PORE NETWORK MODELLING OF SURFACE HETEROGENEITY IN BRINE-FILLED POROUS MEDIA FOR CARBON SEQUESTRATION

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ABSTRACT

Trapping of carbon in deep underground brine-filled reservoirs is a promising approach for the reduction of atmospheric greenhouse gas emissions. However, estimation of the amount of carbon dioxide (CO$_2$) that can be captured in a reservoir remains a challenge. One difficulty lies in the estimation of local capillary pressure effects that arise from mineral surface heterogeneity inherent in underground geological formations. As a preliminary step to address this issue, we present a series of pore network modeling (PNM) simulations of two-phase immiscible flow in 3D structured porous media with contact angle heterogeneity. We present saturation patterns for networks with homogeneous and heterogeneous wettability under typical reservoir conditions, taking into account varying contact angles for CO$_2$ on mica and quartz at supercritical conditions. At lower flow rates, our preliminary results showed higher saturations for the heterogeneous networks than for the homogeneous ones. To characterize the fingering patterns, we have introduced $R$ as the ratio of filled throats to the total network saturation. Based on this measure, the heterogeneous networks demonstrated thicker fingering patterns than the homogeneous networks. These preliminary results highlight the importance of micro-scale surface heterogeneity for the modeling of carbon storage processes.

INTRODUCTION

Carbon capture and storage (CCS) has been proposed as a short- to medium-term solution towards the reduction of carbon dioxide (CO$_2$) emissions into the atmosphere. Underground sequestration of carbon in geological formations is one possible method for realizing this, and involves the injection of CO$_2$ into high-permeability porous reservoirs at supercritical conditions. Once injected, the CO$_2$ displaces the occupying reservoir fluid (oil, gas, or brine) as it migrates upwards, where its upwards migration is arrested by a low-permeability sealing caprock formation. Deep saline aquifers (underground brine-filled geological reservoirs) are being considered as ideal sites due to their large volume capacity and relative global abundance [1].

Within the reservoir, supercritical CO$_2$ forms an immiscible interface with the formation brine. Flow of the CO$_2$ in the geological formation and the associated movement of the immiscible interface are governed by multiphase drainage processes in porous materials, namely the interplay of viscous and capillary forces. This can lead to a variety of possible saturation patterns, depending on the relative strength of these forces [2-5]. Dissolution of one fluid into the other can lead to brine acidification and ion precipitation [6-9]; or formation dry-out, especially near the injection site [10-12]. Knowledge of the formation porosity and pore structure; surface forces; brine properties; and component reactivities are required to predict the expected saturation patterns and the eventual fate of the injected CO$_2$. Prediction of the CO$_2$ storage capacity and
The simulations discussed above [18] involved two-dimensional (2D) continuum simulations with 0.3×0.3 m² grid spacings. Such scales are suitable for reservoir simulations; however, this requires a bulk assumption for the capillary drainage curve of each grid section. As such, structural effects inherent in the pore structure of the material are not considered. Microscale surface effects involving structural and material heterogeneity should be treated on the pore-scale for a full description of microscale interactions. Pore-scale simulations including heterogeneous surface effects are needed to describe local capillary effects, so that appropriately scaled transport phenomena can be determined. This is especially the case if geochemical reactivity is included and pore-scale geometries are simulated.

Pore network modeling (PNM) has been used extensively to describe flow of single or multiphase fluids in geological structures [2, 3, 5, 7, 27-29]. In this technique, a porous structure is represented by a network of discrete pores connected by cylindrical throats [4, 5] with pores placed on a regular lattice [2, 7] or irregular domain based on imaging of real porous rock [29]. The size of the domain depends on the amount of material required for representative modeling. Flow within the porous structure is approximated using a 1D flow model. Computed pore-network quantities, such as saturation patterns and permeability, can be compared to experimental measurements on lab-scale samples.

