the land surface due to its very slow movement and its significant retention (stored in pore spaces in dissolved phase, in adsorbed state on mineral surfaces and also its conversion in geochemical reactions) along the leakage pathway (Ahmad et al., 2015).

So far the major focus has been on the injection of CO₂ in supercritical state as a free-phase in the subsurface reservoir (Matter et al., 2011). Very few studies have been reported in the literature focusing on the injection of CO₂ in dissolved phase. “CO₂-DISSOLVED” is a research project focusing on injecting CO₂ dissolved in brine. The CarbFix Project aims at better understanding the potential of injecting CO₂-charged water into subsurface basalt rock formations (Matter et al. 2011; Aradóttir et al., 2011, 2012; Tollefson, 2013; Alfredsson et al., 2013; Gislason and Oelkers, 2014). Aradóttir et al. (2012) performed reactive transport modelling for injected dissolved CO₂ in the
subsurface basalt rock formation. In their study, 40,000 tonnes of CO$_2$ were injected over a period of 10 years. The simulation was performed in a 2D domain using 100 and 400 meter vertically thick layers extending up to about 2700 m deep. The reactive transport analysis was performed for an extended period of 100 years. These authors reported that about 20% of CO$_2$ was consumed in mineral trapping over the period of 100 years for the 100 m thick reservoir layer.

This study aims at better understanding the injection of CO$_2$ in its dissolved phase (CO$_{2aq}$) in subsurface carbonate reservoirs, including the physical and geochemical interactions with the formation minerals to analyze the amount of CO$_2$ stored in the aqueous and adsorbed states, the amount of CO$_2$ consumed in geochemical reactions as well as change in porosity and permeability of the reservoir resulting from minerals dissolution and precipitation. In this study we consider three carbonate rock forming minerals calcite, dolomite, and siderite for geochemical interactions with the injected dissolved CO$_2$. We also take into account the heat exchange between the injected CO$_2$-saturated brine and the porous media in the reservoir. Various reactive transport modelling scenarios were performed over the period of 10 years of CO$_2$-saturated brine injection in the subsurface carbonate reservoir. The mass of CO$_{2aq}$ injected in the reservoir, its mass stored in aqueous and adsorbed states, and its mass consumed in geochemical reactions were quantified over the injection period of 10 years. Sensitivity analysis was performed to analyze the effect of various parameters like dispersivity, temperature and pH dependent minerals reactions on the levels of CO$_2$ consumption in geochemical reactions.
2. **Numerical modelling technique**

The governing equations were solved using COMSOL Multiphysics where transport and geochemistry were solved sequentially. Initial and boundary conditions required in the transport modelling were obtained from background batch geochemical model (BGM) and CO₂ dissolution model respectively. In this study the species Cl⁻ was assumed to be conservative at a constant concentration of 0.5 mol/(kg water). As one of the options, CO₂ can be dissolved on the land surface in the brine that is pumped out of the targeted subsurface reservoir and the resulting CO₂-saturated brine is injected back in the reservoir (Eke at al., 2011; CO₂-DISsOLVED Project). However, the corrosive nature of brine containing dissolved CO₂ can pose a potential risk of corrosion for the injection pipeline. Alternatively, CO₂ can be transported in a separate line parallel to the one injecting the brine and mixing of these two streams can be achieved within the injection well before their injection in the subsurface reservoir (Alfredsson et al., 2013; Gislason and Oelkers, 2014). We assume mixing of CO₂ and brine to take place at bottom of the well right before injection of the mixture in the reservoir at pressure and temperature conditions corresponding to the upper boundary of the reservoir.

### 2.1 Geochemical reactions system

In this study, we have considered three minerals namely calcite, dolomite, and siderite as the rock forming minerals of an assemblage that represents the carbonate layer in the Rose Run Sandstone (Zerai, 2006). The geochemical system describing the water-rock interaction in the reservoir formation is presented in Table 1.
Table 1: Equilibrium and mineral kinetic reactions considered in this study.

| No. | Reactions |
|-----|-----------|
| (R0)$^1$ | $\text{CO}_2^g \leftrightarrow \text{CO}_{2\text{aq}}$ |
| (R1)$^2$ | $\text{H}_2\text{O} + \text{CO}_{2\text{aq}} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$ |
| (R2)$^2$ | $\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$ |
| (R3)$^2$ | $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$ |
| (R4)$^2$ | $\text{Na}^+ + \text{HCO}_3^- \leftrightarrow \text{NaHCO}_3^-\text{aq}$ |
| (R5)$^2$ | $\text{CaHCO}_3^- \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-$ |
| (R6)$^2$ | $\text{MgHCO}_3^- \leftrightarrow \text{Mg}^{2+} + \text{HCO}_3^-$ |
| (R7)$^2$ | $\text{FeHCO}_3^- \leftrightarrow \text{Fe}^{2+} + \text{HCO}_3^-$ |
| (R8)$^2$ | $\text{Calcite} + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-$ |
| (R9)$^2$ | $\text{Dolomite} + 2\text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{HCO}_3^-$ |
| (R10)$^2$ | $\text{Siderite} + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{HCO}_3^-$ |

$^1$Equilibrium reaction constant was taken from the model of Duan and Sun, 2003 modified by Duan et al., 2006.

$^2$Equilibrium reaction constants were opted from the thermo database of LLNL (Delany and Lundeen, 1990) which is the default database of The Geochemist’s Wrokbench (GWB).

Eight reactions (R0 through R7) represent equilibrium reactions whereas the remaining three reactions (R8 through R10) represent the kinetic reactions of three minerals. Reaction (R0) represents the equilibrium between supercritical free-phase CO$_2$ and its dissolved phase and was only considered in the BGM whilst it was discarded in the subsequent reactive transport model in which free-phase CO$_2$ was not considered.

2.1.1 Background BGM

Background BGM was performed for adjusting the initial pressure and temperature as well as for aqueous species concentration in the reservoir. Initial vertical pressure in the domain was defined as hydrostatic pressure based on a pressure gradient of $1\times10^4$ Pa/m below the land surface (Pruess, 2008). The vertical temperature distribution in the domain was based on a geothermal gradient of 0.03°C/m below the land surface (Pruess, 2008).
Brinkman equations (Eq. (8) and (9)) were used in the background BGM for vertical pressure distribution in the reservoir.

Initial concentration values of aqueous species and the related chemical components were obtained in the background BGM by solving the geochemical system at the CO$_2$ partial pressure ($P_{CO_2}$) of $1\times10^3$ Pa, assuming 0.5 M solution of sodium chloride, while allowing the fluid-minerals interaction until equilibrium. Background BGM calculations were performed assuming a constant temperature of 27°C in the reservoir. All the involved geochemical reactions were defined as a function of temperature.

2.1.2 CO$_2$ dissolution modelling

CO$_2$ dissolution modelling was performed to obtain the CO$_2$-saturated brine composition and the related values of chemical component species required as boundary values required for reactive transport modelling in the injection stage. CO$_2$ dissolution modelling was performed at a temperature of 27°C and pressure of 4.1 MPa for a 0.5 M solution of sodium chloride. These temperature and pressure values correspond to the depth of the upper boundary of the modelled reservoir domain. CO$_2$ pressure was increased from background pressure of $1\times10^3$ Pa to 4.1 MPa. In CO$_2$ dissolution modelling, CO$_2$ was dissolved in the brine fluid of composition given in Table 7 and without including any mineral reactions.
2.2 Reactive transport modelling

2.2.1 Conceptual transport model

The reservoir domain used for CO₂-saturated brine injection consists of a 250 m vertically thick and 500 m wide 2D section (Fig. 1). In the reactive transport model, the system was assumed to be axisymmetric with respect to a vertical axis corresponding to the centerline of the injection well. A 2D cylindrical coordinate system was adopted in which “r” and “z” represents the radial and axial coordinate respectively. The 2D axisymmetric model represents a 3D model with the assumption that no variations in any variable exists around the axis of revolution and this reduces the computational burden significantly compared to a more general 3D model. The upper boundary of the reservoir (z = 0) was assumed located at a depth of 400 m below the land surface, whereas the lower boundary (z = −250) was at 650 m below the land surface.

Figure 1. Schematic of subsurface carbonate reservoir used for CO₂-saturated brine injection.
Injection of CO$_2$-saturated brine was performed through a 0.1 m wide inlet boundary at the left-side ($0 \leq r \leq 0.1$) of top boundary of the reservoir. CO$_2$-charged brine was injected in the reservoir at a constant velocity of about 0.5 m/s that results in nearly 16 kg/s of brine and 0.64 kg/s of dissolved CO$_2$ for a period of 10 years. Symmetry condition exists at left vertical boundary ($r = 0$ m). No-flow conditions were assumed for the upper boundary. Outflow of fluid takes place through the right vertical ($r = 500$ m) and bottom boundary in all the scenarios except for scenario 8 (Table 5) where no-flow was also assumed at bottom boundary. The volume fraction of minerals was calculated from their respective weight percent assuming a porosity of 25% (Table 2). This corresponds to the porosity value of a carbonate reservoir located at a depth of 400 m based on the values reported by Al-Awadi et al., 2009.

| Minerals | Weight percent | Volume fraction in solid mass | Volume fraction including a porosity of 25% |
|----------|----------------|------------------------------|------------------------------------------|
| calcite  | 39             | 0.40                         | 0.30                                     |
| dolomite | 60             | 0.59                         | 0.44                                     |
| siderite | 1              | 6.95×10^{-3}                 | 5.21×10^{-3}                             |

### 2.2.2 Reactive transport for mobile species

The following equation was used to define the reactive transport system for aqueous species (mobile ones) written in terms of chemical components ($u$) (COMSOL):
\[
R_f \theta \frac{\partial u}{\partial t} + (1 - K_d \rho_p)u \frac{\partial \theta}{\partial t} - \nabla \cdot [(D_d + D_e)\nabla u] + \nabla \cdot (vu) = \theta r_{\text{kin}} \quad (1)
\]

\[
R_f = 1 + \frac{\rho_{\text{bulk}}}{\theta} K_d \quad (2)
\]

where \(u\) is the vector of concentration [mol/(kg water)] of six chemical components; \(R_f\) is a diagonal matrix of retardation factors; \(\theta\) is the spatially and temporally varying medium porosity [-]; \(\rho_{\text{bulk}} = (1 - \theta)\rho_p\) is the bulk density [kg/(m\(^3\) bulk volume)] of the porous media that is a function of porosity and particle density; \(\rho_p\) is the particle density [kg/m\(^3\)]; \(K_d\) is a diagonal matrix where the diagonal elements include the sorption partition coefficients corresponding to six chemical components [m\(^3\)/kg]; \(D_d\) is the dispersion tensor [m\(^2\)/s]; \(D_e = \theta D_b I\) is the effective diffusion [m\(^2\)/s] defined as a function of medium porosity with \(D_b\) as the diffusion coefficient of chemical components and \(I\) as the identity tensor; \(v\) is the Darcy’s velocity vector [m/s] updated in space and time and finally \(r_{\text{kin}}\) is the reaction term for consumption or production of chemical components [mol/(s-kg water)]. A total of six chemical components involved in transport equation (1) were written as a linear combination of thirteen aqueous species, participating in seven equilibrium and three mineral kinetic reactions, based on the methodology presented by Saaltink et al. (1998) (Appendix A). The reaction term \((r_{\text{kin}})\) and the equations required for speciation are also presented in Appendix A. This reaction term represents the combined effect of all equilibrium as well as mineral kinetic reactions considered in the modelling (Bethke, 2008). Due to the six chemical components in the transport equation, \(u\) is a vector of size six and \(R_f\) and \(K_d\) are matrices of size 6×6. The transport equation (1) is thus a nonlinear partial differential equation in which the variables, \(\rho_p, \rho_{\text{bulk}}\) as well as the matrices \(R_f\) and \(K_d\) and the vector \(r_{\text{kin}}\) are all nonlinear functions of the local concentration of transport chemical component.
In the simulations the diffusion coefficient of CO$_{2\text{aq}}$ (2.22×10$^{-9}$ m$^2$/s) was calculated at a temperature and pressure of 30.75°C and 5.35 MPa in 0.5 M NaCl brine (Al-Rawajfeh, 2004; Hassanzadeh et al., 2008). These pressure and temperature values correspond to the mean values for the modelled reservoir at a depth between 400 m and 650 m. The same diffusion coefficient was assumed for all the transport chemical components (Gherardi et al., 2007). The dispersivity varied between the various modelling scenarios (Table 5). In order to avoid high dispersion at the inlet boundary and associated high dispersive fluxes, the dispersivity was increased smoothly using a Heaviside function where the dispersivity magnitude was increased with distance.

