Abstract

Geochemical reactions between fluids and carbonate rocks can change porosity and permeability during CO₂ flooding, which may significantly impact well injectivity, well integrity, and oil recovery. Reactions can cause significant scaling in and around injection and production wells leading to high operating costs. Dissolution-induced well integrity issues and seabed subsidence have also been reported as a substantial problem at the Ekofisk field. Furthermore, mineral reactions can create fractures and vugs that can cause injection conformance issues, as has been observed in experiments and pressure transients in field tests. Although these issues are well known, there are differing opinions in the literature regarding the overall impact of geochemical reactions on permeability and injectivity for CO₂ flooding.

In this research, we use fully coupled reactive transport and compositional modeling to understand the interplay between multiphase flow, phase behavior, and geochemical reactions under reservoir and injection conditions relevant in the field. Simulations were carried out using a new compositional simulator (PennSim) based on an implicit pressure explicit composition (IMPEC) multiphase finite-volume formulation that is directly coupled with a reactive transport solver. The compositional and geochemical models were validated separately with CMG-GEOS and CrunchFlow. Phase and chemical equilibrium constraints are solved simultaneously to account for the interaction between phase splits and chemical speciation. The Søreide and Whitson (1992) modified Peng-Robinson equation-of-state (EOS) is used to model component concentrations present in the aqueous and hydrocarbon phases. The mineral reactions are modeled kinetically and depend on the rock-brine contact area and the brine geochemistry, including pH and water composition. Injectivity changes caused by rock dissolution and formation scaling are investigated for a five-spot pattern using several common field injection boundary conditions.

The results show that the type of injection scheme and water used (fresh water, formation water, and seawater) has the same total volume of CO₂ and water injected. For continuous CO₂ injection, very little porosity changes are observed owing to evaporation of water near the injection well. For water-alternating-gas (WAG) injection, however, the injectivity increases from near zero to 50%, depending on the CO₂ slug size, number of cycles, and the total amount of injected water. Simultaneous water-alternating-gas injection (SWAG) shows significantly greater injectivity increases than WAG, primarily because of greater exposure time of the carbonate surface to CO₂-saturated brine coupled with continued displacement of calcite-saturated brine. For simultaneous water-alternating-gas injection (SWAG), carbonate dissolution primarily occurs very near the injection well, where dissolution occurs out to greater distances. Carbonated water flooding (a special case of SWAG) shows even greater increases in injectivity than SWAG because more water is injected in this case, which can continuously sweep out brine saturated with calcite. The results also show that scaling can occur beyond the zone of dissolution depending on the type of water injected. For seawater injection, injectivity first increases and then decreases owing to formation of gypsum. The amount of precipitation depends on the compatibility of the injected brine with the formation water that is equilibrated with high pressure CO₂ and minerals. We consider only gypsum and halite precipitation here, although other types of scale could be easily included.

Introduction

CO₂ flooding is the leading enhanced oil recovery (EOR) method in both sandstone and carbonate reservoirs in the United States (Christensen et al. 2001; Manrique et al. 2007). CO₂ can become miscible with the oil and therefore significantly improve the recovery (Jarrell et al. 2002). Recovery can be adversely impacted if injected CO₂ channels through high permeability layers and causes early breakthrough of solvent and poor sweep. Water is typically injected along with CO₂ to
mitigate poor sweep by improving the effective mobility ratio. Common CO₂ injection methods include continuous gas injection (CGI), water-alternating-gas (WAG), and simultaneous water-alternating-gas (SWAG). Recovery could also be impacted by changes in injectivity or scaling that occurs near wells owing to mineral reactions with brine, especially for carbonate reservoirs.

Injectivity affects the throughput and economics of CO₂ EOR projects (Grigg and Schechter 2001). Changes in injectivity (increases or decreases) during CO₂ injection can be caused by a variety of processes, including relative permeability hysteresis, viscosity improvement, vaporization of oil and water, and changes in porosity and permeability caused by dissolution and precipitation (scaling) in and around wells. Solvent injectivity has generally been observed to decrease in field projects even though CO₂ has a lower viscosity than the fluids it is displacing (Winzinger et al. 1991; Henry et al. 1981).

Rogers and Grigg (2001) stated that one possible reason for observed injectivity decreases is the impact of mineral reactions between brine and carbonates. At the Wasson Denver Unit, pre- and post-pilot core studies showed anhydrate dissolution during the water injection portion of the WAG cycles, although the amount of dissolution was not significant (Mathis and Sears 1984). Patel et al. (1987) concluded from core flood experiments that the sharp decrease of CO₂ injectivity in the tertiary mode was due to the mixed wettability of the carbonate core. The CO₂ and oil had a significantly lower mobility than the water in their experiments. They also observed a significant decrease in Ca²⁺ and SO₄²⁻ concentrations in the effluent, which indicated the occurrence of calcite and anhydrate precipitation. These reactions were not considered, however, as the main reason for the injectivity changes. Prieditis et al. (1991) reported that the different end-point relative permeabilities of brine, oil, and CO₂ contributed to the injectivity differences. They also observed an increase in the injectivity of brine due to the decrease of residual CO₂ because of gas dissolution in brine. In their 4-cycle experiments, the rock dissolution was not significant. Roper et al. (1992) found that injectivity alteration during CO₂ flooding depends on the reservoir heterogeneity, cross flow, and formation of fractures. Again, mineral dissolution or precipitation was concluded to have negligible effects on injectivity.

For several field cases, however, mineral dissolution and/or precipitation are believed to have altered the rock permeability and the injectivity. Kane (1979) reported a nearly 50% injectivity increase at the Kelly Snyder field and attributed the increase to rock dissolution. At the Ekofisk field, which is primarily composed of chalk, dissolution of the carbonates from CO₂ and water injection was believed to cause “water weakening” and seabed subsidence (Korsnes et al. 2008). At the Weyburn site, the composition of produced water before and after CO₂ injection indicates the occurrence of mineral reactions (Emberley et al. 2005). The calcium concentration increased by more than 50% and was believed to be caused by carbonate dissolution, which could impact injectivity. Mineral dissolution also led to spontaneous injectivity improvement during carbonated water injection in a limestone reservoir (El Sheemy 1987).

Experimental studies in core floods have demonstrated that CO₂ injection causes significant porosity and permeability changes. Filho (2012) investigated the interaction between carbonated water and rock under high pressure with carbonated brine injection. The measured porosity increase or decrease was 3% (±) for dolomite and 20% (±) for limestone. The permeability variation was 60% (±) for dolomite and 86% (±) for limestone. In the context of geological carbon sequestration, well integrity has been considered as a primary potential risk due to the interactions among CO₂, wellbore cement, and formation rocks (Carey and Lichtner 2011; Carey et al. 2007; Crow et al. 2010; Frye et al. 2012; Newell and Carey 2012; Keating et al. 2013; Middleton et al. 2012). Cao et al. (2013) injected CO₂-saturated brine through a wellbore cement core for 8 days, and observed an increase in void space by 220%, while permeability increased by over 800%. Brunet et al. (2013) concluded that for CO₂-brine-cement interactions, the permeability could increase by orders of magnitude depending on the initial cement composition and CO₂ content. These experiments demonstrated that permeability can increase (or decrease) more significantly than porosity owing to dissolution (or precipitation) in and around the pore throats. SWAG floods in cores have exhibited wormholes near the inlet caused by dissolution of carbonate minerals (Wellman et al. 2003; Egermann et al. 2005; Izgic et al. 2007). These wormholes increased permeability by up to 100%. Egermann et al. (2010) injected acid to mimic the fluid/rock interactions far from the wellbores and observed increases in permeability by 70%, while porosity increased by only two porosity units. In their experiments, the concentration of SO₄²⁻ was observed to decrease, indicating anhydrate precipitation. For WAG floods, Mohamed and Nasr-El-Din (2013) conducted experiments to compare the permeability loss for a variety of carbonate rocks. Significant permeability damage was observed for heterogeneous rocks and sulfate containing brine, primarily owing to the formation of calcium sulfate scales that plugged the pore throats. They also mentioned that fine migration was an important factor that can cause scaling. In their experiments, porosity changes were not observed.