In an early treatment of wetting in pore network models, Blunt and Scher [30] performed an extensive study of the relevant parameters affecting multiphase flow in porous media. Aker et al. [2] explored 2D pore networks over a range of capillary numbers and viscosity ratios, and presented the associated saturation patterns. A similar model was used by Ferer et al. [3] for simulation of CO₂ sequestration conditions. Al-Futaisi and Patzek [28] developed a 3D PNM with a variety of pore shapes and considered advancing and receding contact angles during primary invasion (drainage) and subsequent imbibition. They found that alteration of the contact angles had significant effects on the capillary pressure and relative permeability curves.

Since capillary pressure is important in determining the overall storage capacity of a reservoir and the security of the caprock seal, the contribution of surface heterogeneities on the throat pressures needs to be considered. To establish a framework for pore-scale simulations involving surface and wettability heterogeneity, we present a series of 3D PNM calculations of model networks composed of two simulated rock types, quartz and mica, with varying contact angles. We examine the effect of surface heterogeneities on the saturation patterns for two model formations made up of varying proportions of quartz and mica. While these values are not intended to be representative of real reservoirs, the contact angle heterogeneity should highlight the importance of these effects.
PORE NETWORK MODEL DESCRIPTION

The pore network model used in this study was a dynamic drainage model adapted from previous works [2, 3], which has been shown to predict saturations patterns for both capillary and viscous fingering regimes. The model describes a two-phase invasion process by a non-wetting fluid (CO₂), displacing in-situ brine (wetting fluid), into a three-dimensional regular lattice. Voids in the model material are treated as pore spaces, and connections between pores as throats. In this study, we consider a three-dimensional regular lattice with pores situated at the nodes of a rectangular grid of grid-spacing \( L \), with each pore joined to its nearest neighbors via tubular throats. This is shown schematically in Figure 1a. Flow inlet and outlet boundary conditions (BCs) are used in the direction of injection flow, which, in our case, was taken to be vertical. Periodic BCs were employed at all other boundaries, as demonstrated by the dashed lines in Fig. 1a.

The pore and throat sizes were set as follows: i) the pore diameters were set randomly as a fraction of the pore-to-pore distance \( L \), according to a normal distribution with standard deviation 0.015; ii) the diameter of the throat connecting each pore to its six nearest neighbors was taken as the diameter of the smallest connecting pore. This is shown schematically for two dimensions in Fig. 1b.

Flow was generated in the network through an initial pressure difference between the inlet and outlet pores. This initial pressure difference was used to initialize the flow fields, which were maintained throughout the simulation. Flow progressed vertically (\( Q_m \) in Fig. 1a) with the inlet along the bottom plane and the outlet at the top. The invasion process was simulated over a series of time steps, and proceeded until breakthrough occurred, which was determined as invasion of an outlet pore.

Modeling equations

The pore network equations have been discussed before [2], so we only briefly describe the model. Flow within the throats is given by 1D Poiseuille flow in a cylinder, so the volumetric flow rate \( q_{\text{throat}} \) is

\[
q_{\text{throat}} = g_{\text{throat}} (\Delta P_j - P_{\text{cap}})
\]

where \( \Delta P_j \) is the pressure difference between connected pores, \( P_{\text{cap}} \) is the capillary pressure, and \( g_{\text{throat}} \) is the throat conductance,

\[
g_{\text{throat}} = \frac{\pi r_{\text{throat}}^4}{8 \mu D L} \left( \frac{1}{x + (1-x)M} \right)
\]

where \( \mu_D \) is the defending fluid viscosity (brine), \( x \) is the fraction of the throat occupied by the defending fluid, so \( x = 0 \) for an invaded throat, and the viscosity ratio is

\[
M = \frac{\mu_1}{\mu_D}
\]

\( \mu_1 \) is the invading fluid viscosity. In the following simulations, we choose \( \mu_D = 10^{-7} \text{N·s·cm}^{-2} \).

