Pore-scale dissolution of CO₂ + SO₂ in deep saline aquifers

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ABSTRACT

We employ Modified Moving Particle Semi-implicit (MMPS) method to study the multi-ion transport of CO₂ and SO₂ in natural porous media at the pore scale level. A new approach has been developed to account for the electrostatic forces. Compared to solving the Poisson-Nernst-Plank equations, this new approach eliminates the restrictions on the size of time step and hence allows for faster simulations. We carry out a series of simulations to study the dissolution of different charged and neutral species resulting from the injection of pure CO₂ and CO₂ + SO₂ in two sandstones, namely Berea and Bentheimer. The pressure, temperature and salinity conditions resemble those encountered in deep saline aquifers and non-ideality of the solution is taken into account by using the Davies activity model. We investigate the impact of pore-scale topology on the dispersion of different ions in both cases of pure CO₂ injection and CO₂ + SO₂ co-injection. Impact of the electrostatic forces on distribution of different ions in the samples is thoroughly studied.

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1. Introduction

Reducing the rate of anthropogenic CO₂ release to the atmosphere is considered an important step toward mitigating global warming and its unwanted consequences. Given the intense reliance of industrial development on fossil fuels, the most viable strategy in this regard seems to be CO₂ capture and storage technology. Among the possible storage scenarios, CO₂ injection into saline aquifers is the most promising. The injected CO₂ to deep saline aquifers can (1) flow updip and accumulate beneath the caprock (structural trapping), (2) migrate into the brine phase and become trapped in the form of isolated clusters (hydrodynamic trapping), (3) dissolve in the brine phase (solubility trapping), and (4) react with the formation minerals to precipitate secondary minerals (mineral trapping). Pore-scale complexities of the formation are among the key players determining the contribution of each of the aforementioned trapping processes on the final fate of the injected CO₂. Therefore, thorough understanding of the pore-scale phenomena pertinent to CO₂ injection in deep saline aquifers is a prerequisite to secure CO₂ sequestration.

Despite the abundance of continuum scale modeling studies of different CO₂ trapping processes, pore-scale studies are few. Moreover, the properties provided by pore-scale models are critical for the continuum scale models. Among the few pore-scale modeling studies on the solubility trapping mechanism in CO₂ sequestration one can point to the studies by Kang et al. (2005), Flukiger and Bernard (2009), and Li et al. (2008) where lattice-Boltzmann and finite volume techniques are used. Additionally, Lopez et al. (2011) used pore-network modeling to study hydrodynamic trapping of CO₂ in reconstructed sandstones.

The aim of this paper is to shed light on the pore-scale complexities of the solubility trapping process which is a precursor to the more long-term mineral trapping process. To do that we use Modified Moving Particle Semi-implicit (MMPS) technique which we have developed earlier (Ovaysi and Piri, 2010). MMPS is a Lagrangian particle-based method used to model pore-scale fluid flow directly in high-resolution images of naturally occurring porous media. In the present work, we add reaction and ion-transport layers on top of the already existing convection-diffusion model (Ovaysi and Piri, 2011). The model is then used to simulate pore-scale CO₂ and SO₂ solubility trapping in saline aquifers. We start by introducing the porous media used in this work. Then we discuss our ion-transport model along with a brief introduction to MMPS. The presentation will then be followed by the results section where we apply the model on the pore-scale images acquired through microtomography imaging.

2. Pore space representation

We use high-resolution images of two naturally occurring sandstones, Berea and Bentheimer, acquired using computed microtomography. The Berea image (Dong, 2007) has 5.345 µm resolution and, with 400 x 400 x 400 voxels dimension, amounts to (2.138 mm³). The Bentheimer image consists of 670 x 670 x 1500 voxels with 6.007 µm resolution which measures 4.025 mm x 4.025 mm x 9.011 mm in x, y, and z directions.
respectively. The Berea sandstone has a 19.6\% porosity and 1.2D permeability whereas our core-scale measurements on the Bentheimer sandstone revealed a 22.2\% porosity and 2.7D permeability.

To make the simulations computationally less expensive, we work with two 0.51 mm × 0.51 mm × 1.09 mm samples (one from each sandstone). Since MMPS is a particle-based method, we assign a particle to each voxel. The microtomography image is then used as a template to mark the solid and void particles. Fig. 1 illustrates the particle representation of the void space for samples A and B from the Berea and Bentheimer sandstones, respectively. Both the solid and void particles take part in MMPS calculations. However, to emphasize on the pore-scale features, we only visualize the void (fluid) particles. Further details of these samples are listed in Table 1.

