

Multi-scale Investigations of Geological Carbon Sequestration in Deep Saline Aquifers

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ACADEMIC ABSTRACT

Geological carbon dioxide (CO₂) sequestration (GCS) in deep saline aquifers is viewed as a viable solution to dealing with the impact of anthropogenic CO₂ emissions on global warming. The trapping mechanisms that control GCS include capillary trapping, structural trapping, dissolution trapping, and mineral trapping. Wettability and density-driven convection play an important role in GCS, because wettability significantly affects the efficiency of capillary trapping, and density-driven convection greatly decreases the time scale of dissolution trapping. This work focuses on the role of wettability on multiphase flow in porous media, density-driven convection in porous media, and their implications for GCS in deep saline aquifers.

Wettability is a critical control over multiphase fluid flow in porous media. However, our understanding on the wettability heterogeneity of a natural rock and its effect on multiphase fluid flow in a natural rock is limited. This work innovatively models the heterogeneous wettability of a rock as a correlated random field. The realistic wetting condition of a natural rock can be reconstructed with in-situ measurements of wettability on the internal surfaces of the rock. A Bentheimer sandstone was used to demonstrate the workflow to model and reconstruct a wettability field.

Relative permeability, capillary pressure-water saturation relation are important continuum-scale properties controlling multiphase flow in porous media. This work employed lattice Boltzmann method to simulate the displacement process. We found that pore-scale surface wettability heterogeneity caused noticeable local scCO₂ and water redistributions under less water-wet conditions at the pore scale. At the continuum scale, the capillary pressure-water saturation curve under the heterogeneous wetting condition was overall similar to that under the homogeneous wetting condition. This suggested that the impact of local wettability heterogeneity on the capillary pressure-water saturation curve was averaged out at the entire-sample scale. The only difference was that heterogeneous wettability led to a negative entry pressure at the primary drainage stage under the intermediate-wet condition. The impact of pore-scale wettability heterogeneity was more noticeable on the relative permeability curves. Particularly, the variation of the scCO₂ relative

permeability curve in the heterogeneous wettability scenario was more significant than that in the homogenous wettability scenario. Results showed that higher wettability heterogeneity (i.e., higher standard deviation and higher correlation length) increased the variations in the CO₂/brine relative permeability curves.

Dissolution of CO₂ into brine is a primary mechanism to ensure the long-term security of GCS. CO₂ dissolved in brine increases the CO₂-brine solution density and thus can cause downward convection. Onset of density-driven instability and onset of convective dissolution are two critical events in the transition process from a diffusion-dominated regime to a convection-dominated regime. In the laboratory, we developed an empirical correlation between light intensity and in-situ solute concentration. Based on the novel and well-controlled experimental methods, we measured the critical Rayleigh-Darcy number and critical times for the onset of density-driven instability and convective dissolution.

To further investigate the impact of permeability heterogeneity on density-driven convection, a three-dimensional (3D) fluidics method was proposed to advance the investigation on density-driven convection in porous media. Heterogeneous porous media with desired spatial correlations were efficiently built with 3D-printed elementary porous blocks. In the experiments, methanol-ethylene-glycol (MEG), was used as surrogate fluid to CO₂. The heterogeneous porous media were placed in a transparent tank allowing visual observations. Results showed that permeability structure controlled the migration of MEG-rich water. Permeability heterogeneity caused noticeable uncertainty in dissolution rates and uncertainty in dissolution rates increases with correlation length.

To sum up, this work comprehensively employed novel experimental methods and large-scale direct simulations to investigate the sequestration of CO₂ in saline aquifers at a pore scale and a continuum scale. The findings advanced our understanding on the role of wettability heterogeneity and permeability heterogeneity on GCS in deep saline aquifers.

Multi-scale Investigations of Geological Carbon Sequestration in Deep Saline Aquifers

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GENERAL AUDIENCE ABSTRACT

Global warming caused by anthropogenic CO₂ emissions is a pressing issue to address of our time. The storage of CO₂ in deep saline aquifers is a promising solution because of saline aquifers' vast storage capacity. Property heterogeneity exists extensively in saline aquifers from a continuum scale to a pore scale. The implications of pore-scale wettability heterogeneity and continuum-scale permeability heterogeneity for the storage of CO₂ in saline aquifers are not clear. This work is to employ novel experimental methods and powerful simulation tools to investigate the role of wettability heterogeneity and permeability heterogeneity on the storage of CO₂ in saline aquifers.

This work measured contact angles on the scanned micro-CT images of a Bentheimer sandstone after a CO₂ flooding. A correlated lognormal wettability model was put forward with the statistical information of the contact angle measurements. Simulations on the CO₂/brine flow in the Bentheimer sandstone were performed. Results showed that the wettability heterogeneity caused noticeable redistributions of CO₂/brine compared to scenarios under homogeneous wettability. Impact of wettability on capillary pressure-water saturation curve was not noticeable because the effects were averaged out through the entire rock sample. The standard deviation and correlation length caused variations on the relative permeabilities. This means that we need to take them into consideration in simulating the migration of CO₂ in saline aquifers at a reservoir scale.

After CO₂ pools beneath the impermeable cap rock, dissolution of CO₂ into brine dominates the trapping process. Convection caused by CO₂ dissolution can greatly accelerate the dissolution rate. The onset of convection is a critical issue and lack of experimental evidence. This work firstly determined the onset time of instability. To further investigate the heterogeneity on the convection, this work proposed a 3D-print-based method to efficiently build heterogeneous porous media with a designed permeability distribution. The experiments were conducted, and results showed that heterogeneity structure of porous media can cause great variations on the dissolution rate of CO₂.

The findings of this work advanced our understanding on the migration of CO₂ in saline aquifers, provided solid basis for assessment and decision on the storage of CO₂ into saline aquifers.

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PREFACE

This dissertation is submitted as a completion of the degree of Doctor of Philosophy at Virginia Polytechnic Institute and State University. This research described here was conducted by the author, Ruichang Guo, under the supervision of Dr. Cheng Chen and Dr. Nino Ripepi in the Department of Mining & Minerals Engineering at Virginia Polytechnic Institute and State University.

This dissertation is established based on four manuscripts, including two peer-reviewed journal papers, one peer-reviewed journal manuscript under review, and one journal manuscript in preparation.

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Chapter 6 is to be submitted for peer review. The work is conducted by Ruichang Guo under the guidance of other co-authors.

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Chapter 1. Introduction

1.1. Background

Addressing climate change has become an urgent and defining issue of our time. As one of the major greenhouse gases, reduction/prevention of CO₂ emission into the atmosphere has been gaining increasing attention in recent decades. Geological carbon sequestration (GCS) has proven a viable practice to offset the carbon emission (Michael et al., 2010). Saline aquifers are considered as one ideal formation for GCS due to its wide distribution and vast storage capacity, which was estimated to be 320 – 10,000 Gt of CO₂ across the world (Bachu, 2002). After the injection of CO₂ in a deep saline aquifer, the CO₂ plumes existing in a supercritical state migrate upward due to buoyancy and spread horizontally when reach the cap rock (Sathaye et al., 2014; Emami-Meybodi et al., 2015). Predicting the migration and ultimate fate of CO₂ in saline aquifers is critical to assessing the time scale and security of GCS (Chang et al., 2020).

The trapping mechanisms of GCS in deep saline aquifers include structural trapping, capillary trapping, dissolution trapping, and mineral trapping (Chen et al., 2013). Immediately after the injection of CO₂, capillary trapping occurs when CO₂ migrates upward and spreads horizontally. Optimizing injection strategy can enhance the capillary trapping (Krevor et al., 2015). Using advanced horizontal drilling can increase capillary trapping efficiency by increasing CO₂ plume sweep (Sams et al., 2004; Guo et al., 2009; Okwen et al., 2011; Tang et al., 2019). The migration and ultimate fate of CO₂ in saline aquifers has been intensively studied in recent decades (Emami-Meybodi et al., 2015). However, we still lack understanding on some critical processes, such as the role of wettability heterogeneity of rocks and experimental observations on the density-driven convection, etc. Wettability is a critical control over the CO₂ migration in saline aquifers. Density driven convection can greatly accelerate the dissolution of CO₂ into brines which favors the long-term security of GCS. This work will focus on these two parts at both the pore scale and the continuum scale.