\( P_{\text{cap}} \) is the capillary pressure due to the presence of a non-wetting/wetting interface and is calculated from the Young-Laplace equation (Eq. 1). To approximate the non-cylindrical shape of the throats, the capillary pressure was described with a sinusoidal function [2]. The formula for the capillary pressure is

\[
P_{\text{cap}} = \frac{2 \gamma \cos \theta}{r_{\text{throat}}^2} \left( 1 - \frac{1}{2} \cos(2\pi x) \right).
\]

where \( \theta \) is the contact angle, and \( \gamma \) is the interfacial surface tension. \( P_{\text{cap}} \) is only calculated if the throat contains an interface. In the following simulations, we use \( \gamma = 0.21 \text{mN·cm}^{-1} \) as the brine-CO₂ surface interfacial tension [3, 31].

Conservation of flux for the network is applied, and Eqs. 2-5 are solved across all pores in the network, at each time step. This leads to a system of \( N \) equations in \( N \) unknowns, which are the pressures in the \( N \) pores. By assuming the pressures do not vary within a pore, the system was solved to determine the pressure at each timestep. A constant flow boundary at the inlet and a constant pressure boundary at the outlet are used. The pressure at the outlet is set to 0 and the inlet flow is determined from the equation for the capillary number, \( C_a \), which is the ratio of viscous to capillary forces, given by

\[
C_a = \frac{\mu}{AY}
\]

where the viscosity \( \mu \) is taken as the defending fluid viscosity, \( \gamma \) is the surface tension, and \( A \) is the total cross sectional area of all inlet pores [2].

The menisci were advanced following Aker et al. [2]. Briefly, the timestep for each iteration is calculated to allow each menisci to advance by a maximal distance, \( \Delta x_{\text{max}}/A \Delta x_{\text{max,j}} \) is determined for each throat at each iteration, and is set to 0.1 when the interface is in the first half of the throat (\( x_i \leq 0.5 \)).
Flow advanced through the throats until an interface reached a pore, at which point the pore was invaded instantly. Upon invasion, all connected throats were invaded by advancing the interfaces into each throat by a fraction of the throat length, given by \( \delta \) [2]. In this way, the values of \( x \) following invasion for all newly invaded throats are \( x_i = 1-\delta \). \( \delta \) was a uniformly distributed random number between 0.01 and 0.05. All other interfaces were advanced as normal when a pore was invaded. The model was iterated until breakthrough occurred, which corresponded to the filling of a single pore at the outlet (top row of pores in Fig. 1a).

**Contact angles and surface heterogeneities.**

We employ CO\(_2\)-brine-solid contact angles determined by Chiquet *et al.* [21]. At the high pressures normally used for sequestration in deep saline aquifers, the contact angles for CO\(_2\) on quartz remain relatively constant over a broad range of salt concentrations. However, for mica, the contact angle is strongly affected by pressure and brine salinity. At pressures near 10 MPa, with salinity on the order of 0.5 M NaCl [1], the contact angles on quartz and mica are taken at 31° and 58°, respectively [21].

The model storage formations are based on compositional studies of the Sleipner sequestration project in the North Sea [19, 20]. Both the sandstone and the shale caprock are formed by a variety of rock-types, including quartz, mica, K-feldspar, and calcite, among others. In this preliminary study, we consider contact angles at supercritical conditions for two surfaces: mica and quartz.

**Computational methodology.**

All simulations were performed using Matlab (v7.11.0.584 R2010b) for a variety of fully coordinated, 50x50 pore networks. The viscosity ratio \( \log(M) \) and the capillary number \( \log(C_a) \) were varied between [-2.0] and [-5.0], respectively. For the 3D simulations, 15x15x40 networks were simulated, with flow in the positive z-direction.

For the heterogeneous wettability computations, a network was created using pseudo-random distributions of throat and pore sizes. A single porosity, \( \phi \approx 0.30 \), was examined which was obtained by setting the mean throat radii to 7.5 \( \mu \)m.