Geological simulation studies have been carried out to understand porosity and permeability alteration in the context of CO₂ sequestration (no oil). Xu et al. (2006) estimated the mineral trapping capacity of CO₂ and reported a decrease in porosity by as much as 50% with supercritical CO₂ injection. André et al. (2007) carried out simulation for the injection of CO₂ saturated brine using a 1D model and reported a porosity increase of 90% within 10 meters around the injection well after 10 years. Mohamed and Nasr-El-Din (2013) used the CMG-GEM simulator to match permeability alteration of their homogeneous and heterogeneous core experiments with WAG. They concluded that local pore structure and the injected sulfate concentration were the most important factors in determining permeability alteration. Wellman et al. (2003) used TRANSTOUGH to match a set of breakthrough curves for SWAG at the field scale and indicated small amounts of mineral dissolution.

Reactive transport models have been applied extensively to understand the physical, chemical and biological processes in earth systems (Steefel and Lasaga 1994; Lichtner 1996; Steefel et al. 2005; Li et al. 2011). Coupled with reactive transport
modeling, compositional modeling can provide an integrative approach to understand the interactions among multiphase flow, phase behavior, and mineral reactions. A few existing simulators in the literature can model oil and gas equilibrium coupled with geochemical reactions. Existing numerical methods include sequential formulations (Delshad et al. 2011; Wei 2012) and fully implicit formulations (Nghiem et al. 2011; Fan et al. 2012). The sequential formulations (Delshad et al. 2011; Wei 2012) solve the chemical reaction equations after solving the phase behavior equations. The fully implicit formulation (Nghiem et al. 2011; Fan et al. 2012) solved the mass conservation, phase equilibrium and chemical reactions simultaneously. The fully implicit scheme could allow for large time steps, however, for kinetic reactions of short time scales, large time steps could lead to numerical errors and non-convergence. These simulators were applied mostly in the context of CO₂ storage while few studies have been carried out for understanding the mineral reactions in various CO₂ injection schemes where oil and gas are presented.

The results of these experiments and field observations indicate that the effect of mineral reactions on CO₂ floods may be highly condition-dependent. Different injection schemes, wettability, injection water compositions, and field conditions can lead to differing impacts of mineral reactions. There is a significant need to predict the impact of mineral reactions on well integrity, CO₂ flood economics, and injectivity alteration. To the best of our knowledge, however, there is no simulator that simultaneously couples kinetic mineral reactions with detailed compositional phase behavior modeling. Further, there is no comparative study of the importance of mineral reactions on dissolution and scaling for common field injection schemes.

In this paper, we develop a numerical scheme that couples reactive transport modeling with detailed compositional simulation using the Peng-Robinson EOS and the modified mixing rules of Soreide-Whitson to model brine-hydrocarbon-solid equilibrium. The numerical solution uses sequential coupling of reactions with flow in an implicit pressure explicit composition (IMPEC) fashion. Because phase behavior and chemical equilibrium are solved simultaneously, this new simulator can better capture the features of CO₂ flooding under complex injection and highly reactive reservoir conditions. We then show with the new simulator the impact of mineral reactions on CO₂ flood injectivity and scale formation in carbonate reservoirs under CGI, SWAG, and WAG. The primary goal of this paper is to understand the complex interplay among phase equilibrium and geochemical reactions and to quantify the extent and magnitude of injectivity alteration arising from hydrocarbon-CO₂-mineral-water interactions.

### Methodology

This section presents the modeled physical processes along with the necessary equations controlling these processes. A brief description of the numerical solution method is also presented.

#### Physical processes.

CO₂ EOR involves multiple processes, including immiscible and miscible multiphase flow, CO₂ dissolution in oil and brine, water vaporization, and aqueous chemical and mineral reactions. Under high injection pressure, a significant amount of CO₂ can dissolve in the brine and form a weak carbonic acid that lowers the pH to around 3.3 to 3.7. The resulting acidic solution may lead to the dissolution of carbonate minerals. Mineral dissolution reactions consume the carbonic acid, which decreases the fugacity of CO₂ in the aqueous phase. The transformation between species CO₂ (hc), CO₂-(aq), HCO₃⁻ and CO₃²⁻ are shown as follows:

\[
\begin{align*}
\text{CO}_2 \ (\text{hc}) & \leftrightarrow \text{CO}_2 \ (\text{aq}) \\
\text{CO}_2 \ (\text{aq}) + \text{H}_2\text{O} & \leftrightarrow \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \\
\text{CaCO}_3 \ (s) & + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^- \\
\end{align*}
\]

where CO₂ (hc) and CO₂ (aq) represent the CO₂ component in the hydrocarbon and aqueous phases. Figure 1 gives the CO₂ solubility in brine as a function of partial pressure with and without calcite. A modified Peng Robinson EOS was used to calculate the hydrocarbon and aqueous phase behavior and CO₂ dissolution following the procedure of Soreide and Whitson (1992) and Mohebbinia et al. (2013). The parameters for the modified PR EOS are shown in Tables 1 and 2. Figure 1 demonstrates that slightly more CO₂ is dissolved into the aqueous phase when calcite dissolution is included. More importantly, however, calcite dissolution can release the Ca²⁺ ions and increase pH, which can lead to precipitation. When sulfate is present, anhydrite or gypsum may precipitate as described by,

\[
\text{CaSO}_4 \ (s) \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}.
\]

Water can vaporize into the gas phase:

\[
\text{H}_2\text{O} \ (\text{aq}) \leftrightarrow \text{H}_2\text{O} \ (\text{hc})
\]

As the water vaporizes, the brine becomes more concentrated, which can lead to the precipitation of halite as follows,

\[
\text{NaCl} \ (s) \leftrightarrow \text{Na}^+ + \text{Cl}^-.
\]
Phase behavior and chemical reactions are tightly coupled. Moreover, the phase behavior affects flow of the components through relative permeability of hydrocarbon and aqueous phases. The following sections describe the partial differential and algebraic equations for the coupled compositional and reactive transport model.

**Phase behavior and reactions.** Material balance equations involve the term “species” (commonly used in reactive transport models) and “component” (commonly used in compositional models). A component is a chemical entity distinguishable from other such quantities by its molecular formula, while a species needs to be distinguishable by its molecular formula and the phase in which it occurs (Nghiem et al. 2011). For example, CO$_2$ (aq) and CO$_2$ (hc) are two species yet one component. Species also includes aqueous ions such as HCO$_3^-$ and minerals such as CaCO$_3$(s). To unify the formulation, we write the phase equilibrium relation as a pseudo-reaction as discussed by Nghiem et al. (2011). For example, the following phase equilibrium relation is treated as a pseudo-reaction:

$$\text{CO}_2 \text{(hc)} \leftrightarrow \text{CO}_2 \text{(aq)}.$$  

In this way, we can represent the mass transfer between all species using the language of geochemists. Further, the term “reaction” also includes the phase equilibrium relations, equilibrium-controlled chemical reactions, and kinetic-controlled chemical reactions unless indicated otherwise.

Any linearly independent set of reactions (Smith and Missen 1982) can be written in the form

$$\emptyset \leftrightarrow \sum_{i=1}^{n_s} \bar{v}_{ir} A_i, r = 1, \ldots, n_r,$$

where $\emptyset$ represents the empty set; $n_s$ is the total number of species; $\bar{v}_{ir}$ is the original stoichiometric coefficient of species $i$ in reaction $r$; $A_i$ is the chemical formula of species $i$; and $n_r$ is the total number of reactions. It is possible to transform the set of reactions to its canonical form (Lichtner 1985; Lichtner 1996), which also consists of $n_r$ reactions,

$$\sum_{j=1}^{n_p} v_{ij} A_j \leftrightarrow A_i, i = n_p + 1, \ldots, n_s,$$

in which a single species $A_i$, referred to as secondary species, is written in terms of the primary species $A_j$; $v_{ij}$ is the stoichiometric coefficients based on the canonical form of reaction formula and is constructed from the original stoichiometry matrix (composed of $\bar{v}_{ij}$), following the method in Steefel and Macquarrie (1996). Each reaction is related to a secondary species regardless of the type of the reaction, so the numbers of secondary species and independent reactions are equal. Here the secondary species include species in the hydrocarbon, aqueous and solid phases. The parameter $n_p$ is the number of primary species and is given by,

$$n_p = n_s - n_r.$$

In the canonical form, the species are ordered in such a way that the first $n_p$ species are primary species, and reaction $r$ corresponds with the species $n_p + r$. One such reaction system and its stoichiometry matrix is shown in Appendix I.

