Capillary processes increase salt precipitation during CO$_2$ injection in saline formations

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An important attraction of saline formations for CO$_2$ storage is that their high salinity renders their associated brine unlikely to be identified as a potential water resource in the future. However, high salinity can lead to dissolved salt precipitating around injection wells, resulting in loss of injectivity and well deterioration. Earlier numerical simulations have revealed that salt precipitation becomes more problematic at lower injection rates. This article presents a new similarity solution, which is used to study the relationship between capillary pressure and salt precipitation around CO$_2$ injection wells in saline formations. Mathematical analysis reveals that the process is strongly controlled by a dimensionless capillary number, which represents the ratio of the CO$_2$ injection rate to the product of the CO$_2$ mobility and air-entry pressure of the porous medium. Low injection rates lead to low capillary numbers, which in turn are found to lead to large volume fractions of precipitated salt around the injection well. For one example studied, reducing the CO$_2$ injection rate by 94% led to a tenfold increase in the volume fraction of precipitated salt around the injection well.

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1. Introduction

An important aspect of many international CO\textsubscript{2} emissions reduction plans involves storing CO\textsubscript{2} within the pore space of brine-containing aquifers, often referred to as saline formations (Nordbotten & Celia 2006; MacMinn et al. 2010). The reason for choosing saline formations as opposed to freshwater aquifers is the idea that brine is sufficiently saline that it is unlikely to be suitable for exploitation as a future water resource. However, the dissolved salt within the brine can lead to operational problems (Miri and Hellevang 2016).

When CO\textsubscript{2} is injected into a saline formation, there is a high interfacial area between the CO\textsubscript{2} and the brine. Consequently, there is dissolution of CO\textsubscript{2} into the brine and evaporation of the water into the CO\textsubscript{2}-rich phase (Spycher et al. 2003). Surrounding the injection well, a dry-out zone develops where the water in the brine is completely evaporated. A consequence of this evaporation is that the dissolved salt precipitates as a solid phase, leading to significant loss of permeability around the injection well. Ultimately, this process can lead to complete deterioration of the injection well (Miri and Hellevang 2016).

A number of numerical modeling studies have been undertaken to investigate important controls on salt precipitation in the dry-out zone. Zeidouni et al. (2009) derived an analytical solution using method of characteristics (MOC) to estimate the volume fraction of precipitated salt in the dry-out zone (hereafter referred to as \( C_{30} \)) due to CO\textsubscript{2} injection in saline formations. They concluded that the distribution of precipitated salt was uniform within the dry-out zone.

An important limiting assumption was that there is a local pressure equilibrium between the CO\textsubscript{2}-rich and aqueous phases. The difference between the pressures of a non-wetting and wetting phase (the CO\textsubscript{2}-rich and aqueous phases, respectively, in this con-
Capillary processes increase salt precipitation

Capillary processes increase salt precipitation. Pruess and Muller (2009) explored the same problem using the numerical reservoir simulator, TOUGH2, with the CO₂ storage module, ECO2N (Pruess and Spycher 2007). When capillary pressure is set to zero, \( C_{30} \) is found to be insensitive to injection rate. However, when capillary pressure is accounted for, \( C_{30} \) is found to increase with reducing CO₂ injection rate.

A physical explanation is provided as follows (Pruess and Muller 2009): capillary pressure is significantly increased as the wetting saturation is reduced. This can lead to a reversing in the direction of the wetting pressure gradient, which in turn results in counter-current flow, whereby brine flows in the opposite direction to the injected CO₂. The counter-current flow provides additional brine to the dry-out zone leading to an increased availability of salt for precipitation. The counter-current flow rate is driven by phase saturation gradients. As the injection rate increases, the counter-current flow becomes less significant in comparison.

Kim et al. (2012) extended the work of Pruess and Muller (2009) by performing a wider sensitivity analysis. They found that the value of \( C_{30} \) was significantly increased for scenarios involving high permeability and low injection rates. Furthermore, contrary to Zeidouni et al. (2009), they found that \( C_{30} \) was non-uniform, with the highest values present at the edge of the dry-out zone. This localized increase in salt precipitation is attributed to the combined effects of gravity and capillary pressure driven counter-current flow.

Li et al. (2013) found that smoother capillary pressure curves lead to faster dissolution of CO₂ into the aqueous phase. This is presumably because smoother capillary pressure curves lead to more capillary diffusion of the CO₂-rich phase and hence greater interfacial area between the CO₂-rich phase and the aqueous phase.

The suite of numerical simulations described by Pruess and Muller (2009) and Kim et
H. L. Kelly and S. A. Mathias (2012) have provided significant insight into the processes that control salt precipitation during CO₂ injection in saline formations. However, probably due to the perceived computational expense of numerically simulating this problem to an adequate accuracy, a more widespread sensitivity analysis has not been undertaken to further understand this process.

Analytical solutions have been developed to better understand many other aspects of the CO₂ storage process. Nordbotten & Celia (2006) developed a similarity solution to study the propagation rate of a CO₂ plume and its associated dry-out zone during injection of CO₂ into a cylindrical saline formation. Hesse et al. (2007, 2008) and MacMinn et al. (2010, 2011) developed MOC solutions to study the migration of CO₂ plumes following the cessation of injection. Mathias et al. (2011a) extended the analytical solution of Nordbotten & Celia (2006) to estimate the resulting pressure buildup within an injection well. Mathias et al. (2011b) combined the work of Mathias et al. (2011a) and Zeidouni et al. (2009) to study the role of partial miscibility between the CO₂ and brine on pressure buildup. More recently, Mathias et al. (2014) derived a MOC solution to estimate the temperature distribution around a CO₂ injection in a depleted gas reservoir. There are many other such examples in the literature. However, all the analytical solutions presented to date revolve around the CO₂ transport problem reducing to a hyperbolic partial differential equation (PDE), such that MOC or some variant can be used for the solution procedure. The difficulty of accounting for capillary pressure is that this leads to a diffusive component within the equations, rendering MOC inadequate in this regard.

Unrelated to CO₂ storage, McWhorter and Sunada (1990) derived a similarity solution to look at two-phase immiscible flow around an injection well, which explicitly captures the counter-current flow associated with capillary pressure effects. In the past, their solution has not been commonly used due to difficulties with evaluating the necessary
non-linear multiple integrals associated with their equations (Fucik et al. 2007). However, more recently, Bjornara and Mathias (2013) have provided a more efficient evaluation procedure by re-casting the equations as a boundary value problem, which they then solve using a Chebyshev polynomial differentiation matrix (Weideman and Reddy 2000). The objective of this study is to use the method of Bjornara and Mathias (2013) and extend the similarity solution of McWhorter and Sunada (1990) to account for partial miscibility of phases, so as to study the control of capillary pressure on salt precipitation during CO$_2$ injection in saline formations.

The outline of this article is as follows. First, a PDE to describe partially miscible three phase flow is presented. This is then reduced to an ordinary differential equation (ODE) by application of a similarity transform. The resulting boundary value problem is solved using a Chebyshev polynomial differentiation matrix. The necessary equations are then presented to determine the volume fraction of precipitated salt in the dry-out zone. A set of verification examples are presented based on a gas-displacing-oil scenario, previously presented by Orr (2007). A CO$_2$-injection-in-a-saline-formation scenario is then presented, which is compared with simulation results from TOUGH2 for verification. Finally, a wider sensitivity analysis is conducted to better understand the main controls in this context.

2. Mathematical model

A homogenous, cylindrical and porous saline formation is invoked with a thickness of $H$ [L] and an infinite radial extent. The pore space is initially fully saturated with a brine of uniform NaCl concentration. Pure CO$_2$ is injected at a constant rate of $Q_0$ [L$^3$T$^{-1}$] into the center of the saline formation via a fully penetrating injection well of infinitesimally small radius. The permeability of the saline formation is horizontally
isotropic. However, a necessary simplifying assumption is that the vertical permeability
is significantly smaller than the horizontal permeability such that gravity effects can be
neglected. In this way, during the injection phase, fluid flow can be treated as a one-
dimensional radially symmetric process.