One heterogeneous and two homogeneous networks were constructed. To construct model homogeneous and heterogeneous formations, the amounts of mica and quartz in realistic formations were considered. The relative compositions of these two minerals were then used to form the fractions in the model. For instance, the sandstone formation contains 76% quartz and 5% mica. The model formation was only comprised of these two minerals, so the relative model composition is 0.94:0.06 quartz:mica. The heterogeneous and homogeneous compositions for our model are shown in Table 1, along with the compositions reported in the literature [1].

In all cases, the final saturation profile was determined upon breakthrough. The 3D networks normally required less than 100 minutes computation to achieve breakthrough; however, at lower capillary numbers (10\(^{-3}\)), this required up to 11 hours, in some cases.

**RESULTS & DISCUSSION**

We begin by presenting 3D pore-network saturation patterns at breakthrough over a range of transport parameters. Figure 2 shows saturation patterns at two capillary numbers (10\(^0\) and 10\(^3\)) and viscosity ratios (10\(^0\) and 10\(^3\)), for three surface regimes: homogeneous (high \( P_{cap} \)), homogeneous (low \( P_{cap} \)), and heterogeneous. In Fig. 2, pores filled with CO\(_2\) are represented as green cubes. For clarity, brine-filled pores are not shown. In all cases, the mean pore network porosity was approximately \( \phi=0.30 \). Figure 3 shows saturation profiles for the high and low flows along the flow direction, averaged across the X- and Y-axes.

The saturation patterns in Fig. 2 are nearly identical at the higher capillary number (10\(^3\)), whereas at the lower \( C_a \), the heterogeneous patterns show a greater degree of saturation than either homogeneous network. This is the case at both viscosity ratios tested (10\(^0\) and 10\(^3\)). The trend is quantified in Fig. 3, where on the right (\( C_a=10^3 \)), the profiles for all three regimes follow similar trends. However, at the low \( C_a \) (10\(^2\)), the saturation is consistently higher for the heterogeneous surface, above 60% of the flow thickness, at all three viscosity ratios tested.

The effects of the surface heterogeneities on final saturation are further compared in Fig. 4, which shows the saturations at breakthrough over three values for M, \( C_a \), and surface heterogeneity. At the higher values of \( C_a \) (10\(^2\) and 10\(^3\)), which corresponds to higher flow rates, there is little or no difference between the three surface heterogeneities simulated.

**Table 1** –Formation composition from [1] for the model sandstone and shale, and the relative fractions employed in this study.

<table>
<thead>
<tr>
<th>(a)</th>
<th>Sandstone (based on [19])</th>
<th>Shale (based on [20])</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model from [1]</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>76 %</td>
<td>Quartz</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>7 %</td>
<td>K-feldspar</td>
</tr>
<tr>
<td>Calcite</td>
<td>7 %</td>
<td>Calcite</td>
</tr>
<tr>
<td>Mica</td>
<td>5 %</td>
<td>Mica</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>3 %</td>
<td>Plagioclase</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>20 %</td>
<td>Other</td>
</tr>
<tr>
<td><strong>Model Formation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Quartz</td>
<td>0.94</td>
<td>0.57</td>
</tr>
<tr>
<td>% Mica</td>
<td>0.06</td>
<td>0.43</td>
</tr>
</tbody>
</table>
At the lowest capillary number, however, the heterogeneous network saturation was higher than the homogeneous networks by about 7%, at $M=10^0$. The increase was smaller at the lower $M$ values.

We can explain the increase in saturation for the heterogeneous network as follows. Recall that identical networks were used for the homogeneous and heterogeneous networks, so that the throat diameters were the same for each surface regime. Since the saturation patterns for the $C_a = 10^0$ and $10^{-3}$ cases are similar, we only consider the $10^{-5}$ regime. At the highest viscosity ratio ($10^0$), the two homogeneous cases have the same saturation (45%). This can be attributed to the fact that the only difference in these networks is that the contact angles, and therefore the capillary entry pressures in most throats decreases, going from a uniformly high-$P_{cap}$ to low-$P_{cap}$ regime. Since all the throat radii remain the same, the capillary pressure distribution retains the same shape, and is simply shifted to lower values. As a result, the invading fluid follows the same pathway for both homogeneous networks, leading to identical patterns.