At the pore scale, the wettability heterogeneity of a natural rock is complex and is rarely investigated. The wettability of a porous medium is usually characterized as static contact angle (CA) and can be homogeneous or heterogeneous. The role of homogeneous wettability on multiphase flow in porous media has been intensively studied (Pan et al., 2004; Li et al., 2005; Boek

et al., 2017;Leclaire et al., 2017). However, Studies on realistic rock strongly suggest that the wettability of a realistic rock is heterogeneous (Morrow, 1975;Bradford and Leij, 1995;Hwang et al., 2006;Rucker et al., 2019). Previous studies commonly modeled heterogeneous wettability as a combination of two certain wettability, usually one is water-wet, and the other is non-water-wet. This heterogeneous wettability model can be further classified as fractional wettability and mixed wettability, depending on whether the distribution of wettability is a function of pore size. Fractional wettability model assumes that the distribution of wetting surface is independent of pore size, while mixed wettability model assumes that the rock surface of small pores is water-wet while rock surface of large pores is non-water-wet. The overall wettability of a porous medium is usually modified by changing the proportion of wetting/nonwetting surface for fractional wettability model or changing alteration severity for mixed wettability model. Recently published in-situ measurements of wettability suggested that the wettability of a realistic rock covers a wide spectrum of CAs rather than two certain CAs (Saraji et al., 2013;Andrew et al., 2014;Alhammadi et al., 2017;Mutailipu et al., 2017;AlRatrout et al., 2018;Arshadi et al., 2020;Guo et al., 2020;Liu et al., 2020). Guo et al. (2020) modeled the heterogeneous wettability of a realistic rock as a Gaussian stochastic field based on recent in-situ CA measurements, which is closer to realistic wetting condition of rocks. To advance the power of simulation in predicting multiphase flow in porous media with complex wettability, it is needed to accurately describe the realistic wettability and incorporate detailed wettability information into simulation model (Akai et al., 2019).

Density-driven convection is common in many natural processes, such as weather system (Hodges and Thorncroft, 1997), oceanic currents (Polyakov and Doronin, 1999;Takahashi et al., 2018), groundwater (Van Dam et al., 2009), and could also find applications in many engineering, including GCS (Michael et al., 2010), electronic devices (Ordonez-Miranda et al., 2016), and microfluidics systems (Zehavi et al., 2016), etc. GCS, as a promising solution to mitigate the impact of CO₂ emission on global climate, has been gaining increasing attention in recent years (Mahmoodpour et al., 2019;Tang et al., 2019). The feasibility of GCS has been proved in field operations (Michael et al., 2010;Sathaye et al., 2014).

This density-driven convection is analogous to the thermal convection, also expressed as Rayleigh-Benard convection (Riaz et al., 2006;Xu et al., 2006). Observations in the literatures showed that fully developed convective dissolution in a Rayleigh-Darcy system can be categorized by five critical events: 1) onset of convective instability. 2) onset of convective dissolution. 3) unsteady-

flux peak. 4) constant flux regime. 5) convective shutdown (Slim, 2014; Emami-Meybodi et al., 2015). The onset of convective instability indicates the start of perturbation growth while onset of convective dissolution the significant increase of dissolution rate caused by convection. The criteria of early-stage events, onset of convective instability and convective dissolution, controls the short-term security of GCS after the emplacement of CO₂. Whether convection will occur, when the stratification of CO₂-brine system becomes unstable and when convective dissolution will occur are questions of significance, which have been intensively investigated.

The stability of this stratification is controlled by the balance of convection and diffusion, expressed as Rayleigh number, Ra. Whether convection will occur is controlled by critical Ra, Ra_{cr}. The classic Ra_{cr} for onset of convective instability is $4\pi^2$ (Xu et al., 2006). Slim and Ramakrishnan (2010) employed linear stability analysis (LSA) to investigate Ra_{cr} and suggested that no instability occurs for thin convection layers when $Ra < 32.5$ and the prerequisite for onset of instability independent of layer thickness is $Ra \geq 75$. Chen et al. (2013) used continuum-scale-lattice-Boltzmann direct simulations to investigate convective dissolution in porous media and found that the critical Ra in heterogeneous porous media can be up to 250. Field observation in heterogeneous formation found the critical Ra can be as low as 20 (Sathaye et al., 2014).

The instability-onset time indicates when the stratification of CO₂-brine system becomes unstable. Almost all of previous studies are theoretical analysis or numerical simulation. The theoretical studies on onset of instability usually consider a two-layer stratification of CO₂ or water/brine, which was primarily studied by researchers with a LSA method (Ennis-King and Paterson, 2005; Ennis-King et al., 2005; Hassanzadeh et al., 2006; Riaz et al., 2006; Xu et al., 2006; Kim et al., 2008; Wessel-Berg, 2009; Javaheri et al., 2010; Slim and Ramakrishnan, 2010; Bestehorn and Firoozabadi, 2012; Cheng et al., 2012; Kim and Choi, 2012; Kim, 2013; Meulenbroek et al., 2013; Meybodi and Hassanzadeh, 2013; Myint and Firoozabadi, 2013; Tilton et al., 2013; Elenius et al., 2014; Kim, 2014; Kim, 2014; Kim, 2015). Some researchers used direct simulation method to investigate the instability-onset time (Elenius and Johannsen, 2012; Chen et al., 2013; Slim, 2014).

In these studies, the instability-onset time is usually expressed as $t_{cr1}^* = C_1 Ra^{-2}$, where t_{cr1}^* is the dimensionless onset time of convective instability. Due to the difference in the methods, boundary conditions and perturbations used in these studies, the coefficient C_1 ranges from 31.14 to 167.6.

The onset of convective dissolution has also been intensively investigated (Emami-Meybodi et al., 2015). The most practical measure of the onset of convective dissolution is flux growth (Slim, 2014). Most of the studies were using direct numerical simulations (Riaz et al., 2006; Farajzadeh et al., 2007; Hassanzadeh et al., 2007; Hidalgo et al., 2009; Pau et al., 2010; Andres and Cardoso, 2011; Cheng et al., 2012; Elenius and Johannsen, 2012; Azin et al., 2013; Meybodi and Hassanzadeh, 2013; Slim, 2014). Similar to the onset time of instability, the onset time of convective dissolution can also be expressed in the form of $t_{cr2}^* = C_2 Ra^{-2}$. Due to the different initial perturbations in the numerical simulations, the coefficient C_2 also varies in a large range from 500 to 5619. Mahmoodpour et al. (2019) experimentally investigated convective dissolution with CO₂ and brine using a high-pressure visual Hele-Shaw cell. Estimation of C_2 with data in one example case is 12348. So far, no experiment was done to systematically investigate the onset of convective dissolution.

To sum up, further investigations are still needed to examine the critical physical processes from a pore scale to a continuum scale.

1.2. *Research objectives and work scope*

The goal of this work is to investigate the role of pore-scale wettability heterogeneity in multiphase flow in a CO₂-brine-rock system and density-driven flow in the dissolution trapping of CO₂ in deep saline aquifers. At a pore scale, the existing heterogeneous wettability model is not enough to represent realistic wetting conditions in a saline aquifer. The displacement process in a CO₂-brine-rock system under complex wetting conditions is rarely investigated. At a macroscopic scale, critical parameters, such as critical Rayleigh number and critical instability onset time, are commonly studied by theoretical analysis or direct numerical simulations. Furthermore, the establishment of a complex permeability field is a challenge in lab experiments. To advance the studies associated with these challenges, the research tasks in both experimental and numerical ways are listed as follows:

- 1) Heterogeneous wettability modeling and wettability reconstruction of a natural rock.
- 2) The role of wettability heterogeneity on relative permeability in a CO₂-brine-rock system.

- 3) The role of wettability heterogeneity on immiscible displacement in a CO₂-brine-rock system.
- 4) Experimental investigation on density-driven instability and convective dissolution in porous media.
- 5) Using novel 3D printing to study the role of permeability heterogeneity on miscible density-driven convection in porous media.

1.3. Organization of this dissertation

The dissertation consists of seven chapters. Chapter 1 introduces the background and significance of the experimental and numerical investigations of geological carbon sequestration in deep saline aquifers. The research objectives and study scope are also included in this chapter.

In Chapter 2, the modeling and reconstruction of a heterogeneous wetting condition of a natural rock were illustrated. In-situ measurements of wettability on a Bentheimer sandstone were conducted. The mean, standard deviation, and correlation length were extracted from the measurements. The heterogeneous wettability field can be generated with a large-scale random field generation method, such as FFT-MA, and KLE. A Kriging method was used to condition the generated wettability field to reconstruct the wettability field of the Bentheimer sandstone.