Now we will describe the material mixture that resides within the pore-space. Consider
a mixture of three components: \(i = 1, 2\) and 3. Components 1 and 2 are mutually soluble
and can reside within both a non-wetting fluid phase and a wetting fluid phase, denoted
hereafter as \(j = 1\) and 2, respectively. Component 3 can dissolve into phase 2 and
precipitate to form a solid phase, denoted hereafter as \(j = 3\). However, component 3 is
assumed not to be able to reside in phase 1 and components 1 and 2 are assumed not to
be able to reside in phase 3. In the context of a CO\(_2\)-H\(_2\)O-NaCl system, \(i = 1, 2\) and 3
for CO\(_2\), H\(_2\)O and NaCl, respectively. All components are assumed to be incompressible
and not to experience volume change on mixing, such that component densities can be
treated as constant throughout.

The volume fraction of component \(i\) for the combined mixture, \(C_i \ [\cdot]\), is defined by
\[
C_i = \sum_{j=1}^{3} \sigma_{ij} S_j
\]  
(2.1)
where \(\sigma_{ij} \ [\cdot]\) is the volume fraction of component \(i\) in phase \(j\) and \(S_j \ [\cdot]\) is the volume
fraction of phase \(j\) for the combined mixture, often referred to as the saturation of
phase \(j\).

With no additional assumptions, it can be said that
\[
\sum_{i=1}^{3} C_i = \sum_{i=1}^{3} \sigma_{ij} = \sum_{j=1}^{3} S_j = 1
\]  
(2.2)
Capillary processes increase salt precipitation and

\[
\sigma_{ij} = \begin{cases} 
C_i, & C_i \notin (c_{12}(1 - S_3), c_{11}(1 - S_3)), \quad i \in \{1, 2\}, \ j \in \{1, 2\} \\
0, & C_i \in [0, 1], \quad i \in \{1, 2\}, \ j \in \{3\} \\
0, & C_3 \in [0, 1], \quad i = 3, \ j = 1 \\
\frac{C_3}{S_2}, & C_3 \in (0, c_{32}S_2), \quad i = 3, \ j = 2 \\
c_{32}, & C_3 \in [c_{32}S_2, 1], \quad i = 3, \ j = 2 \\
1, & C_3 \in [0, 1], \quad i = 3, \ j = 3 
\end{cases}
\] (2.3)

where \(c_{ij}[-]\) is the constant equilibrium volume fraction of component \(i\) in phase \(j\). It further follows that

\[
S_1 = \begin{cases} 
0, & C_1 \leq c_{12}(1 - S_3) \\
\frac{C_1 - c_{12}(1 - S_3)}{c_{11} - c_{12}}, & c_{12}(1 - S_3) < C_1 < c_{11}(1 - S_3) \\
1 - S_3, & C_1 \geq c_{11}(1 - S_3) 
\end{cases}
\] (2.4)

and

\[
S_3 = \begin{cases} 
0, & 0 \leq C_1 \leq 1, \quad C_3 < c_{32}S_2 \\
\frac{C_3 - c_{32}}{1 - c_{32}}, & C_1 \leq c_{12}(1 - S_3), \quad C_3 \geq c_{32}S_2 \\
\frac{(c_{11} - c_{12})C_3 - (c_{11} - C_1)c_{32}}{(1 - c_{32})c_{11} - c_{12}}, & c_{12}(1 - S_3) < C_1 < c_{11}(1 - S_3), \quad C_3 \geq c_{32}S_2 \\
C_3, & C_1 \geq c_{11}(1 - S_3), \quad C_3 \geq c_{32}S_2 
\end{cases}
\] (2.5)

Under the above set of assumptions, fluid flow is controlled by the following set of one-dimensional radially symmetric mass conservation equations

\[
\phi \frac{\partial C_i}{\partial t} = -\frac{1}{r} \frac{\partial}{\partial r} \left( r \sum_{j=1}^{2} q_j \sigma_{ij} \right), \quad i \in \{1, 2, 3\}
\] (2.6)

where \(\phi[-]\) is the saline formation porosity, \(t\) [T] is time, \(r\) [L] is radial distance from the injection well and \(q_j\) [LT\(^{-1}\)] is the flow of phase \(j\) per unit area, which can be found from
Darcy’s law

\[ q_j = -\frac{kk_{rj}}{\mu_j} \frac{\partial P_j}{\partial r}, \quad j \in \{1, 2\} \]  

(2.7)

where \( k \) [L^2] is the saline formation permeability and \( k_{rj} [\cdot] \), \( \mu_j [\text{ML}^{-1}\text{T}^{-1}] \) and \( P_j [\text{ML}^{-1}\text{T}^{-2}] \) are the relative permeability, dynamic viscosity and pressure of phase \( j \), respectively.

A detailed discussion with regards to justification for the above set of assumptions is provided in Section 4 below.

The difference between the non-wetting and wetting phase pressure is referred to as the capillary pressure, \( P_c [\text{ML}^{-1}\text{T}^{-2}] \), i.e.,

\[ P_c = P_1 - P_2 \]  

(2.8)

Because the component densities are assumed to be constant, the system of equations is divergence free and

\[ \sum_{j=1}^{2} q_j = \frac{Q_0}{2\pi Hr} \]  

(2.9)

Substituting Eqs. (2.7) and (2.8) into Eq. (2.9), solving for the partial derivatives of \( P_j \) and then substituting these back into Eq. (2.7) leads to

\[ q_j = \frac{Q_0 f_j}{2\pi Hr} + \frac{(-1)^j k k_{r1} f_2}{\mu_1} \frac{\partial P_c}{\partial r} \]  

(2.10)

where, with further consideration of Eq. (2.4),

\[ f_j = \begin{cases} 
\frac{[1 + (-1)^j]}{2}, & C_1 \leq c_{12}(1 - S_3) \\
\frac{k_{rj}}{\mu_j} \left( \sum_{j=1}^{2} \frac{k_{rj}}{\mu_j} \right)^{-1}, & c_{12}(1 - S_3) < C_1 < c_{11}(1 - S_3) \\
\frac{[1 + (-1)^j]}{2}, & C_1 \geq c_{11}(1 - S_3) 
\end{cases} \]  

(2.11)

Also note that there is no capillary pressure gradient when only one fluid phase is present, i.e.,

\[ \frac{\partial P_c}{\partial r} = 0, \quad C_1 \notin (c_{12}(1 - S_3), c_{11}(1 - S_3)) \]  

(2.12)
Capillary processes increase salt precipitation

Substituting Eq. (2.10) into Eq. (2.6), therefore leads to

\[
\frac{\partial C_i}{\partial \tau} = -\frac{\partial F_i}{\partial \xi} \tag{2.13}
\]

where

\[
F_i = \begin{cases} 
\sigma_{i2}, & C_1 \leq c_{12}(1 - S_3) \\
\sum_{j=1}^{2} f_j \sigma_{ij} + \left( \frac{k_{r1} f_2}{Ca} \sum_{j=1}^{2} (-1)^j \sigma_{ij} \right) \xi \frac{\partial \psi}{\partial \xi}, & c_{12}(1 - S_3) < C_1 < c_{11}(1 - S_3) \\
\sigma_{i1}, & C_1 \geq c_{11}(1 - S_3) \end{cases} \tag{2.14}
\]

and

\[
\tau = \frac{Q_0 t}{\pi \phi H r_c^2} \tag{2.15}
\]

\[
\xi = \frac{r^2}{r_c^2} \tag{2.16}
\]

\[
\psi = \frac{P_c}{P_{c0}} \tag{2.17}
\]

where \(r_c\) [L] is an arbitrary reference length, \(P_{c0}\) [ML\(^{-1}\)T\(^{-2}\)] is a reference “air-entry” pressure for the porous medium of concern and \(Ca\) [-] is a dimensionless constant often referred to as the capillary number, found from

\[
Ca = \frac{Q_0 \mu_1}{4 \pi H k P_{c0}} \tag{2.18}
\]

The capillary number represents the ratio of the \(CO_2\) injection rate to the product of the \(CO_2\) mobility and air-entry pressure of the porous medium. It compares the relative effect of the frictional resistance associated with fluid movement with the surface tension, which acts across the interface between the \(CO_2\)-rich phase and the aqueous phase. Small values of \(Ca\) imply that capillary processes are important.