For the heterogeneous case, the capillary entry pressure distribution has now been entirely altered compared to the homogeneous cases, due to the new distribution of contact angles. As a result, the fluid pathway for the heterogeneous network was not identical to the homogeneous cases, leading to a different saturation. Because of the contact angle heterogeneity, this pathway will no longer be determined simply the largest throat sizes, but will also depend on the mineral type. Since only a single simulation was performed at for each condition, we cannot conclude that the increase in saturation is due to the heterogeneous surface. Further simulations are required for validation.

Concerning the lower values of $M$ ($10^{-1}$ and $10^{-2}$), the homogeneous low-$P_{cap}$ and the heterogeneous formations yielded similar, higher saturations than the homogeneous high-$P_{cap}$. The shift towards lower capillary pressures could correspond to a shift from capillary force dominated to viscous force dominated, which would be expected to lead to higher saturations. Again, as this is a preliminary study, further simulations are required to verify this statement.
Finally, we turn our attention to the shape of the CO₂ front as a way to describe the degree of fingering for the three surface regimes tested. To make this comparison, we introduce \( R \) as the ratio of the fraction of filled throats to the total saturation. This value can qualitatively illustrate the shape of the front and can serve as a bulk measure for the relative thickness of the fingering. Figure 5 shows \( R \) over a range of \( C_a \) and \( M \) values. At high flow (\( C_a = 10^0 \)), all the networks behaved identically, and had the same general shape of the flow-front, for both stable displacement (\( M = 10^0 \)) and viscous fingering (\( M = 10^{-1} \) and \( 10^{-2} \)). At lower flow rates, the heterogeneous surface resulted in lower \( R \) ratios than the homogeneous surfaces. This indicates that there are fewer interfaces for the saturation level for the heterogeneous surface, which could correspond to thicker, more dense fingering patterns. However, more quantitative techniques are required to fully validate this measurement for observing the thickness of fingering patterns.

**CONCLUSION**

We have presented preliminary 3D pore network model results for a regularly-spaced two-phase porous media with contact angle heterogeneity. This model described the invasion of a brine-filled reservoir with surface heterogeneity by CO₂ at supercritical conditions. The model was explored over a range of capillary numbers \( C_a \) (\( 10^{-7} - 10^0 \)) and viscosity ratios \( M \) (\( 10^{-2} - 10^0 \)), values relevant to carbon sequestration in deep underground geological formations. Initial simulations behaved as expected, demonstrating stable displacement, viscous fingering, and capillary fingering for pore network models.

At the highest flow rate explored, over the range of viscosity simulated, the breakthrough saturation patterns were independent of the surface regime – all followed similar stable displacement or viscous fingering patterns. However, at low flow rates (lower capillary number), the saturations were higher by up to 7\% for the heterogeneous surfaces than the homogeneous ones. This indicates that surface heterogeneity must be considered when simulating deep underground reservoirs for carbon sequestration. The shape of the displacement fronts of the various networks were described with the parameter \( R \) introduced here. Its behavior, namely that the heterogeneous surface caused a decrease in \( R \) at lower flow rates, indicates that the surface heterogeneity demonstrates a qualitative effect on the shape of the front.

While the model networks considered here are not intended to mimic real geological formations, they have been used here to determine the impact of surface heterogeneity on breakthrough saturations. While porosity effects would likely dominate the trapping capabilities of the storage formations, such heterogeneities need to be accounted for when evaluating carbon dioxide storage security. More comprehensive models of mineral type correlation lengths are needed to characterize the effects of contact angle distributions, as well as networks based on computed tomography pore structure analyses, including mineral types. Only two mineral types have been considered in this analysis, as these are the only two to have been considered in the literature for supercritical CO₂, to the best of the authors’ knowledge. Further experimental studies to characterize the surface properties of other CO₂-brine-mineral systems are required. Finally, while buoyancy is likely not important for these small networks with the flow rates used here, a more comprehensive analysis of its effects will be required for future studies.

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