Each independent reaction is controlled by an equation that relates the concentration of involved species. There are $n_r$ such equations where

$$n_r = n_{\text{pheq}} + n_{\text{cheq}} + n_{\text{mkin}}$$

and $n_{\text{pheq}}$ is the number of phase equilibrium relations; $n_{\text{cheq}}$ is the number of equilibrium-controlled chemical reactions; and $n_{\text{mkin}}$ is the number of kinetically controlled mineral reactions. The mass transfer of species between phases and in reactions are described by fugacity equations for phase equilibrium, the mass action law for chemical reaction equilibrium, and transition state theory (TST) rate laws for reaction kinetics.

Fugacity equations describe the equilibrium condition of mass transfer between phases, namely

$$\sum_{s=1}^{n_s} v_{rs} \log f_s = 0, \quad r = 1, \ldots, n_{\text{pheq}}$$

where $f_s$ is the fugacity (psi) of species $s$ that depends on the choice of equation of state, mole fractions of the species in the
same phase with species \( s \), the phase pressure \( P_f \) (psia) and temperature (Sandler 2006). A modified PR EOS is used in this research to accurately model the \( \text{CO}_2 \) dissolution and water vaporization (Søreide and Whitson 1992). Although Eq (1) is written in a general form, it is only meaningful when only two species are involved in a phase equilibrium relation, with the stoichiometric coefficient set to 1 or –1. One example of such relation is

\[
\log f_{\text{CO}_2(hc)} - \log f_{\text{CO}_2(aq)} = 0.
\]

The mass action law for the equilibrium controlled chemical reaction \( r \) is given by

\[
a_{n_p+1} = \frac{1}{K_{eq,r}} \prod_{p=1}^{n_p} a_{p}^{v_{p}}, \quad r = n_{pheq} + 1, \ldots, n_{pheq} + n_{cheq},
\]

where \( K_{eq,r} \) is the equilibrium constant (dimensionless) for reaction \( r \); \( a_{n_p+1} \) is the activity (dimensionless) of the secondary species that is associated with reaction \( r \). In this paper, we do not consider the reactions in phases other than the aqueous phase and at the mineral surface. For an aqueous species, the extended Debye-Huckel model is used to calculate the activity coefficient \( \gamma_f \) (Helgeson et al. 1970). The activity for the species in the solid phase is unity. One example of equilibrium-controlled reactions is

\[
\text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{CO}_2(aq) + \text{H}_2\text{O}.
\]

In canonical form, the reaction is written as

\[
\text{HCO}_3^- \leftrightarrow (-1) \text{H}^+ + \text{CO}_2(aq) + \text{H}_2\text{O}.
\]

For the above reaction, the mass action law (Eq. (2)) is written as

\[
a_{HCO_3} = \frac{1}{K_{eq}} (a_{H^+})^{-1} (a_{CO}_2(aq))^1 (a_{H2O})^1.
\]

For mineral reactions that are kinetically controlled, the reactions have finite conversion rates. An ordinary differential equation (ODE) needs to be solved for such a reaction (Langmuir et al. 1997). For the mineral reaction \( r \), the mass consumption due to the dissolution/precipitation reaction gives

\[
\frac{\partial m_{n_p+1}}{\partial t} = \sum_{i=1}^{n_{path}} R_{r,i} \quad r = n_{pheq} + n_{cheq} + 1, \ldots, n_r,
\]

where \( m_{n_p+1} \) is the moles of mineral species that is the secondary species associated with reaction \( r \); \( R_{r,i} \) is the reaction rate of the reaction \( r \) along the \( i^{th} \) reaction path (mol/day); and \( n_{path} \) is the number of reaction paths. Here the reaction paths refer to the reaction mechanisms, e.g. acidic or neutral, that the mineral dissolution may follow (Chou et al. 1989). The TST rate law is expressed as

\[
R_{r,i} = A_s k_{r,i} \exp \left( - \frac{E_a}{RT} \right) \prod_{i=1}^{n_s} a_{i}^{n_{li}} \left( \frac{IAP_i}{K_{eq,r}} \right)^{l-1}
\]

where \( A_s \) is the bulk surface area of mineral species \( s \) associated with reaction \( r \) and is calculated from the specific surface area (SSA) and the mineral mass; \( k_{r,i} \) is the reaction rate constant of the \( i^{th} \) path (mol/m²·s); \( E_a \) is the activation energy (J/mol); \( R \) is the universal gas constant (8.31 J/mol·K); \( T \) is the temperature (K); \( n_{li} \) is the dependent exponent of species \( i \) for path \( l \); \( IAP_i \) is the ionic activity product; \( K_{eq,r} \) is the equilibrium constant; and the subscript \( r \) indicates that these variables are for reaction \( r \). A detailed description and explanation of the TST rate law can be found in Brantley et al. (2008). One example of such reactions is

\[
\text{CaCO}_3(s) \leftrightarrow (-1) \text{H}^+ + \text{Ca}^{2+} + \text{HCO}_3^-,
\]

for which the ODE is written as
\[
\frac{\partial m_{\text{CaCO}_3}}{\partial t} = A_{\text{CaCO}_3} k \exp \left( - \frac{E_a}{RT} \right) a_H^+ \left( 1 - \frac{a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}}{K_{eq} a_{H^+}} \right).
\]

Equations (1), (2) and (3) form a reaction equation system with \( n_r \) equations. This system shows how the phase equilibrium is coupled with geochemical reaction equilibrium and kinetics.

**Mass conservation.** With the definition of primary species and secondary species, the mass conservation for primary species \( p \) is written without an explicit reaction term as

\[
\frac{\partial N_p}{\partial t} + \nabla \cdot F_p + Q_p = 0
\]  

(4)

where the total moles of a primary species is defined as

\[
N_p = \sum_{i=0}^{n_s} v_{ip}m_i
\]  

(5)

and \( m_i \) is the moles of species \( i \) (mol) and \( v_{ip} \) is the \((i,p)\) entry in the stoichiometry matrix \( S_{n_s \times n_p} \) (dimensionless). Per unit bulk volume, \( m_i \) is calculated as

\[
m_i = \phi \xi_j S_{ij} x_{ij}
\]  

(6)

where \( \phi \) is porosity (dimensionless); \( \xi_j \) is the index of the phase that contains species \( i \); \( \xi_j \) is the molar density of phase \( j_i \) (mol/ft\(^3\)); and \( S_{ij} \) is the saturation of phase \( j_i \) (dimensionless). The total molar flow rate (mol/day) is expressed as

\[
F_p = \sum_{i=0}^{n_s} v_{ip}f_i.
\]  

(7)

The species molar rate \( f_i \) is expressed as

\[
f_i = \xi_j x_{ij} u_{ji} - \phi S_{ij} D \nabla (\xi_j x_{ij})
\]  

(8)

where \( u_{ji} \) is the volumetric flow rate of phase \( j_i \) (ft\(^3\)/day); \( D \) is the diffusion/dispersion coefficient tensor (ft\(^2\)/day). The well rate is expressed from the total molar rate,

\[
Q_p = \sum_{q=0}^{n_s} v_{ip}q_i
\]  

(9)

where \( q_i \) is the molar rate (mol/day) of the source/sink term for species \( i \). The convention used here is that a sink is positive. The generalized total molar concentration and flux are also discussed in Lichtner (1996). **Equation (4)** degenerates to the general mass conservation equation for the compositional model if there are no reactions. Moreover, for cases with phase equilibrium constraints, reaction equilibrium constraints, and reaction kinetic relations, Eq. (4) holds without an explicit reaction term. This form of the mass conservation equation enables an operator splitting method that solves the transport and other constraints sequentially.

**Darcy’s law.** The phase flow volumetric rate is a function of pressure

\[
u_j = - \frac{k_{r_j}}{\mu_j} \left( \nabla p_j - g_j \nabla Z \right)
\]

where \( k \) is the permeability (md); \( k_{r_j}, \mu_j \) and \( g_j \) are the relative permeability (dimensionless), viscosity (cp), and specific gravity factor (psi/ft) of the \( j \)th phase respectively. The phase pressure is related to the reference pressure by capillary pressure as follows

\[
p_j = P + P_{cj}.
\]
The oil phase pressure is chosen as the reference pressure.