With regards to the initial condition and boundary conditions, let \(C_{iI}\) [-] represent a uniform initial value of \(C_i\) in the saline formation and \(C_{i0}\) [-] represent a constant boundary value of \(C_i\) at the injection well for \(i \in \{1, 2, 3\}\).
2.1. Writing capillary pressure in terms of $C_1$

As CO$_2$ is injected into the saline formation, H$_2$O evaporates from the brine leaving NaCl behind as a precipitate in a dry-out zone that develops around the injection well. Following the commencement of CO$_2$ injection, there are therefore three distinct zones within the saline formation that should be considered (see Fig. 1): (1) The dry-out zone, which surrounds the injection well and contains only precipitated salt and CO$_2$ in the non-wetting fluid phase. (2) The full mixture zone, which surrounds the dry-out zone and contains CO$_2$, H$_2$O and NaCl, distributed between the wetting and non-wetting fluid phases. (3) The initial saline formation fluid zone, which surrounds the full mixture zone and contains only H$_2$O and NaCl in a wetting fluid phase.

Inspection of Eqs. (2.13) and (2.14) reveals that the problem is hyperbolic for $C_1 \notin (c_{12}(1 - S_3), c_{11}(1 - S_3))$ and not hyperbolic for $C_1 \in (c_{12}(1 - S_3), c_{11}(1 - S_3))$, because of the $\partial \psi / \partial \xi$ term. For the CO$_2$ injection scenario described above, both Zones 1 and 3 are hyperbolic. In contrast, Zone 2 is not hyperbolic. The discontinuities that separate the three zones are shock waves, which must satisfy the Rankine-Hugoniot condition (e.g. Orr 2007).

Within Zone 2, the displacement of a wetting phase by a non-wetting phase represents a continuous drainage cycle such that $\psi$ can be treated as a unique function of $S_2$. Furthermore, because $S_3 = 0$ and $S_2 = 1 - S_1$, it follows, from Eq. (2.4), that

$$S_2 = \begin{cases} 
1, & C_1 \leq c_{12} \\
\frac{c_{11} - C_1}{c_{11} - c_{12}}, & c_{12} < C_1 < c_{11} \\
0, & C_1 \geq c_{11} 
\end{cases} \quad (2.19)$$

and

$$\frac{\partial S_2}{\partial C_1} = \frac{1}{(c_{12} - c_{11})}, \quad C_1 \in (c_{12}, c_{11}) \quad (2.20)$$
Capillary processes increase salt precipitation such that it can be said that
\[
\frac{\partial \psi}{\partial \xi} = \frac{1}{(c_{12} - c_{11})} \frac{\partial \psi}{\partial S_2} \frac{\partial C_1}{\partial \xi} \tag{2.21}
\]
In this way, Eq. (2.14) can be substantially simplified to get
\[
F_i = \alpha_i - \beta_i \xi \frac{\partial C_1}{\partial \xi} \tag{2.22}
\]
where
\[
\alpha_i = \begin{cases} 
C_i, & C_1 \notin (c_{12}, c_{11}), \; i \in \{1, 2\} \\
\sum_{j=1}^{2} f_j c_{ij}, & C_1 \in (c_{12}, c_{11}), \; i \in \{1, 2\} \\
f_2 \sigma_{32}, & C_1 \in [0, 1], \quad i = 3
\end{cases} \tag{2.23}
\]
and
\[
\beta_i = \begin{cases} 
0, & C_1 \notin (c_{12}, c_{11}), \; i \in \{1, 2, 3\} \\
G \sum_{j=1}^{2} (-1)^j c_{ij}, & C_1 \in (c_{12}, c_{11}), \; i \in \{1, 2\} \\
G \sigma_{32}, & C_1 \in (c_{12}, c_{11}), \; i = 3
\end{cases} \tag{2.24}
\]
When \(\text{Ca} \to \infty\) and \(\sigma_{32} = 0\), the above problem reduces to the hyperbolic problem solved by Orr (2007) using the MOC. When \(c_{11} = 1, c_{12} = 0\) and \(\sigma_{32} = 0\), the above problem reduces to the immiscible two-phase flow problem with capillary pressure, previously solved by McWhorter and Sunada (1990) and Bjornara and Mathias (2013). The \(G\) term in Eq. (2.25) is analogous to the \(G\) term in Eq. (16) of Bjornara and Mathias (2013).
2.2. Relative permeability and capillary pressure functions

Relative permeability is calculated from Corey curves but with relative permeability assumed to linearly increase with saturation to one beyond residual saturations:

\[
k_{rj} = \begin{cases} 
0, & S_j \leq S_{jc} \\
_k r_{j0} \left( \frac{S_j - S_{jc}}{1 - S_{ic} - S_{2c}} \right)^{n_j}, & S_{jc} < S_j < 1 - S_{ic}, \quad i \neq j \\
_k r_{j0} + (1 - k_{rj0}) \left( \frac{S_j - 1 + S_{ic}}{S_{ic}} \right), & S_j \geq 1 - S_{ic}
\end{cases}
\] (2.26)

Dimensionless capillary pressure, \(\psi\), is calculated using the empirical equation of van Genuchten (1980) in conjunction with, following Oostrom et al. (2016) and Zhang et al. (2016), the dry-region extension of Webb (2000):

\[
\psi = \begin{cases} 
(S_{e}^{-1/m} - 1)^{1/n}, & S_2 > S_{2m} \\
\psi_d \exp \left[ \ln \left( \frac{\psi_{m}}{\psi_d} \right) \frac{S_2}{S_{2m}} \right], & S_2 \leq S_{2m}
\end{cases}
\] (2.27)

where \(S_e \) [-] is an effective saturation found from

\[
S_e = \frac{S_2 - S_{2c}}{1 - S_{2c}}
\] (2.28)

and \(k_{rj0} \), \(S_{jc} \) [-] and \(n_j \) [-] are the end-point relative permeability, residual saturation and relative permeability exponent for phase \(j\), respectively, \(m \) [-] and \(n \) [-] are empirical exponents associated with van Genuchten’s function, \(\psi_d = P_{cd}/P_{c0} \) [-] where \(P_{cd} \) [ML^{-1}T^{-2}] is the capillary pressure at which “oven-dry” conditions are said to have occurred (according to Webb (2000), this is taken to be \(10^9 \) Pa) with

\[
S_{2m} = (1 - S_{2c}) S_{em} + S_{2c}
\] (2.29)

and

\[
\psi_{m} = (S_{em}^{-1/m} - 1)^{1/n}
\] (2.30)

where \(S_{em} \) [-] is a critical effective saturation at which the switch over between the van Genuchten’s function and Webb’s extension take place, defined in the subsequent sub-section.
Capillary processes increase salt precipitation

Differentiation of (2.27) with respect to $S$ leads to

$$
\frac{\partial \psi}{\partial S_2} = \begin{cases} 
\psi/(1 - S_2c)mnS_c(S_c^{1/m} - 1), & S_2 > S_{2m} \\
\frac{\psi}{S_{2m}} \ln \left( \frac{\psi_m}{\psi_d} \right), & S_2 \leq S_{2m}
\end{cases}
$$

(2.31)

The van Genuchten capillary pressure function has been widely used in many previous CO$_2$ injection studies (e.g. Pruess and Muller 2009; Kim et al. 2012; Mathias et al. 2013; Oostrom et al. 2016; Zhang et al. 2016). The Corey relative permeability functions have previously been useful in describing CO$_2$-brine relative permeability data from at least 25 different experiments from the international literature (Mathias et al. 2013).