In Chapter 3, the impact of wettability heterogeneity on relative permeabilities were investigated. The heterogeneity wettability fields were characterized with mean, spatial heterogeneity and correlation length. The wetting condition of the Bentheimer sandstone was used as a reference case. In the simulation, a powerful hybrid CPU/GPU accelerated LBM code was used.

In Chapter 4, the impact of wettability heterogeneity on the pore-scale distribution of CO₂/brine, relative permeability, capillary pressure-water saturation relation displacement under a complex heterogeneous wetting condition was presented. In this chapter, the wetting conditions were extended to strongly water-wet, weakly water-wet, and intermediate wet conditions.

In Chapter 5, experimental investigation on density driven flow in homogeneous porous media was demonstrated. A novel experimental method was used to determine the critical onset time of density-driven instability. High-resolution imaging technology was used imaging the density-

driven flow process. MEG was used as surrogate fluids of CO₂. The spatial and temporal distribution of MEG can be extracted, and critical onset time can be inferred.

In Chapter 6, an innovative 3D-print technology-based method was used to build heterogeneous porous media with controlled permeability heterogeneity structure. MEG was used as a surrogate fluid of CO₂. The spatial and temporal distribution of MEG can be extracted, and the total transferred MEG mass can be inferred.

In Chapter 7, Conclusions and future work were presented.

1.4. Novelty and contributions

The studies in this dissertation employ innovative methods to investigate the role of wettability heterogeneity in the migration of CO₂ in saline aquifers and the role of density-driven convection in the dissolution of CO₂ in saline aquifers. The findings provide new ideas and understanding on the trapping mechanisms of GCS. The novelty and contributions are summarized as follow.

- 1) Modeling pore-scale heterogeneous wettability of a natural rock as a random field that incorporates subpore-scale heterogeneity and spatial correlation of wettability of a natural rock.
- 2) First investigation on the role of wettability heterogeneity and spatial correlation on immiscible displacement in a CO₂-brine-rock system.
- 3) First experimental determination of critical Ra number and critical onset time of instability in the density-driven convection in porous media.
- 4) An efficient method to construct heterogeneous permeability field assisted by 3D printing.

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Chapter 2. Modeling and Reconstructing Heterogeneous Wettability of a Natural Rock

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Abstract

Wettability is a critical control over multiphase fluid flow in porous media. However, our understanding on the wettability heterogeneity of a natural rock and its effect on multiphase fluid flow in a natural rock is limited because the wettability heterogeneity of a rock is at a subpore level making it a challenge to perform in-situ measurements of wettability on the internal surfaces of a porous medium. This study proposed a method to model and reconstruct the heterogeneous wettability of a natural rock. A Bentheimer sandstone was used to demonstrate the workflow. Local wettability of the sandstone was measured as static contact angles which were performed on the X-ray micro-computed tomography images of the sandstone. The heterogeneous wettability of the Bentheimer sandstone was modeled as a stationary random field which is characterized by mean, standard deviation and correlation length. This model takes account of subpore heterogeneity of wettability and comprehensively includes primary controlling factors, such as minerals, roughness, nonaqueous materials and pore geometry. A fast Fourier transform moving average (FFT-MA) method was used to generate large heterogeneous wettability fields. A Kriging method was used to condition the wettability field generated by the FFT-MA. The wetting condition of the Bentheimer sandstone was reconstructed by mapping the conditioned heterogeneous wettability field onto the Bentheimer sandstone. This work provided basis for advancing our understanding of the implication of subpore wettability heterogeneity on multiphase flow in porous media.

Key Words: wettability heterogeneity, in-situ measurement of contact angle, wetting condition reconstruction, immiscible displacement, porous media

2.1. Introduction

Multiphase flow in porous media is a ubiquitous phenomenon which can be found in many natural and engineered processes, such as groundwater flow (Cueto-Felgueroso and Juanes, 2008; Arshadi et al., 2020), oil and gas recovery (Culligan et al., 2006; Qin et al., 2019), geological CO₂ sequestration (Szulczewski et al., 2012; Guo et al., 2021). Along with pore structure of porous media and fluid properties, wettability is also one principal control on multiphase flow in porous media which significantly affects both pore-scale properties, such as fluids configuration and displacement patterns, and continuum-scale properties, such as capillary pressure and relative permeability (Guo et al., 2020; Qin et al., 2020). Wettability describes the relative preference of multiple fluids to spread over a solid surface (Craig, 1993). The fluid-fluid interfaces are curved if the affinity of the solid surface to the two fluids are different. The pressure difference between two sides of the fluid-fluid surface is balanced by the surface tension. At the contact line of the solid and the two fluids, the interface forms an angle against the solid surface. Both the pressure difference between wetting phase and non-wetting phase at the continuum scale and contact angles at the pore scale can represent the effect of wettability. Therefore the wetting condition of a porous medium is commonly characterized by capillary pressure-water saturation relation or contact angle (McClure et al., 2007).

In the capillary pressure-fluid saturation (P_c - S_w) relation, the capillary pressure was measured as the equilibrium pressure different between continued ganglia of nonwetting phase and wetting phase in a porous medium. The capillary pressure-fluid saturation can also be converted into a single index to describe wetting conditions of a porous medium, such as Amott and USBM indices (Amott, 1959; Donaldson et al., 1969). The P_c - S_w relation, Amott index, and USBM index are Darcy-scale measurements of the wetting condition of a porous medium, which is the comprehensive results of complex fluid-fluid and fluid-solid interactions at the pore scales. However, there are gaps between Darcy-scale wettability measurements and pore-scale intrinsic wettability, because the Darcy-scale wettability measurements fails in describing complex displacement dynamics, such as hysteresis, and existing pore-scale wettability heterogeneity models can not accurately describe the wetting condition of a natural rock. The P_c - S_w relation is also affected by the wettability distribution pattern of a porous medium (Guo et al., 2022). Hiller et al. (2019) investigated the impact of wettability heterogeneity on capillary pressure and found that under heterogeneous wetting condition in porous media built by spheres with different wettability, P_c - S_w relation can vary a lot even when the average wettability of the porous media is

the same. From a fundamental point of view, characterization of the wetting conditions of natural rocks requires intensive investigation on implications of pore-scale wettability on Darcy-scale properties.

Although much efforts were made to advance our understanding on the pore-scale wettability of a natural rock, how the pore-scale heterogeneous wettability is upscaled onto Darcy-scale properties are still not clear (Rucker et al., 2020). The challenges in in-situ measurements of the intrinsic wettability at subpore scales and quantifying the controlling factors on subpore scale wettability hindered these efforts. The subpore controls on wettability of a natural rock include surface mineral, roughness, nonaqueous materials absorbed on the solid surface, etc. Different minerals have different wettability and most natural minerals are water-wet. Wettability is strongly related to surface roughness (AlRatrout et al., 2018). Absorption of nonaqueous materials onto solid surfaces can alter the wettability from water-wet to neutral- or oil-wet (Buckley, 1998; Javanbakht et al., 2017). The complex distribution pattern of these controlling factors makes quantifying subpore scale wettability even more challenging. The wettability distribution depends on the grain sizes of minerals (Arshadi et al., 2020) and the effective surface area exposed to the pore space. Hassenkam (2009) quantified the grain size of chalk showing that the chalk grain sizes have a broad range from several millimeters to tens of nanometers (Hassenkam et al., 2009). Lai et al. (2015) investigated the distribution of minerals of six natural rocks and found that there is a discrepancy between the surface area fraction and volumetric fraction of minerals. Hassenkam (2009)'s investigation also showed that roughness heterogeneity is at a subpore scale. AlRatrout et al. (2018) made in-situ measurements of roughness and contact angle on a limestone suggesting that the correlation length of roughness was approximately the pore size and the distribution of contact angles strongly related to roughness. The distribution of nonaqueous materials is determined by the saturation history of a porous medium in the process where petroleum hydrocarbons migrate into an oil and gas reservoir, or nonaqueous contaminants invade into a soil (Skauge et al., 2007; Kumar et al., 2012). Because the distribution of the nonaqueous materials is related to pore geometry, the distribution of resulting oil-wet surfaces was assumed to be a function of pore geometry (Skauge et al., 2007). Understanding the distribution pattern of pore-scale wettability is important to characterize the wetting condition of a porous medium.