3. Model description

The first step to modeling the reactive transport of CO\(_2\) in saline aquifers at the pore scale is the solution of the incompressible Navier–Stokes equations, i.e.,

\[
\frac{D\mathbf{v}}{Dt} = -\frac{1}{\rho} \nabla P + \frac{\mu}{\rho} \nabla^2 \mathbf{v} + \mathbf{g}
\]  

(1)

\[
\nabla \cdot \mathbf{v} = 0
\]

(2)

where \(\mathbf{v}\) is the velocity vector, \(\rho\) is density, \(\mu\) is viscosity, \(\mathbf{g}\) is the gravity vector, and \(P\) is pressure.

We use MMPS to solve Eqs. (1) and (2) for the porous media presented in Section 2. The advantages of using a Lagrangian

![Image of pressure distribution in particle representation with color bars]
Fig. 2. Mole fraction of water at $t = 0$ in a $24 \mu m \times 24 \mu m \times 120 \mu m$ tube with $2 \mu m$ resolution used to test the accuracy of the proposed multi-ion transport model.

Fig. 3. Comparison of the results obtained using our proposed method against the results obtained after solving the Poisson–Nernst–Planck equations (PNP) for (a) $H^+$ and (b) $CO_3^{2-}$ concentrations along the length of the test tube at four different times during the simulations.
Based on our simulations, molecular diffusion accounts for close to 70%, electrical coupling less than 30%, and chemical reactions less than 1% of the total transport. Though, these numbers can vary in other cases depending on the reaction rates and diffusion coefficients of the chemical species present in the system. The contribution of molecular diffusion in the overall rate of change for species $i$ in a non-ideal solution is represented by (Marchand et al., 2001)

$$\frac{\partial C_i}{\partial t} = D_i ( \nabla^2 C_i + \nabla \cdot (C_i \nabla \ln \gamma_i) )$$  \hspace{1cm} (4)

where $D_i$ is the molecular diffusion coefficient and $\gamma_i$ is the activity coefficient of species $i$. We use the Davies equation (Samson et al., 1999) to calculate the activity coefficients of ions. The activity coefficients of neutral species are assumed to be unity. A similar approach as in Ovaysi and Piri (2011) is employed to solve Eq. (4). The non-ideal term in Eq. (4), however, is an addition to a convection–diffusion equation which is also handled by a similar approach as in Ovaysi and Piri (2011).

To account for the electrical coupling of the ions, the conventional approach (Marchand et al., 2001) is to define

$$\frac{\partial C_i}{\partial t} = \frac{D_i z_i F}{RT} \nabla \cdot (C_i \nabla \Phi)$$  \hspace{1cm} (5)

where $z_i$ is the charge of the species $i$, $F$ is Faraday constant, $R$ is gas constant, $T$ is temperature, and $\Phi$ is electrostatic potential that is calculated using Poisson's equation, i.e.,

$$\nabla^2 \Phi = -\frac{F}{\epsilon} \sum_{i} z_i C_i$$  \hspace{1cm} (6)

where $\epsilon$ is the dielectric permittivity of the aqueous phase and $N$ is the number of species. However, due to the large multiplier of $F/\epsilon$ on the right-hand-side of Eq. (6), any deviation from the electroneutrality condition of

$$\sum_{i} z_i C_i = 0$$  \hspace{1cm} (7)

will lead to a significant change in the electrostatic field which in turn instantaneously corrects the local ion concentrations in favor

Fig. 4. The scCO$_2$/brine interface is placed at the inlet of the porous system to allow for molecular diffusion of species across the interface.

Fig. 5. Progression of the CO$_2$ plume due to pure CO$_2$ dissolution in samples A (left) and B (right) at (a) $t = 0.2$ s, (b) $t = 10$ s, and (c) $t = 20$ s. Only the particles with $C_{CO_2} > 0.01$ M at the first 0.65 mm of the samples are shown.
of Eq. (7). Therefore, Newman and Thomas-Alyea (2004) recommend to solve for only Eq. (7). This would eliminate the need to solve for the system of linear equations arised from Poisson’s equation. However, the solution to Eq. (7) is not unique in the presence of more than two ions. Eqs. (5) and (6) guarantee a unique and physically accurate solution to Eq. (7). In practice, however, Eqs. (5) and (6) greatly restrict the time step size, making the simulations computationally very expensive. To overcome this, we recommend Eqs. (8) and (9) presented below in place of Eqs. (5) and (6).