2.3. Determination of $S_{em}$

Considering Eq. (2.31), Webb (2000) defines $S_{em}$ as the effective saturation at which

$$
\frac{\psi_m}{(1 - S_2c)mnS_c(S_c^{1/m} - 1)} = \frac{\psi_m}{S_{2m}} \ln \left( \frac{\psi_m}{\psi_d} \right)
$$

(2.32)

Substituting Eqs. (2.30) and (2.29) into Eq. (2.32) and rearranging leads to

$$
S_{em} = \frac{S_{em} + S_{2c}(1 - S_{2c})^{-1}}{mn(S_c^{1/m} - 1) \ln \left( (S_c^{1/m} - 1)^{1/n} \psi_d^{-1} \right)}
$$

(2.33)

which must be solved iteratively. Webb (2000) suggests that four to five iterations are sufficient. However, this will be strongly dependent on the initial estimate of $S_{em0}$ applied.

For $S_{2c} > 0$, a good initial estimate of $S_{em}$, $S_{em0}$, can be obtained by assuming $S_{em0} \ll 1$ such that Eq. (2.33) reduces to

$$
S_{em0} = \frac{S_{2c}(1 - S_{2c})^{-1}}{\ln \left( S_{em0} \psi_d^{nm} \right)}
$$

(2.34)

which can be rearranged to get

$$
W \exp(W) = z
$$

(2.35)

where

$$
z = \frac{S_{2c}\psi_d^{nm}}{(1 - S_{2c})}
$$

(2.36)
and

\[ W = \frac{S_{2c}}{(1 - S_{2c})S_{em0}} \]  

(2.37)

Note that the functional inverse of \( z(W) \) in Eq. (2.35), \( W(z) \), is given by the Lambert \( W \) function. Furthermore, because \( z \) is always positive and real, \( W(z) = W_0(z) \), otherwise referred to as the zero branch, which has the following asymptotic expansion (Corless et al. 1996)

\[ W_0(z) = L_1 - L_2 + \frac{L_2}{L_1} + O\left(\left[\frac{L_2}{L_1}\right]^2\right) \]  

(2.38)

where \( L_2 = \ln L_1 \) and \( L_1 = \ln z \).

In this way, it can be said that

\[ S_{em0} = \frac{S_{2c}}{(1 - S_{2c})W_0(z)} \]  

(2.39)

where \( z \) is found from Eq. (2.36).

Examples of the iterative calculation of \( S_{em} \) from initial guesses obtained from Eq. (2.39) are presented in Table 1. When \( S_{2c} \leq 0.3 \), it can be seen that convergence is achieved after just two iterations. When \( S_{2c} = 0.5 \), three iterations are required. When \( S_{2c} = 0.7 \), six iterations are required. The increase in the number of iterations required with increasing \( S_{2c} \) is due to reducing validity of the \( S_{em} \ll 1 \) assumption.

2.4. Application of a similarity transform

The partial differential equation in Eq. (2.13) can be reduced to an ordinary differential equation by application of the following similarity transform

\[ \lambda = \frac{\xi}{\tau} \]  

(2.40)

Substituting Eq. (2.40) into Eqs. (2.13) and (2.22) leads to

\[ \frac{dF_i}{dC_i} = \lambda \]  

(2.41)
Capillary processes increase salt precipitation

Table 1. Examples of the iterative calculation of $S_{em}$ for different values of $S_{2c}$ (as indicated in the top row) using Eq. (2.33) with $m = 0.5$, $P_{c0} = 19.6$ kPa and $P_{cd} = 10^9$ Pa. The initial guess, $S_{em0}$, is calculated using Eq. (2.39).

<table>
<thead>
<tr>
<th>Iteration / $S_{2c}$</th>
<th>0.1</th>
<th>0.3</th>
<th>0.5</th>
<th>0.7</th>
</tr>
</thead>
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<td>0</td>
<td>0.016496</td>
<td>0.05104</td>
<td>0.11525</td>
<td>0.2472</td>
</tr>
<tr>
<td>1</td>
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<td>0.061087</td>
<td>0.13012</td>
<td>0.29011</td>
</tr>
<tr>
<td>2</td>
<td>0.018927</td>
<td>0.061082</td>
<td>0.13051</td>
<td>0.29695</td>
</tr>
<tr>
<td>3</td>
<td>0.018927</td>
<td>0.061082</td>
<td>0.13051</td>
<td>0.29825</td>
</tr>
<tr>
<td>4</td>
<td>0.018927</td>
<td>0.061082</td>
<td>0.13051</td>
<td>0.29850</td>
</tr>
<tr>
<td>5</td>
<td>0.018927</td>
<td>0.061082</td>
<td>0.13051</td>
<td>0.29855</td>
</tr>
<tr>
<td>6</td>
<td>0.018927</td>
<td>0.061082</td>
<td>0.13051</td>
<td>0.29856</td>
</tr>
<tr>
<td>7</td>
<td>0.018927</td>
<td>0.061082</td>
<td>0.13051</td>
<td>0.29856</td>
</tr>
</tbody>
</table>

and

$$F_i = \alpha_i - \beta_i\lambda \frac{dC_1}{d\lambda} \quad (2.42)$$

Differentiating both sides of Eq. (2.41) with respect to $C_i$ yields

$$\frac{d^2 F_i}{dC_i^2} = \frac{d\lambda}{dC_i} \quad (2.43)$$

which on substitution into Eq. (2.42), along with Eq. (2.41), and rearranging leads to

$$\frac{d^2 F_1}{dC_1^2} + \frac{\beta_1}{(F_1 - \alpha_1)} \frac{dF_1}{dC_1} = 0 \quad (2.44)$$

In the event that the boundary and initial values of $C_1$, $C_{10}$ and $C_{11}$, respectively, are \notin (c_{12}, c_{11}), the boundary conditions for Eq. (2.44) must satisfy the Rankine-Hugoniot conditions (similar to Orr 2007, p. 75):

$$\frac{dF_1}{dC_1} = \frac{\alpha_{10} - F_1}{C_{10} - C_1}, \quad C_1 \geq c_{11} \quad (2.45)$$
\[ \frac{dF_1}{dC_1} = \frac{\alpha_{1I} - F_1}{C_1 - C_1}, \quad C_1 \leq c_{12} \quad (2.46) \]

where \( \alpha_{10} \) and \( \alpha_{1I} \) represent the boundary and initial values of \( \alpha_1 \) associated with \( C_{10} \) and \( C_{1I} \), respectively. Alternatively, when \( C_{10} \) and \( C_{1I} \) are \( \in (c_{12}, c_{11}) \)

\[ F_1 = \alpha_{10}, \quad C_1 = C_{10} \]
\[ F_1 = \alpha_{1I}, \quad C_1 = C_{1I} \quad (2.47) \]

An efficient way of expressing both Eqs. (2.46) and (2.47) simultaneously is to state instead:

\[ (C_{10} - C_1) \frac{dF_1}{dC_1} + F_1 = \alpha_{10}, \quad C_1 = \tilde{C}_{10} \]
\[ (C_{1I} - C_1) \frac{dF_1}{dC_1} + F_1 = \alpha_{1I}, \quad C_1 = \tilde{C}_{1I} \quad (2.48) \]

where

\[ \tilde{C}_{10} = H(C_{10} - c_{11})c_{11} + H(c_{11} - C_{10})C_{10} \quad (2.49) \]
\[ \tilde{C}_{1I} = H(c_{12} - C_{1I})c_{12} + H(C_{1I} - c_{12})C_{1I} \quad (2.50) \]

and \( H(x) \) is a Heaviside function.

2.5. Pseudospectral solution

Following Bjornara and Mathias (2013), the boundary value problem described in the previous section is solved using a Chebyshev polynomial differentiation matrix, \( D \) (Weideman and Reddy 2000).