2.2.3 Mass conservation of immobile species (minerals)

Because the minerals involved were considered immobile and therefore do not appear in transport equation (1), additional mass conservation equations for these minerals are needed. Mass conservation for the three involved minerals undergoing kinetic reactions was expressed by the following ordinary differential equation (ODE) (Ahmad et al., 2015):

$$\frac{\partial \mathbf{c}_{\text{m, bulk}}}{\partial t} = -\theta \rho_b \mathbf{r}_m$$  \hspace{1cm} (3)

where $\mathbf{c}_{\text{m, bulk}}$ is a vector of size 3 representing the concentration [mol/(m$^3$ bulk volume)] of three minerals calcite, dolomite and siderite whereas $\rho_b$ is the fluid density. The initial values of mineral concentrations were calculated from their respective initial volume fraction in the porous reservoir for an assumed initial reservoir porosity of 0.25. The reaction term ($\mathbf{r}_m$) is also a vector of size 3 representing the kinetic reactions of three minerals. Mineral kinetic reactions are
defined in terms of rate constants, concentration of aqueous species involved and the reactive surface area of the respective mineral (Lasaga et al., 1994):

\[ r_m = k_m A_m \left[ 1 - \frac{Q_m}{K_m} \right] \quad (4) \]

where \( k_m \) is the temperature-dependent kinetic rate constant of the mineral [mol/(s-m²)], \( A_m \) is the mineral reactive surface area [m²/(kg water)] updated in time and space, \( K_m \) is the equilibrium constant, modelled as a function of temperature and \( Q_m \) is the ion activity product of the mineral.

The temperature dependency of the kinetic rate constants is described by the Arrhenius equation (Lasaga, 1984):

\[ k_m = k_{25} \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] \quad (5) \]

where \( R \) is the gas constant taken equal to 8.314 J/(mol-K), \( T \) is absolute temperature [K], \( E_a \) is the activation energy of the mineral [J/mol] and \( k_{25} \) is the rate constant [mol/(s-m²)] of mineral at 25°C. The parameters and the initial values used for the variables in Eq. (3) through (5) are presented in Table 3 for the minerals calcite, dolomite, and siderite.

**Table 3. Parameters and initial values of variables used in Eq. (3)-(5) for minerals calcite, dolomite, and siderite.**

| Mineral  | \( k_{25} \) [mol/(s-m²)] | \( E_a \) [KJ/mol] | \( A_m \) [m²/(kg water)] | \( c_{m,bulk} \) [mol/(m³ bulk volume)] |
|----------|--------------------------|----------------|--------------------------|----------------------------------|
| calcite  | 1.60×10^{-9}             | 41.87          | 21.67                    | 8216.67                          |
| dolomite | 0.6×10^{-9}              | 41.87          | 31.53                    | 7377.96                          |
| siderite | 0.6×10^{-9}              | 41.87          | 0.37                     | 181.94                           |
The effects of pH do not appear in the mineral’s kinetic rate constants defined by Eq. (5).

The fact that injected CO$_2$-saturated brine is highly acidic, with low-pH, makes it important to define the minerals kinetic rate constant taking this dependence into account. Therefore, the kinetic rate constants ($k_m$) were also modelled using the following expression that considers acid, neutral and base mechanisms (Palandri and Kharaka, 2004):

$$k_m = k_{25,H} a_H^{n_H} \exp \left[ \frac{E_a,H}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] + k_{25,\nu} a_{\nu}^{n_{\nu}} \exp \left[ \frac{E_a,\nu}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right]$$

$$+ k_{25,OH} a_{OH}^{n_{OH}} \exp \left[ \frac{E_a,OH}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right]$$

(6)

where the subscripts $H$, $\nu$, and $OH$ represent the acid, neutral and base mechanisms respectively and $a_H$ represents the activity of H$^+$. The values of parameters used in Eq. (6) are given in Table 4. For minerals calcite and dolomite all three mechanisms were included whereas for mineral siderite, the rate constant was defined by acidic and neutral mechanisms alone (Xu et al., 2007).

| Mineral   | Acid mechanism | Neutral mechanism | Base mechanism |
|-----------|----------------|-------------------|---------------|
|           | $k_{25,H}$ mol/(s-m$^2$) | $n_H$ | $E_{a,H}$ KJ/mol | $k_{25,\nu}$ mol/(s-m$^2$) | $E_{a,\nu}$ KJ/mol | $k_{25,OH}$ mol/(s-m$^2$) | $n_{OH}$ | $E_{a,OH}$ KJ/mol |
| calcite*  | 0.50            | 1.0 | 14.3             | 1.55×10$^{-6}$ | 23.5 | 3.31×10$^{-4}$ | 1.0 | 35.4             |
| dolomite* | 1.74×10$^{-4}$  | 0.5 | 56.7             | 2.51×10$^{-9}$ | 95.3 | 4.27×10$^{-6}$ | 0.5 | 45.7             |
| siderite**| 6.46×10$^{-4}$  | 0.5 | 36.1             | 1.26×10$^{-9}$ | 62.76 | 0.0 | -- | -- |

Table 4. Parameters used in Eq. (6).

---

*Svensson and Dreybrodt, 1992; **Initial values were calculated from initial volume fraction (corresponding to reservoir porosity of 0.25) of minerals in porous rock formation. The minerals reactive surface area was taken equal to 10% of the respective minerals physical surface area (Johnson et al., 2004)."
The mineral reactive surface area was calculated from the number of mineral grains based on the geometric approach (Johnson et al., 2004; Marini, 2007). Mineral kinetic reactions cause variations in concentration of mineral (Eq. (3)) and thus the number of mineral grains. This results in variations in their reactive surface area. The variations in the minerals reactive surface area were modelled using the following relationship:

\[ A_m = 0.1 \left( \frac{A_g}{\theta_{\rho_b} V_g} \right) (M V c_{m, bulk}) \]  

(7)

where \( A_g \) and \( V_g \) are the physical surface area and volume of a mineral grain (assumed spherical with a radius of 1.65×10^{-5} \text{ m}) respectively; \( MV \) is the molar volume of mineral [\text{ m}^3/\text{mol}]. The mineral reactive surface area is much lower than its geometric surface area and was thus taken equal to 10\% of the latter (Johnson et al., 2004).

2.2.4 Velocity field for the transport system

Brinkman equations were used to describe the velocity field in the reactive transport system formed by Eq. (1) and (2). Brinkman equations combine the continuity equation with the momentum balance equation to define the flow in porous media:

\[
\frac{\partial (\rho \theta \rho_b)}{\partial t} + \nabla \cdot (\rho_b \theta \mathbf{v}) = 0 \tag{8}
\]

\[
\frac{\rho_b}{\theta} \left[ \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \right] \mathbf{v} = -\nabla p + \nabla \cdot \left[ \mu_b \left\{ (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) - \frac{2}{3} (\nabla \cdot \mathbf{v}) \mathbf{I} \right\} \right] - \left( \frac{\mu_b}{\kappa} \right) \mathbf{v} + \mathbf{F} \tag{9}
\]

where \( \rho_b \) is the density [\text{kg/m}^3]; \( \mu_b \) is the dynamic viscosity [\text{kg/(m-s)}] of CO\text{2}-saturated NaCl brine; \( p \) is the pressure [\text{Pa}]; \( \kappa \) is the permeability of the porous medium [\text{m}^2]. Gravitational influence was accounted through the force term \( \mathbf{F} = -\rho_b g \) with \( g \) as the gravitational
acceleration vector \([9.81 \text{ m/s}^2]\). The use of Brinkman equations for solving the flow problem in porous media is reported in various studies (Popov et al., 2009; Gulbransen et al., 2010; Sajjadi et al., 2014; Chabonan et al., 2015; Golfier et al., 2015; Basirat et al., 2015). The density and viscosity of brine were calculated as a function of temperature, pressure and dissolved species \((\text{Na}^+, \text{Cl}^-, \text{and CO}_{2\text{aq}})\). However, in this study the values of temperature and pressure were based on constant vertical gradients in the reservoir for computation of brine density and viscosity. The brine density was computed using the model of Duan et al. (2008) whereas the viscosity was based on the formulations presented by Man and Duan (2009). The equations related to \text{CO}_2- saturated brine density and viscosity are presented in the Appendix B and Appendix C respectively.

**2.2.5 Heat transfer in porous media**

The temperature of the injected \text{CO}_2-saturated brine can be expected to be relatively lower than the prevailing temperature in the reservoir. The example may be the heat recovery from the hotter brine, either for power production or heating purposes that is pumped out of the reservoir and its subsequent injection back in the reservoir carrying dissolved \text{CO}_2 (\text{CO}_2\text{-DISSOLVED project}; Wolf et al., 2009; Ganjdanesh et al., 2014). In this study brine injection was performed at varying temperatures (27, 17 and 7°C). Thus the injected brine may shift the cooling effects through thermal exchanges between the resident brine and the porous media in the reservoir. The resulting cooling in the reservoir may affect the geochemical reactions defined as a function of temperature. Heat-exchange between the injected \text{CO}_2-saturated brine and the porous media of the reservoir was modelled using the following heat transfer equation (Bear and Bachmat, 1990; COMSOL):
\[(\rho C_p)_{eq} \frac{\partial T}{\partial t} + \rho_b C_{p,b} \mathbf{v} \cdot \nabla T = \nabla \cdot (\lambda_{eq} \nabla T) + \nabla \cdot (k_d \nabla T) \tag{10}\]

where

\[(\rho C_p)_{eq} = (1 - \theta)\rho_{pm} C_{p,pm} + \theta \rho_b C_{p,b} \tag{11}\]

and

\[\lambda_{eq} = (1 - \theta)\lambda_{pm} + \theta \lambda_b \tag{12}\]

where \(T\) is the temperature [K]; \((\rho C_p)_{eq}\) is the equivalent volumetric heat capacity of fluid-solid system at constant pressure [J/(m\(^3\)-K)]; \(\lambda_{eq}\) is the equivalent volumetric thermal conductivity of fluid-solid system [W/(m-K)]; \(\mathbf{v}\) is the fluid velocity representing the Darcy velocity defined through Brinkman equations; \(\rho_{pm}\) is density of the porous medium; \(C_{p,pm}\) is heat capacity of the porous media [J/(kg-K)]; \(C_{p,b}\) is heat capacity of the fluid [J/(kg-K)]; \(\lambda_{pm}\) is thermal conductivity of porous media; \(\lambda_b\) is thermal conductivity of the brine [W/(m-K)] and \(k_d = \rho_b C_{p,b} D\) is the dispersive thermal conductivity. Thermal dispersion \((D)\) was defined as a function of thermal dispersivity taken equal to 1 m. Thermal conductivity of porous media was taken equal to 2.51 W/(m-K) and specific heat capacity of rock was taken equal to 920 J/(kg-K) (Pruess, 2005). The relations for heat capacity and thermal conductivity of CO\(_2\)-saturated brine are presented in Appendix D.

### 2.2.4 Medium porosity

Over the time, minerals dissolution or precipitation causes changes in mineral fractions (through Eq. (3)) which in turn change the porosity of the porous media. The temporal and spatial
variation in porosity was modelled as a function of variations in volume fractions of the minerals in the porous media by:

\[ \theta = 1 - VF_{rock,p} \]  

where \( VF_{rock,p} = \sum_m VF_{m,p} \) is sum of volume fractions of all the minerals forming the porous rock media and the term \( VF_{m,p} = v_{m,p}/V_{rock,p} \) \([\text{m}^3 \text{ of mineral}/(\text{m}^3 \text{ of porous rock medium})]\) is the volume fraction of the mineral expressed as the ratio of the mineral volume to the total volume of porous rock including porosity. It is important to mention here that none of the minerals was allowed to completely dissolve and disappear from the transport domain. Medium porosity was kept below unity by setting a minimum threshold concentration value of all kinetic minerals equal to \(1 \times 10^{-7} \) \([\text{mol}/(\text{m}^3 \text{ bulk volume})]\) in Eq. (3).

### 2.2.5 Medium permeability

The initial value of medium permeability was computed from initial values of porosity and specific surface area of rock using the Kozeny-Carman relation (Bear and Cheng, 2010):

\[ \kappa_0 = C \frac{\theta_0^3}{(1-\theta_0)^2(A_{rock,SSAV})^2} \]  

where \( C \) is taken equal to 0.2 and \( A_{rock,SSAV} \) is the specific surface area of the solid rock per unit volume of solid rock \([\text{m}^2/\text{m}^3]\) which depends on the mineral composition forming the porous media (Bear and Cheng, 2010). For the considered combination of initial porosity (0.25) and initial minerals volume fraction (Table 2) we found an initial permeability of the reservoir as \(6.46 \times 10^{-13} \text{ m}^2\). Evolution of medium permeability was modelled as a
function of varying medium porosity by the following Kozeny-Carman relation (Xu et al., 2014):

\[
\kappa = \kappa_0 \frac{(1-\theta_0)^2 \theta^2}{(1-\theta)^2 \theta_0^2} \tag{15}
\]

2.2.4 Various injection scenarios

Eight scenarios of reactive transport modelling were performed (Table 5) for an injection period of 10 years to investigate the role of various parameters on the mass conversion/consumption of CO\(_2\) in reactions and variations in medium porosity and permeability linked to minerals dissolution and precipitation. In all these scenarios geochemical reactions (equilibrium as well as minerals kinetics) were defined as a function of temperature.