**Volume constraint.** The total volume of the fluids in the porous media must be equal to the volume of the pore space,

\[ V_t = V_b \phi \]  

(10)

where \( V_t \) is the total volume of the fluids (ft\(^3\)) and \( V_b \) is the bulk volume (ft\(^3\)). The value of \( V_t \) is a function of species mass, pressure and temperature through an equation of state. Furthermore, the temporal derivative of both sides of Eq. (10) gives

\[ \frac{\partial V_t}{\partial P} \frac{\partial P}{\partial t} + \sum_{i=1}^{n_p} \frac{\partial V_t}{\partial N_p} \frac{\partial N_p}{\partial t} = V_b \frac{\partial \phi}{\partial t} \]  

(11)

where subscript \( p \) is the index for the primary species. By combining Eq. (11) with Eq. (4), we can obtain the partial differential equation for pressure, in the same form as the volume balance equation for standard compositional models (Chang 1990),

\[ \left( V_b \frac{\partial \phi}{\partial P} - \frac{\partial V_t}{\partial P} \right) \frac{\partial P}{\partial t} - V_b \sum_{p=1}^{n_p} \frac{\partial V_t}{\partial N_p} (\nabla \cdot F_p + Q_p) = 0. \]  

(12)

In summary, there are \( n_s - n_r \) mass conservation equations, Eq. (4), \( n_r \) reaction equations, Eqs. (1) - (3), and a volume balance equation, Eq. (12). There are also \( n_s + 1 \) primary unknowns, consisting of \( n_s \) species moles (\( m_i \)) and the variable for pressure \( P \). All other variables (\( u_j, m_i, S_j, \xi_j \)) are functions of the primary unknowns.

**Calculation of Injectivity.** Injectivity can be defined in various ways. In this paper, the injectivity is calculated as

\[ \text{Injectivity} = \frac{Q_{inj}}{P_{bhp} - P_{avg}} \]  

(13)

where \( P_{bhp} \) is the injection well bottom hole pressure (psi); \( Q_{inj} \) is the injection rate at reservoir conditions (ft\(^3\)); and \( P_{avg} \) is the pattern average pressure. The injection rate \( Q_{inj} \) is given by:

\[ Q_{inj} = WI \lambda_T (P_{bhp} - P_{wb}) \]  

(14)

where \( WI \) is the well index calculated from Peaceman’s model for a grid-block centered vertical well:

\[ WI = \frac{2\pi k_w h}{\log \left( \frac{r_e}{r_w} \right) + S}. \]  

(15)

In Eq. (15), \( k_w \) is the effective permeability for an injection well (md); \( h \) is the grid block thickness in the well direction (ft); \( r_e \) is the effective radius for the well block (ft); \( r_w \) is the wellbore radius (ft); \( S \) is the skin factor (dimensionless); and \( \lambda_T \) is the total mobility of the fluid in the well block given by:

\[ \lambda_T = \sum_{j=1}^{n_p} \frac{k_{rj}}{\mu_j} \]  

(16)

where \( k_{rj} \) and \( \mu_j \) are evaluated at the well block. The skin factor \( S \) is zero here, although precipitation or dissolution near the wellbore could be modeled as infinitesimal skin. The effect of mineral reactions on injectivity is accounted for through the change in permeability \( k_w \). **Equation (14)** indicates that there is a positive correlation between \( \lambda_T \) and the injectivity. However, the injectivity is not a local concept since the pattern average pressure \( P_{avg} \) is used in Eq. (13). The injectivity is normalized with the injectivity at the end of the secondary waterflood (Patel et al. 1987),

\[ \text{Normalized Injectivity} = \frac{\text{Injectivity}}{\text{Waterflood Injectivity}}. \]  

(17)
At the beginning of CO₂ injection, the normalized injectivity is therefore equal to 1.0. The normalized injectivity indicates the relative magnitude between injectivity in secondary and tertiary modes.

**Numerical solution.** We used the finite volume method to discretize the PDEs. The grid-block size varies spatially, with small grid blocks near the well to obtain grid-convergence. For each control volume \( k \), the pressure \( P_{k} \) and mole number \( N_{p, k} \) are assumed to be at the geometric center. The volumetric flow rate is evaluated at the interface between two control volumes using a central finite difference scheme. The temporal discretization uses a generalized non-iterative IMPEC solution, which treats the pressure variable in Eq. (12) using the backward Euler method and the total moles of primary species in Eq. (4) using the forward Euler method. The IMPEC solution is an operator splitting approach that solves the flow, transport and thermodynamic equilibrium equations. The IMPEC solution used in this paper generalizes the IMPEC formulation (Watts 1986; Chang 1990) to a coupled system with reactions. After the pressure is solved by a multi grid linear solver, the total moles of each primary species are calculated explicitly. A flash calculation is performed after pressure and mole numbers are calculated. The flash calculation yields the molar concentrations of each species so that Eqs. (1), (2) and (3) are satisfied under the constraint of Eq. (5). The inputs for the flash calculations are \( P, T \) and \( N_{p} \) \((p = 1, \ldots, n_{prl})\). The set of equations can be solved by successive substitution or the Newton-Raphson method. The last step is to update the properties that include the effects of mineral reactions on porous media properties such as changing permeability and porosity. The overall calculation procedure for one time step is shown in Fig. 2.

**Results and discussion**

The developed code (PennSim Toolkit 2013) was validated separately with CMG-GEM for the compositional modeling part and CrunchFlow for the reactive transport part (CMG 1995; Steefel 2009). The simulation results matched exactly for a series of benchmark problems. In the following, we focus on the injectivity alteration due to geochemical reactions in different injection schemes. Here first contact miscibility between CO₂ and oil was assumed to avoid the computational cost and instability in multiple contact miscibility simulation, while still reflecting the chemical aspects of CO₂ flooding on injectivity. The model system includes the representative oil, gas and ionic species in the hydrocarbon (hc) and aqueous (aq) phase. The species considered include \( \text{C}_{10} \) (hc), \( \text{C}_{10} \) (aq), \( \text{CO}_2 \) (hc), \( \text{CO}_2 \) (aq), \( \text{H}_2 \text{O} \) (hc), \( \text{H}_2 \text{O} \) (aq), \( \text{H}^+ \), \( \text{Ca}^{2+} \), \( \text{Cl}^- \), \( \text{Na}^+ \), \( \text{SO}_4^{2-} \), \( \text{HCO}_3^- \), \( \text{CO}_3^{2-} \), \( \text{OH}^- \), calcite (\( \text{CaCO}_3 \)), halite (\( \text{NaCl} \)) and gypsum (\( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \)). The critical properties and binary interaction parameters for the modified PR EOS are listed in Tables 1 and 2. The Debye-Hückel parameters for the aqueous species are from the EQ3/6 database (Wolery et al. 1990).

A 2-D five spot pattern is modeled as the base case using a stretched structured grid as shown in Fig. 3. The reservoir is homogeneous and isotropic in porosity and permeability with values of 0.1 and 10 md, respectively. This porosity and permeability is within the measured range for many carbonate reservoirs (Ehrenberg et al. 2006). The initial pressure was 3000 psi and the temperature was 105°F. The oil was 100% \( \text{C}_{10} \). The two phase Corey’s relative permeability model was used. The end-point permeability is 0.5 for the hydrocarbon phase and 0.3 for the aqueous phase to reflect a water wet condition. The initial water saturation is 0.8; the pattern had already been flooded to residual oil saturation. The reservoir rock is assumed to be limestone, which consists of 80% calcite and 10% quartz by bulk volume fraction, leaving 10% porosity. Quartz dissolution is orders of magnitude slower than calcite dissolution and is considered non-reactive within the time frame of the simulations. The specific surface area (SSA) of the calcite was set to 0.001 m²/g. This value is two orders of magnitude smaller than the measured surface area in the laboratory (0.1 m²/g) because reaction rates measured in the field are generally 2 to 5 orders of magnitude smaller because of physical and chemical heterogeneity, longer residence time, and smaller water-rock contact area (Wellman et al. 2003; Li et al. 2006; Li et al. 2014). The injection well in the five-spot is in the lower left corner with a constant reservoir volumetric rate of 200 ft³/day (average pattern velocity of 0.6 ft/day). The compositions of different types of waters, including formation water, fresh water and seawater are given in Table 3. These waters were injected in separate simulations to examine their effects on injectivity. These injection compositions do not lead to precipitation upon mixing under surface conditions. The production well is in the upper right corner grid block as shown in Fig. 3 with a constant bottom hole pressure of 3000 psi. The permeability porosity relation is the Carman-Kozeny relation with an exponent of 5.0 following Mohamed and Nasr-El-Din (2013). The input parameters are summarized in Table 4 and are case dependent.