The coordinate space for the Chebyshev nodes is \( x \in [-1, 1] \). However, the solution space for \( F_1 \) is \( C_1 \in [\tilde{C}_{1I}, \tilde{C}_{10}] \). Therefore the Chebyshev nodes, \( x_k \), need to be mapped to the \( C_1 \) space by the following transform

\[ C_1 = \frac{\tilde{C}_{10} + \tilde{C}_{1I}}{2} + \left( \frac{\tilde{C}_{10} - \tilde{C}_{1I}}{2} \right) x \quad (2.51) \]

Consequently, it is necessary to introduce an appropriately transformed differentiation
Capillary processes increase salt precipitation

matrix, \( \mathbf{E} \), where

\[
\mathbf{E} = \frac{dx}{dC_1} \mathbf{D} \tag{2.52}
\]

and from Eq. (2.51)

\[
\frac{dx}{dC_1} = \frac{2}{C_{10} - C_{1f}} \tag{2.53}
\]

By applying the Chebyshev polynomial on the internal nodes and the Robin boundary conditions in Eq. (2.48) on the end nodes, Eq. (2.44) can be written in matrix form (similar to Piche and Kanninen (2009) and Bjornara and Mathias (2013))

\[
\mathbf{R}(\mathbf{F}) = \begin{bmatrix}
\mathbf{E}^{(2)}_{2,N-1,:} \mathbf{F} + \mathbf{I}_{2,N-1,:} \cdot \text{diag} \left[ \frac{\beta_1}{F_1 - \alpha_1} \right] \mathbf{E}^{(1)} \mathbf{F} \\
(C_N - C_{1f}) \mathbf{E}^{(1)}_{N,:} \mathbf{F} - \mathbf{I}_{N,:} \mathbf{F} + \alpha_{1f} \\
(C_{1} - C_{10}) \mathbf{E}^{(1)}_{1,:} \mathbf{F} - \mathbf{I}_{1,:} \mathbf{F} + \alpha_{10}
\end{bmatrix} \tag{2.54}
\]

where \( \mathbf{R} \) is the residual vector, \( \mathbf{F} \) is the solution vector for the dependent variable \( F_1 \), \( \mathbf{C} \) is the vector containing the corresponding values of \( C_1 \) and \( N \) denotes the number of Chebyshev nodes to be solved for. The two last rows on the right-hand side of Eq. (2.54) impose the Robin boundary conditions. Also note that \( \mathbf{E}^{(n)} \) can be obtained from \( \mathbf{E}^{(n)} \).

The solution vector, \( \mathbf{F} \), can be obtained by Newton iteration, whereby new iterations, \( \mathbf{F}_{(i+1)} \), are obtained from

\[
\mathbf{F}_{(i+1)} = \mathbf{F}_{(i)} - \left( \frac{\partial \mathbf{R}}{\partial \mathbf{F}} \right)^{-1} \mathbf{R} \left( \mathbf{F}_{(i)} \right) \tag{2.55}
\]

where \( \frac{\partial \mathbf{R}}{\partial \mathbf{F}} \) is the Jacobian matrix defined as

\[
\frac{\partial \mathbf{R}}{\partial \mathbf{F}} = \begin{bmatrix}
\mathbf{E}^{(2)}_{2,N-1,:} + \mathbf{I}_{2,N-1,:} \cdot \text{diag} \left[ \frac{\beta_1}{F_1 - \alpha_1} \right] \mathbf{E}^{(1)} - \mathbf{I}_{2,N-1,:} \cdot \text{diag} \left[ \frac{\beta_1}{(F_1 - \alpha_1)^2} \right] \mathbf{E}^{(1)} \mathbf{F} \\
(C_N - C_{1f}) \mathbf{E}^{(1)}_{N,:} - \mathbf{I}_{N,:} \\
(C_{1} - C_{10}) \mathbf{E}^{(1)}_{1,:} - \mathbf{I}_{1,:}
\end{bmatrix} \tag{2.56}
\]

Note that \( F_1 \) is bounded by \( \alpha_1 \) and \( \alpha_{10} \). Therefore, a good initial guess is to set \( F_1 = \alpha_{10} \). Following Bjornara and Mathias (2013), an additional correction step should
be applied in the Newton iteration to force the solution, $F_1$, to be less than $\alpha_1$. The Newton iteration loop is assumed to have converged when the mean absolute value of $R \leq 10^{-9}$. With 100 Chebyshev nodes (i.e., $N = 100$), convergence is typically achieved with less than 200 iterations.

2.6. Dealing with salt precipitation in the dry-out zone

Now consider the case where pure CO$_2$ is injected into a porous medium (i.e., $\alpha_{10} = 1$) initially fully saturated with brine (i.e., $\alpha_{1f} = 0$). Let $\sigma_{32}$ be the volume fraction of NaCl in phase 2 throughout the system. In this way, the volume fraction of H$_2$O in phase 2 prior to CO$_2$ injection is $(1 - \sigma_{32})$.

Let $r_0$ [L] and $r_I$ [L] be the radial extents of the dry-out zone and injected CO$_2$ plume respectively. At any given time, the volume of H$_2$O evaporated by the CO$_2$, $V_e$ [L$^3$], can be found from

$$V_e = 2\pi \phi H (1 - c_{11}) \int_{r_0}^{r_I} r S_1 dr$$  \hspace{1cm} (2.57)

The volume of salt precipitated in the dry-out zone, $V_s$ [L$^3$], is found from

$$V_s = \frac{\sigma_{32} V_e}{1 - \sigma_{32}}$$  \hspace{1cm} (2.58)

The volume of the dry-out zone where the salt is precipitated, $V_d$ [L$^3$], is found from

$$V_d = \pi \phi H r_0^2$$  \hspace{1cm} (2.59)

Another quantity of interest is the volume of CO$_2$ dissolved in the brine, $V_c$ [L$^3$], which can be found from

$$V_c = 2\pi \phi H c_{12} \int_{r_0}^{r_I} r (1 - S_1) dr$$  \hspace{1cm} (2.60)

Considering the definition of $\lambda$ in Eq. (2.40) in conjunction with Eqs. (2.15) and (2.16)

$$r_0^2 = \frac{Q_0 t \lambda_0}{\pi \phi H} \quad \text{and} \quad r_I^2 = \frac{Q_0 t \lambda_I}{\pi \phi H}$$  \hspace{1cm} (2.61)
Capillary processes increase salt precipitation

where, recall Eqs. (2.41) and (2.48), $\lambda_0$ and $\lambda_I$ can be found from

$$\lambda_0 = \frac{dF_1}{dC_1} \bigg|_{C_1 = c_{11}} \quad \text{and} \quad \lambda_I = \frac{dF_1}{dC_1} \bigg|_{C_1 = c_{12}}$$

(2.62)

In this way it can be understood that:

$$V_e = (1 - c_{11})Q_0 t \int_{\lambda_0}^{\lambda_I} S_1 d\lambda$$

(2.63)

$$V_d = Q_0 t \lambda_0$$

(2.64)

$$V_c = c_{12}Q_0 t \int_{\lambda_0}^{\lambda_I} (1 - S_1) d\lambda$$

(2.65)

Noting that the rates at which $V_e$ and $V_d$ grow with time are constant it can also be understood that the volume fraction of precipitated salt, $C_3$, will be both uniform within the dry-out zone and constant with time. The value of $C_3$ within the dry-out zone, hereafter denoted as $C_{30}$, can be found from

$$C_{30} = \frac{(1 - c_{11})\sigma_{32}}{(1 - \sigma_{32})\lambda_0} \int_{\lambda_0}^{\lambda_I} S_1 d\lambda$$

(2.66)

Given that $C_{10} = 1 - C_{30}$, $C_{1I} = 0$, $\alpha_{10} = 1$ and $\alpha_{1I} = 0$, the boundary conditions in Eq. (2.48) reduce to

$$\frac{dF_1}{dC_1} = \frac{1 - F_1}{1 - C_{30} - c_{11}}, \quad C_1 = c_{11}$$

$$\frac{dF_1}{dC_1} = \frac{F_1}{c_{12}}, \quad C_1 = c_{12}$$

(2.67)

Values of $C_{30}$ can be obtained iteratively by repeating the procedures outlined in Section 2.5 with successive estimates of $C_{30}$ obtained from Eq. (2.66). Using an initial guess of $C_{30} = 0$, this process is found to typically converge after less than 60 iterations.