A constant temperature of 27°C (T constant) was considered in the reservoir in scenarios 1 through 5 and in scenario 8. Sorption of species on the rock surfaces was considered in scenario 2 through a sorption partition coefficient (K\(_d\)) taken equal to 2.50x10\(^{-4}\) m\(^3\)/kg (Heller and Zoback, 2014; Ahmad et al., 2015). The significance of various parameters like dispersivity, temperature and the kinetic rate constant of minerals were also investigated as part of the sensitivity analysis. The role of temperature was studied in scenarios 6 and 7. In scenarios 6 and 7, the brine was injected at a temperature of 17°C and 7°C respectively thereby modelling the heat transport and its exchange between the injected cooler brine and the porous media (T flow). In scenario 8, the role of pH on the minerals kinetic rate constant was investigated. In this scenario, the minerals reaction rate...
constants were defined as a function of pH by employing the rate expression defined in Eq. (6).

### Table 5. Various brine injection scenarios.

| Scenarios | Injection temperature \((T_{\text{inj}})\) [°C] | Temperature conditions in the reservoir | Expression for mineral kinetic rate constant | Sorption | Longitudinal dispersivity \((D_L)\) | Transverse dispersivity \((D_T)\) |
|-----------|------------------------------------------|----------------------------------------|-------------------------------------------|----------|---------------------------------|---------------------------------|
| 1         | 27                                       | constant                               | Eq. (5)                                   | No       | 50                              | 5                               |
| 2         | 27                                       | constant                               | Eq. (5)                                   | Yes      | 50                              | 5                               |
| 3         | 27                                       | constant                               | Eq. (5)                                   | No       | 10                              | 1                               |
| 4         | 27                                       | constant                               | Eq. (5)                                   | No       | 100                             | 10                              |
| 5         | 27                                       | constant                               | Eq. (5)                                   | No       | 100                             | 50                              |
| 6         | 17                                       | flow                                   | Eq. (5)                                   | No       | 100                             | 50                              |
| 7         | 7                                        | flow                                   | Eq. (5)                                   | No       | 100                             | 50                              |
| 8         | 27                                       | constant                               | Eq. (6)                                   | No       | 100                             | 50                              |

**2.2.5 Calculation of mass consumption of CO\(_2\) in reactions**

In addition to these reactive transport scenarios given in Table 5, an equal number of mass transport scenarios were also performed where no geochemical reactions (those presented in Table 1) were included. The comparison of mass balance between the mass transport scenario and the corresponding reactive transport scenario gives an accurate estimate of CO\(_2\) mass conversion in geochemical reactions. The consumption of CO\(_2\) in geochemical reactions was calculated based on the cumulative quantities of CO\(_{2aq}\) injected in the reservoir, mass stored in the aqueous and adsorbed states, and the mass leaving the reservoir domain through the outlet boundary over the considered injection time of 10 years.
2.2.5 Initial and boundary values

The initial values of pressure, temperature, concentration of dissolved species and related chemical components were obtained from the background BGM. The boundary values of involved six chemical components representing the composition of CO$_2$-saturated brine to be injected were obtained from CO$_2$ dissolution modelling. Boundary values of primary and secondary species were defined in terms of transport chemical components. The initial numerical solution from the background BGM was stored and used as initial conditions in the subsequent transport modelling. This approach requires only definition of the boundary concentration values of the chemical components. Boundary values in terms of chemical components obtained from CO$_2$ dissolution modelling performed at CO$_2$ pressure of 4.1 MPa and temperature of 27°C are presented in Table 6.

Table 6. Boundary values (sub-index $bc$) for chemical components.

| Chemical component* | Concentration [mol/(kg water)] |
|--------------------|--------------------------------|
| $u$HCO$_3$bc       | 5.915×10$^{-3}$                |
| $u$Na$_{bc}$       | 0.5                            |
| $u$Ca$_{bc}$       | 2.670×10$^{-3}$                |
| $u$Mg$_{bc}$       | 2.568×10$^{-4}$                |
| $u$Fe$_{bc}$       | 3.058×10$^{-5}$                |
| $u$CO$_2$bc        | 0.902                          |

* $u$ represents the chemical component.
3 Results

3.1 Composition of resident brine in the reservoir

The composition of resident brine in the reservoir was obtained from the background BGM. For a constant temperature of 27°C assumed in the reservoir, the brine composition is given in column 2 of Table 7. For temperature gradient considered in the reservoir, the brine composition at lower boundary of the reservoir is given in column 3 of Table 7. The solution equilibrated at pH values of 7.26 and 7.29 at top and bottom boundaries of the reservoir respectively. At a background CO₂ pressure of 1×10³ Pa, the dissolution and precipitation of the minerals were found to be negligible, and this provides justification of assuming constant mineral reactive surface area as well as constant porosity and permeability of the reservoir in the background BGM. Geochemical conditions obtained from the background BGM were in equilibrium with respect to the considered carbonate minerals calcite, dolomite and siderite.

| Species          | Concentration [mol/(kg water)] (top boundary of the reservoir) | Concentration [mol/(kg water)] (lower boundary of the reservoir) |
|------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| CO₂aq            | 2.885×10⁻⁴                                                  | 2.436×10⁻⁴                                                  |
| HCO₃⁻            | 4.582×10⁻³                                                  | 4.221×10⁻³                                                  |
| Na⁺              | 0.499                                                        | 0.499                                                        |
| Cl⁻              | 0.500                                                        | 0.500                                                        |
| H⁺               | 5.518×10⁻⁸                                                  | 5.079×10⁻⁸                                                  |
| OH⁻              | 4.012×10⁻⁷                                                  | 5.147×10⁻⁷                                                  |
| CO₃²⁻            | 1.606×10⁻⁵                                                  | 1.655×10⁻⁵                                                  |
| NaHCO₃aq         | 1.243×10⁻⁵                                                  | 1.096×10⁻⁴                                                  |
| Ca²⁺             | 2.617×10⁻³                                                  | 2.398×10⁻³                                                  |
| Mg²⁺             | 2.529×10⁻⁴                                                  | 2.247×10⁻⁴                                                  |
Fe$^{2+}$ 2.990×10^{-5} 2.676×10^{-5}
CaHCO$_3^+$ 5.308×10^{-5} 4.595×10^{-5}
MgHCO$_3^+$ 3.938×10^{-6} 3.284×10^{-6}
FeHCO$_3^+$ 6.865×10^{-7} 5.405×10^{-7}

3.2 Composition of CO$_2$-saturated brine

CO$_2$ solubility modelling was performed at the pressure (4.1 MPa) and temperature (27°C) conditions representative of the upper boundary of the reservoir. In the solubility modelling, CO$_2$ was dissolved in the resident brine of composition given in column 2 of Table 7. Table 8 shows the composition of CO$_2$-saturated brine, to be injected in the geological reservoir, obtained from solubility modelling performed at 27°C. Concentration of dissolved CO$_2$ in the resulting CO$_2$-saturated brine increased from a value of 2.89×10^{-4} mol/(kg water) to a value of 0.902 mol/(kg water). Increased concentration of dissolved CO$_2$ resulted in a decrease in pH of brine from 7.26 to a value of 3.78. According to the solubility modelling performed at a temperature of 27°C and pressure of 4.1 MPa, about 25.2 kg of brine fluid is needed to dissolve one kg of CO$_2$.

| Species          | concentration [mol/(kg water)] |
|------------------|--------------------------------|
| CO$_2$aq         | 0.902                          |
| HCO$_3^-$        | 4.738×10^{-3}                  |
| Na$^+$           | 0.499                          |
| Cl$^-$           | 0.5                            |
| H$^+$            | 1.669×10^{-4}                  |
| OH$^-$           | 1.327×10^{-10}                 |
| CO$_3^{2-}$      | 5.526×10^{-9}                  |
| NaHCO$_3$aq      | 1.285×10^{-3}                  |
| Ca$^{2+}$        | 2.615×10^{-3}                  |
\[
\begin{array}{|c|c|}
\hline
\text{Ion} & \text{Concentration} \\
\hline
\text{Mg}^{2+} & 2.528 \times 10^{-4} \\
\text{Fe}^{2+} & 2.987 \times 10^{-5} \\
\text{CaHCO}_3^+ & 5.484 \times 10^{-5} \\
\text{MgHCO}_3^+ & 4.070 \times 10^{-6} \\
\text{FeHCO}_3^+ & 7.092 \times 10^{-7} \\
\hline
\end{array}
\]

The saturation state of resulting CO\(_2\)-saturated brine fell well below unity and thus got
under-saturated with respect to the considered minerals calcite, dolomite and siderite (Table 9). The lower saturation state of CO\(_2\)-saturated brine to be injected with respect to
the minerals involved may cause intense and successive dissolution of the minerals
particularly near the injection point in the reservoir during the injection stage.

**Table 9.** Saturation state of CO\(_2\)-saturated brine with respect to considered carbonate minerals.

| Mineral   | Saturation state of CO\(_2\)-saturated brine with respect to minerals |
|-----------|---------------------------------------------------------------------|
| Calcite   | 3.42 \times 10^{-4}                                                 |
| Dolomite  | 1.17 \times 10^{-7}                                                 |
| Siderite  | 3.42 \times 10^{-4}                                                 |

3.3. **Reactive transport**

3.3.1. **Mass of CO\(_{2aq}\) injected in the reservoir**

For brine injection at a constant velocity of 0.5 m/s through 0.1 m wide inlet boundary,
nearly \(2 \times 10^5\) tonnes of CO\(_{2aq}\) were injected in the reservoir over the period of 10 years in
all the injection scenarios. However, small variations in mass injection were observed due
to varying dispersive and diffusive mass fluxes through the injection boundary between
the scenarios (Fig. 2a and b).
The overall mass balance of CO$_2$aq [tonnes] injected in the reservoir after simulation time of 10 years is presented in Table 10. The maximum injected mass was found nearly 2.42×10$^5$ tonnes in scenario 8. Total mass of CO$_2$aq injected in the reservoir represents the sum of the mass due to advection, dispersion and diffusion through the injection boundary. The split of injected mass is also presented in terms of advective, dispersive and diffusive mass fluxes through the inlet boundary. The same advective mass inflow results from the same injection velocity used in all the scenarios. However, observed variations in CO$_2$aq mass injection between the scenarios is mainly due to different dispersive fluxes. In scenario 8, the complete dissolution of medium in near vicinity of the injection boundary caused higher dispersive fluxes resulting in higher mass injection compared to rest of the scenarios.
### Table 10. CO$_{2aq}$ mass balance [in tonnes] in various injection scenarios after 10 years of simulation.

| Injection scenarios                        | Scenario 1   | Scenario 2   | Scenario 3   | Scenario 4   | Scenario 5   | Scenario 6   | Scenario 7   | Scenario 8   |
|-------------------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Total mass injected in the reservoir      | 2.04×10$^5$  | 2.05×10$^5$  | 2.01×10$^5$  | 2.02×10$^5$  | 2.18×10$^5$  | 2.18×10$^5$  | 2.17×10$^5$  | 2.42×10$^5$  |
| Mass entered due to advection             | 2.00×10$^5$  | 2.00×10$^5$  | 2.00×10$^5$  | 2.00×10$^5$  | 2.00×10$^5$  | 2.00×10$^5$  | 2.00×10$^5$  | 2.00×10$^5$  |
| Mass entered due to diffusion             | 2.77×10$^6$  | 4.07×10$^6$  | 3.62×10$^6$  | 7.43×10$^6$  | 6.70×10$^6$  | 6.04×10$^6$  | 5.60×10$^6$  | 4.68×10$^6$  |
| Mass entered due to dispersion            | 3.50×10$^4$  | 5.24×10$^4$  | 7.14×10$^4$  | 1.96×10$^4$  | 1.75×10$^4$  | 1.75×10$^4$  | 1.75×10$^4$  | 4.15×10$^4$  |
| Mass left the domain (bottom boundary)    | 7.24×10$^1$  | 6.50×10$^1$  | 2.92×10$^1$  | 1.12×10$^1$  | 9.57×10$^1$  | 9.59×10$^1$  | 9.57×10$^1$  | 0.00         |
| Mass left the domain (right side boundary)| 3.39×10$^1$  | 3.16×10$^1$  | 3.51×10$^1$  | 3.37×10$^1$  | 3.38×10$^1$  | 3.09×10$^1$  | 3.09×10$^1$  | 6.02×10$^1$  |
| Mass stored in aqueous state              | 1.77×10$^5$  | 5.91×10$^5$  | 1.84×10$^5$  | 1.82×10$^5$  | 1.84×10$^5$  | 1.84×10$^5$  | 1.83×10$^5$  | 2.03×10$^5$  |
| Mass stored in adsorbed state             | 0.00         | 1.24×10$^3$  | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| Mass consumed in geochemical reactions    | 1.95×10$^5$  | 2.28×10$^5$  | 1.44×10$^4$  | 2.57×10$^4$  | 2.56×10$^4$  | 2.57×10$^4$  | 2.60×10$^5$  | 3.97×10$^4$  |
| Mass conversion of CO$_{2aq}$ (%)         | 9.61         | 1.11×10$^1$  | 7.17         | 1.17×10$^1$  | 1.18×10$^1$  | 1.18×10$^1$  | 1.20×10$^1$  | 1.65×10$^1$  |
| Error in mass balance (%)                 | -1.84×10$^1$ | -1.08×10$^1$ | -4.56×10$^1$ | -1.94×10$^1$ | -6.36×10$^1$ | -6.44×10$^1$ | -6.44×10$^1$ | -4.85×10$^1$ |
| Mass left the domain (%)                  | 3.57         | 4.71×10$^2$  | 1.47         | 5.10         | 4.41         | 4.42         | 4.41         | 2.49×10$^2$  |