\[
\left( \frac{DC_i}{Dt} \right)_{\text{electrical coupling}} = -\lambda z_i C_i \tag{8}
\]

where \( \lambda \) is calculated using

\[
\lambda = \frac{\sum_{i=1}^{N} z_i C_i + \Delta t \sum_{i=1}^{N} z_i (DC_i/Dr)_{\text{diffusion}}}{\Delta t z_i^2 C_i} \tag{9}
\]

which is obtained by combining Eqs. (7), (8), and first-order time integration of \( C_i \). This formulation does not impose any further restriction on the size of time step other than the ones defined by Courant–Friedrichs–Lewy (CFL) condition (Ovaysi and Piri, 2010) which, in the present work, is used to ensure the convergence of the numerical solution to the Navier–Stokes equations. Eqs. (8) and (9) are solved locally for each fluid particle. These equations are implied from Eqs. (5) and (6) by separating the variables \( z_i \) and \( C_i \).

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**Fig. 6.** Progression of the HCO\(_3\) plume due to pure CO\(_2\) dissolution in samples A (left) and B (right) at (a) \( t = 0.2 \) s, (b) \( t = 10 \) s, and (c) \( t = 20 \) s. Only the particles with \( C_{HCO3} > 0.00017 \) M at the first 0.65 mm of the samples are shown.

**Fig. 7.** Progression of $\text{HCO}_3^-$ concentration due to pure CO\(_2\) dissolution in samples A (left) and B (right) at (a) \( t = 0.2 \) s, (b) \( t = 10 \) s, and (c) \( t = 20 \) s. Only the particles with \( C_{\text{HCO}_3^-} > 8.8 \times 10^{-6} \) at the first 0.65 mm of the samples are shown.
from the rest of the right hand side of Eq. (5) which is constant relative to the concentration of different ions. It should be stressed that Eqs. (8) and (9) are valid only in systems with neutral solid boundaries similar to the systems we study here. Furthermore, these equations are solely developed to expedite the numerical simulations and cannot be used for analytical purposes.

Finally, in Table 3 we list a series of reactions that are believed to ensue following the injection of a mixture of CO$_2$ and SO$_2$ in deep saline aquifers (Ellis et al., 2010). We assume the reactions happen instantaneously and therefore, to account for the last term of Eq. (3), we first need to rearrange the reactions in their canonical form (Lichtner et al., 1996). Then, using the stoichiometric relations and the mass action equations for the above-mentioned chemical reactions and also Eq. (3) for all the species, a nonlinear system of equations is obtained for each fluid particle. The unknowns of this system of equations are $\frac{DC}{DC_{\text{chemical reactions}}}$ for the reactive species which are calculated locally for each fluid particle. For more information on these calculations consult Lichtner et al. (1996).

4. Verification

In a previous study (Ovaysi and Piri, 2010), MMPS has been validated against analytical, numerical, and experimental data available in the literature. In particular, the accuracy of MMPS in capturing the correct velocity field in packed beds was proven. Furthermore, it was shown that MMPS can accurately predict the longitudinal dispersion coefficient in natural porous media under a wide range of Peclet numbers, including the flow regimes

\[ \text{Fig. 8. Progression of CO}_2^2^- \text{ concentration due to pure CO}_2 \text{ dissolution in samples A (left) and B (right) at (a) } t = 0.2 \text{ s, (b) } t = 10 \text{ s, and (c) } t = 20 \text{ s. Only the particles with} \quad c_{\text{CO}_2^2^-} > 3.75 \times 10^{-11} \text{ at the first 0.65 mm of the samples are shown.} \]

\[ \text{Fig. 9. Progression of pH due to pure CO}_2 \text{ dissolution in samples A (left) and B (right) at (a) } t = 0.2 \text{ s, (b) } t = 10 \text{ s, and (c) } t = 20 \text{ s. Only the particles with pH < 5.8 at the first 0.65 mm of the samples are shown.} \]
dominated by inertia and turbulence. The results of that study was successfully compared against the experimental data in the literature in Ovaysi and Piri (2011).