The integrals in Eqs. (2.65) and (2.63) can be found by trapezoidal integration.
3. Sensitivity analysis

3.1. Gas displacing oil

As a first example, the gas-displacing-oil scenario previously presented in Figs. 4.13 and 4.15 of Orr (2007) is adopted. The parameters describing the scenario include $c_{11} = 0.95$, $c_{12} = 0.20$, $\sigma_{32} = 0$, $\mu_2/\mu_1 = 2$, $S_{1c} = 0.05$, $S_{2c} = 0.1$, $k_{r10} = k_{r20} = 1$ and $n_1 = n_2 = 2$. For the pseudospectral solution, a value for the van Genuchten (1980) parameter, $m$, is set to 0.5.

Plots of $C_1$ against $dF_1/dC_1$ (which, recall, is equal to $\xi/\tau$) for this scenario are shown in Fig. 2. The different subplots show the effect of varying the boundary volume fraction, $C_{10}$, and the initial volume fraction, $C_{1I}$. The different colors relate to different assumed values of $C_a$. Increasing $C_a$ can be thought of as analogous to an increased injection rate. The $C_a \to \infty$ curves were obtained from the MOC solutions previously presented in Figs. 4.13 and 4.15 of Orr (2007). The finite $C_a$ value solutions were obtained using the pseudospectral solution described above, with 100 Chebyshev nodes.

When $C_a = 100$, the pseudospectral solution is virtually identical to the infinite-$C_a$-MOC solutions. As $C_a$ is decreased, the solution becomes more diffused. In Figs. 2a, d, e and f, the infinity $C_a$ results exhibit a trailing shock, which represents a dry-out zone where all the liquid oil has been evaporated by the gas. Of particular interest is that decreasing $C_a$ leads to a reduction in the thickness of the dry-out zone, ultimately leading to its complete elimination.

3.2. CO$_2$ injection in a saline formation

Here the CO$_2$-injection-in-a-saline-formation scenario, previously presented by Mathias et al. (2013), is revisited. The example involves injecting pure CO$_2$ at a constant rate via a fully penetrating injection well at the center of a cylindrical, homogenous and confined
Capillary processes increase salt precipitation

Table 2. Relevant model parameters used for the CO₂ injection in saline formation scenario, previously presented by Mathias et al. (2013).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ injection rate</td>
<td>15 kg s⁻¹</td>
</tr>
<tr>
<td>Porosity, φ</td>
<td>0.2</td>
</tr>
<tr>
<td>Initial pressure</td>
<td>10 MPa</td>
</tr>
<tr>
<td>Temperature</td>
<td>40 °C</td>
</tr>
<tr>
<td>Mass fraction of salt in brine, X₃₂</td>
<td>0.15</td>
</tr>
<tr>
<td>Critical gas saturation, S₁c</td>
<td>0.0</td>
</tr>
<tr>
<td>Residual water saturation, S₂c</td>
<td>0.5</td>
</tr>
<tr>
<td>End-point relative permeability for CO₂, k₉₁₀</td>
<td>0.3</td>
</tr>
<tr>
<td>End-point relative permeability for brine, k₉₂₀</td>
<td>1.0</td>
</tr>
<tr>
<td>Relative permeability exponents, n₁, n₂</td>
<td>3</td>
</tr>
<tr>
<td>Formation thickness, H</td>
<td>30 m</td>
</tr>
<tr>
<td>Permeability, k</td>
<td>10⁻¹³ m²</td>
</tr>
</tbody>
</table>

saline formation, initially fully saturated with brine. Relevant model parameters are presented in Table 2. In this case, components 1, 2 and 3 are CO₂, H₂O and NaCl, respectively, and phases 1, 2 and 3 represent a CO₂-rich phase, an H₂O rich phase and precipitated salt, respectively.

The relevant fluid properties are obtained using equations of state (EOS) and empirical equations provided by Batzle and Wang (1992), Fenghour et al. (1998), Spycher et al. (2003) and Spycher and Pruess (2005). Mathias et al. (2011a) found that when using analytical solutions in this context, to account for the relatively high compressibility of CO₂, it is important to use an estimate of the final pressure rather than the initial pressure for calculating the fluid properties relating to CO₂. Mathias et al. (2013) found that, for the scenario described in Table 2, the well pressure increased by just over 5 MPa.
after ten years. Therefore, for the current study, fluid properties are calculated using 15 MPa as opposed to 10 MPa.

The EOS of Spycher et al. (2003) and Spycher and Pruess (2005) provide equilibrium mole fractions as opposed to volume fractions. Pruess and Spycher (2007) show how mole fractions can be converted to mass fractions, $x_{ij} [-]$, which can be converted to volume fractions, $\sigma_{ij} [-]$, using (similar to Orr 2007, p. 19)

$$\sigma_{ij} = \frac{\rho_j x_{ij}}{\rho_{ij}}$$ (3.1)

where $\rho_{ij} [\text{ML}^{-3}]$ is the density of component $i$ in phase $j$ and $\rho_j [\text{ML}^{-3}]$ is the composite phase density, which can be found from

$$\rho_j = \left( \sum_{i=1}^{N_c} x_{ij} \rho_{ij} \right)^{-1}$$ (3.2)

where $N_c [-]$ is the number of components present. Because the pseudospectral solution above assumes component densities remain constant throughout, a decision is made that

$\rho_{12} = \rho_{11}$, $\rho_{21} = \rho_{22}$ and $\rho_{32} = \rho_{33}$.

Table 3 shows how the various fluid properties vary with depth below sea-level in this context. Depth is related to pressure by assuming hydrostatic conditions and then adding 5 MPa to allow for pressure induced by CO$_2$ injection. Depth is related to temperature by assuming a geothermal gradient of 40°C per km. It can be seen that the volume fractions are largely unaffected by depth. However, the variation in brine viscosity and CO$_2$ density are more noticeable.

A comparison of results from the pseudospectral solution with those from the TOUGH2 simulation reported by Mathias et al. (2013) is shown in Fig. 3, alongside results for when $Ca \to \infty$, obtained using a MOC solution similar to that previously presented by Zeidouni et al. (2009) and Mathias et al. (2011b). Mathias et al. (2013) assumed $P_{c0} = 19.6$ kPa. Considering the other parameters in Tables 2 and 3, this leads to a Ca value of 1.7.
Capillary processes increase salt precipitation

Table 3. Relevant model parameters used for the CO₂ injection in a saline formation scenario with a brine salinity of 150 ppt.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (MPa)</td>
<td>15</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>40</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td>Density of CO₂, ρ₁₁ (kg m⁻³)</td>
<td>754</td>
<td>704</td>
<td>673</td>
</tr>
<tr>
<td>Density of H₂O, ρ₂₂ (kg m⁻³)</td>
<td>998</td>
<td>992</td>
<td>984</td>
</tr>
<tr>
<td>Density of NaCl, ρ₃₃ (kg m⁻³)</td>
<td>2160</td>
<td>2160</td>
<td>2160</td>
</tr>
<tr>
<td>Volume fraction of CO₂ in phase 1, c₁₁ (-)</td>
<td>0.999</td>
<td>0.998</td>
<td>0.996</td>
</tr>
<tr>
<td>Volume fraction of CO₂ in phase 2, c₁₂ (-)</td>
<td>0.041</td>
<td>0.043</td>
<td>0.045</td>
</tr>
<tr>
<td>Volume fraction of NaCl in phase 2, σ₃₂ (-)</td>
<td>0.075</td>
<td>0.074</td>
<td>0.073</td>
</tr>
<tr>
<td>Dynamic viscosity of CO₂, μ₁ (cP)</td>
<td>0.064</td>
<td>0.057</td>
<td>0.054</td>
</tr>
<tr>
<td>Dynamic viscosity of brine, μ₂ (cP)</td>
<td>0.963</td>
<td>0.730</td>
<td>0.573</td>
</tr>
</tbody>
</table>

There is excellent correspondence between the MOC solution, the TOUGH2 results and the pseudospectral solution when Ca = 1.7.