Contact angle is a common measure of local wettability of a solid surface. Rising/captive bubble techniques are used to characterize the wettability of a substrate of different minerals (Lee et al.,

2003). The measured wettability of different minerals can be used to infer the wettability of a rock with known mineral compositions. However, the surface of mineral substrates are usually clean and smooth, not representing the intrinsic wettability of internal surfaces of a rock. The advent of X-ray micro-computed tomography (micro-CT) with a micron resolution enables in-situ measurement of wettability on the internal surfaces of a rock (Andrew et al., 2014; Pak et al., 2015; Khishvand et al., 2016). The wettability is a comprehensive outcome of the interaction between fluids and internal surfaces with varying minerals, roughness and absorbed nonaqueous materials. The contact angle measurements can even be affected by pore geometry. The complexity of these controlling factors on wettability determines that the wettability of a natural rock is also complex, which has been repeatedly confirmed by recently published in-situ experimental measurements of the wettability of a natural rock (Andrew et al., 2014; AlRatrout et al., 2017; Dalton et al., 2018; Arshadi et al., 2020; Guo et al., 2020).

Previous studies usually modeled heterogeneous wettability of a natural rock as a mixture of two types of wettability, with one being water-wet and the other being oil-wet. Depending on whether the distribution of water-wet and oil-wet surfaces is a function of pore size, the heterogeneous wettability was commonly categorized into two types: fractional wettability and mixed wettability (O'Carroll et al., 2005; Skauge et al., 2007). Fractional wettability assumes that the water-wet and oil-wet surfaces randomly distributed in a porous medium, while mixed wettability assumes that the randomly distributed water-wet and oil-wet surfaces also depends on pore sizes (i.e., surfaces of larger pores are oil-wet, and surfaces of smaller pores or fractures are water-wet) (Skauge et al., 2007). Many studies were conducted on the immiscible displacement process under heterogeneous wetting conditions (Bradford and Leij, 1995; Masalmeh, 2003; Hwang et al., 2006; Murison et al., 2014; Zhao et al., 2018; Bakhshian and Hosseini, 2019). These studies showed that wettability heterogeneity had noticeable impact on macroscopic properties of immiscible displacement, such as P_c - S_w relation and relative permeability. Although great progresses have been made in modeling wettability heterogeneity, it is still challenging to explicitly incorporate subpore heterogeneity of mineral, roughness, and nonaqueous materials in wettability models. There is no unified heterogeneous wettability model that can quantitatively describe various heterogeneous wettability and enable systematic comparison of the implication of different wettability heterogeneity on multiphase flow in a porous medium.

Significant challenges exist in attempting to explore subpore-scale wettability heterogeneity of a rock. To resolve this problem, we modeled the wettability of a rock as a stationary random field which was characterized with mean, standard deviation, and correlation length of contact angles. A workflow to reconstruct the wettability of a rock with measured contact angles was proposed and demonstrated with a CO₂-brine-rock system as an example. The in-situ measurements of static contact angles were performed on a Bentheimer sandstone after one cycle of CO₂ flooding. The wettability field of the Bentheimer sandstone was constructed with fast Fourier transform moving average (FFT-MA) method and a Kriging method. This work provided basis for advancing our understanding of the implication of subpore wettability heterogeneity on multi-phase flow in porous media.

2.2. *Materials and methods*

2.2.1. *Rock sample*

The digital image of the rock was cut from a Bentheimer sandstone after one cycle of core flooding experiment at U.S. Department of Energy (DOE)'s National Energy Technology Laboratory (NETL). The size of the Bentheimer core sample was 2.54 cm in length and 0.64 cm in diameter. The experimental apparatus and protocol were illustrated in our previous studies (Dalton et al., 2018;Guo et al., 2020). A $400 \times 400 \times 400$ -pixel³ digital rock sample was extracted from the core sample and the resolution was 5 μ m/ pixel. The porosity of the Bentheimer sandstone was measured as 25.3%, the average grain size 133 μ m, and average pore diameter 58 μ m.

2.2.2. *Modeling wettability conditions*

In recently published studies, the in-situ measured CAs behaved a log-normal distribution and were correlated (Andrew et al., 2014;AlRatrou et al., 2017;Dalton et al., 2018;Arshadi et al., 2020;Guo et al., 2020). In this study, we model the wettability of a rock as a correlated random field with a log-normal distribution and a correlation function, $C_Y(x,y)$. The wettability was measured as static contact angle, θ . The wettability field, Y , was defined as $Y = \log(\theta)$. The mean

and variance of Y are μ and σ^2 , respectively. The mean and variance of CAs can be calculated by $E(\theta) = e^{\mu + \sigma^2/2}$ and $Var(\theta) = (e^{\sigma^2} - 1)e^{2\mu + \sigma^2}$ (Chen et al., 2013).

In this study, we used a FFT-MA method to generate the random fields. The correlation function was decomposed as a convolution product of two functions, $C_Y = g * \bar{g}$, where $\bar{g}$ is the transpose of g (i.e., $\bar{g}(x) = g(-x)$). The stochastic process Y with mean and covariance function C_Y can be generated by $Y = \bar{Y} + g * Z$, where Z is uncorrelated normal deviates (i.e., Gaussian white noise). This FFT-MA method is an efficient way in generating large stochastic processes, because it can avoid expensive Cholesky decomposition of the correlation function.

2.2.3. Conditioning wettability fields by Simple Kriging

Simple Kriging (SK) method provides linear estimates to the true unknown value in a random field with the measured value of the variable at limited locations. The conditional wettability field, Y_{cs} , is calculated as

$$Y_{cs}(\mathbf{x}) = Y_{us}(\mathbf{x}) + Y_{SK}(\mathbf{x}) - Y_{SK,us}(\mathbf{x}), \quad (2-1)$$

where $\mathbf{x}$ is unsampled locations; Y_{us} is the unconditional wettability; Y_{SK} is the wettability kriged from measured wettability; $Y_{SK,us}$ is the wettability kriged from simulated wettability. unconditional wettability field can be generated by the FFT-MA method in section 2.2.2. The kriged wettability Y_{SK} and $Y_{SK,us}$ are calculated as

$$Y_{SK}(\mathbf{x}) = \sum_{\alpha=1}^n \lambda_{\alpha}(\mathbf{x}) Y(\mathbf{x}_{\alpha}) \quad (2-2)$$

$$Y_{SK,us}(\mathbf{x}) = \sum_{\alpha=1}^n \lambda_{\alpha}(\mathbf{x}) Y_{us}(\mathbf{x}_{\alpha}) \quad (2-3)$$

where λ_{α} are Kriging weights; $Y(\mathbf{x}_{\alpha})$ are measured wettability; $Y_{us}(\mathbf{x}_{\alpha})$ are simulated wettability.

2.3. Results and discussion

2.3.1. In-situ measurements of static contact angles

An automatic contact angle measurement tool was used to perform the in-situ measurements of static contact angles on the Bentheimer sandstone (AlRatrou et al., 2017). The contact angles were measured based on the interfaces and 9575 contact angles were measured. From **Figure 2-1a**, it is observed that the distribution of contact angles followed a lognormal distribution. The mean of contact angles is 51.12° . The standard deviation is 26.04° . The covariance of the contact angles was calculated and illustrated in Figure 2-1-b. The correlation length is measured as 10.42 pixels (i.e., $50.21 \mu\text{m}$).

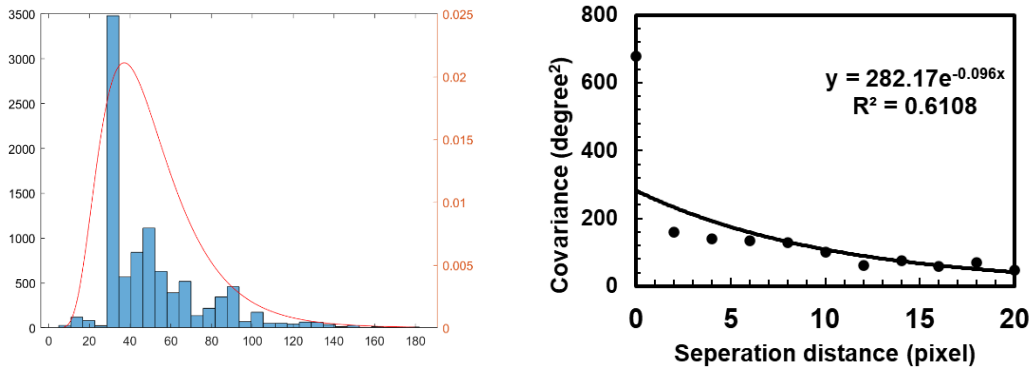


Figure 2 - 1. (a) Counts of measured contact angles. The solid line is the fitted lognormal distribution model. The mean is 51.12° . The standard deviation is 26.04° . (b) Covariance of measured contact angles. The correlation length was estimated as $50.21 \mu\text{m}$.