As discussed previously, one goal of this paper is to understand how mineral dissolution/precipitation changes the permeability and the injectivity under different injection schemes, including continuous gas injection (CGI), water alternating CO₂ injection (WAG) and simultaneous water alternating gas injection (SWAG). This research does not exclude the importance of other properties like wettability alteration and relative permeability hysteresis.

**Continuous Gas Injection (CGI).** CGI is commonly used for gravity drainage reservoirs (Christensen et al. 2001). Although water is not injected, there remains some potential for mineral reactions with a large volume of formation water in place. The formation water composition is shown in Table 3 and is initially in solid-aqueous equilibrium with calcite. Other input parameters are shown in Table 4. Pure CO₂ in the supercritical state was injected for 1.0 pore volume (2250 days).

The evolution of multiple variables at the injection well block in the first 20 days is shown in Fig. 4. As shown in Fig. 4A, CO₂ total concentration in the aqueous phase increased sharply, indicating quick equilibrium between the aqueous and CO₂.
phases. Correspondingly, pH decreased sharply as CO₂ dissolved, as shown in Fig. 4B. When water is saturated with CO₂, the pH decreased to 3.3 at the CO₂ partial pressure of 3000 psi. As a result, calcite dissolved rapidly under this highly acidic condition, which consumed the hydrogen ions and in turn increased the pH to a value of 4.2. Fig. 4C shows the saturation index (SI) of calcite and halite, where the value indicates the tendency for continued precipitation (SI > 1), dissolution (SI < 1), or no change (SI = 1). The calcite SI increased to 1.0 within the first day, indicating the calcite reached equilibrium in the wellbore grid block, which explains the fast increase of pH within the first day. Fig. 4C also indicates that the aqueous phase reached equilibrium with calcite much faster than for halite. This is because there was originally no halite in place and the increase of the halite saturation index is only because of water vaporization. In addition, halite also has a much higher solubility than calcite. Figure 4D shows the water saturation history at the injection well block. As pure CO₂ contacted connate water, water was displaced by CO₂ and simultaneously vaporized into the hydrocarbon phase. The water saturation decreased sharply to 0.38 in the first 0.5 days in a piston-like displacement. The aqueous phase is immobile below a water saturation of 0.32, indicating that the saturation decrease afterwards is not due to water flow, but instead is the result of water vaporization. Correspondingly, concentrations of the ion species, including Na⁺, increased to as high as 7 mol/kg-water, as shown in Fig. 4E. The aqueous solution was saturated with halite after day 7, leading to halite precipitation. Figure 4F shows that the volume fraction of halite reaches 0.0017, accounting for 2% of the pore volume after 12 days.

Figure 5A shows the water saturation profile along the diagonal streamline between the injector and producer (the shortest streamline in the five-spot pattern as shown by the red line in Fig. 3). On day 667, there were two shocks, one is the Buckley-Leverett shock at around 30 ft and the other is the slow water vaporization front at around 15 ft (Buckley and Leverett 1941). Figure 5B shows the profile of C mâ©. The oil bank was produced along the streamline on around day 800. After 1125 days, the swept area was almost free of C mâ©. The high displacement efficiency is the result of the displacement being first contact miscible. Figures 5C and 5D show the spatial distribution of the halite volume fraction and porosity along the diagonal streamline. The porosity change caused by halite precipitation near the injection well was small (less than 0.002). The halite precipitated when the water vaporized completely within 15 ft of the injection well. Figure 6 shows that the normalized injectivity increased by a factor of about five. However this increase is mainly because of the increase in total mobility owing to low CO₂ viscosity, not the change in porosity.

In summary, the simulation results show that halite precipitation and porosity reduction was localized within a distance of about 3 to 40 ft from the injection well. At the field pattern scale, the reaction induced formation damage was minimal because of negligible changes in porosity and permeability. Reactions played a negligible role in CGI injection primarily because no water was injected to dilute the mineral-saturated aqueous phase. Injectivity increased primarily because of the lower viscosity of CO₂.

**Simultaneous water-alternating-gas injection (SWAG).** For SWAG, three different sets of injection water composition were used, including formation water, seawater, and freshwater to understand the role of injection water in affecting injectivity (see Table 3). We also consider carbonated waterflooding in this section, which is a limiting case of SWAG where CO₂ saturated water is injected (no free gas is injected).

**SWAG using formation water.** In primary and secondary recovery, a common practice is to inject the produced water into the reservoir to maintain reservoir pressure and increase recovery. In this case, the injection water is the formation water. Figure 7A shows the calcite volume fraction along the diagonal streamline between the injector and producer. Calcite dissolution occurred within 10 ft of the injection well. This region is small because calcite dissolution is fast and quickly increased the saturation index and pH. The size of the dissolution region depends on the injection rate and can extend outward until it reaches a distance where the water is saturated with that mineral. That is, larger injection flow rates increase the size of the dissolution region. Figure 7B shows that the porosity increased by as much as 0.07 in the injection well block. Most of the porosity increase is in the vicinity of the injection well, indicating that the porosity alteration was a localized phenomenon for the rate of 200 ft³/day. The change in porosity also depends on the injection duration. At the injection well block, the porosity increased at the rate of 0.012 per year. If injection continues, the porosity at the injection well would increase further until all calcite is consumed. Figure 7C shows that at the injection well block, permeability increased from 10 md to 160 md over the simulation duration. Figures 7D and 7E show that the oil bank has low mobility compared to the trailing gas. The mobility of water is between the oil and gas component mobilities. The oil bank therefore builds up as CO₂ moves forward.

Figure 7F shows the pressure profiles after 7, 667, and 1125 days. The pressure at any particular location decreases with time because the total fluid mobility increases with time. On 667 days, as the low mobility oil front approached the production well, the transmissibility between the field and production well decreased. The reservoir pressure increased because the production well was operated at fixed pressure. This explains the temporal evolution of the bottom-hole pressure and field average pressure in Fig. 8A. The injection well pressure and the field average pressure sharply increased after 667 days due to the breakthrough of the oil bank. Since the production well had fixed bottom-hole pressure and the injection well had fixed volumetric rate, the injection well bottom-hole and pattern average pressure increased. After the oil bank broke through, the total fluid mobility was high and the field pressure decreased. Figure 8B shows that the normalized injectivity increased much more with mineral reactions than without mineral reactions. The injectivity measures how well the injection well is connected to the reservoir and is positively correlated to the total fluid mobility. For both cases (with or without mineral reactions), the total fluid mobility increases as the gas is injected (see Fig. 7E) so that injectivity increased. For the case with mineral reactions, the calcite dissolution increased the porosity and permeability significantly (shown in Figs. 7A, 7B, and
The comparison in Fig. 8B indicates that more than 60% of the injectivity increase is because of calcite dissolution. A small oscillation in the injectivity is observed when the oil bank reached the production well.

The spatial distribution of pH and Ca\(^{2+}\) concentration are highly correlated as shown in Figs. 9A and 9B. The increase of pH and Ca\(^{2+}\) near the injection well is because mineral dissolution consumed the H\(^+\) ions. Figure 9C shows the CO\(_2\) (aq) total concentration, which represents the fronts of the injected fluid containing CO\(_2\). The spatial-temporal evolution of CO\(_2\) mirrors the change in pH. The difference between the pH and CO\(_2\) (aq) indicates that the pH was controlled not only by CO\(_2\) dissolution but also by mineral dissolution. CO\(_2\) dissolution is assumed to be in equilibrium while the calcite dissolution is assumed to be controlled by reaction kinetics. Therefore, CO\(_2\) lowered the pH instantaneously while the mineral elevated pH response was delayed. Figure 9D shows the profile of the nonreactive tracer Cl. Comparison of Ca\(^{2+}\) and Cl profiles indicates that the Ca\(^{2+}\) front moved faster than the tracer in the aqueous phase. Thus, the increase of the Ca\(^{2+}\) concentration with distance is a result of the reactions rather than the transport of injected water. This also indicates that CO\(_2\) in the hydrocarbon phase travels faster than the aqueous phase.

Compared with the CGI case, the porosity and permeability increase is much more significant with SWAG because the continuous injection of water increased the contact time between CO\(_2\) in the vapor and unsaturated brine, which allows for much more calcite dissolution and therefore injectivity increase.