A value of $P_{c0} = 19.6$ kPa is often used to describe saline formations in a CO₂ storage context (Rutqvist et al. 2007; Zhou et al. 2008; Mathias et al. 2013; Zhu et al. 2015, e.g.). Experimental analysis looking at four different sandstone reservoirs revealed a range of $P_{c0}$ values from 1.3 to 7.1 kPa (Oostrom et al. 2016). Smaller values of $P_{c0}$ imply larger pore diameters.

A hallmark of hyperbolic theory is that the problem can be reduced to a fundamental wave structure which constitutes the solution. In Fig. 3, it can be seen that such a wave structure is largely preserved, despite the inclusion of capillary diffusion. Furthermore, the wave velocity of the leading shock is virtually independent of Ca for the range of Ca.
values studied. However, decreasing $Ca$ leads to a more diffused spreading wave caused by the increase in capillary diffusion, which in turn leads to a reduction in the wave velocity of the trailing shock, as also seen in Fig. 2a. The decrease in steady-state $CO_2$ saturation in the dry-out zone is caused by an increase in the volume fraction of precipitated salt (recall that $C_{10} = 1 - C_{30}$).

For the scenarios depicted in Fig. 3, $C_{30}$ is found to be insensitive to $Ca$ for $Ca$ values greater than or equal to 1.7. However for $Ca$ values less than 1.7, the volume of the dry-out zone is significantly reduced and the volume fraction of precipitated salt is significantly increased. The value of $C_{30}$ for $Ca = 0.2$ is almost double the value for $Ca = 1.7$. The value of $C_{30}$ for $Ca = 0.1$ is around ten times that of when $Ca = 1.7$. The $Ca = 1.7$ scenario described in Table 2 assumes an injection rate of 15 kg s$^{-1}$. The results shown in Fig. 3 therefore suggest that reducing the injection rate down to 1.8 kg s$^{-1}$ would lead to a doubling of the volume fraction of precipitated salt around the injection well. Furthermore, reducing the injection rate from 15 kg s$^{-1}$ down to 0.9 kg s$^{-1}$ would lead to an almost ten times larger volume fraction of precipitated salt around the injection well.

For the hyperbolic case when $Ca \rightarrow \infty$, it is common to study plots of $F_1$ and $C_1$ (Orr 2007). Fig. 4a shows plots of $F_1$ against $C_1$ for all the values of $Ca$ presented in Fig. 3 along with a plot of $\alpha_1$. The MOC solution (i.e., with $Ca \rightarrow \infty$), which sits almost exactly underneath the $Ca = 1.7$ line, intersects the $\alpha_1$ line at tangents, which is symptomatic of satisfying the shock waves satisfying the Rankine-Hugoniot condition. To better visualize the results for finite $Ca$ values, $(1 - F_1)$ is shown on a log-scale in Fig. 4b. Here it can be seen that the models approach a value of $F_1 = 1$ at different $C_1$ values depending on the volume fraction of precipitated salt. The volume fraction of precipitated salt increases with decreasing $Ca$. Fig. 4c shows a close-up view of the trailing shocks on linear axes.
Capillary processes increase salt precipitation

for further reference. For finite Ca values, the $F_1$ lines never actually intersect the $a_1$
line except at where $C_1 = 0$. The reason for this is due to $\beta_1$, which is plotted in Fig.
4d. The highest values of $\beta_1$ are at the center of the two-phase region, $C_1 \in (c_{12}, c_{11})$. $\beta_1$
smoothly grades down to zero as it reaches the single-phase regions, $C_1 \notin (c_{12}, c_{11})$.

A further sensitivity analysis is presented in Fig. 5. The three depth scenarios presented
in Table 3 are applied with three different brine salinities. Fig. 5a shows how the volume
of the dry-out zone decreases with decreasing Ca. The size of the dry-out zone increases
with increasing depth. In contrast, brine salinity has very little impact on dry-out zone
volume.

Fig. 5b shows the volume of the evaporated water also reduces with decreasing Ca. At
first this seems surprising given that capillary pressure effects should bring more water
into the dry-out zone. However, the effect of the capillary pressure is also to spread the
CO$_2$ out further (see leading edge of CO$_2$ plumes in Fig. 3). As a consequence, more CO$_2$
is dissolved (see Fig. 5c). Consequently, less of the CO$_2$-rich phase is available for water
from the brine to evaporate into. The volume of evaporated water increases with depth
because the equilibrium volume fraction of water in the CO$_2$-rich phase increases with
depth (see Table 3). The volume of dissolved CO$_2$ is insensitive to depth but decreases
with increasing brine salinity. The latter is because the solubility limit of CO$_2$ in brine
decreases substantially with increasing salinity (Spycher and Pruess 2005).

Fig. 5d shows how volume fraction of precipitated salt in the dry-out zone, $C_{30}$, super-
linearly increases with decreasing Ca. For Ca $> 0.25$, the quantity of precipitated salt is
mostly controlled by brine salinity. However, for Ca $< 0.25$, depth plays an increasingly
important role, with higher levels of salt precipitation in shallower formations. This is
because the dry-out zone increases with depth, despite increasing water evaporation with
depth. Fig. 6 shows the same results as Fig. 5d but with $C_{30}$ normalized by dividing by
the salinity of the brine, $X_{32}$. Here it can be seen that $C_{30}$ almost linearly scales with $X_{32}$.

The volume fraction of precipitated salt is also strongly controlled by the relative permeability parameters, $k_{rj0}$, $S_{jc}$ and $n_j$ (Zhang et al. 2016). The analysis performed to provide Fig. 6 was repeated for the 1000 m depth scenario for each of the six groups of relative permeability parameters presented in Table 4. These six parameter sets were selected from a database of 25 core experiments previously compiled by Mathias et al. (2013). The six cores were selected to provide a representative range of possible outcomes, given the wide variability generally observed in such data sets.

From Fig. 7 it can be seen that the high Ca values of $C_{30}$ range from 0.019 to 0.044. Furthermore, the critical Ca value below which $C_{30}$ superlinearly increases ranges from 0.025 to 10. Comparing these results with the parameter sets in Table 4 it can be seen that when the relative permeability for brine is more linear, the value of $C_{30}$ at high values of Ca tends to be lower. However, this linearity also leads to the superlinearly increasing of $C_{30}$ with decreasing Ca to occur at a relatively low value of $C_{30}$ (see for example Cardium #1 and Basal Cambrian). Exactly the opposite happens when the relative permeability for brine is highly non-linear (see for example Paaratte and Tuscaloosa). This is probably due to counter-current flow of water being less efficient when relative permeability is highly non-linear.

4. Discussion of key modeling assumptions

4.1. Incompressible fluids

Fluid densities are assumed to be independent of pressure. The compressibilities of H$_2$O and NaCl are commonly ignored. For pressures and temperatures associated with depleted gas reservoirs, the compressibility of CO$_2$ is very high and has a significant impact
Capillary processes increase salt precipitation

Table 4. Relative permeability parameters for six different sandstone cores (after Mathias et al. 2013). Note that for each core \( k_{r20} = 1 \) and \( S_{1c} = 0 \). Data for Cardium #1, Basal Cambrian and Viking #1 was originally obtained by Bennion and Bachu (2008). Data for Otway was originally obtained by Perrin and Benson (2010). Data for Paaratte and Tuscaloosa was originally obtained by Krevor et al. (2012).

<table>
<thead>
<tr>
<th>Unit</th>
<th>( k_{r10} )</th>
<th>( S_{2c} )</th>
<th>( n_1 )</th>
<th>( n_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardium #1</td>
<td>0.526</td>
<td>0.197</td>
<td>1.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Basal Cambrian</td>
<td>0.545</td>
<td>0.294</td>
<td>5.0</td>
<td>1.8</td>
</tr>
<tr>
<td>Otway</td>
<td>0.332</td>
<td>0.558</td>
<td>3.2</td>
<td>2.9</td>
</tr>
<tr>
<td>Viking #1</td>
<td>0.659</td>
<td>0.437</td>
<td>6.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Paaratte</td>
<td>0.328</td>
<td>0.389</td>
<td>3.0</td>
<td>4.6</td>
</tr>
<tr>
<td>Tuscaloosa</td>
<td>0.077</td>
<td>0.703</td>
<td>3.2</td>
<td>4.7</td>
</tr>
</tbody>
</table>

on fluid movement (Mathias et al. 2014). However, for \( \text{CO}_2 \) injection in saline formations, fluid pressures are expected to be hydrostatic or above. Under these conditions, providing a sensible reference pressure is used to determine the fluid properties of \( \text{CO}_2 \) (i.e., an estimate of pressure towards the end of the injection cycle), the compressibility of \( \text{CO}_2 \) has been found to have a negligible effect in this context (Mathias et al. 2011a,b).