**3.3.2. CO$_{2aq}$ mass balance and its consumption in reactions**

Dissolution of minerals calcite, dolomite, and siderite resulted in the conversion thus the consumption of CO$_2$. Dissolution of calcite causes conversion of CO$_2$ into other ions H$^+$ and HCO$_3^-$ in a ternary CaCO$_3$-H$_2$O-CO$_2$ system (Kaufmann and Dreybrodt, 2007). However, precipitation of these minerals releases CO$_2$ back into the brine (Dreybrodt et al., 1997). Dissolution of carbonate minerals in the reservoir converted the mass of injected dissolved CO$_2$ into its associated bicarbonate ions. This is a result of the pH-buffering effect of the carbonate dissolution reactions, and the corresponding transformation of carbonic acid into bicarbonate (e.g., sum of reactions R1 + R10). The consumption of injected CO$_{2aq}$ in geochemical reactions in various scenarios over the period of 10 years is presented in Fig. 3. Fig. 3a and b show the cumulative mass consumption whereas Fig. 3c and d show its corresponding percentage mass.
consumption. From the mass balance calculations, the cumulative mass consumption of CO$_2$ in chemical reactions was found to be $1.95 \times 10^4$, $2.28 \times 10^4$, $1.44 \times 10^4$, $2.57 \times 10^4$, $2.56 \times 10^4$, $2.57 \times 10^4$, $2.60 \times 10^4$, $3.02 \times 10^4$ tonnes in scenarios 1 through 8 respectively (Fig. 3a, b and Table 10). In scenarios 1 through 8 the mass consumption of CO$_2$ was found as 9.61%, 11.09%, 7.17%, 11.72%, 11.76%, 11.83%, 11.97% and 16.47% respectively of its total mass injected (Fig. 3c, d and Table 10).

**Figure 3.** Mass consumption of CO$_2$ in geochemical reactions; cumulative mass conversion in scenarios 1 to 5 (a) and in scenarios 5 to 8 (b); percent mass conversion in scenarios 1 to 5 (c) and in scenarios 5 to 8 (d).
Keeping rest of the parameters the same, the sorption process included in scenario 2 resulted in higher cumulative mass consumption of CO$_2$ in geochemical reactions as compared to corresponding no-sorption scenario 1. Cumulative mass consumption of CO$_2$ in sorption scenario 2 is higher than that in no-sorption scenario 1 over the entire simulation time (Fig. 3a). However, different trends are observed for percent mass consumption in scenarios 1 and 2. In the initial times, the percent mass consumption is lower in sorption scenario 2 compared to no-sorption scenario 1 whereas it becomes the opposite towards the later times (Fig. 3c). It can also be observed that for the used partition coefficient in scenario 2, the injected mass of CO$_{2aq}$ is partitioned between the aqueous state (28.78%) and the adsorbed state (60.19%) in the reservoir (Table 10).

Higher dispersivity values used in scenario 5 caused higher cumulative and percent mass consumption of CO$_2$ as compared to the rest of the corresponding scenarios 1, 3 and 4 (Fig. 3a and c). The lowest dispersivity resulted in lowest mass consumption in scenario 3. For the range of temperature (7 to 27°C) used in this study, the effects of temperature were observed to be negligible on the mass consumption of CO$_2$ in reactions. Comparison between the mass consumption in scenarios 5, 6 and 7 shows insignificant effect of temperature on the mass consumption of CO$_2$ in reactions (Fig. 3b and d). The mineral kinetic reactions defined as a function of pH in scenario 8, caused increased minerals dissolution with associated higher pore volume and higher mass consumption of CO$_2$ in reactions.
A maximum of 5.10% of injected mass left the transport domain through the outflow boundaries in scenario 4 over the period of 10 years. Only insignificant quantities flow out of the domain in scenarios 2 and 8 (less than about 0.05%). Sorption in scenario 2 decreases the quantities in aqueous state and reduces the mass outflow. However, in scenario 8 the lower mass outflow is mainly due to the fact that the bottom boundary was assumed to be insulated with no-flow conditions and thus the outflow could only take place through the right sided boundary. In scenario 8, the bottom boundary was modelled with no-flow conditions for improved solver convergence.

3.3.3. Medium porosity and permeability variations

Injected brine saturated with CO₂ was not only low in pH but also highly under-saturated with respect to the carbonate minerals calcite, dolomite and siderite. Geochemical interactions of injected brine with the reservoir minerals initiated mineral dissolution in the vicinity of the injection point. In the reactive transport model the minerals were allowed to either dissolve or precipitate depending upon the geochemical conditions driven by injected CO₂-saturated brine. The reaction zone advanced with the lateral and downward movement of CO₂-saturated brine in the reservoir.

Dissolution and precipitation of minerals resulted in variations in medium porosity and permeability. Fig. 4 shows the porosity variations in the vicinity of the injection point, for the reactive transport scenarios 1 through 8, after 10 years of simulation time. In scenarios 1 through 5, the medium porosity reached a value of 0.437 from its initial value of 0.25 in the vicinity of the injection point and extending up to about 25 m in the reservoir (Fig. 4a to e). In these
scenarios, the maximum value of porosity was observed as same with the exception of its spread linked to the different values of dispersivity. The highest porosity values were observed as 0.36 and 0.32 in scenarios 6 and 7 respectively, which shows that decrease in temperature lowered the increase in porosity close to injection point compared to scenarios 1 through 5 (Fig. 4f and g).

However, low temperatures at the injection point and cooling transfer in the reservoir in scenarios 6 and 7 caused overall higher mineral dissolution towards deeper place with an overall higher increase in pore volume in these scenarios compared to scenarios 1 through 5 (Table 11). The highest porosity increase was observed in scenario 8 (Fig. 4h) where it became nearly 1 (upper porosity limit of 0.999) due to almost complete dissolution of carbonate minerals. In scenario 8, a decrease in porosity was also observed due to minerals precipitation taken place in the reservoir. In this scenario, the medium porosity decreased to a value of 0.20 from the initial porosity value of 0.25 in some locations in the reservoir. Variations in permeability were also observed as linked to the minerals dissolution and precipitation. The medium permeability reached a value of $1.33 \times 10^{-5}$ m$^2$ from an initial value of $6.46 \times 10^{-13}$ m$^2$ near the inlet boundary in scenario 8.
Figure 4. Variations in medium porosity [-] in various reactive transport scenarios from initial porosity value of 0.25; (a) scenario 1; (b) scenario 2; (c) scenario 3; (d) scenario 4; (e) scenario 5; (f) scenario 6; (g) scenario 7; and (h) scenario 8.
Variations in total pore volume of the reservoir resulted from minerals dissolution and precipitation over time. Total pore volume in the reservoir in various reactive transport scenarios at the end of the 10 years of simulation period is presented in Table 11. Comparing the reactive transport scenarios, it can be observed that higher mineral dissolution resulted in higher total pore volume in the reservoir (Table 11) and higher quantities of CO$_2$ mass consumption through geochemical reactions (Table 10).

Table 11. Variations in total pore volume in the reservoir after 10 years.

| Scenario | initial pore volume [$m^3$] | increase in pore volume [$m^3$] | % increase |
|----------|-----------------------------|---------------------------------|------------|
| Scenario 1 | 4.91×10$^7$ | 1.55×10$^4$ | 3.17×10$^{-2}$ |
| Scenario 2 | 4.91×10$^7$ | 1.81×10$^4$ | 3.70×10$^{-2}$ |
| Scenario 3 | 4.91×10$^7$ | 1.13×10$^4$ | 2.31×10$^{-2}$ |
| Scenario 4 | 4.91×10$^7$ | 2.03×10$^4$ | 4.14×10$^{-2}$ |
| Scenario 5 | 4.91×10$^7$ | 2.06×10$^4$ | 4.19×10$^{-2}$ |
| Scenario 6 | 4.91×10$^7$ | 2.06×10$^4$ | 4.20×10$^{-2}$ |
| Scenario 7 | 4.91×10$^7$ | 2.08×10$^4$ | 4.24×10$^{-2}$ |
| Scenario 8 | 4.91×10$^7$ | 3.30×10$^4$ | 6.73×10$^{-2}$ |

4. Discussions

As a result of the solubility of CO$_2$ in the NaCl brine, pH of CO$_2$-saturated brine dropped down to a value of 3.78 from its initial value of 7.26 in the resident brine. CO$_2$ was dissolved in the brine in the absence of any geochemical interactions with the minerals. This significant drop in pH is mainly due to the absence of any buffer to the solution which is otherwise provided by the carbonate minerals in the subsurface (Lagneau, et al., 2005; Hellevang, 2006; Pokrovsky et al. 2009; Gaus, 2010). Thus dissolution of CO$_2$ in the brine turned the resulting CO$_2$-saturated brine more acidic with high geochemical reactivity.
The injected CO$_2$-saturated brine that was highly under-saturated with respect to carbonate minerals caused intense dissolution of these minerals resulting in an increase in medium porosity in close vicinity of the injection point. Over the time, the continued production of Ca$^{2+}$, Mg$^{2+}$, Fe$^{2+}$, HCO$_3^-$ ions into the brine solution from minerals dissolution and their transport in the reservoir brought the chemical conditions towards saturation with respect to these minerals away from the injection point. This resulted in lowering the dissolution of minerals away from the injection point. In addition to minerals dissolution we also observed their precipitation in some locations where the brine solution became saturated with respect to minerals. This resulted in a decrease in porosity particularly in scenario 8 where the minerals kinetics was modelled as pH dependent.

In the initial times, the sorption process reduced the mass in aqueous state participating in reactions, which resulted in lower mass consumption of CO$_2$ in scenario 2 compared to that in scenario 1. However, over the time, the sorption process lowered the concentration of species (Ca$^{2+}$, Mg$^{2+}$, Fe$^{2+}$, HCO$_3^-$, CaHCO$_3^+$, MgHCO$_3^+$ and FeHCO$_3^+$) in aqueous phase, resulting in lower saturation state with respect to minerals (calcite, dolomite, and siderite) than the saturation states prevailing in scenario 1. This produced higher mineral dissolution with higher percent mass consumption in scenario 2 than in scenario 1 at later times. Although the cumulative mass consumed in scenario 4 is higher than that in scenario 5, the percent mass consumption is lower in the former than that in the latter. This is due to the fact that the percent mass consumption was calculated in relation to the cumulative mass inflow. Higher dispersivity in scenario 4 caused higher mass inflows than in scenario 5, resulting in lower percent mass consumption in scenario 4 compared to scenario 5.
The lowest temperature (7°C) at the inlet boundary in scenario 7 decreased the mineral dissolution due to lower reaction rates with decrease in temperature. However, the lower temperature (7°C) at the inlet boundary, and consequently in the reservoir, increased the reaction equilibrium constant of the minerals calcite, dolomite and siderite. The equilibrium constant in scenario 7 were found to be 93.07, 1409.9 and 1.32 for minerals calcite, dolomite and siderite respectively compared to the corresponding values of 48.36, 283.91 and 0.55 in the scenarios where the inlet temperature was 27°C. Due to increase in equilibrium constant of the minerals with decreasing temperature, higher concentration of reaction products (e.g. Ca$^{2+}$ and HCO$_3^-$ for calcite) and lower concentration of reactants (H$^+$) are needed to reach the saturation state with respect to the respective minerals. Thus, over the time the minerals continued to dissolve despite the lower mineral reaction rate with decreasing temperature, and reached almost the same mineral dissolution with same mass consumption of CO$_2$ in reactions and increase in pore volume in scenarios 5 and 6 (Table 10 and 11).

In scenario 8, the mineral kinetics defined as a function of pH resulted in highest reaction rates of minerals driven by lower pH CO$_2$-saturated brine. For example, for calcite the pH dependent reaction rate constant increased to a value of 7.13×10$^{-5}$ mol/(s-m$^2$) compared to 1.79×10$^{-9}$ mol/(s-m$^2$) when the reaction rate was defined without considering the pH dependence. The increased reaction rate constant resulted in almost complete mineral dissolution, causing the medium porosity to become almost 1 in close vicinity of the inlet boundary.
4. Conclusions

In this study we have explored a relatively safer way of CO$_2$ geological storage in relatively shallow carbonate reservoir. Injection of CO$_2$-saturated brine was performed in the subsurface carbonate reservoir at a depth of 400 m below the land surface. Injected brine saturated with CO$_2$ being low in pH and highly under-saturated with respect to the considered carbonate minerals exhibited higher minerals reactivity with significant mass consumption of CO$_2$. Almost complete dissolution of carbonate minerals was observed in close vicinity of the injection point due to their intense dissolution driven by low-pH CO$_2$-saturated brine.