In this paper, in the absence of analytical/experimental data on the transport of multiple ions, we examine the accuracy of our proposed equations, i.e., Eqs. (8) and (9), in capturing the correct physics of multi-ion transport. To do that, we studied the diffusion of a brine saturated with SO$_2$ + CO$_2$ in a 1 M brine (free of SO$_2$ and CO$_2$) at 40 °C and 12.7 MPa, see Table 2 for brine compositions. For this test, we place the SO$_2$ + CO$_2$ rich brine at the entrance of a 120 μm long tube with square cross section that measures 24 μm at each side, see Fig. 2. The tube is initially filled with the 1 M brine that is free of SO$_2$ and CO$_2$. Upon starting the simulations, a series of reactions (see Table 3) ensue that result in the production of multiple ions as well as few neutral species. Overall, 17 species are present in the system of which 11 are charged. To simplify the comparisons, we only present the concentrations of H$^+$ and CO$_3^{2-}$ along the length of the tube in Fig. 3. The results of

---

**Table 2**

<table>
<thead>
<tr>
<th>Component</th>
<th>Brine</th>
<th>CO$_2$ rich brine</th>
<th>CO$_3$ + SO$_2$ rich brine</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>55.56</td>
<td>55.56</td>
<td>55.56</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.8995</td>
<td>0.8975</td>
<td>0.899</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.0098</td>
<td>0.0097</td>
<td>0.0099</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1.099</td>
<td>1.0989</td>
<td>1.0988</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0</td>
<td>0.9972</td>
<td>0.9989</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>0</td>
<td>0</td>
<td>0.0099</td>
</tr>
</tbody>
</table>
Fig. 11. Ca²⁺ profile after pure CO₂ dissolution in sample A in the presence and absence of electrostatic forces.

Table 3
Equilibrium constants taken from Ellis et al. (2010) at 40 °C and 12.7 MPa for 1 M NaCl brine.

<table>
<thead>
<tr>
<th>Index</th>
<th>Reaction</th>
<th>log Keq</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂O → H⁺ + OH⁻</td>
<td>-13.49</td>
</tr>
<tr>
<td>2</td>
<td>SO₂ + H₂O → H₂SO₃⁻ + H⁺</td>
<td>-0.042</td>
</tr>
<tr>
<td>3</td>
<td>H₂SO₃⁻ + H₂O → H₂SO₄⁻ + H⁺</td>
<td>-1.93</td>
</tr>
<tr>
<td>4</td>
<td>HSO₄⁻ + SO₂ + H⁺</td>
<td>-7.24</td>
</tr>
<tr>
<td>5</td>
<td>SO₂ + H₂O → ½H₂SO₃⁻ + ½H⁺ + ½H₂O</td>
<td>5.68</td>
</tr>
<tr>
<td>6</td>
<td>HSO₄⁻ → SO₄²⁻ + H⁺</td>
<td>-2.12</td>
</tr>
<tr>
<td>7</td>
<td>CO₂ + H₂O → H₂CO₃⁻</td>
<td>-2.77</td>
</tr>
<tr>
<td>8</td>
<td>H₂CO₃⁻ → HCO₃⁻ + H⁺</td>
<td>-6.27</td>
</tr>
<tr>
<td>9</td>
<td>HCO₃⁻ → CO₃²⁻ + H⁺</td>
<td>-10.16</td>
</tr>
</tbody>
</table>

The proposed method are obtained by solving Eq. (3) with the electrical coupling term computed using Eqs. (8) and (9). Whereas, in the Poisson–Nernst–Planck (PNP) case, the electrical coupling term is computed using Eqs. (5) and (6). As shown in Fig. 3 the results obtained using our proposed method are as accurate as those computed using Eqs. (3) and (6). Furthermore, our proposed method does not impose any restriction on the size of the time step leading to faster simulations.

5. Results and discussions

Given its critical temperature and pressure (31.1 °C and 7.38 MPa), CO₂ will exist as a supercritical fluid in deep saline aquifers. In this section, we study the dissolution of supercritical CO₂ phase (scCO₂) in brine. To do that, we first saturate the

Fig. 12. Progression of pH due to CO₂ + SO₂ dissolution in sample A in the presence (left) and absence (right) of electrostatic forces at (a) t = 0.2 s, (b) t = 10 s, and (c) t = 20 s. Only the particles with pH < 2.53 at the first 0.65 mm of the sample are shown.
samples A and B with 1 M neutral brine. We then, as shown in Fig. 4, introduce the brine solution equilibrated with CO₂ (or CO₂ + SO₂) at the inlet of the sample, see Table 2 for brine compositions. The assumption is that the CO₂/brine interface is located at the inlet of the sample (left side in Fig. 1(a) and (b)) and is constantly feeding the sample with CO₂ (or CO₂ + SO₂) saturated brine solution. The CO₂ and SO₂ solubilities in the brine solution are based on the data reported by Ellis et al. (2010) which are calculated for 1 M brine at 40 °C and 12.7 MPa. Also, Table 4 lists the molecular diffusion coefficients used in the present study. To simulate a realistic scenario, we establish a background aquifer velocity of 10 cm/yr (3 × 10⁻⁹ m/s) (Bachu et al., 1994) by applying 8 × 10⁻⁶ Pa and 4 × 10⁻⁸ Pa

**Table 4**

Molecular diffusion coefficients of different ions in water at 40 °C taken from Newman and Thomas-Alyea (2004) and Ellis et al. (2010).