4.2. No volume change on mixing

Component densities are assumed to be uniform across phases. In fact, the densities of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) are both higher in the aqueous phase as compared to in the \( \text{CO}_2 \)-rich phase. For a wide range of different \( \text{CO}_2 \) injection scenarios, this volume change on mixing is found to lead to an increase in volumetric flow rate of around 0.05% in Zone 2 and a
decrease in volumetric flow rate of around 5% in Zone 3 (see Table 2 of Mathias et al. 2011b). See section 2.1 above for an explanation of the zone numbers.

With regards to NaCl, the density of precipitated NaCl, $\rho_{33}$, is 2160 kg m$^{-3}$. Using Eq. (3.2) in conjunction with the EOS for brine given by Batzle and Wang (1992), it can be shown that the density of NaCl dissolved in brine, $\rho_{32}$, is around 2800 kg m$^{-3}$. In the above analysis we have set $\rho_{32} = \rho_{33}$ such that the model precipitates the correct volume of salt in the dry-out zone. The consequence is that the volume fractions of water and CO$_2$ in the brine are underestimated by around 2%.

Fig. 3 compares model results from TOUGH2 with those from the similarity solution. TOUGH2 properly incorporates fluid compressibility and volume change on mixing and there is negligible difference between the two models.

4.3. Ignoring gravity effects

As stated earlier, another important assumption is that the vertical permeability of the formation is sufficiently low that gravity effects can be ignored. Extreme changes in density and/or viscosity can lead to instabilities and fingering phenomena, which cannot be represented using one-dimensional models. Indeed, Kim et al. (2012) found that buoyancy driven flow, associated with the different densities of brine and CO$_2$, played an important part in controlling the spatial distribution of precipitated salt around an injection well. However, this was mostly after the cessation of injection. During the injection phase, gravity segregation within the dry-out zone was much less significant and no viscous fingering was observed.

Mathias et al. (2011b) presented a comparison of simulation results where gravity was accounted for and ignored using TOUGH2 and the MOC solution of Zeidouni et al. (2009), respectively. For a 100 m thick isotropic saline formation, gravity was found to have a strong effect on the leading edge of the CO$_2$ plume. However, gravity effects
were found to be negligible on the dry-out zone development and the associated volume fraction of the precipitated salt. For a 50 m thick isotropic saline formation, gravity effects were found to be negligible throughout.

The dry-out zone is generally unaffected by gravity segregation due to the larger velocities situated close around the injection well, which are mostly horizontal due to the horizontal driving force provided by the injection well boundary (Mathias et al. 2011b). From the discussion above it is expected that gravity effects are unlikely to significantly affect the dry-out zone in the 30 m thick saline formations studied in this current article, at least for the lower capillary numbers studied. However, as the capillary numbers are increased, the horizontal injection velocities will become less significant and gravity will play a more important role. However, our analysis has shown that excessive salt precipitation can also develop in the absence of gravity effects due to the counter-current imbibition associated with capillary pressure.

5. Summary and conclusions

A new similarity solution has been presented to study the role of capillary pressure on salt precipitation during CO$_2$ injection in a saline formation. Dimensional analysis has revealed that the problem is largely controlled by a capillary number, $Ca = Q_0\mu_1/(4\pi H k P_c)$, where $H$ [L] is the formation thickness, $k$ [L$^2$] is permeability, $P_c$ [ML$^{-1}$T$^{-2}$] is an air-entry pressure associated with the porous medium, $Q_0$ [L$^3$T$^{-1}$] is the injection rate and $\mu_1$ [ML$^{-1}$T$^{-1}$] is the dynamic viscosity of CO$_2$. The volume fraction of precipitated salt around the injection well, $C_{30}$ [-], is found to superlinearly increase with decreasing $Ca$. Subsequent sensitivity analysis also reveals that $C_{30}$ linearly scales with the salinity of brine. $C_{30}$ is found to reduce with increasing storage depth. This latter point is largely attributed to the equilibrium volume fraction of water in
the CO$_2$-rich phase increasing with depth. Relative permeability parameters are found to have a significant effect on the value of $C_a$ below which $C_{30}$ superlinearly increases. For highly non-linear relative permeabilities, $C_{30}$ remains stable for much lower capillary numbers.

The new similarity solution represents a significant extension of the work of Zeidouni et al. (2009) by accounting for capillary pressure and an extension of the work of Bjornara and Mathias (2013) by accounting for radially symmetric flow, partial miscibility and salt precipitation.

In one scenario studied, reducing the CO$_2$ injection rate from 15 kg s$^{-1}$ to 0.9 kg s$^{-1}$ led to almost a ten times larger volume fraction of precipitated salt. In the past, pressure buildup in injection wells has been widely perceived to increase monotonically with CO$_2$ injection rate. However, these results clearly demonstrate that as injection rate is decreased the volume fraction of precipitated salt around the injection well will significantly increase leading to potentially significant loss of injectivity. It follows that below a critical threshold, pressure buildup can be expected to increase with reducing injection rates as well. The similarity solution presented in this article can serve as a useful tool to determine the critical capillary number at which these effects are likely to take place.

Acknowledgements

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Capillary processes increase salt precipitation


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**Figure 1.** A schematic diagram illustrating the distribution of CO$_2$, water and salt around a CO$_2$ injection well in a saline formation.
Capillary processes increase salt precipitation

Figure 2. Sensitivity analysis based on gas-displacing-oil examples. The infinite Ca value curves were obtained from the method of characteristics solutions presented in Figs. 4.13 and 4.15 of Orr (2007). The finite Ca value curves were obtained using the pseudospectral solution documented in the current article.
Figure 3. Plots of CO$_2$ saturation against radial distance after injecting 4.73 Mt of CO$_2$ whilst assuming a range of different capillary numbers, Ca. The TOUGH2 results are from the simulations previously presented by Mathias et al. (2013). Other associated model parameters are presented in Table 2. The results for Ca → ∞ were obtained using a method of characteristics solution, also presented by Mathias et al. (2013). The results for finite Ca values were obtained using the pseudospectral solution.
Capillary processes increase salt precipitation

\[ F_1, \alpha_1, \beta_1 \text{ against } C_1 \text{ for the simulation results presented in Fig. 3.} \]
Figure 5. Sensitivity analysis based around the scenario presented in Fig. 3. The different colors relate to different brine salinities, as indicated in the legend. The solid lines, dashed lines and dash-dotted lines represent results obtained using fluid properties calculated assuming the saline formation exists at a depth of 1000 m, 1500 m and 2000 m, respectively (based on hydrostatic pressure conditions and a geothermal gradient of 40°C per km as in Table 3). a) shows plots of the ratio of dry-out zone volume ($V_d$) to injected CO$_2$ volume ($Q_0t$) against capillary number (Ca). b) shows plots of the ratio of volume of evaporated water ($V_e$) to $Q_0t$ against Ca. c) shows plots of the ratio of volume of dissolved CO$_2$ ($V_c$) to $Q_0t$ against Ca. d) shows plots of precipitated salt volume fraction in the dry-out zone ($C_{30}$) against Ca.
Capillary processes increase salt precipitation

Figure 6. The same as Fig. 5d except that salt volume fraction, $C_30$, is divided by the salinity of the brine, $X_{32}$.

Figure 7. Plot of normalized precipitated salt volume fraction, $C_{30}$, against capillary number, Ca, using the 1000 m depth model scenario described in Tables 2 and 3 in conjunction with the different relative permeability parameters given in Table 4.