The variations in minerals dissolution and precipitation, related variations in medium porosity and permeability and mass consumption of injected CO$_2$$_{aq}$ in geochemical reactions were seen as a complex function of spatial distribution of temperature, dispersivity, pH and the sorption process when included in the transport analysis. The proper evaluation of sorption properties of carbonate minerals is very important for the quantification of additional CO$_2$ mass stored in adsorbed state in the reservoir.

This study has quantified the mass of CO$_2$ stored in aqueous and adsorbed states, its mass converted into other ions in relation to its mass injected in the reservoir during the injection period. Storage of injected mass of dissolved CO$_2$ in the reservoir occurred mainly in the form of aqueous and adsorbed states and ionic trapping through mineral reactions in the carbonate rock formation. Although negligible mineral trapping of CO$_2$ was observed in the modelled carbonate rock formation, this study provided insights into the response of carbonate rock formation to injected CO$_2$$_{aq}$. Large volumes of brine may involve for injection of bulk quantities of dissolved
CO₂. For safer and increased sequestration of CO₂ in the form of mineral trapping, future modelling studies may focus on the injection of CO₂aq in multi-mineralogical systems like sandstone or basalt rock formations.

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Appendix A: Finding the component species involved in the reactive transport system from the aqueous species participating the equilibrium and mineral kinetic reactions

The equilibrium and kinetic reactions ((R1)-(R10) in Table 1) involve thirteen aqueous chemical species (HCO$_3^-$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, Fe$^{2+}$, CO$_{2aq}$, H$^+$, OH$^-$, CO$_3^{2-}$, NaHCO$_3$aq, CaHCO$_3^+$, MgHCO$_3^+$, FeHCO$_3^+$). Using the formulation of Saaltink et al. 1998, six chemical components were written as a linear combination of involved thirteen aqueous species:

\[
\begin{align*}
    u_{HCO_3} &= c_{HCO_3} - c_{H^+} + c_{OH^-} + 2c_{CO_3^{2-}} + c_{NaHCO_3} + c_{CaHCO_3} + c_{MgHCO_3} + c_{FeHCO_3} \\
    u_{Na} &= c_{Na^+} + c_{NaHCO_3} \\
    u_{Ca} &= c_{Ca^{2+}} + c_{CaHCO_3} \\
    u_{Mg} &= c_{Mg^{2+}} + c_{MgHCO_3} \\
    u_{Fe} &= c_{Fe^{2+}} + c_{FeHCO_3} \\
    u_{CO_2} &= c_{CO_{2aq}} + c_{H^+} - c_{OH^-} - c_{CO_3^{2-}} 
\end{align*}
\]

(A.1)

A vector of component concentrations ($u$) that is involved in the transport Eq. (1) and (2) can be written as under:
By expressing all the aqueous species involved in the geochemical reactions (equilibrium plus kinetic) into chemical component species, the required number of transport equations are now reduced to six (number of chemical component species) from originally thirteen (number of aqueous species). The reaction term involved in the transport Eq. (1) can be written in the following form:

\[ r_{\text{kin}} = \begin{cases} 
  r_{\text{HCO}_3} &= 2r_{\text{calcite}} + 4r_{\text{dolomite}} + 2r_{\text{siderite}} \\
  r_{\text{Na}} &= 0r_{\text{calcite}} + 0r_{\text{dolomite}} + 0r_{\text{siderite}} \\
  r_{\text{Ca}} &= r_{\text{calcite}} + r_{\text{dolomite}} + 0r_{\text{siderite}} \\
  r_{\text{Mg}} &= 0r_{\text{calcite}} + r_{\text{dolomite}} + 0r_{\text{siderite}} \\
  r_{\text{Fe}} &= 0r_{\text{calcite}} + 0r_{\text{dolomite}} + r_{\text{siderite}} \\
  r_{\text{CO}_2} &= -r_{\text{calcite}} - 2r_{\text{dolomite}} - r_{\text{siderite}} 
\end{cases} \] (A.2)

This reaction term \( r_{\text{kin}} \) presents the combined effect of all the equilibrium as well as minerals kinetic reactions on the consumption or production of chemical components (Bethke, 2008). Minerals kinetic reactions \( r_m \) have been described by Eq. (4).

A.1 Speciation
Transport of chemical components through Eq. (1) requires computing the concentration of all thirteen aqueous species, involved in the equilibrium and kinetic reactions, at every node of the computational domain. The following thirteen algebraic equations (A.3 through A.15) result from seven equilibrium and three mineral kinetic reactions ((R1) through (R7) and (R8) through (R10) respectively presented in Table 1). These algebraic equations were solved as a function of transported chemical component species to compute the concentration of aqueous species:

\[
\left( c_{\text{CO}_2\text{aq}} \gamma_{\text{CO}_2\text{aq}} K_{\text{CO}_2\text{aq}} \right) - \left( c_{\text{H}^+} + c_{\text{H}^+} c_{\text{HCO}_3^{\gamma}} \right) = 0 \quad (A.3)
\]

\[
\left( K_{\text{H}_2\text{O}} \right) - \left( c_{\text{H}^+} c_{\text{HCO}_3^{\gamma}} \right) = 0 \quad (A.4)
\]

\[
\left( c_{\text{HCO}_3^{\gamma}} K_{\text{HCO}_3^{\gamma}} \right) - \left( c_{\text{H}^+} c_{\text{HCO}_3^{\gamma}} c_{\text{CO}_3^{\gamma}} c_{\text{CO}_3^{\gamma}} \right) = 0 \quad (A.5)
\]

\[
\left( c_{\text{Na}^+} c_{\text{Na}^+} c_{\text{HCO}_3^{\gamma}} c_{\text{Na}^+} \right) - \left( c_{\text{NaHCO}_3\text{aq}} c_{\text{NaHCO}_3\text{aq}} \right) = 0 \quad (A.6)
\]

\[
\left( c_{\text{CaHCO}_3^+} c_{\text{CaHCO}_3^+} K_{\text{CaHCO}_3^+} \right) - \left( c_{\text{Ca}^{2+}} c_{\text{Ca}^{2+}} c_{\text{HCO}_3^{\gamma}} c_{\text{HCO}_3^{\gamma}} \right) = 0 \quad (A.7)
\]

\[
\left( c_{\text{MgHCO}_3^+} c_{\text{MgHCO}_3^+} K_{\text{MgHCO}_3^+} \right) - \left( c_{\text{Mg}^{2+}} c_{\text{Mg}^{2+}} c_{\text{HCO}_3^{\gamma}} c_{\text{HCO}_3^{\gamma}} \right) = 0 \quad (A.8)
\]

\[
\left( c_{\text{FeHCO}_3^+} c_{\text{FeHCO}_3^+} K_{\text{FeHCO}_3^+} \right) - \left( c_{\text{Fe}^{2+}} c_{\text{Fe}^{2+}} c_{\text{HCO}_3^{\gamma}} c_{\text{HCO}_3^{\gamma}} \right) = 0 \quad (A.9)
\]
\[ u\text{HCO}_3^- \left( c\text{HCO}_3^- - c\text{H}^+ + c\text{OH}^- + 2c\text{CO}_3^{2-} + c\text{NaHCO}_3\text{aq} + c\text{CaHCO}_3^+ + c\text{MgHCO}_3^+ + c\text{FeHCO}_3^+ \right) = 0 \]  
(A.10)

\[ u\text{Na} - \left( c\text{Na}^+ + c\text{NaHCO}_3\text{aq} \right) = 0 \]  
(A.11)

\[ u\text{Ca} - \left( c\text{Ca}^{2+} + c\text{CaHCO}_3^+ \right) = 0 \]  
(A.12)

\[ u\text{Mg} - \left( c\text{Mg}^{2+} + c\text{MgHCO}_3^+ \right) = 0 \]  
(A.13)

\[ u\text{Fe} - \left( c\text{Fe}^{2+} + c\text{FeHCO}_3^+ \right) = 0 \]  
(A.14)

\[ u\text{CO}_2 - \left( c\text{CO}_2\text{aq} + c\text{H}^+ - c\text{OH}^- - c\text{CO}_3^{2-} \right) = 0 \]  
(A.15)

In the equations above, the symbol \( \gamma_i \) represents the activity coefficient of aqueous species. The activity coefficients of \( \text{CO}_2\text{aq} \) was computed from Duan and Sun, 2003. Activity coefficients of charged species were computed from extended Debye-Hückel function (B-dot equations) whereas those of electrically neutral species were found from the relations presented by Bethke (2008) (Ahmad et al., 2015). The activity of water was taken as unity.

Appendix B: Density of \( \text{CO}_2 \)-saturated \( \text{NaCl} \) brine
B.1 Methodology

By treating the mixture of H\textsubscript{2}O and NaCl as a solvent, the H\textsubscript{2}O+NaCl+CO\textsubscript{2} ternary system can be obtained by adding CO\textsubscript{2} to the mixture of H\textsubscript{2}O+NaCl (Duan et al. 2008). The density [kg/m\textsuperscript{3}] of the ternary solution (H\textsubscript{2}O+NaCl+CO\textsubscript{2}) is given by the relation (Duan et al. 2008);

\[
\rho_{\text{ternary}} = 1000 \frac{x_{\text{H}_2\text{O}}M_{\text{H}_2\text{O}} + x_{\text{CO}_2}M_{\text{CO}_2} + x_{\text{NaCl}}M_{\text{NaCl}}}{V_{\text{ternary}}} \tag{B.1}
\]

The molar volume [cm\textsuperscript{3}/mol] of the ternary system can be found from the relation (Duan et al. 2008);

\[
V_{\text{ternary}} = x_{\text{H}_2\text{O}}V_{\text{H}_2\text{O}} + x_{\text{NaCl}}V^B_{\varphi, \text{NaCl}} + x_{\text{CO}_2}V^B_{\varphi, \text{CO}_2} \tag{B.2}
\]

where \(V_{\text{H}_2\text{O}}\) is the molar volume of pure water, \(V^B_{\varphi, \text{NaCl}}\) is the apparent molar volume of NaCl in water, \(V^B_{\varphi, \text{CO}_2}\) is the apparent molar volume of CO\textsubscript{2} in the ternary system whereas \(x_{\text{H}_2\text{O}}, x_{\text{NaCl}}, \text{and } x_{\text{CO}_2}\) represent the molar fraction of water, NaCl and CO\textsubscript{2} respectively in the ternary system. Since the brines in the CO\textsubscript{2} sequestration environments are usually dilute to the degree that the effect of salt on \(V^B_{\varphi, \text{CO}_2}\) can be neglected and therefore \(V^B_{\varphi, \text{CO}_2}\) can be approximated with the apparent molar volume of CO\textsubscript{2} in pure water (Duan et al. 2008). Therefore the equation (B.2) can be written as;

\[
V_{\text{ternary}} = x_{\text{H}_2\text{O}}V_{\text{H}_2\text{O}} + x_{\text{NaCl}}V^B_{\varphi, \text{NaCl}} + x_{\text{CO}_2}V^B_{\varphi, \text{CO}_2} \tag{B.3}
\]
where superscript \( B \) represent the binary. Mole fraction of \( \text{CO}_2, \text{H}_2\text{O} \) and \( \text{NaCl} \) was obtained from the relations (Li et al., 2011):

\[
x_{\text{CO}_2} = \frac{m_{\text{CO}_2}}{m_{\text{H}_2\text{O}} + m_{\text{NaCl}} + m_{\text{CO}_2}} \tag{B.4}
\]

\[
x_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{m_{\text{H}_2\text{O}} + m_{\text{NaCl}} + m_{\text{CO}_2}} \tag{B.5}
\]

\[
x_{\text{NaCl}} = \frac{m_{\text{NaCl}}}{m_{\text{H}_2\text{O}} + m_{\text{NaCl}} + m_{\text{CO}_2}} \tag{B.6}
\]

where \( M_{\text{CO}_2} = 44.01 \) [g/mol] is molecular weight of \( \text{CO}_2 \), \( M_{\text{H}_2\text{O}} = 18.015 \) [g/mol] is molecular weight of \( \text{H}_2\text{O} \), \( M_{\text{NaCl}} = 58.443 \) [g/mol] is molecular weight of \( \text{NaCl} \), \( m_{\text{H}_2\text{O}} = 55.51 \) [mol/kg], \( m_{\text{NaCl}} \) is molality [mol/kg] of \( \text{NaCl} \) solution, and \( m_{\text{CO}_2} \) is the molality [mol/kg] of \( \text{CO}_2 \) which was found from the solubility model of Duan and Sun, 2003 and Duan et al., 2006.