<table>
<thead>
<tr>
<th>Species</th>
<th>D_D (m²/s) × 10⁹</th>
<th>Species</th>
<th>D_D (m²/s) × 10³</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>9.312</td>
<td>HCO₃⁻</td>
<td>1.24</td>
</tr>
<tr>
<td>OH⁻</td>
<td>5.26</td>
<td>CO₂²⁻</td>
<td>0.968</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.334</td>
<td>H₂SO₄⁻</td>
<td>2.31</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.792</td>
<td>HSO₃⁻</td>
<td>1.02</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.032</td>
<td>SO₂²⁻</td>
<td>1.01</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.94</td>
<td>HSO₃⁻</td>
<td>1.45</td>
</tr>
<tr>
<td>SO₂</td>
<td>2.316</td>
<td>SO₂²⁻</td>
<td>1.12</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>1.5</td>
<td>H₂S</td>
<td>1.33</td>
</tr>
</tbody>
</table>

**Fig. 13.** Progression of HSO₄⁻ due to CO₂ + SO₂ dissolution in sample A in the presence (left) and absence (right) of electrostatic forces at (a) t = 0.2 s, (b) t = 10 s, and (c) t = 20 s. Only the particles with C_HSO₄⁻ > 0.0086 M at the first 0.65 mm of the sample are shown.

**Fig. 14.** Progression of SO₄²⁻ due to CO₂ + SO₂ dissolution in sample A in the presence (left) and absence (right) of electrostatic forces at (a) t = 0.2 s, (b) t = 10 s, and (c) t = 20 s. Only the particles with C_SO₄²⁻ > 0.0032 M at the first 0.65 mm of the sample are shown.
pressure difference across samples A and B, respectively. This yields a very low Peclet number, i.e., $Pe < 1 \times 10^{-4}$, which places the dispersion regime in a zone dominated by molecular diffusion in both samples A and B. In practice, the above conditions prevail when the CO$_2$ stored through residual and structural trapping gets exposed to fresh brine due to small background velocity of the aquifer. In both cases, the supercritical phase gradually shrinks by diffusing into the surrounding aqueous phase at very low Peclet numbers. Also, to speed up the simulations that follow, we used a multi-GPU accelerated code (Ovaysi and Piri, 2012) that was developed recently.

5.1. Pure CO$_2$ dissolution

Shown in Fig. 5 is the visualization of CO$_2$ dispersion in the brine phase in samples A and B. Following the reaction route specified in Table 3, H$_2$CO$_3$ is formed in the presence of CO$_2$, see Fig. 6. Carbonic acid then dissociates in two stages to give H$^+$, HCO$_3^-$, and CO$_3^{2-}$ ions. The bicarbonate and carbonate ions reach their peak concentrations at the inlet of the sample with a gradual dilution towards the outlet as seen in Figs. 7 and 8. Noteworthy in these figures, despite having an inferior molecular diffusion coefficient, the carbonate ions spread faster than the bicarbonate ions. To further investigate this, we show pH progression in these samples in Fig. 9. As expected, the hydrogen ions spread faster due to their much higher molecular diffusion coefficient compared to all the other ions present in the system, see Table 4. However, their dispersion rate is compromised by reactions (8) and (9) listed in Table 3. A closer look at Figs. 6, 7 and 9 reveals that the H$^+$ produced by reactions (8) and (9) quickly disperses throughout the system. This further shifts these reactions to the right in favor of production of the HCO$_3^-$ and CO$_3^{2-}$ ions. The HCO$_3^-$ ion, however, is further consumed in reaction (9) leading to an overall slower dispersion rate for HCO$_3^-$ compared to that of CO$_3^{2-}$.