2.3.2. Reconstructed wettability

With the mean, standard deviation and correlation lengths calculated from the measured contact angles and locations, the wettability field was generated and shown in **Figure 2-2a**. To better demonstrate the distribution of wettability, the contact angles of all the solid phase were plotted on the figures. However, only the wettability of the internal surfaces function in the CO_2 flooding. Figure 2-2b is the conditioned wettability of the Bentheimer sandstone with measured contact angles. Compared with the unconditioned wettability in the enlarged area with measurements of contact angles, it is observed that the distribution of wettability was adjusted and smoothly transitioned the rest area of the sandstone.

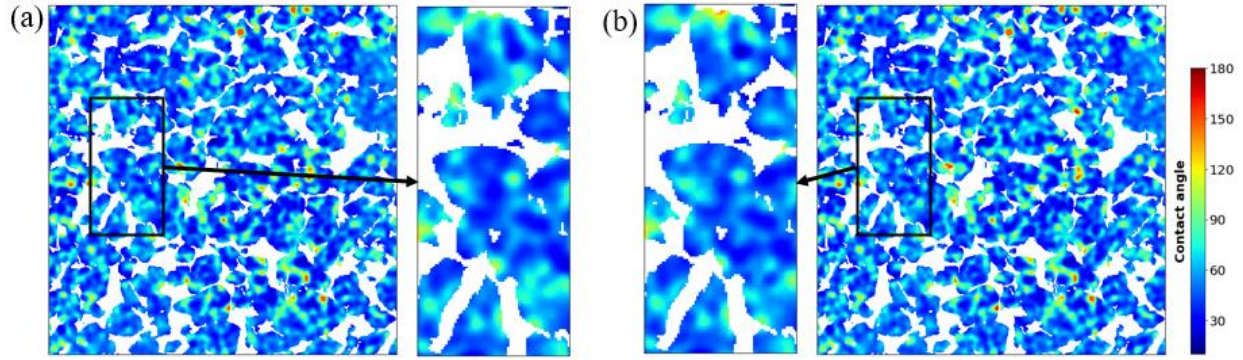


Figure 2-2. (a) Generated wettability field following lognormal distribution. (b) Conditioned wettability field with measured contact angles. At the locations with contact angle measurements, the surrounding region was smoothly adjusted to approximate realistic wettability.

2.4. Conclusion

Wettability is a critical control over the multiphase flow in porous media, which has practical implications for GCS in saline aquifers. Experimental observations repeatedly confirmed that the wettability of a natural rock is heterogeneous and correlated. This work performed in-situ measurements of wettability of a Bentheimer sandstone after a CO₂ flooding. Based on the measured contact angles, it was observed that the distribution of followed a lognormal distribution. A new model was proposed to model heterogeneous wettability as a correlated random field. Efficient large random fields generation field methods, such as fast Fourier Transformation Moving Average, or Karhunen Loeve Expansion, can be used to generate the wettability fields. Conditioning the generated wettability field with measured contact angles, the wetting condition of a given sandstone can be reconstructed. This innovative model is able to describe subpore heterogeneity of wettability of a rock, which provides basis for comprehensive investigations on the multiphase flow in natural rocks.

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Chapter 3. The Role of the Spatial Heterogeneity and Correlation Length of Surface Wettability on Multiphase Flow in 3D Porous Media

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Abstract

Relative permeability, which depends strongly on the surface wettability of a porous medium, plays a critical role in multiphase flow in the porous medium and has important applications in geological CO₂ sequestration, oil and gas recovery, and contaminated groundwater remediation. Although numerous studies have attempted to understand the influences of surface wettability, capillary number (Ca), and viscosity ratio, the role of the spatial variation and correlation length of surface wettability on multiphase flow in three-dimensional (3D) porous media has not been unraveled due to the challenges in the measurement and representation of realistic rock surface wettability. In this work, we conducted in-situ measurements of surface contact angle (CA) in a Bentheimer sandstone after supercritical CO₂ (scCO₂) flooding using micro-computed tomography (micro-CT), and found that the pore-scale CA distribution on rock surfaces followed a log-normal distribution associated with a spatial correlation length. Based on the statistical information from CT scanning, a Gaussian random field was used to model CA distributions that had desired standard deviations and spatial correlation lengths, which were then adjusted within a certain range of values for sensitivity analyses to study their combined effects on the multiphase flow in the porous medium simulated using the lattice Boltzmann (LB) method. The LB multiphase flow numerical model was accelerated using hybrid, multicore parallel computing to overcome the challenges in simulating multiphase flow in a large 3D domain having 800×800×600 pixels. The simulation results showed that the surface wettability heterogeneity (i.e., standard deviation of CA) had a lesser effect on the relative permeability of the wetting fluid (water) but a more significant impact on the relative permeability of the non-wetting fluid (scCO₂). The Corey model was used to fit the LB-simulated relative permeability curves of water and scCO₂ and showed that the variations in the relative permeability curves for both water and scCO₂ increased as the standard

deviation and spatial correlation length of CA increased. These findings suggested that a larger standard deviation of rock surface CA, combined with a longer spatial correlation length of CA distribution, led to larger variations in the relative permeability curves of the rock. This study illustrated that it was not sufficient to only use a spatially-averaged CA to describe the role of rock surface wettability on multiphase flow properties in a 3D porous medium. Instead, the impacts of both the standard deviation and spatial correlation length of CA must be accounted for. This is the first study that explored the spatial correlation lengths associated with CA distributions on sandstone surfaces and comprehensively investigated the roles of both spatial variation and correlation length of CA on multiphase flow properties in 3D porous media. The optimized LB multiphase flow model was proved a powerful tool to study the interplays and combined effects of these statistical parameters, which had critical applications in numerous natural and engineering processes that involved multiphase flow in porous media.

3.1. Introduction

Multiphase flow in porous media has a wide range of applications, including oil and gas recovery (Orr and Taber 1984), geological CO₂ sequestration (Chen and Zhang 2010, Szulczewski et al. 2012, Chen et al. 2013), and contaminated groundwater remediation (Keller et al. 2000, Davis et al. 2009). Fluid-fluid displacement processes and the associated microscopic properties in a porous medium, such as capillary pressure and relative permeability, depend strongly on the wettability on the solid surface (Landry et al. 2014). Although the rapid development of experimental technologies has allowed for in-situ measurements of surface wettability within porous media (Andrew et al. 2014, Dalton et al. 2018, Maziar Arshadi 2020), accurate representation and reproduction of complex and heterogeneous surface wettability still remain a challenge.

Surface wettability indicates the tendency of a fluid to adhere to solid surfaces resulting from intermolecular interactions with the solid surface and other immiscible fluids (Zhao et al. 2018). Macroscopic characterization of the wetting status of a rock is given by the Amott–Harvey index (Amott 1959) or USBM index (Donaldson et al. 1969). Surface wettability is commonly characterized by the measurement of water’s contact angle (CA) (Maziar Arshadi 2020), which is the angle between the water/solid interface and the water/non-aqueous-fluid interface. According to (Iglauer et al. 2015), a CO₂-water-rock system is completely water-wet for a CA of 0°, strongly

water-wet for 0° - 50° , weakly water-wet for 50° - 70° , intermediate wet for 70° - 110° , weakly CO_2 -wet for 110° - 130° , strongly CO_2 -wet for 130° - 180° , and completely CO_2 -wet for 180° . The CA can be uniformly and nonuniformly distributed over the solid surface. Uniform (i.e., homogeneous) wettability indicates that the CA throughout the entire solid surface in a porous medium is the same (Hwang et al. 2006), whereas nonuniform (i.e., heterogeneous) wettability indicates that the CA value varies spatially over the rock surface. Heterogeneous wettability on solid surfaces can be further categorized into two scenarios: fractional wet and mixed wet. Fractional wet, in a CO_2 -water-rock system, in general assumes that water-wet and CO_2 -wet solid surfaces coexist and the spatial distribution of these two types of surfaces is heterogeneous (Bradford and Leij 1996). On the other hand, mixed wet assumes that the spatial distribution of surface wettability depends on the pore size; solid surfaces in smaller pores and fractures are water-wet whereas solid surfaces in larger pores and fractures are CO_2 -wet (Salathiel 1973, Valvatne and Blunt 2004).