The molar volume of water [cm\(^3\)/mol] required in equation (B.3) can be calculated from the relation:

\[
V_{\text{H}_2\text{O}} = 10^6 VM_{\text{H}_2\text{O}} \tag{B.7}
\]

where \( V \) is the specific volume of water [m\(^3\)/kg] and \( M_{\text{H}_2\text{O}} = 18.015 \times 10^{-3} \) [kg/mol] is the molar mass of water. The specific volume and the density of water were obtained from Cooper.
and Dooley (2007) and the equations are presented in section B.2. Apparent molar volume of CO$_2$ was obtained from the relation (Duan et al. 2008);

\[ V^B_{\phi,CO_2} = V_{H_2O} (1 + A_1 + A_2P) \]  

(B.8)

\[ \begin{align*} 
A_1 &= A_{11}T^2 + A_{12}T + A_{13} + A_{14}T^{-1} + A_{15}T^{-2} \\
A_2 &= A_{21}T^2 + A_{22}T + A_{23} + A_{24}T^{-1} + A_{25}T^{-2} 
\end{align*} \]  

(B.9)

Parameters for equation (B.9) are listed in Table B 1.

| Parameter | Value | Parameter | Value |
|-----------|-------|-----------|-------|
| $A_{11}$  | 0.38384020E-3 | $A_{21}$ | -0.57709332E-5 |
| $A_{12}$  | -0.55953850 | $A_{22}$ | 0.82764653E-2 |
| $A_{13}$  | 0.30429268E3 | $A_{23}$ | -0.43813556E1 |
| $A_{14}$  | -0.72044305E5 | $A_{24}$ | 0.10144907E4 |
| $A_{15}$  | 0.63003388E7 | $A_{25}$ | -0.86777045E5 |

$V^B_{\phi,NaCl}$ is the apparent molar volume of NaCl in water which can be found from model of Rogers and Pitzer, 1982, which is also used by Mao and Duan, 2008. Equations for calculation of apparent molar volume of NaCl in water and the required di-electric constant of water are presented in section B.3.

B.2 Specific volume and density of pure water

Calculations of specific volume and density of pure water were based on formulation of Cooper and Dooley (2007). Specific volume [m$^3$/kg] of pure water is related through;
\[
V = \left( \frac{\partial g}{\partial p} \right)_T \tag{B.10}
\]

\[
V \frac{p}{RT} = \pi \gamma \pi \tag{B.11}
\]

where \( g \) is the Gibbs free energy which in dimensionless form is given by the relation:

\[
g\left( \frac{p}{RT}, \pi \right) = \gamma (\pi, \tau) = \sum_{i=1}^{34} n_i (7.1 - \pi)^{I_i} (\tau - 1.222)^{J_i} \tag{B.12}
\]

Equation (B.12) can cover the following pressure and temperature conditions relevant to CO\(_2\) geological storage:

\[
p_S(T) \leq p \geq 100 \text{MPa} \quad 273.15 \text{K} \leq T \geq 623.15 \text{K}
\]

Here \( p_S(T) \) is the saturation pressure of water which is found from the following relations:

\[
p_S = p^* \left[ \frac{2C}{-B + (B^2 - 4AC)^{0.5}} \right]^4 \tag{B.13}
\]

\[
\begin{align*}
A &= 9^2 + n_1 9 + n_2 \\
B &= n_3 9^2 + n_4 9 + n_5 \\
A &= n_6 9^2 + n_7 9 + n_8 \\
\end{align*}
\]

\[
\psi = \frac{T_S}{T^*} + \frac{n_9}{\left( \frac{T_S}{T^*} \right)^{-n_{10}}}
\]
with $p^* = 1$ MPa, $T^* = 1$ K, $T_s = T$ and coefficient $n_1$ to $n_{10}$ are given in Table B 2.

### Table B 2: Parameters for equation (B.13) (Cooper and Dooley, 2007).

| $i$ | $n_i$          | $i$ | $n_i$          |
|-----|---------------|-----|---------------|
| 1   | 0.116 705 214 527 67E4 | 6   | 0.149 151 086 135 30E2 |
| 2   | $-0.724 213 167 032 06E6$ | 7   | $-0.482 326 573 615 91E4$ |
| 3   | $-0.170 738 469 400 92E2$ | 8   | 0.405 113 405 420 57E6 |
| 4   | 0.120 208 247 024 70E5  | 9   | $-0.238 555 575 678 49$ |
| 5   | $-0.323 255 503 223 33E7$ | 10  | 0.650 175 348 447 98 E3 |

Relation for specific volume [m$^3$/kg] of pure water takes the form;

$$V = \frac{RT}{p^* \gamma \pi} \quad (B.14)$$

where $\pi = p/p^*$, $\tau = T^*/T$, $p$ is pressure [Pa], $p^* = 16.53 \times 10^6$ [Pa], $T^* = 1386$ [K] and $R = 0.461526 \times 10^3$ [J/(kg K)] is the specific gas constant of ordinary water. Parameters for equation (B.12) are listed in Table B 3. Here, $\gamma \pi$ is the dimensionless form of Gibbs free energy and is obtained by taking the derivative of $\gamma(\pi, \tau)$ with respect to pressure at constant temperature;

$$\gamma \pi = \left[ \frac{\partial \gamma}{\partial \pi} \right]_\tau = \sum_{i=1}^{34} -n_i I_i (7.1 - \pi)^{I_i-1} (\tau - 1.222)^{J_i} \quad (B.15)$$

Density of water [kg/m$^3$] is calculated from the relation;

$$\rho_{H_2O} = \frac{1}{V} \quad (B.16)$$
**Table B 3:** Parameters of equation (B.12) (Cooper and Dooley, 2007).

| $i$ | $I_i$ | $J_i$ | $n_i$ |
|-----|-------|-------|-------|
| 1   | 0     | -2    | 0.14632971213167 |
| 2   | 0     | -1    | -0.84548187169114 |
| 3   | 0     | 0     | -0.37563603672040E1 |
| 4   | 0     | 1     | 0.33855169168385E1 |
| 5   | 0     | 2     | -0.95791963387872 |
| 6   | 0     | 3     | 0.15772038513228 |
| 7   | 0     | 4     | -0.16616417199501E-1 |
| 8   | 0     | 5     | 0.81214629983568E-3 |
| 9   | 1     | -9    | 0.28319080123804E-3 |
| 10  | 1     | -7    | -0.60706301565874E-3 |
| 11  | 1     | -1    | -0.18990068218419E-1 |
| 12  | 1     | 0     | -0.32529748770505E-1 |
| 13  | 1     | 1     | -0.21841717175414E-1 |
| 14  | 1     | 3     | -0.5283857969930E-4 |
| 15  | 2     | -3    | -0.47184321073267E-3 |
| 16  | 2     | 0     | -0.30001780793026E-3 |
| 17  | 2     | 1     | 0.47661393906987E-4 |
| 18  | 2     | 3     | -0.44141845330846E-5 |
| 19  | 2     | 17    | -0.7269496297594E-15 |
| 20  | 3     | -4    | -0.31679644845054E-4 |
| 21  | 3     | 0     | -0.28270797985312E-5 |
| 22  | 3     | 6     | -0.85205128120103E-9 |
| 23  | 4     | -5    | -0.22425281908000E-5 |
| 24  | 4     | -2    | -0.6517122895601E-6 |
| 25  | 4     | 10    | -0.14341729937924E-12 |
| 26  | 5     | -8    | -0.40516996860117E-6 |
| 27  | 8     | -11   | -0.12734301741641E-8 |
| 28  | 8     | -6    | -0.17424871230634E-9 |
| 29  | 21    | -29   | -0.68762131295551E-18 |
| 30  | 23    | -31   | 0.14478307828521E-19 |
| 31  | 29    | -38   | 0.26335781662795E-22 |
| 32  | 30    | -39   | -0.11947622640071E-22 |
| 33  | 31    | -40   | 0.18228094581404E-23 |
| 34  | 32    | -41   | -0.93537087292458E-25 |
B.3 Apparent molar volume of NaCl in water and di-electric constant of water

$V_{\phi,NaCl}^B$ is the apparent molar volume of NaCl in water [cm$^3$/mol] and is found from the model of Rogers and Pitzer, 1982. The relation for apparent molar volume of NaCl is as under (Mao and Duan, 2008);

$$V_{\phi,NaCl}^B = V_\phi^0 + v|z_+ z_-|A_r h\left(I_m\right) + 2v+v_+m_{NaCl}RT \left(B_v + v_+z_+m_{NaCl}C_v\right) \quad (B.17)$$

$V_\phi^0$ is the apparent molar volume of the NaCl at infinite dilution and is found from the relation (Mao and Duan, 2008);

$$V_\phi^0 = \frac{V(m_r)}{m_r} - \frac{1000}{m_r \rho_{H_2O}} - V|z_+ z_-|A_r h\left(I_m\right) - 2v+v_+RT \left(B_v m_r + v_+z_+C_v m_r^2\right) \quad (B.18)$$

where;

$v = v_{Na} + v_{Cl}$

$v_+ = v_{Na} = 1$; number of cations per solute formula unit

$v_- = v_{Cl} = 1$; number of anions per solute formula unit

$z_+ = z_{Na} = 1$; charge of Na ion

$z_- = z_{Cl} = -1$; charge of Cl ion

$V(m_r)$ is the solution volume assuming that 1 kg water contains NaCl equal to the reference molality ($m_r = 6$ mol/kg) and is found from the relation (Mao and Duan, 2008);

$$V(m_r) = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + p \left(c_5 + c_6 T + c_7 T^2 + c_8 T^3\right) \quad (B.19)$$
where \( p \) is pressure [MPa] and \( T \) is the temperature [K].

\( B_V \) and \( C_V \) are the second and third virial coefficients respectively given by the relations (Mao and Duan, 2008);

\[
B_V = \frac{c_9}{T - 227} + c_{10} + c_{11}T + c_{12}T^2 + \frac{c_{13}}{647 - T} + p\left(\frac{c_{14}}{T - 227} + c_{15} + c_{16}T + c_{17}T^2 + \frac{c_{18}}{647 - T}\right)
\]

(B.20)

\[
C_V = \frac{c_{19}}{T - 227} + c_{20} + c_{21}T + c_{22}T^2 + \frac{c_{23}}{647 - T}
\]

(B.21)

Parameters \((c_1 - c_{23})\) used in equation (B.19) through equation (B.21) are listed in Table B 4.

| Parameter | Value       | Parameter | Value       |
|-----------|-------------|-----------|-------------|
| \(c_1\)   | 1.06607098E3| \(c_{13}\) | -5.05734723E-2 |
| \(c_2\)   | -8.39622456E-3| \(c_{14}\) | -1.32747828E-4 |
| \(c_3\)   | 5.35429127E-4| \(c_{15}\) | 4.77261581E-6  |
| \(c_4\)   | 7.55373789E-7| \(c_{16}\) | -1.76888377E-8 |
| \(c_5\)   | -4.19512335E-1| \(c_{17}\) | 0            |
| \(c_6\)   | 1.45082899E-3| \(c_{18}\) | 6.40541237E-4  |
| \(c_7\)   | -3.47807732E-6| \(c_{19}\) | 3.07698827E-4  |
| \(c_8\)   | 0           | \(c_{20}\) | -1.64042763E-4 |
| \(c_9\)   | 1.10913788E-2| \(c_{21}\) | 7.06784935E-7  |
| \(c_{10}\) | 1.14498252E-3| \(c_{22}\) | -6.50338372E-10 |
| \(c_{11}\) | -5.51181270E-6| \(c_{23}\) | -4.50906014E-4 |
| \(c_{12}\) | 7.05483955E-9 |           |              |

Ionic strength \((I_{m_r})\) for reference molality \((m_r = 6 \text{ mol/kg})\) in equation (B.18) is related through:
\[ I_{m_r} = \frac{1}{2} \left( v_{Na} z_{Na}^2 + v_{Cl} z_{Cl}^2 \right) m_r \]  
(B.22)

\[ h(I_{m_r}) = \frac{\log \left( 1 + b I_{m_r}^{0.5} \right)}{2b} \]  
(B.23)

Ionic strength \((I_m)\) for variable molality in equation (B.17) is found from the relations;

\[ I_m = \frac{1}{2} \left( v_{Na} z_{Na}^2 + v_{Cl} z_{Cl}^2 \right) m_{NaCl} \]  
(B.24)

\[ h(I_m) = \frac{\log \left( 1 + b I_m^{0.5} \right)}{2b} \]  
(B.25)

In equation (B.23) and equation (B.25), the value of \(b = 1.2\ \text{kg}^{0.5}/\text{mol}^{0.5}\).

Debye-Hückel co-efficient for the apparent molar volume \((A_v)\) \([\text{cm}^3\cdot\text{kg}^{0.5}/\text{mol}^{1.5}]\) was given by the relation (Fernández et al. 1997);

\[ A_v = 2A_{\varphi}RT \left[ 3\left( \frac{\partial e}{\partial \rho} \right)_T - \left( \frac{\partial \rho}{\partial \rho} \right)_T \right] \]  
(B.26)

where the Debye-Hückel slope for the osmotic co-efficient \([\text{kg}^{0.5}/\text{mol}^{0.5}]\) is related to the Debye-Hückel coefficient for the limiting slope of the activity by the relation (Bradley and Pitzer, 1979);

\[ A_{\varphi} = \frac{A_v}{3} \]  
(B.27)
Debye-Hückel coefficient for the limiting slope of the activity has the following relation (Fernández et al. 1997):

\[ A_\gamma = \left( 2\pi N_A \rho M_{w} \right)^{1/2} \left[ e^2 / (4\pi e_0 kT) \right]^{3/2} \]  

(B.28)

Parameters for equation (B.28) are listed in Table B 5.