Due to the low background velocity, molecular diffusion is dominant in both samples and hence pore connectivity does not play a major role in the transport of species. Therefore, transport of the species in both samples A and B is comparable. The only exception is distribution of the low pH (more acidic) particles in the samples. As clearly seen in Fig. 9, low pH particles at the inlet of sample A are more pronounced compared to those in sample B. This is due to the superior connectivity of sample B which creates a medium where H$^+$ ions come in better contact with a fresh supply of neutral brine far from the interface. This helps to further neutralize the acidic front in the more conductive fluid channels of both samples A and B, though sample B has a higher density of conductive fluid channels. Acidity of the less conductive or dead-end fluid channels which are more present in sample A, on the other hand, remains high throughout the simulations which could indicate a higher chance for mineral reactions in these areas.

Using the method of moments as described in Ovaysi and Piri (2011), we have computed the longitudinal dispersion coefficients for the different species. Fig. 10 illustrates variation of the longitudinal dispersion coefficients versus time for CO$_2$, H$_2$CO$_2$, H$^+$, HCO$_3^-$, and CO$_3^{2-}$ in samples A and B. It should be noted that, due to their extremely low velocities, none of the fluid particles enters the downstream section during the 20s simulations. Therefore, concentration in the downstream section, which is equal to the original brine concentration, remains fixed throughout the simulation. Consequently, a steady-state concentration profile establishes between the two fixed boundaries at the inlet and outlet. This leads to a zero rate of growth for the plume and hence a zero rate of dispersion after steady state is reached. Also, the plotted values in these figures are strongly influenced by the reactions listed in Table 3 and hence a slightest change in the concentration of one species triggers a redistribution of other species. As such, the computed dispersion coefficients in Fig 10 can be used as a tool to assess the reactivity of the species. For instance, according to reaction number 7 in Table 3, H$_2$CO$_3$ is produced when CO$_2$ comes in contact with water. Therefore, since water is present everywhere in the pore space, presence of the dissolved CO$_2$ translates to the
presence of H$_2$CO$_3$ which is also supported by Figs. 5 and 6 for samples A and B. This explains why the computed dispersion coefficients of these two components overlap throughout the simulation for both samples. As explained earlier, dispersion rate of the bicarbonate and carbonate ions are increased due to the fast dispersion of the hydrogen ions and the dissociation reactions of carbonic acid. In fact, dispersion of the bicarbonate and carbonate ions is primarily controlled by the dispersion pattern of the hydrogen ion. This can be better understood by studying the pH front in Fig. 9 at $t = 10$ s where the hydrogen ions are introduced to large pores in the middle of sample B. According to Ovakyi and Piri (2011), this translates to a slight increase in the dispersion coefficient of H$^+$ as similar features in the sample have already been scanned by the plume of H$^+$. Since H$^+$ passes quickly through this conductive area of sample B, the balance of both reactions (8) and (9) is shifted more to the right which results in an increase in CO$_3^{2-}$ production and hence an increase in its dispersion coefficient as calculated in the present work. However, passage of the hydrogen ion through this conductive area is quick and the next fluid channels are not as conductive leading to less dispersion of the hydrogen ions and consequently slower production of the carbonate ions. Overall, the net result of this interaction is a pulse of CO$_2^{2-}$ production that results in a peak for the longitudinal dispersion coefficient of carbonate ions.

To investigate the impact of electrostatic forces on distribution of the different ions present in the system, we also simulated the dissolution of scCO$_2$ in sample A in the absence of the electrical coupling term in Eq. (3). Knowing that the system is electroneutral at $t = 0$, the only factor to change the balance of the electrostatic forces is production of the cations and anions resulting from dissociation of carbonic acid. However, carbonic acid's rate of dissociation is very low and the produced ions are in very small quantities. Therefore, no detectable change in the distribution of H$^+$, HCO$_3^-$, or CO$_2^{2-}$ was observed in the absence of the electrostatic forces. Nonetheless, production of H$^+$, and particularly its fast rate of dispersion, slightly impacted the distribution of Ca$^{2+}$ at the inlet of the sample, see Fig. 11. It is evident from this figure that, in the presence of electrostatic forces, the hydrogen cations repel the

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**Fig. 16.** Progression of pH due to CO$_2$ + SO$_2$ dissolution in sample B at (a) $t = 0.2$ s, (b) $t = 10$ s, and (c) $t = 20$ s. Only the particles with pH = 2.53 at the first 0.65 mm of the sample are shown.