In the past few decades, the development of high-resolution X-ray micro-computed tomography (micro-CT) has provided a powerful tool for direct observations of internal pore structure and fluid and particle distribution within porous media at the pore scale (Chen et al. 2008, Chen et al. 2009, Iglauer et al. 2011, Silin et al. 2011, Kumar et al. 2012). This non-invasive, three-dimensional (3D) visualization technology made it possible to conduct in-situ, pore-scale CA measurements on solid surfaces in a porous medium (Andrew et al. 2014, Dalton et al. 2018, Blunt et al. 2019, Maziar Arshadi 2020). With pore structure and fluid distributions characterized at the pore and subpore scales, numerical modeling has widely been used as a tool to study multiphase flow in the porous medium as well as its interactions with the pore geometry and surface wettability (Fan et al. 2018, Fan et al. 2019). Pore-scale direct simulation methods are capable of accounting for detailed information on microscopic flow, which makes it possible to investigate the underlying complex physics and key mechanisms in multiphase flow in porous media. Through recent developments, the color gradient lattice Boltzmann (LB) method has become a promising numerical method for simulating multiphase flow in complex 3D porous media because of its advantage in dealing with complex boundaries within porous media, simplicity in optimization through parallel computing, and capability to incorporate new physics (Shi and Tang 2018, Zhao et al. 2018, Yi et al. 2019, Wang et al. 2020). Particularly, the continuous growth of computer performance and development of parallel computing devices, such as graphics processing units (GPUs) (Chen et al. 2016), have greatly enhanced the LB method's capabilities in modeling multiphase flow in large-scale 3D

porous media. Landry et al. investigated relative permeability in a bead-packed porous medium having altered wetting conditions. They found that the variation in surface wettability did not influence the wetting phase relative permeability noticeably but caused a significant decrease in the non-wetting phase relative permeability (Landry et al. 2014). Hwang et al. (2006) studied the impact of fractional wettability on the capillary pressure and relative permeability curves. They found that a greater fraction of non-water-wetting solid surfaces caused a higher water relative permeability at a given water saturation (Hwang et al. 2006). Zhao et al. (2018) investigated the impact of fractional-wet solid surfaces on the relative permeability of computer-generated two-dimensional (2D) porous media. They found that the relative permeability curves of water and oil were not bounded between the pure water-wet relative permeability curves and pure oil-wet relative permeability curves (Zhao et al. 2018).

Table 3-1 gives a comprehensive literature review that summarizes the recent studies on multiphase flow dynamics within porous media that have homogeneous and heterogeneous surface wettability. It can be found that most existing studies on the effects of heterogeneous surface wettability made assumptions of fractional-wet or mixed-wet solid surfaces. Generally speaking, in numerical modeling of fractional-wet and mixed-wet scenarios in a CO₂-water-rock system, binary CA values are assigned to rock surfaces, i.e., a CA smaller than 90° is assigned to the water-wet surfaces whereas a CA larger than 90° is assigned to the CO₂-wet surfaces. Furthermore, there are in general no spatial correlation patterns associated with the distribution of the CAs over the rock surfaces, as discussed before. However, our recent works (Dalton et al. 2018, Fan et al. 2019) on in-situ measurements of CAs in sandstone samples using micro-CT illustrated that the spatial variation of CA on sandstone surfaces can be continuous, which leads to a possibility that there may be a spatial correlation length associated with CA distributions on sandstone surfaces. AlRatrout et al. (2017) studied spatial correlations of CAs in three carbonate cores. Their findings suggested that CA distribution was spatially correlated in carbonates and the correlation length was not larger than the average pore size (AlRatrout et al. 2017). However, the impact of the spatial distribution pattern of CAs on macroscopic multiphase flow properties in 3D porous media remains unknown.

This study aims to answer these fundamental questions in order to: i) find out if there exist spatial correlation patterns associated with the distribution of CAs on sandstone surfaces; ii) unravel the role of spatial correlation length of CA distribution on multiphase flow in porous media; and iii)

understands the interactions and combined effects between the CA's spatial heterogeneity and correlation length. The workflow of this study is organized in the following order. First, brine and scCO₂ injection experiments were conducted on a Bentheimer sandstone core and then the core was scanned using X-ray micro-CT. Second, in-situ CA measurements were conducted on the scCO₂ ganglia trapped in the sandstone, and advanced image analyses were used to extract the variogram and covariance functions for the CA distribution on the sandstone surface. Third, based on the standard deviation and spatial correlation length of CA measured from the micro-CT scans, autocorrelated Gaussian random fields were used to generate nine realizations of CA distribution in the sandstone; the values of the standard deviation and spatial correlation length of CA were shifted slightly from the reference values measured from the micro-CT scans, and then 3D LB multiphase flow modeling was used for comprehensive sensitivity analyses to unravel how the shifts in CA standard deviation and correlation length affect the relative permeability curves in the system. By incorporating advanced optimization techniques, such as GPU parallel computing and morphological drainage, the LB simulator in this study is capable of performing large-scale multiphase flow simulations on a domain having 800×800×600 pixels.

Table 3 - 1. Literature review of related studies on the impact of homogeneous and heterogeneous surface wettability on multiphase flow in porous media. “lu” denotes the lattice length unit in the LB modeling, which is equal to one pixel length in micro-CT imaging.

Studies	Porous media	Fluids	Methods	Domain size (lu ² or lu ³)	Resolution (μm/lu)	Surface wettability	Relative permeability measurement?
This work	Bentheimer sandstone	Water /scCO ₂	Experiment and LB modeling	3D: 800×800×600	1.66	Autocorrelated Gaussian random fields	Yes
(Wang et al., 2020)	Bentheimer sandstone	Fluids with a viscosity ratio of 1 and interfacial tension of 0.05 N/m	LB modeling	3D: 500×500×500	5.3	Homogeneous	No
(Fan et al., 2019)	Berea sandstone	Water/scCO ₂	LB modeling	3D: 800×800×600	2.36	Homogeneous	Yes
(Maziar Arshadi, 2020)	Arkose	N/A ¹	Experiment and pore network modeling	3D: 3×3×3 mm ³	0.73	Fractional wet	No
(Zhao et al., 2018)	Computer-generated solid spheres	N/A	LB modeling	2D: 460×400	N/A	Fractional wet	Yes
(Gu et al., 2018)	Berea sandstone	N/A	LB modeling	2D: 2644×2117	N/A	Homogeneous wet	Yes
(Shi and Tang, 2018)	Computer-generated sphere packs	N/A	LB modeling	3D: 128×128×128	N/A	Homogeneous wet	No
(Zhao et al., 2017)	Tight sandstone	N/A	LB modeling	2D: 3600×1920	N/A	Homogeneous wet	Yes
(Landry et al., 2014)	Glass and polyethylene bead packs	Brine/kerosene	Experiment and LB modeling	3D: 100×100×100 3D: 200×200×200	26	Homogeneous and mixed wet	No
(Dou and Zhou, 2013)	Computer-generated square blocks	N/A	LB modeling	2D: 200×101	N/A	Homogeneous wet	No
(Ghassemi and Pak, 2011)	Computer-generated spheres	Formamide/N-Nonanol	Experiment and LB modeling	2D: 261×261	20	Homogeneous wet	No
(Hwang et al., 2006)	Mixture of quartz sand and organosilane-treated sand	Water/oil	Experiment	N/A	N/A	Fractional wet	No
(Huang and Lu, 2009)	Computer-generated square blocks	N/A	LB modeling	2D: 400×400	N/A	Homogeneous wet	No
(Li et al., 2005)	Computer-generated sphere packs	Fluids with a viscosity ratio between 1 and 3.35	LB modeling	3D: 96×96×96	N/A	Homogeneous wet	No
(Masalmeh, 2003)	Carbonate	Water/oil	Experiment	N/A	N/A	Mixed wet	No
(Bradford and Leij, 1995)	Mixture of octadecyltrichlorosilane-treated and untreated sands	Water/air, water/oil, and water/ail/oil	Experiment	N/A	N/A	Fractional wet	No

1. “N/A” denotes “not available”.