Table B 5: Parameters for equation (B.28).

| Parameter | Value | Parameter | Value |
|-----------|-------|-----------|-------|
| \pi       | 3.142 | \( M_{H_2O} \); molar mass of water | 0.018015268 [kg/mol] |
| \( N_A \); Avogadro’s number | 6.0221367E23 (1/mol) | \( R \); gas constant | 8.3144621 [J/(mol-K)] |
| \( \rho \); molar density of water | \( \rho_{H_2O} / M_{H_2O} \) (mol/m³) | \( \varepsilon_0 \); permittivity of free space | 8.8542E-12 [C²/J/m] |
| \( \rho_{H_2O} \); mass density of pure water | (kg/m³) | \( e \); elementary charge | 1.60217733E-19 (C) |
| \( k \); Boltzmann’s constant | 1.380658E-23 (J/K) | \( \varepsilon \); di-electric constant of water | equation (C.18) |

First derivative of di-electric constant of water with respect to pressure at constant temperature used in equation (B.26) was found from the relation (Fernández et al. 1997):

\[ \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T = \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T \left( \frac{\partial \rho}{\partial \rho} \right)_T \]  

(B.29)

where \( \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T \) was calculated from the relations (Fernández et al. 1997);
\[
\left( \frac{\partial \varepsilon}{\partial \rho} \right)_T = \frac{4B_1 \varepsilon}{4 - 4B} + \frac{A_1 + 5B_1 + 0.5C^{-0.5}}{4 - 4B} \left[ 2A_1 + 18B_1 + 2AA_1 + 10(A_1B + AB_1) + 18BB_1 \right]
\]

(B.30)

\[
A_1 = \frac{A}{\rho} + \left( \frac{A}{g} \right) \left( \frac{\partial g}{\partial \rho} \right)_T
\]

\[
B_1 = \frac{B}{\rho}
\]

\[
C = 9 + 2A + 18B + A^2 + 10AB + 9B^2
\]

(B.31)

The correlation factor \( g \) was found from the relation (Fernández et al. 1997):

\[
g = 1 + \sum_{k=1}^{11} N_k \left( \frac{\rho}{\rho_c} \right)^{i_k} \left( \frac{T_c}{T} \right)^{j_k} + N_{12} \left( \frac{\rho}{\rho_c} \right)^{T \over 228} \left( 1 \right)^{-q}
\]

(B.32)

\( \rho \) is the molar density of water (defined in Table B.5), \( \rho_c = \frac{322}{M_{H_2O}} \) mol/m\(^3\) is critical molar density of water, \( T_c = 647.096 \) K is the critical temperature of water, \( q = 1.2 \) is a constant whereas the values of \( N_k, i_k, j_k \) are listed in Table B 6.

Table B 6: Parameters \( (N_k, i_k, j_k, \) and \( q) \) for equation (B.32) (Fernández et al. 1997).

| \( k \) | \( i_k \) | \( j_k \) | \( N_k \) |
|-------|--------|--------|--------|
| 1     | 1      | 0.25   | 0.978224486826 |
| 2     | 1      | 1      | -0.957771379375 |
| 3     | 1      | 2.5    | 0.237511794148 |
| 4     | 2      | 1.5    | 0.714692244396 |
| 5     | 3      | 1.5    | -0.298217036956 |
| 6     | 3      | 2.5    | -0.108863472196 |
| 7     | 4      | 2      | 0.949327488264E-1 |
The following relation gives the value of \( \left( \frac{\partial g}{\partial \rho} \right)_T \) which is obtained from equation (B.32) above:

\[
\left( \frac{\partial g}{\partial \rho} \right)_T = \frac{1}{\rho_c} \sum_{k=1}^{11} N_{ki} \left( \frac{\rho}{\rho_c} \right)^{ik-1} \left( \frac{T_c}{T} \right)^{jk} + \frac{N_{12}}{\rho_c} \left( \frac{T}{228} - 1 \right)^{-q}
\]  \hspace{1cm} (B.33)

Di-electric constant of water (\( \epsilon \)) required in equation (B.26) and equation (B.28) was found from the formulation of Fernández et al. 1997:

\[
\epsilon = \frac{1 + A + 5B + \sqrt{9 + 2A + 18B + A^2 + 10AB + 9B^2}}{4 - 4B}
\]  \hspace{1cm} (B.34)

where

\[
A = \frac{N_A \mu^2}{\varepsilon_0 k} \frac{\rho g}{T}
\]  \hspace{1cm} (B.35)

\[
B = \frac{N_A \alpha}{3 \varepsilon_0} \rho
\]  \hspace{1cm} (B.36)

whereas \( \mu = 6.138 \times 10^{-30} \) C-m is dipole moment of water and \( \alpha = 1.636 \times 10^{-40} \) C²/(J-m²) is mean molecular polarizability of water.
The term $\left( \frac{\partial \rho}{\partial p} \right)_{T}$ in equation (B.29) is the derivative of density of water with respect to pressure at constant temperature which is found from the following relation based on equation (B.12) and equation (B.15):

\[
\left( \frac{\partial \rho}{\partial p} \right)_{T} = -\frac{1}{v^2} \left( \frac{RT}{p^*} \sum_{i=1}^{34} (I_i^2 - I_i) n_i (7.1 - \pi) I_i^{-2} (\tau - 1.222) J_i \right)
\]  

(B.37)

Where $\pi = p / p^*$, $\tau = T^* / T$, $p$ is pressure [Pa], $p^* = 16.53 \times 10^6$ Pa, $T^* = 1386$ K and $R = 0.461526 \times 10^3$ J/(kg-K) is the specific gas constant of ordinary water.
Appendix C. Viscosity of CO₂-saturated NaCl brine

According to Mao and Duan (2009), the viscosity of brine (NaCl+H₂O) can be determined from the following relationship:

\[ \mu_{sol} = \mu_r \mu_{H_2O} \]  \hspace{1cm} (C.1)

where \( \mu_{sol} \) represents the solution viscosity \([\text{kg/(m-s)}]\), \( \mu_r \) refers to relative viscosity, and \( \mu_{H_2O} \) is the viscosity of pure water \([\text{kg/(m-s)}]\). The relative viscosity is found from the following relationship:

\[ \mu_r = \exp(A m + B m^2 + C m^3) \]  \hspace{1cm} (C.2)

where \( m \) is the molality \([\text{mol/(kg water)}]\) of salt (NaCl) and \( A, B, \) and \( C \) are polynomials as a function of temperature \( T \) \([\text{K}]\):

\[
\begin{align*}
A &= a_0 + a_1 T + a_2 T^2 \\
B &= b_0 + b_1 T + b_2 T^2 \\
C &= c_0 + c_1 T
\end{align*}
\]  \hspace{1cm} (C.3)

The parameters \( a_i, b_i \) and \( c_i \) are given in Table C 1.

| \( i \) | \( a_i \) | \( b_i \) | \( c_i \) |
|-----|-----|-----|-----|
| 0   | -0.21319213 | 0.69161945E-1 | -0.2598886E-2 |
| 1   | 0.1365159E-2  | -0.2729226E-3 | 0.7798923E-5  |
| 2   | -0.1219176E-5 | 0.2085245E-6 | —— |
The viscosity of pure liquid water is calculated from the following relationship:

\[ \mu_{\text{H}_2\text{O}} = \exp \left( \sum_{i=1}^{5} d_i T_i^{-3} + \sum_{i=6}^{10} d_i \rho_{\text{H}_2\text{O}} T_i^{-8} \right) \]  

(C.4)

where the density of pure water (\( \rho_{\text{H}_2\text{O}} \)) is found from Cooper and Dooley (2007) and the parameters (\( d_i \)) are given in Table C 2.

| \( i \) | \( d_i \)   | \( i \) | \( d_i \)   |
|--------|-----------|--------|-----------|
| 1      | 0.28853170E7 | 6      | -0.19283851E7 |
| 2      | -0.11072577E5 | 7      | 0.56216064E4   |
| 3      | -0.90834095E1 | 8      | 0.13827250E2   |
| 4      | 0.30925651E-1  | 9      | -0.47609523E-1 |
| 5      | -0.27407100E-4 | 10     | 0.35545041E-4   |

The viscosity of CO\(_2\)-saturated NaCl brine (\( \mu_m \)) is found from the following mixing rule (Laliberte, 2007):

\[ \ln \mu_m = w_{\text{sol}} \ln \mu_{\text{sol}} + w_{\text{CO}_2} \ln \mu_{\text{CO}_2} \]  

(C.5)

where \( w_{\text{sol}} \), \( w_{\text{CO}_2} \), \( \mu_{\text{sol}} \), and \( \mu_{\text{CO}_2} \) are the mass fraction of NaCl brine solution, mass fraction of CO\(_2\) dissolved in NaCl brine, viscosity of NaCl brine and viscosity of CO\(_2\) respectively. Viscosity of CO\(_2\) was found from the formulation of Chung et al., 1988 whereas the required molar volume of CO\(_2\) was found from Peng Robinson equation of state (Peng and Robinson, 1976).
APPENDIX D: Heat capacity and thermal conductivity of CO$_2$-saturated brine

The specific heat capacity [J/(kg-K)] of brine fluid was calculated from the following mass averaged relation, considering the only contribution of CO$_2$ in water, while neglecting the contribution of all other dissolved species in the water:

\[
C_{p,b} = \frac{C_{p,g}m_g + C_{p,w}m_w}{m_g + m_w}
\]  
(D.1)

Here the specific heat capacity [J/(kg-K)] of CO$_2$ ($C_{p,g}$) and specific heat capacity [J/(kg-K)] of water ($C_{p,w}$) were found from the following relations (COMSOL):

\[
C_{p,g} = 459.913258 + 1.86487996T - 0.00212921519T^2 + 1.22488004E - 6T^3
\]

\[
C_{p,w} = 12010.1471 - 80.4072879T + 0.309866854T^2 - 5.38186884E - 4T^3 + 3.62536437E - 7T^4
\]

here T [K] is temperature and mass fraction of CO$_2$ ($m_g$ [kg/(kg water)]) and water ($m_w$ [kg/(kg water)]) are as under;

\[
m_g = \frac{c_{CO_2,aq}MW_{CO_2}}{1000}
\]

\[
m_w = \frac{55.509MW_w}{1000}
\]

where $MW_w = 18.015$ g/mol and $MW_{CO_2} = 44.01$ g/mol are the molecular weight of water and CO$_2$ respectively.
Thermal conductivity \([W/(m\cdot K)]\) of brine fluid with dissolved \(CO_2\) was calculated from the following mass averaged relation:

\[
k_b = \frac{k_g m_g + k_w m_w}{m_g + m_w}
\]  

(D.2)

where \(k_g\) and \(k_w\) are the thermal conductivities \([W/(m\cdot K)]\) of \(CO_2\) and water respectively and were found from the following relations (COMSOL):

\[
k_w = -0.869083936 + 0.008948803455 - 1.58366345E^2 + 7.97543259E - 9T^3
\]

\[
k_g = -0.00132472616 + 4.13956923E - 5T + 6.70889081E - 8T^2 - 2.11083153E - 11T^3
\]
Figure Captions

Figure 1. Schematic of subsurface carbonate reservoir used for CO₂-saturated brine injection.

Figure 2. CO₂aq mass injection in the reservoir over the period of 10 years; (a) injection scenarios 1 through 5 and (b) injection scenarios 5 through 8.

Figure 3. Mass consumption of CO₂ in geochemical reactions; cumulative mass conversion in scenarios 1 to 5 (a) and in scenarios 5 to 8 (b); percent mass conversion in scenarios 1 to 5 (c) and in scenarios 5 to 8 (d).

Figure 4. Variations in medium porosity [-] in various reactive transport scenarios from initial porosity value of 0.25; (a) scenario 1; (b) scenario 2; (c) scenario 3; (d) scenario 4; (e) scenario 5; (f) scenario 6; (g) scenario 7; and (h) scenario 8.
Table 1: Equilibrium and mineral kinetic reactions considered in this study.

| No. | Reactions                                      |
|-----|------------------------------------------------|
| (R0)$^1$ | $CO_{2g} \leftrightarrow CO_{2aq}$         |
| (R1)$^2$ | $H_2O + CO_{2aq} \leftrightarrow H^+ + HCO_3^-$ |
| (R2)$^2$ | $H_2O \leftrightarrow H^+ + OH^-$           |
| (R3)$^2$ | $HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$    |
| (R4)$^2$ | $Na^+ + HCO_3^- \leftrightarrow NaHCO_3{aq}$ |
| (R5)$^2$ | $CaHCO_3^- \leftrightarrow Ca^{2+} + HCO_3^-$ |
| (R6)$^2$ | $MgHCO_3^- \leftrightarrow Mg^{2+} + HCO_3^-$ |
| (R7)$^2$ | $FeHCO_3^- \leftrightarrow Fe^{2+} + HCO_3^-$ |
| (R8)$^2$ | $Calcite + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$ |
| (R9)$^2$ | $Dolomite + 2H^+ \leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$ |
| (R10)$^2$ | $Siderite + H^+ \leftrightarrow Fe^{2+} + HCO_3^-$ |

$^1$Equilibrium reaction constant was taken from the model of Duan and Sun, 2003 modified by Duan et al., 2006.