**SWAG using seawater.** Due to the existence of sulfate (SO\(_4^{2-}\)), seawater injection can lead to CaSO\(_4\) precipitation, which often takes many forms including CaSO\(_4\), CaSO\(_4\)\(\cdot\)\(H_2\)\(\cdot\)\(H_2O\), and CaSO\(_4\)\(\cdot\)\(2H_2\)\(\cdot\)\(O\). Here we assume that all CaSO\(_4\) precipitates as CaSO\(_4\)\(\cdot\)\(2H_2\)\(\cdot\)\(O\) (gypsum), one of the most common scales found in the field. The injection water is compatible with the formation water under surface conditions, but not under reservoir conditions with the presence of calcite.

Figure 10A shows the porosity profile in the vicinity of the injection well, where the porosity decreases at around 7 ft from the injection well. Figures 10B and 10C show the resulting gypsum and calcite volume fractions along the shortest streamline (diagonal streamline) between the injector and producer. Similar to the previous case with injected formation water (Fig. 7A), calcite dissolved within 20 ft of the injection well. The Ca\(^{2+}\) concentration increases as the water flows into the reservoir, while the SO\(_4^{2-}\) concentration is relatively constant as SO\(_4^{2-}\) is transported with the injected water. At some distance from the injection well, CaSO\(_4\) reaches its equilibrium concentration and precipitates out. The precipitation is some distance from the well because it takes time for Ca\(^{2+}\) to reach sufficiently high concentration for CaSO\(_4\) precipitation to occur. With continued injection the bulk volume fraction of gypsum increases with time, while calcite continues to dissolve around the injection well. The net effect is the continued formation of scale (gypsum) beyond 7 ft from the injection well. Depending on the relative magnitude of the calcite dissolution rate and the injection rate, gypsum can precipitate at different locations. Figures 10D and 10E show that the porosity increased within 5 ft of the injector, but decreased suddenly 7 ft away. The permeability profile shows a similar trend, but to a larger extent. The injectivity first increased and then decreased, depending on the combined effect of calcite dissolution and subsequent gypsum precipitation (Fig. 10F). Compared with the previous case with injected formation water, the formation has a 20% injectivity decrease on day 2,250.

**Comparison of SWAG using fresh water, formation water, and seawater.** Fresh water can be used to avoid scaling because minerals are generally more soluble in fresh water. Fresh water however could cause clay swelling depending on the clay type. Figure 11A shows that when injecting fresh water, dissolution was only significant around the injection well, which is similar to the results in Fig. 7A. However, in this case the size of the dissolution region increased significantly. Figures 11B and 11C compare the porosity and permeability profiles after 2250 days for different injection waters. The porosity and permeability increased more when fresh water is injected compared to the other two water compositions. Figure 11D shows that the injectivity increased 80% with fresh water injection, compared to a 20% decrease with seawater injection. The comparison emphasizes the importance of the injection water composition, even if the injected water is compatible with the formation water under surface conditions.

**Carbonated water injection.** Carbonated water injection (CWI) is a special case of SWAG when injected water is saturated with CO\(_2\). CWI is sometimes used to improve sweep efficiency (by viscosity reduction) and to increase oil solubility (Puon et al. 1988). In Fig. 12A, we compare the porosity alteration in CWI and SWAG cases using formation water. In these simulations, the gas water volume ratio is 1:1 for SWAG and is zero for CWI. The CWI case shows a similar, however larger porosity increase than for SWAG, primarily because more injected water in the CWI cases leads to more calcite dissolution. Figure 12B shows that the aqueous phase in SWAG maintains low pH because of the increased supply of CO\(_2\). For CWI, 1.0 pore volume of water is injected while for SWAG, 0.5 pore volume of water is injected. Therefore, per unit volume of water injected, the calcite dissolved in the SWAG case is almost twice that in the CWI case.

The simulation results for all of the above cases show that the aqueous and mineral reactions are important in determining the porosity, permeability and the injectivity. Calcite dissolution typically occurs around the injection well in these injection cases. If the injection water contains sulfate, however, precipitation occurs at a distance further away from the injection well.

**Effect of specific surface area.** The mineral reaction rates depend on the intrinsic reaction rate constant and the specific surface area (SSA). For calcite, the laboratory measured SSA ranges from 0.01 to 2 m\(^2\)/g (Walter and Morse 1984). The rock is usually crushed into fine powder and then the SSA is measured by adsorption with a BET isotherm (Walter and Morse 1984). This measured value tends to be too large for the reactions at the field scale, where various conditions exist to reduce the reaction rates (Lichtner 1996; Li et al. 2006; Li et al. 2014). In addition, for multiphase flow, the water-rock contact area also depends on wettability so that a smaller fraction of the rock surface is in direct contact with the reactive aqueous phase (Izgec et al. 2007). SSA can also be calculated from a geometric model of the pore space for calcite grains, where a smaller
value is more typical (0.0003 to 0.2 m²/g) (Brosse et al. 2005). Here we used a small value of 0.001 m²/g for the base case and varied the SSA value from 0.01 to 0.0001 m²/g to understand the role of SSA in SWAG floods. The formation water was used as the injection fluid. Simulation results show that for these three values, the total dissolved volume is almost the same (relative difference is less than 0.5%). However, the dissolution profile differs significantly, as shown in the porosity profile in Fig. 13A. For large SSA, the reaction rate is fast and the dissolution is only in the injection well block. For small SSA, the reaction rate is relatively slow and the dissolution region extends outward so that the porosity increase for the injection block is not as large. Figure 13B shows the comparison of injectivity for the three values of SSA. The base case gives the largest injectivity implying that there is an optimum value for maximum injectivity. Larger SSA leads to more localized dissolution and therefore flow is still restricted more by the rock outside this zone. Smaller SSA extends the permeability increase to a much larger zone, however with lower overall impact on injectivity.

**Water-alternating-gas (WAG) injection.** WAG is the most commonly used method for CO₂ EOR (Christensen et al. 2001; Rogers and Grigg 2001). It is challenging to simulate WAG when both gas dissolution and water vaporization are considered because of the rapid disappearance and reappearance of the hydrocarbon and aqueous phases and the reaction rates considered. The disappearance of the hydrocarbon phase is naturally modelled with a cubic equation-of-state (EOS) compositional model. When the aqueous phase disappears, the solute precipitates out as the solute concentrations in the aqueous phase become larger. This precipitation is challenging to simulate owing to the time scales of the reactions. Here we used a pseudo solid phase to store the un-precipitated solute following the approach of Farshidi et al. (2013). When the water saturation becomes so small that the ionic strength is greater than 10 mol/kg water, the chemical speciation is terminated and the solutes are stored in the pseudo solid phase.

WAG injection was simulated with the same total volume (CO₂ and water) at reservoir conditions in a 1:1 volume ratio. The mineral reactions cause significantly different effects on injectivity alteration for a varying number of WAG cycles. In Fig. 14A, the porosity of the injection well block after 2250 days is plotted with respect to slug size. The slug size here refers to the volume of each gas cycle. As the slug size decreases, the porosity exhibits a highly nonlinear response and approaches its value for SWAG since both used the same CO₂/water volume ratio. Surprisingly, it takes more than 1000 cycles to achieve a similar porosity increase as SWAG however. WAG floods for a practical number of cycles (< 10) do not exhibit a significant change in porosity for the cases studied. Figure 14B shows that the porosity change is monotonic with the number of WAG cycles and will increase if given sufficient injection time even for a practical number of cycles. The highly nonlinear behavior in Fig. 14A occurs because dissolution requires a sufficient supply of unsaturated water to pass through a particular location as was seen for SWAG floods. For WAG, the coexistence of CO₂ and water at the injection block is only maintained for a short time when a few cycles are used so that porosity does not change as significantly.

Figure 14C demonstrates the hydrocarbon (gas) saturation history at the injection well block in a three-cycle WAG case. In the gas cycle, the residual water and oil were vaporized and only the solvent (gas) remains. In the water cycle, the trapped gas (20% saturation) is dissolved and only the aqueous phase exists. Both phenomena lead to either solvent or aqueous phase at the injection well block for most of the simulation. As the mineral reactions require low pH from CO₂ dissolution and water flux to transport the solute, the mineral dissolution is significantly reduced with only CO₂ or water present in the grid block at particular times. Figure 14D compares the injectivity history for three cycles and ten cycles. As expected, the gas cycle has much larger injectivity than for water injection. The maximum and minimum injectivity in each cycle increases slightly from cycle to cycle. The injectivity is likely to be dominated by relative permeability hysteresis and viscosity of the injected fluids in this case, not the mineral reactions. In addition, trapped CO₂ can act as a continued source of acidity and can significantly impact the extent of mineral reactions. For SWAG, however, mineral reactions are significant and can greatly increase or decrease injectivity.