3.2. *Materials and methods*

3.2.1. *Core flooding experiment and micro-CT imaging*

The core flooding experiment and X-ray micro-CT imaging were performed at U.S. Department of Energy (DOE)'s National Energy Technology Laboratory (NETL). The experimental setup was the same as in our previous studies (Dalton et al. 2018, Fan et al. 2019), as illustrated in **Figure 3-1**. One reactor and three ISCO pumps were used in the experiment. A 12-volt heater was used to control the temperature. The core sample was a Bentheimer sandstone core with 1.0 inches in length and 0.25 inch in diameter. Before core flooding, a 5 wt% potassium iodide (KI) brine was exposed to scCO₂ for 24 hours to allow the brine to be fully saturated with scCO₂. The Bentheimer core was placed in a confining sleeve, and aluminum spacers were attached to both ends of the core sample to eliminate the capillary end effects. The core was then placed in a pressurized vessel which was mounted on the sample stage in a Zeiss Versa xrm-400 micro-CT scanner. KI was added to reduce the impact of clay swelling and to enhance the X-ray attenuation contrast between brine and scCO₂, which was necessary for the micro-CT to differentiate the wetting-phase fluid (brine) and the non-wetting-phase fluid (scCO₂) in the Bentheimer sandstone (Dalton et al. 2018).

The core was initially saturated by brine. One cycle of the core flooding experiment involved a scCO₂ injection (i.e., Step 1: drainage) followed by a brine injection (i.e., Step 2: imbibition). The flowrate was 0.1 ml/min, and 10 pore volumes (3.1 ml) of each fluid in each step were injected through the sample. The flow rate led to a Ca of 1.3×10^{-7} , which was in the range (between 3×10^{-9} and 3×10^{-5}) of the Ca encountered in CO₂ aquifer storage projects (Wei et al. 2014). During the core flooding experiment, the pore pressure was 1800 psi and the confining pressure was 2100 psi. The flow-through temperature was 24 °C for all injections. After Step 2, the sample was set to a shut-in condition, the temperature was increased to the supercritical condition (48 °C), and the sample sat for 24 hours before micro-CT scanning, which allowed CO₂ to transition into the supercritical state and fluid distribution to settle in the steady state. Two drainage-imbibition cycles were conducted and micro-CT scanning with a resolution of 1.66 μ m per pixel length was used to visualize the scCO₂/brine distribution at the pore scale after each cycle of core flooding. For simplicity, hereafter we refer to the wetting fluid as water, although the wetting fluid used in the experiments was actually CO₂-saturated 5 wt% KI brine.

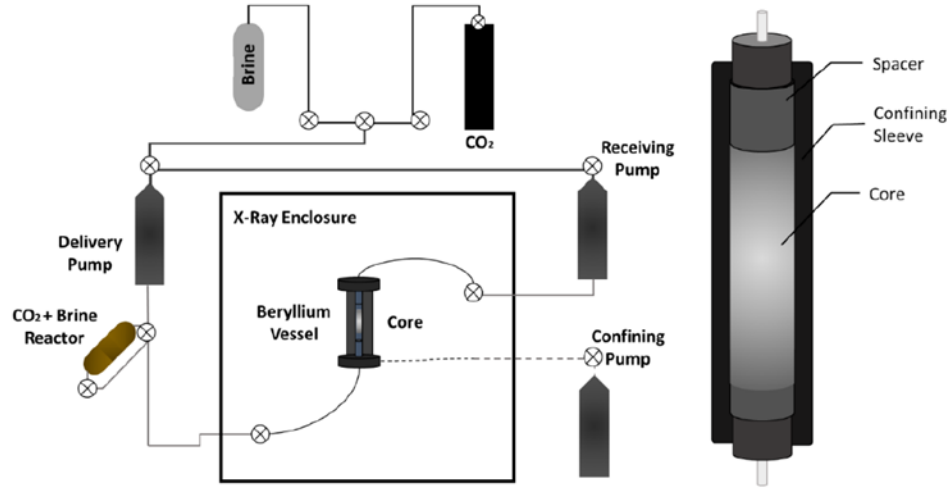


Figure 3 - 1. U.S. DOE-NETL core flooding experiment setup.

3.2.2. Generation of autocorrelated contact angle distributions

Representation of the heterogeneity in rock surface wettability is critical to study the role of wettability heterogeneity on the multiphase flow properties in porous media. In this study, the spatial pattern of the surface wettability heterogeneity was characterized by the standard deviation and correlation length of the static CAs, which were measured using micro-CT scanning after the fluid distribution settled in the steady state. Based on the CT scanning results, the surface CA distribution was found log-normally distributed. Therefore, in this study we modeled the logarithm of CA, $Y = \log(\theta)$, using an autocorrelated Gaussian random field with a given correlation function, where θ is the CA. Assuming the mean and standard deviation of Y are μ_Y and σ_Y respectively, the mean and variance of θ were calculated using $\mu_\theta = e^{\mu_Y + \sigma_Y^2/2}$ and $\sigma_\theta^2 = (e^{\sigma_Y^2} - 1) \cdot e^{2\mu_Y + \sigma_Y^2}$ respectively (Chen and Zeng, 2015). The correlation function between points $\mathbf{x}$ and $\mathbf{y}$ in the 3D space, $c_Y(\mathbf{x}, \mathbf{y})$, had an exponential form: $c_Y(\mathbf{x}, \mathbf{y}) = \sigma_Y^2 \exp\left[-(|x_1 - y_1|/L_1 + |x_2 - y_2|/L_2 + |x_3 - y_3|/L_3)\right]$, where L_1 , L_2 , and L_3 were the correlation lengths in the three principal directions.

To efficiently generate a large-scale 3D random field, in this paper the Karhunen-Loève expansion method was used to solve the computational challenges (Zhang and Lu, 2004). The correlation function, $c_Y(\mathbf{x}, \mathbf{y})$, can be decomposed as (Zhang and Lu, 2004):

$$c_Y(\mathbf{x}, \mathbf{y}) = \sum_{n=1}^{\infty} \lambda_n \psi_n(\mathbf{x}) \psi_n(\mathbf{y}) \quad (3-1)$$

where λ_n and $\psi_n(\mathbf{x})$ are the n^{th} eigenvalues and eigenfunctions, respectively. The Gaussian random field can then be generated using the Karhunen-Loève expansion:

$$\mathbf{Y}(\mathbf{x}) = \langle \mathbf{Y}(\mathbf{x}) \rangle + \sum_{n=1}^{\infty} \xi_n \sqrt{\lambda_n} \psi_n(\mathbf{x}) \quad (3-2)$$

where ξ_n are independent zero-mean Gaussian random variables with unit variance.

In this process, the calculation of eigenvalues and eigenfunctions can be computationally expensive. For a computational domain of $800 \times 800 \times 600$ pixels, there are 3.8×10^8 grid nodes, which leads to a challenge for the computations of eigenvalues and eigenfunctions. This challenge was addressed by analytically calculating the eigenvalues and eigenfunctions from the exponential correlation function. For a 3D field, the eigenvalues and eigenfunctions can be analytically calculated as:

$$\lambda_n = \frac{4L_1L_2L_3\sigma_Y^2}{\left[L_1^2 \left(\omega_i^{(1)} \right)^2 + 1 \right] \left[L_2^2 \left(\omega_j^{(2)} \right)^2 + 1 \right] \left[L_3^2 \left(\omega_k^{(3)} \right)^2 + 1 \right]} \quad (3-3)$$

and

$$\psi_n(\mathbf{x}) = \psi_i(x_1) \psi_j(x_2) \psi_k(x_3) \quad (3-4)$$

where $\psi_i(x_1)$, $\psi_j(x_2)$, and $\psi_k(x_3)$ are the eigenfunctions in the three principal directions and can be calculated independently in each direction using:

$$\psi_n(x_i) = \frac{1}{\sqrt{(L_i^2 \omega_n^2 + 1) D_i / 2 + L_i}} \left[L_i \omega_n \cos(\omega_n x_i) + \sin(\omega_n x_i) \right] \quad i = 1, 2, 3 \quad (3-5)$$

where ω_n are the positive roots of the characteristic equation $(L_i^2 \omega^2 - 1) \sin(\omega D_i) = 2L_i \omega \cos(\omega D_i)$, and D_i is the side length of the computational domain in each direction. Once the eigenvalues and eigenfunctions in the three principal directions are calculated, the $\mathbf{Y}$ field can be generated using Equation 3-2.