$^2$Equilibrium reaction constants were opted from the thermo database of LLNL (Delany and Lundeen, 1990) which is the default database of The Geochemist’s Workbench (GWB).

Table 2. Composition of minerals for a carbonate reservoir opted from Zerai et al., 2006.

| Minerals | Weight percent | Volume fraction in solid mass | Volume fraction including a porosity of 25% |
|----------|----------------|------------------------------|-------------------------------------------|
| Calcite  | 39             | 0.40                         | 0.30                                      |
| Dolomite | 60             | 0.59                         | 0.44                                      |
| Siderite | 1              | $6.95 \times 10^{-3}$       | $5.21 \times 10^{-3}$                     |

Table 3. Parameters and initial values of variables used in Eq. (3)-(5) for minerals calcite, dolomite, and siderite.

| Mineral | $k_{25}^*$ [mol/(s-m$^2$)] | $E_a^*$ [KJ/mol] | $A_m^{**}$ [m$^2$/kg water)] | $c_{m,bulk}^{**}$ [mol/(m$^3$ bulk volume)] |
|---------|-----------------------------|------------------|-------------------------------|---------------------------------------------|
| Calcite | $1.60 \times 10^{-9}$      | 41.87            | 21.67                         | 8216.67                                     |
| Dolomite| $0.6 \times 10^{-9}$       | 41.87            | 31.53                         | 7377.96                                     |
| Siderite| $0.6 \times 10^{-9}$       | 41.87            | 0.37                          | 181.94                                      |

$^*$Svensson and Dreybrodt, 1992; **Initial values were calculated from initial volume fraction (corresponding to reservoir porosity of 0.25) of minerals in porous rock formation. The minerals reactive surface area was taken equal to 10% of the respective minerals physical surface area (Johnson et al., 2004).
Table 4. Parameters used in Eq. (6).

| Mineral    | Acid mechanism | Neutral mechanism | Base mechanism |
|------------|----------------|-------------------|----------------|
|            | $k_{25,H}$  | $n_H$ | $E_{a,H}$ | $k_{25,nu}$ | $E_{a,nu}$ | $k_{25,OH}$ | $E_{a,OH}$ |
| calcite*   | 0.50 | 1 | 14.3 | 1.55×10^{-6} | 23.5 | 3.31×10^{-4} | 1 | 35.4 |
| dolomite*  | 1.74×10^{-4} | 0.5 | 56.7 | 2.51×10^{-9} | 95.3 | 4.27×10^{-6} | 0.5 | 45.7 |
| siderite** | 6.46×10^{-4} | 0.5 | 36.1 | 1.26×10^{-9} | 62.76 | 0 | -- | -- |

*Palandri and Kharaka, 2004; **Xu et al., 2007.

Table 5. Various brine injection scenarios.

| Scenarios | Injection temperature ($T_{inj}$) [°C] | Temperature conditions in the reservoir | Expression for mineral kinetic rate constant | Sorption | Dispersivity [m] |
|-----------|---------------------------------------|----------------------------------------|---------------------------------------------|-----------|-----------------|
|           |                                       |                                        |                                             |           | Longitudinal dispersivity ($D_L$) | Transverse dispersivity ($D_T$) |
| 1         | 27                                    | constant                               | Eq. (5)                                    | No        | 50              | 5               |
| 2         | 27                                    | constant                               | Eq. (5)                                    | Yes       | 50              | 5               |
| 3         | 27                                    | constant                               | Eq. (5)                                    | No        | 10              | 1               |
| 4         | 27                                    | constant                               | Eq. (5)                                    | No        | 100             | 10              |
| 5         | 27                                    | constant                               | Eq. (5)                                    | No        | 100             | 50              |
| 6         | 17                                    | flow                                   | Eq. (5)                                    | No        | 100             | 50              |
| 7         | 7                                     | flow                                   | Eq. (5)                                    | No        | 100             | 50              |
| 8         | 27                                    | constant                               | Eq. (6)                                    | No        | 100             | 50              |

Table 6. Boundary values (sub-index $bc$) for chemical components.

| Chemical component* | Concentration [mol/(kg water)] |
|---------------------|---------------------------------|
| $^{\mu}$HCO$_3_{bc}$ | $5.915\times10^{-3}$            |
| $^{\mu}$Na$_{bc}$   | 0.5                             |
| $^{\mu}$Ca$_{bc}$   | $2.670\times10^{-3}$            |
| $^{\mu}$Mg$_{bc}$   | $2.568\times10^{-4}$            |
| $^{\mu}$Fe$_{bc}$   | $3.058\times10^{-5}$            |
| $^{\mu}$CO$_2_{bc}$ | 0.902                           |

* $^{\mu}$ represents the chemical component.
Table 7. Composition of resident brine in the reservoir obtained from background BGM.

| Species      | concentration [mol/(kg water)] (top boundary of the reservoir) | concentration [mol/(kg water)] (lower boundary of the reservoir) |
|--------------|------------------------------------------------------------------|------------------------------------------------------------------|
| CO$_{2}^{aq}$ | 2.885×10$^{-4}$                                                  | 2.436×10$^{-4}$                                                  |
| HCO$_{3}^{-}$ | 4.582×10$^{-3}$                                                  | 4.221×10$^{-3}$                                                  |
| Na$^{+}$     | 0.499                                                            | 0.499                                                            |
| Cl$^{-}$     | 0.500                                                            | 0.500                                                            |
| H$^{+}$      | 5.518×10$^{-8}$                                                  | 5.079×10$^{-8}$                                                  |
| OH$^{-}$     | 4.012×10$^{-7}$                                                  | 5.147×10$^{-7}$                                                  |
| CO$_{3}^{2-}$ | 1.606×10$^{-5}$                                                  | 1.655×10$^{-5}$                                                  |
| NaHCO$_{3}^{aq}$ | 1.243×10$^{-3}$                                  | 1.096×10$^{-4}$                                                  |
| Ca$^{2+}$    | 2.617×10$^{-3}$                                                  | 2.398×10$^{-3}$                                                  |
| Mg$^{2+}$    | 2.529×10$^{-4}$                                                  | 2.247×10$^{-4}$                                                  |
| Fe$^{2+}$    | 2.990×10$^{-5}$                                                  | 2.676×10$^{-5}$                                                  |
| CaHCO$_{3}^{+}$ | 5.308×10$^{-5}$                                  | 4.595×10$^{-5}$                                                  |
| MgHCO$_{3}^{+}$ | 3.938×10$^{-6}$                                  | 3.284×10$^{-6}$                                                  |
| FeHCO$_{3}^{+}$ | 6.865×10$^{-7}$                                  | 5.405×10$^{-7}$                                                  |

Table 8. Composition of CO$_{2}$-saturated brine obtained from CO$_{2}$ dissolution modelling.

| Species      | concentration [mol/(kg water)] |
|--------------|--------------------------------|
| CO$_{2}^{aq}$ | 0.902                          |
| HCO$_{3}^{-}$ | 4.738×10$^{-3}$                |
| Na$^{+}$     | 0.499                          |
| Cl$^{-}$     | 0.5                             |
| H$^{+}$      | 1.669×10$^{-4}$                |
| OH$^{-}$     | 1.327×10$^{-10}$               |
| CO$_{3}^{2-}$ | 5.526×10$^{-9}$                |
| NaHCO$_{3}^{aq}$ | 1.285×10$^{-3}$          |
| Ca$^{2+}$    | 2.615×10$^{-3}$                |
| Mg$^{2+}$    | 2.528×10$^{-4}$                |
| Fe$^{2+}$    | 2.987×10$^{-5}$                |
| CaHCO$_{3}^{+}$ | 5.484×10$^{-5}$                |
| MgHCO$_{3}^{+}$ | 4.070×10$^{-6}$                |
| FeHCO$_{3}^{+}$ | 7.092×10$^{-7}$                |
Table 9. Saturation state of CO$_2$-saturated brine with respect to considered carbonate minerals.

| Mineral      | Saturation state of CO$_2$-saturated brine with respect to considered carbonate minerals |
|--------------|----------------------------------------------------------------------------------------|
| Calcite      | 3.42×10^{-4}                                                                           |
| Dolomite     | 1.17×10^{-7}                                                                           |
| Siderite     | 3.42×10^{-4}                                                                           |

Table 10. CO$_{2aq}$ mass balance [in tonnes] in various injection scenarios after 10 years of simulation.

| Injection scenarios | Scenario 1 | Scenario 2 | Scenario 3 | Scenario 4 | Scenario 5 | Scenario 6 | Scenario 7 | Scenario 8 |
|---------------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Total mass injected in the reservoir | 2.04×10^5 | 2.05×10^5 | 2.01×10^5 | 2.20×10^5 | 2.18×10^5 | 2.18×10^5 | 2.17×10^5 | 2.42×10^5 |
| Mass entered due to advection | 2.00×10^4 | 2.00×10^3 | 2.00×10^3 | 2.00×10^3 | 2.00×10^3 | 2.00×10^3 | 2.00×10^3 | 2.00×10^3 |
| Mass entered due to diffusion | 2.77×10^{-6} | 4.07×10^{-6} | 3.62×10^{-6} | 7.43×10^{-6} | 6.70×10^{-6} | 6.04×10^{-6} | 5.60×10^{-6} | 4.68×10^{-5} |
| Mass entered due to dispersion | 3.50×10^{-4} | 5.24×10^{-3} | 7.14×10^{-3} | 1.96×10^{-4} | 1.75×10^{-4} | 1.75×10^{-4} | 1.75×10^{-4} | 4.15×10^{-4} |
| Mass left the domain (bottom boundary) | 7.24×10^{3} | 6.50×10^{3} | 2.92×10^{3} | 1.12×10^{4} | 9.57×10^{3} | 9.57×10^{3} | 9.57×10^{3} | 0.00       |
| Mass left the domain (right side boundary) | 3.39×10^{4} | 3.16×10^{4} | 3.51×10^{4} | 3.37×10^{4} | 3.38×10^{4} | 3.09×10^{4} | 3.09×10^{4} | 6.02×10^{4} |
| Mass stored in aqueous state | 1.77×10^{4} | 5.91×10^{4} | 1.84×10^{4} | 1.82×10^{4} | 1.84×10^{4} | 1.84×10^{4} | 1.83×10^{4} | 2.03×10^{4} |
| Mass stored in adsorbed state | 0.00 | 1.24×10^{5} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Mass consumed in geochemical reactions | 1.95×10^{4} | 2.28×10^{4} | 1.44×10^{4} | 2.57×10^{4} | 2.56×10^{4} | 2.57×10^{4} | 2.60×10^{4} | 3.97×10^{4} |
| Mass conversion of CO$_{2aq}$ (%) | 9.61 | 1.11×10^{-1} | 7.17 | 1.17×10^{-1} | 1.18×10^{-1} | 1.18×10^{-1} | 1.20×10^{-1} | 1.65×10^{-1} |
| Error in mass balance (%) | -1.84×10^{4} | -1.08×10^{4} | -4.56×10^{4} | 1.94×10^{4} | -6.36×10^{4} | -6.44×10^{4} | -6.44×10^{4} | -4.85×10^{4} |
| Mass left the domain (%) | 3.57 | 4.71×10^{4} | 1.47 | 5.10 | 4.41 | 4.42 | 4.41 | 2.49×10^{4} |
Table 11. Variations in total pore volume in the reservoir after 10 years.

| Scenario | initial pore volume [m³] | increase in pore volume [m³] | % increase |
|----------|--------------------------|-----------------------------|------------|
| Scenario 1 | $4.91 \times 10^7$    | $1.55 \times 10^4$       | $3.17 \times 10^{-2}$ |
| Scenario 2 | $4.91 \times 10^7$    | $1.81 \times 10^4$       | $3.70 \times 10^{-2}$ |
| Scenario 3 | $4.91 \times 10^7$    | $1.13 \times 10^4$       | $2.31 \times 10^{-2}$ |
| Scenario 4 | $4.91 \times 10^7$    | $2.03 \times 10^4$       | $4.14 \times 10^{-2}$ |
| Scenario 5 | $4.91 \times 10^7$    | $2.06 \times 10^4$       | $4.19 \times 10^{-2}$ |
| Scenario 6 | $4.91 \times 10^7$    | $2.06 \times 10^4$       | $4.20 \times 10^{-2}$ |
| Scenario 7 | $4.91 \times 10^7$    | $2.08 \times 10^4$       | $4.24 \times 10^{-2}$ |
| Scenario 8 | $4.91 \times 10^7$    | $3.30 \times 10^4$       | $6.73 \times 10^{-2}$ |