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**Fig. 17.** Progression of HSO$_3^-$ (left) and SO$_2^{2-}$ (right) due to CO$_2$ + SO$_2$ dissolution in sample B at (a) $t = 0.2$ s, (b) $t = 10$ s, and (c) $t = 20$ s. Concentrations are in molar. Only the particles with Ca$^{2+} > 0.0086$ M (left) or Ca$^{2+} > 0.0032$ M (right) at the first 0.65 mm of the sample are shown.
divalent calcium cations leading to a sharp increase in Ca$^{2+}$ concentration at the inlet of the sample. This repulsion force, however, is negligible on Na$^+$ for two reasons: First, Na$^+$ is present in much higher concentrations than Ca$^{2+}$ and the very weak repulsion forces from a dilute solution of H$^+$ cannot cause significant change in the saturation of Na$^+$; Second, Na$^+$ is monovalent and receives a smaller repulsion force from H$^+$ compared to the repulsion force exerted on the divalent Ca$^{2+}$. Also, no significant change was observed in the concentration of Cl$^-$ in the absence of electrostatic forces. This can be attributed to the high concentration of Cl$^-$ compared to the low quantities of H$^+$ produced in the system. We also see a decrease in Ca$^{2+}$ concentration at the inlet of the sample in the absence of the electrostatic forces. This is caused due to the production of other species in the system which leads to the dilution of Ca$^{2+}$ at the inlet.

5.2. CO$_2$ and SO$_2$ dissolution

Based on the emission data published in Miller and Van Atten (2004), a 99% CO$_2$ and 1% SO$_2$ composition was chosen for the scCO$_2$ phase which comes in contact with the brine phase at the inlet of the samples. This composition, however, is greatly altered in the brine phase due to the vastly different solubilities of CO$_2$ and SO$_2$ in brine. Composition of the CO$_2$ + SO$_2$ saturated brine, which represents the scCO$_2$/brine interface and is placed at the inlet of the samples, is listed in Table 2. Once this interface comes in contact with the brine solution, SO$_2$ is entirely consumed in the hydrolysis and disproportionation reactions that ensue and its saturation is not detectable in any of the samples. As shown in Fig. 12 the high dissociation rate of sulfuric acid leads to the formation of a strongly acidic front in sample A. Besides H$^+$, progression of the
other products of sulfuric acid dissociation, i.e., HSO₄⁻ and SO₄²⁻, in sample A are shown in Figs. 13 and 14, respectively. To study the impact of electrostatic forces on the distribution of these anions, similar to the study in Section 5.1, we also carried out a second simulation in sample A for CO₂ + SO₂ dissolution in the absence of the electrical coupling term in Eq. (3). In the above figures, we also illustrate the progression of the hydrogen, bisulfate, and sulfate ions in sample A in the absence of electrostatic forces where we notice a decline in the concentration of H⁺ (increase in pH) and an increase in the concentration of both HSO₄⁻ and SO₄²⁻. This can be explained by the vastly different molecular diffusion coefficients of the hydrogen cation compared to those of the bisulfate and sulfate anions. In the absence of electrostatic forces, these ions diffuse independently which means that H⁺ quickly diffuses away from its production site, leaving behind a dilute solution of H⁺.

On the other hand, HSO₄⁻ and SO₄²⁻, which have much smaller molecular diffusion coefficients stay close to their production sites. This yields a higher concentration for these ions in the absence of electrostatic forces. However, in reality, the electrostatic forces are present which requires the cations and anions to be coupled, leading to a slower rate of diffusion for H⁺ and a faster rate of diffusion for HSO₄⁻ and SO₄²⁻. Consequently, compared to the case in which the electrostatic forces were ignored, H⁺ stays closer to its production site, i.e., primarily the inlet, and HSO₄⁻ and SO₄²⁻ move away from the inlet faster. Interestingly, the maximum HSO₄⁻ concentration observed in the presence of electrostatic forces is 30% smaller than that obtained in the absence of electrostatic forces. In the case of SO₄²⁻, this number is 60%. Considering these values, it is evident that the divalent sulfate anion has received a twice stronger pull from the hydrogen cation compared to the pull on the monovalent...
bisulfate anion. The graphs in Fig. 15 support the statements above where, in the presence of electrostatic forces, longitudinal dispersion coefficient of H⁺ has inched above those of HSO₄⁻ and SO₄²⁻. It is also clear that in the presence of electrostatic forces, the electrical coupling of the ions leads to a greater variation of their respective dispersion coefficients. However, since the dispersion coefficients continuously decline towards zero, no conclusive remarks can be made regarding how the electrostatic forces might influence the time scale of asymptotic behavior.