**Conclusions**

We presented a compositional model with reactions in carbonate reservoirs and studied the impact of mineral reactions (precipitation and dissolution) on the injectivity for various 2-D five-spot first contact miscible floods involving continuous gas injection (CGI), simultaneous water and gas injection (SWAG), and water-alternating-gas injection (WAG). The results demonstrate the capability of the new simulator in coupling phase behavior and chemical reactions, and in predicting injectivity alteration. The key conclusions are:

- Under the injection rate of 200 ft³/day, calcite dissolution is generally localized at the immediate vicinity of the injection well. This dissolution region is typically limited within 20 ft from the injection well.
- Continuous CO₂ gas injection (CGI) does not lead to significant porosity change due to the lack of injected water to flush out the dissolved products of calcite dissolution.
- Simultaneous CO₂ and water injection (SWAG) leads to significant calcite dissolution because of the co-existence of CO₂ and water, which dissolves calcite.
- The composition of the injection water plays an important role in determining injectivity alteration. The injectivity significantly increased when the formation water and fresh water were injected. With the injection of sulfate-containing seawater, gypsum precipitation at some distance away from the injection well led to reduced injectivity.
- Carbonated water flooding affects injectivity more than SWAG (at 1:1 CO₂ volume ratio) because more CO₂-containing water is in contact with the rock.
- Calcite dissolution and the corresponding porosity changes increase with the number of cycles, ultimately approaching that of SWAG. It takes more than 1000 cycles to approach SWAG for the cases studied.
- Precipitation and dissolution occur at different places within the reservoir and can occur in various patterns based on injection schemes.

The simulation results indicate that the impact of mineral reactions on injectivity can depend strongly on particular conditions, which may contribute to the disagreement in the literature about its importance in altering reservoir properties. Both injection schemes and injection water composition are important. For SWAG, the mineral reactions can increase injectivity by 50% for the cases studied. In all cases, the water composition changed significantly when mineral reactions were considered. This research also indicates that CO₂-water-mineral contact drives the areal extent and the magnitude of the mineral reactions, indicating total injected water volume flow rates can play a key role in determining the ultimate impacts of mineral reactions.

Acknowledgments
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Nomenclature
\( a_s \) = activity of species \( s \) (dimensionless)
\( (aq) \) = aqueous phase
\( A_l \) = chemical formula of species \( l \)
\( A_s \) = specific surface area of the mineral species \( s \)
\( D \) = diffusion/displacement coefficient tensor \((ft^2/day)\)
\( E_a \) = activation energy \((J/mol)\)
\( F_p \) = total molar rate of the primary species \( p \) \((lbmol/day)\)
\( f_i \) = molar rate of species \( i \)
\( f_s \) = fugacity of species \( s \)
\( g_j \) = specific gravity factor of the \( j^{th} \) phase \((psi/ft)\)
\( (hc) \) = hydrocarbon phase
\( IAP_r \) = ionic activity product of reaction \( r \)
\( K_{eq,r} \) = equilibrium constant of reaction \( r \)
\( k \) = permeability \((md)\)
\( k_{r,j} \) = relative permeability of phase \( j \)
\( k_{r,l} \) = reaction constant of reaction \( r \) along the \( l^{th} \) path \((mol/m^2-s)\)
\( m_i \) = moles of species \( i \) \((lbmol)\)
\( n_p \) = number of primary species
\( n_r \) = number of reactions
\( n_{ph,eq} \) = number of the phase equilibrium relations
\( n_{cheq} \) = number of the equilibrium-controlled chemical reactions
\( n_{m,kin} \) = number of the kinetic-controlled chemical reactions
\( n_{sec} \) = number of secondary species
\( n_s \) = number of species
\( N_p \) = total moles of the primary species \( p \)
\( P_j \) = pressure of phase \( j \) \((Pa)\)
\( P_{bhp} \) = bottom hole pressure
\( P_{cj} \) = capillary pressure between phase \( j \) and a reference phase
\( Q_p \) = total molar rate of primary species \( p \) \((lbmol/day)\)
\( q_i \) = molar rate of species \( i \) \((lbmol/day)\)
\( R \) = universal gas constant \((8.31 J/mol-K)\)
\( R_{k,l} \) = reaction rate of reaction \( k \) along the \( p^{th} \) path
\( r_e \) = effective well block radius
\( (s) \) = the solid phase
\( S_j \) = saturation of phase \( j \) (dimensionless)
\( S \) = skin factor
\[ S_{n_s \times n_p} = \text{the stoichiometry matrix} \]
\[ T = \text{temperature (K)} \]
\[ u_j = \text{volumetric flow rate of phase } j \ (\text{m}^3/\text{day}) \]
\[ V_b = \text{bulk volume} \]
\[ V_f = \text{total fluids volume} \]
\[ WI = \text{well index} \]
\[ x_{ij} = \text{mole fraction of species } i \text{ in phase } j \]
\[ \bar{v}_{ip} = \text{the } (i, p) \text{ entry in the stoichiometry matrix for the reactions in the original form} \]
\[ v_{ip} = \text{the } (i, p) \text{ entry in the stoichiometry matrix for the reactions in canonical form} \]
\[ \lambda_T = \text{total fluid mobility (1/cp)} \]
\[ \xi_j = \text{molar density of phase } j \ (\text{lbmol}/\text{ft}^3) \]
\[ \gamma_i = \text{activity coefficient of species } i \ (\text{kg-water/mol}) \]
\[ \phi = \text{porosity (dimensionless)} \]
\[ \emptyset = \text{the empty set} \]
\[ \rho = \text{density (kg/m}^3) \]
\[ \mu_j = \text{viscosity of phase } j \ (\text{cp}) \]

References


El Sheemy, M. M. 1987. Water Injection Performance: Case Study and Related Spontaneous Injectivity Improvement. Paper SPE 15740 presented at the Middle East Oil Show, Bahrain, 7-10 March. [http://dx.doi.org/10.2118/15740-MS]


Table 1: Critical property of the components

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<th>Name</th>
<th>Pc (psi)</th>
<th>Tc (R)</th>
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<th>Vc (ft^3/lbmol)</th>
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<tr>
<td>C10</td>
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Table 2: Binary interaction coefficients (Mohebbinia et al. 2013)

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<th></th>
<th>CO2</th>
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<th>H2O</th>
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<td>C10</td>
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<tr>
<td>H2O</td>
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Table 3 - Brine compositions used in this research. The seawater composition is from Haarberg et al. (1992). The formation water composition is from Austad et al. (2011). The unit of the concentrations is molality (mol/kg water). The pH is dimensionless.

<table>
<thead>
<tr>
<th>Seawater (SW)</th>
<th>Formation water (FW)</th>
<th>Fresh water (FW)</th>
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<td>CO2 (aq)</td>
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</tr>
<tr>
<td>Ca2+</td>
<td>0.001</td>
<td>0.437</td>
</tr>
<tr>
<td>Cl-</td>
<td>0.662</td>
<td>3.643</td>
</tr>
<tr>
<td>Na+</td>
<td>0.594</td>
<td>2.62</td>
</tr>
<tr>
<td>SO4²⁻</td>
<td>0.032</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 4 – Input parameters for the simulation cases.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well pattern</td>
<td>Five-spot</td>
</tr>
<tr>
<td>Pattern size</td>
<td>300 ft x 300 ft x 50 ft</td>
</tr>
<tr>
<td>Formation mineralogy (volume fraction)</td>
<td>0.8 calcite, 0.1 nonreactive minerals, 0.1 pore space</td>
</tr>
<tr>
<td>Calcite specific surface area</td>
<td>1 m$^2$/kg</td>
</tr>
<tr>
<td>Initial pressure</td>
<td>3000 psi</td>
</tr>
<tr>
<td>Temperature</td>
<td>105 °F</td>
</tr>
<tr>
<td>Average porosity</td>
<td>0.1</td>
</tr>
<tr>
<td>Average permeability</td>
<td>10 md</td>
</tr>
<tr>
<td>Oil composition</td>
<td>0.999 C$_{10}$, 0.001 C$_1$</td>
</tr>
<tr>
<td>Initial water saturation</td>
<td>0.8</td>
</tr>
<tr>
<td>Injection rate</td>
<td>200 ft$^3$/day at reservoir condition</td>
</tr>
<tr>
<td>Injection time</td>
<td>2250 days</td>
</tr>
<tr>
<td>Production condition</td>
<td>Constant bottom hole pressure of 3000 psia</td>
</tr>
</tbody>
</table>

Figure 1- The CO$_2$(aq) total mole fraction in aqueous phase with varying CO$_2$ partial pressure at 77°F. The curves were calculated by flash calculations with and without calcite reactions.
Begin one time-step calculation

**Pressure solver (Eq. (12))**
Calculate the Jacobian matrix for implicit pressure solution
Use multigrid preconditioned linear solver to solve the pressure

**Transport solver (Eq. (4))**
Calculate flux between blocks using the new pressure and old transmissibility
Calculate the total moles of the primary species in each grid block

**Flash and reaction solver (Eqs. (1)(2)(3)(5))**
Use Newton Raphson method to solve the chemical equilibrium, kinetic and phase equilibrium equations

**Property update**
Calculate the porosity and permeability from the moles of mineral species

Proceed to next time-step

---

**Figure 2 – Flow chart of the IMPEC solution scheme for one time step.**

---

**Figure 3 - The grid blocks for the five-spot pattern used in this research.** The block size near the injection well is 2 ft, but increases to 20 ft away from the well. The domain is gridded this way to capture the fast varying processes near the well. The diagonal red line is the shortest streamline. The blue dot at the lower left corner is the injector. The red dot at the upper right corner is the producer.**
Figure 4 - Evolution of the properties at the injection well block in the first 20 days of CO₂ injection for CGI. (A) CO₂ total concentration (mol/kg water) in aqueous phase. The total concentration is the sum of the concentration of CO₂ (aq), HCO₃⁻, and CO₃²⁻. (B) pH. (C) Saturation index of calcite and halite. (D) Water saturation. (E) Na⁺ concentration. (F) Halite volume fraction.
Figure 5 – Profiles along the diagonal streamline of the five-spot pattern for CGI. (A) Water saturation. (B) $C_{10}$ overall molar fraction. (C) Halite volume. (D) Porosity.

Figure 6 - Normalized injectivity evolution for CGI flood. The small notch at around 800 days is due to the rapid pressure change that occurs when the oil bank breaks through.
Figure 7 – Profiles along the diagonal streamline of the five-spot pattern using SWAG with formation water injection. (A) Calcite volume fraction. (B) Porosity. (C) Permeability. (D) Water saturation. (E) Total fluid mobility. (F) Pressure.
Figure 8 – Evolution of SWAG with formation water injection. (A) Injector bottom hole pressure and field average pressure. (B) Injectivity. The red curve is the calculated injectivity with reactions considered. The blue curve is the calculated injectivity without reactions.

Figure 9 – Profiles along the diagonal streamline of the five-spot pattern using SWAG with formation water injection. (A) pH. (B) Ca\(^{2+}\) concentration. (C) CO\(_2\) total concentration. (D) Cl\(^-\) concentration.
Figure 10 – Profiles and evolution of SWAG with seawater injection. (A) Porosity in the vicinity of the injection well. (B) Gypsum volume fraction. (C) Calcite volume fraction. (D) Porosity. (E) Permeability. (F) Normalized injectivity evolution.
Figure 11 – Profiles along the diagonal streamline of the five-spot pattern using SWAG. (A) Porosity for SWAG with fresh water injected. Profiles at 2250 days for SWAG with fresh water, seawater and formation water injection. (B) Porosity. (C) Permeability. (D) Injectivity evolution.

Figure 12 - Profiles along the diagonal streamline of the five-spot pattern and evolution of CWI and SWAG with formation water injection. (A) Porosity. (B) pH at 667 days.
Figure 13 – Profiles along the diagonal streamline of the five-spot pattern using SWAG with formation water injection and variable specific surface area (SSA). (A) Porosity. (B) Normalized injectivity. Units for SSA are m$^2$/g-solid.

Figure 14 – (A) Porosity at 2250 days for different SWAG values. (B) Porosity temporal evolution at the injection well block. (C) Hydrocarbon phase saturation history at the injection well block for the 3 cycle WAG case. (D) Normalized injectivity for 3-cycle and 10-cycle WAG injection using FW.
Appendix

This section lists all the reactions in the model system and illustrates the stoichiometry matrix. In the model system, we have 17 species, and eight of them are selected as the primary species and ordered as

\[
\begin{pmatrix}
C_{10}(hc) \\
H_2O (hc) \\
CO_2(aq) \\
H^+ \\
Ca^{2+} \\
Cl^- \\
Na^+ \\
SO_4^{2-}
\end{pmatrix}.
\]

The moles of all the species are related to the primary species by the reactions in the canonical form as shown in Table A-1. Based on the relations in Table A-1, the stoichiometry matrix \( S \) is written as

\[
S = (v_t)_{17 \times 8} =
\begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & -2 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & -2 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & -2 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\
0 & 2 & 0 & 0 & 1 & 0 & 0 & 1
\end{pmatrix}.
\]

The total moles of the primary species is calculated from

\[
N_p = \sum_{i=0}^{n_s} v_{ip} m_i.
\]

The total moles of primary species \( p \) is a weighted sum of the moles of all the species, where the weight of each species is the entry of the \( p^{th} \) column in the stoichiometry matrix \( S \).
Table A-1: The reactions and their type used in the model system. The reactions are written in the canonical form (Lichtner 1985). The equilibrium constants at 105 °F are from Wolery et al. (1990). The equilibrium constants were obtained by interpolating between the values at the reference temperature. The dependence of the equilibrium constants on pressure is not included.

<table>
<thead>
<tr>
<th>Relations</th>
<th>Relation type</th>
<th>Equilibrium Constants (log(<em>{10}K</em>{eq}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(<em>{10}) (hc) ↔ C(</em>{10}) (hc)</td>
<td>self</td>
<td>-</td>
</tr>
<tr>
<td>H(_2)O (aq) ↔ H(_2)O (aq)</td>
<td>self</td>
<td>-</td>
</tr>
<tr>
<td>CO(_2) (aq) ↔ CO(_2) (aq)</td>
<td>self</td>
<td>-</td>
</tr>
<tr>
<td>H(^+) ↔ H(^+)</td>
<td>self</td>
<td>-</td>
</tr>
<tr>
<td>Ca(^{2+}) ↔ Ca(^{2+})</td>
<td>self</td>
<td>-</td>
</tr>
<tr>
<td>Cl(^-) ↔ Cl(^-)</td>
<td>self</td>
<td>-</td>
</tr>
<tr>
<td>Na(^+) ↔ Na(^+)</td>
<td>self</td>
<td>-</td>
</tr>
<tr>
<td>SO(_4)(^2-) ↔ SO(_4)(^2-)</td>
<td>self</td>
<td>-</td>
</tr>
<tr>
<td>HCO(_3^-) ↔ CO(_2) (aq) + (-1) H(^+)</td>
<td>reaction equilibrium</td>
<td>6.34</td>
</tr>
<tr>
<td>CO(_3)(^2-) ↔ CO(_2) (aq) + (-2) H(^+)</td>
<td>reaction equilibrium</td>
<td>16.32</td>
</tr>
<tr>
<td>OH(^-) ↔ H(_2)O + (-1) H(^+)</td>
<td>reaction equilibrium</td>
<td>13.99</td>
</tr>
<tr>
<td>C(<em>{10}) (aq) ↔ C(</em>{10}) (hc)</td>
<td>phase equilibrium</td>
<td>-</td>
</tr>
<tr>
<td>CO(_2) (hc) ↔ CO(_2) (aq)</td>
<td>phase equilibrium</td>
<td>-</td>
</tr>
<tr>
<td>H(_2)O (hc) ↔ H(_2)O (aq)</td>
<td>phase equilibrium</td>
<td>-</td>
</tr>
<tr>
<td>Calcite ↔ CO(_2) (aq) + (-2) H(^+) + Ca(^{2+})</td>
<td>reaction kinetic</td>
<td>8.23*</td>
</tr>
<tr>
<td>Halite ↔ Na(^+) + Cl(^-)</td>
<td>reaction equilibrium</td>
<td>1.59</td>
</tr>
<tr>
<td>Gypsum ↔ 2 H(_2)O (aq) + Ca(^{2+}) + SO(_4)(^2-)</td>
<td>reaction equilibrium</td>
<td>-3.56</td>
</tr>
</tbody>
</table>

*The kinetic rate constant of calcite dissolution used here is 10\(^{-6.19}\) mol/m\(^2\)-s (Svensson and Dreybrodt 1992)