Another factor contributing to the formation of a highly acidic area at the inlet of sample A is the poor connectivity of this sample. The produced hydrogen ions in sample A are mostly trapped at the inlet, due to the very turturous network of fluid channels existing in this sample. On the contrary, fluid channels in sample B are not only better connected but also wider, which provide a more efficient pathway for the produced species to travel away from their production sites. Evolution of pH in sample B is shown in Fig. 16 where the low pH front has scanned more length of the sample compared to that in sample A. Also, a better dispersion of the hydrogen ions in sample B has translated to a rather dilute solution of H⁺ at the inlet. Furthermore, as shown in Fig. 17, compared to sample A, concentration of the bisulfate and sulfate ions at the inlet remain higher in sample B. This can be explained by the concentration profile of other ions present in the system, namely the mineral ions of Na⁺, Ca²⁺, and Cl⁻. As shown in Figs. 18–20, these ions are distributed quite differently in samples A and B. We use the profile of these ions in the absence of electrostatic forces as a base case where the mineral ions are not altered by these forces. In sample A, due to its poor connectivity, the produced ions cannot move considerably and hence are forced to neutralize their electrical charge by
themselves. This has led to less alteration of the mineral ions, except for Ca\textsuperscript{2+} which, as explained earlier in Section 5.1, is a divalent cation that exists in smaller quantities and therefore more susceptible to alteration. In sample B, on the other hand, the produced ions are not restricted by porous system and therefore can rely on the existing mineral ions in the system to reach an electroneutral state. Therefore, in sample B, H\textsuperscript{+} does not need to couple with HS\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-}. Hence, as shown in Fig. 15, the hydrogen cation can disperse faster as the mineral ions are present throughout the system. However, this alters the concentration of the mineral ions in areas away from the inlet as seen in Figs. 18–20. The slow diffusing bisulfate and sulfate anions, also, are less dependent on the hydrogen cation and instead couple with the mineral ions at the inlet of sample B.

Being a neutral component, identical to Section 5.1, CO\textsubscript{2} diffuses throughout both samples A and B to produce H\textsubscript{2}CO\textsubscript{3}. However, due to its low dissociation rate, the produced carbonic acid acts as a buffer for sulfuric acid. Therefore, both the bicarbonate and carbonate ions are present only in trace quantities of less than 10\textsuperscript{-12} M. Though, these ions are even less present in sample B due to the fact that H\textsuperscript{+} is strongly present throughout the system. Therefore, the diffused CO\textsubscript{2} in the presence of SO\textsubscript{2} can only give H\textsubscript{2}CO\textsubscript{3}. Since, most of the diffused SO\textsubscript{2} is consumed in the production of sulfuric acid, sulfurous acid is rarely produced. Even then, this weak acid acts as another buffer for sulfuric acid. Hence, sulfuric acid and its dissociation products are not present in any of the samples in noticeable quantities.

6. Conclusions

In this study, the particle-based method of MMPS was extended to model reactive multi-ion transport of charged and neutral species resulting from the dissolution of CO\textsubscript{2} and CO\textsubscript{2} + SO\textsubscript{2} in deep saline aquifers. We observed that, in the case of pure CO\textsubscript{2} dissolution, a weakly acidic front (pH \approx 4.8) establishes at areas close to the scCO\textsubscript{2}/brine interface. This acidic front spreads throughout the system, though at a faster rate in samples with good connectivity. Since the produced ions resulting from the dissolution of pure CO\textsubscript{2} are in small quantities, the electrostatic forces only slightly affect the transport of species. Dissolution of CO\textsubscript{2} + SO\textsubscript{2}, on the other hand, leads to the production of large quantities of charged species which are significantly influenced by the electrostatic forces. These forces can then greatly alter the mineral makeup of the brine, a phenomenon that cannot be observed in the absence of electrostatic forces. We also observed that the highly acidic front (pH \approx 1.53) is firmly maintained in porous media with poor connectivity. In addition to using a multi-GPU accelerated code, to expedite the simulations, we also chose relatively small subsets of the two sandstones studied here. Although previous studies (Ovaysi, 2010) indicate improved connectivity in larger samples (for samples smaller than REV size), based on the early results of our simulations on larger samples, we believe these small subsets offer enough pore-scale details to examine the physics of multi-ion transport at this scale. We intend to extend the current model to include mineral reactions which would eventually help improve the current understanding of CO\textsubscript{2} trapping mechanisms and hence lead to the design of better optimized CO\textsubscript{2} sequestration strategies.

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References