3.2.3. Multiphase flow simulation plan for sensitivity analyses

The standard deviation and spatial correlation length of the CAs in the Bentheimer sandstone were measured as 9° and 71 pixel lengths, respectively, of which the details will be discussed in Section 3.1. Therefore, we used 9° and 71 pixel lengths as the reference values for the standard deviation and spatial correlation length of CA, respectively, and then adjust these values within a certain range for comprehensive sensitivity analysis to investigate the respective and combined effects of the standard deviation and correlation length of CA on the relative permeability curves in the rock. Specifically, various CA distributions, which had different combinations of CA standard deviation and CA correlation length, were generated on the Bentheimer sandstone surface using the Gaussian random field method described in Section 3.2.2. Pore-scale LB modeling was then used to simulate the multiphase flow in these pore geometries and to calculate the relative permeability curves. In this study, the 3D microstructure of the Bentheimer sandstone was reconstructed from the micro-CT images. The computational domain for LB modeling has dimensions of 800×800×600 lu³, which means that there were 800 lattices in the x and y directions and 600 lattices in the z direction. The spatial resolution was 1.66 μm per lu. In this study, one lattice length unit in LB modeling, lu, was equal to one pixel length in the micro-CT imaging.

Table 3-2 illustrates the comprehensive combinations of the standard deviation and spatial correlation length of CA. Specifically, the standard deviation of CA took values of 2°, 9°, and 18°, and the spatial correlation length of CA took values of 35, 71, and 105 pixel lengths. The central block of the table shows the reference values (i.e., a CA standard deviation of 9° and a CA correlation length of 71 pixel lengths) measured from the laboratory micro-CT scanning. In the same row in the table, the standard deviation of CA increases from left to right whereas the spatial correlation length stays constant. In the same column in the table, the spatial correlation length of CA increases from top to bottom whereas the standard deviation stays constant. The minimum dimension of the computational domain (600 pixel lengths) was nearly six times larger than the

maximum spatial correlation length (105 pixel lengths), which suggests that sufficient statistical information was included in the generated Gaussian random fields and thereby the ergodicity requirement was satisfied. According to our previous research (Chen et al. 2013, Chen and Zeng 2015), when a Gaussian random field meets the ergodicity requirement, the simulated system behaviors depend primarily on the statistical parameters (i.e., standard deviation and spatial correlation length of the random variable) and are relatively insensitive to the local heterogeneity in each specific realization.

Table 3 - 2. Comprehensive sensitivity analysis to study the respective and combined effects of standard deviation and correlation length of surface CAs. Y is the logarithm of contact angle, $\log(\theta)$.

$\mu_Y = 3.3623, \sigma_Y = 0.1000;$ $\mu_\theta = 29^\circ; \sigma_\theta = 2^\circ;$ $L = 35$ pixels	$\mu_Y = 3.3213, \sigma_Y = 0.3033;$ $\mu_\theta = 29^\circ, \sigma_\theta = 9^\circ;$ $L = 35$ pixels	$\mu_Y = 3.2044; \sigma_Y = 0.5709$ $\mu_\theta = 29^\circ, \sigma_\theta = 18^\circ;$ $L = 35$ pixels
$\mu_Y = 3.3623, \sigma_Y = 0.1000;$ $\mu_\theta = 29^\circ, \sigma_\theta = 2^\circ;$ $L = 71$ pixels	$\mu_Y = 3.3213, \sigma_Y = 0.3033;$ $\mu_\theta = 29^\circ, \sigma_\theta = 9^\circ;$ $L = 71$ pixels	$\mu_Y = 3.2044; \sigma_Y = 0.5709;$ $\mu_\theta = 29^\circ, \sigma_\theta = 18^\circ;$ $L = 71$ pixels
$\mu_Y = 3.3623, \sigma_Y = 0.1000;$ $\mu_\theta = 29^\circ, \sigma_\theta = 2^\circ;$ $L = 105$ pixels	$\mu_Y = 3.3213, \sigma_Y = 0.3033;$ $\mu_\theta = 29^\circ, \sigma_\theta = 9^\circ;$ $L = 105$ pixels	$\mu_Y = 3.2044; \sigma_Y = 0.5709;$ $\mu_\theta = 29^\circ, \sigma_\theta = 18^\circ;$ $L = 105$ pixels

3.2.4. Lattice Boltzmann simulation of multiphase flow in porous media

The LB method is a mesoscopic kinetic equation based method for solving the Navier-Stokes equations (Chen et al., 1992) and has demonstrated excellent capabilities in simulating complex multiphase flow in porous media (McClure et al., 2014) because of its advantages in the explicit evolution equation (Chen et al., 2008; Chen et al., 2009; Jiang et al., 2014; Landry et al., 2014; Li et al., 2016; Liu et al., 2016), simplicity in parallel computing (Coon et al., 2014; McClure et al., 2014; Chen et al., 2016), and capabilities of incorporating new physics such as fluid-solid interactions at solid surfaces (Han and Cundall, 2013; Yang et al., 2019). The color-gradient LB multiphase flow model was employed in this study.

The LB method discretizes fluids into particle distributions which are transported on discrete velocity space. In this work, the fluid momentum was calculated in the D3Q19 (19 velocity vectors in 3D space) lattice model to recover the momentum equations. The velocity vectors for the D3Q19 scheme are (McClure et al., 2014):

$$\begin{aligned}
\mathbf{e}_0 &= (0, 0, 0)c, \mathbf{e}_1 = (1, 0, 0)c, \mathbf{e}_2 = (-1, 0, 0)c, \\
\mathbf{e}_3 &= (0, 1, 0)c, \mathbf{e}_4 = (0, -1, 0)c, \mathbf{e}_5 = (0, 0, 1)c, \mathbf{e}_6 = (0, 0, -1)c, \\
\mathbf{e}_7 &= (1, 1, 0)c, \mathbf{e}_8 = (-1, 1, 0)c, \mathbf{e}_9 = (1, -1, 0)c, \mathbf{e}_{10} = (-1, -1, 0)c, \quad . \\
\mathbf{e}_{11} &= (0, 1, 1)c, \mathbf{e}_{12} = (0, -1, 1)c, \mathbf{e}_{13} = (0, 1, -1)c, \mathbf{e}_{14} = (0, -1, -1)c, \\
\mathbf{e}_{15} &= (1, 0, 1)c, \mathbf{e}_{16} = (-1, 0, 1)c, \mathbf{e}_{17} = (1, 0, -1)c, \mathbf{e}_{18} = (-1, 0, -1)c
\end{aligned} \tag{3-6}$$

In the D3Q19 multi-relaxation-time (MRT) approach, the moments are calculated by

$$m_i = \sum_{q=0}^{Q-1} M_{i,q} f_q \tag{3-7}$$

where m_i are the moments, M_{iq} is the transform matrix converting fluid distribution to moments, and f_q is the particle distribution function in the q direction.

The moments relax to their equilibrium value m_i^{eq} at rates specified by relaxation coefficients Λ_i and then the momentum transport equation in the D3Q19 MRT LB equation is written as

$$f_q(\mathbf{x} + \mathbf{e}_q \Delta t, t + \Delta t) - f_q(\mathbf{x}, t) = M_{qi}^* \Lambda_i (m_i^{eq} - m_i) \quad q = 0, 1, 2, \dots, 18 \tag{3-8}$$

where $f_q(\mathbf{x}, t)$ is the particle distribution function at location $\mathbf{x}$ at time t moving along the q^{th} direction; $f_q(\mathbf{x} + \mathbf{e}_q \Delta t, t + \Delta t)$ is the particle distribution function at the adjacent lattice location after the streaming step; M_{qi}^* is the inverse of M_{iq} .

The right hand side of Equation 8 represents the collision term. An anisotropic stress tensor was added to the collision term to simulate interfacial tension:

$$\begin{aligned}
m_1^{eq} &= (j_x^2 + j_y^2 + j_z^2) + \alpha |\mathbf{C}| \\
m_9^{eq} &= (2j_x^2 - j_y^2 - j_z^2) + \alpha \frac{|\mathbf{C}|}{2} (2n_x^2 - n_y^2 - n_z^2) \\
m_{11}^{eq} &= (j_y^2 - j_z^2) + \alpha \frac{|\mathbf{C}|}{2} (n_y^2 - n_z^2) \\
m_{13}^{eq} &= j_x j_y + \alpha \frac{|\mathbf{C}|}{2} n_x n_y \\
m_{14}^{eq} &= j_y j_z + \alpha \frac{|\mathbf{C}|}{2} n_y n_z \\
m_{15}^{eq} &= j_x j_z + \alpha \frac{|\mathbf{C}|}{2} n_x n_z
\end{aligned} \tag{3-9}$$

where j_x , j_y , and j_z are fluid momentum in the x, y, and z directions, respectively; α is the parameter controlling the interfacial tension; $\mathbf{C}$ is the color gradient; n_x , n_y , and n_z are the components of the unit norm vector, $\mathbf{n}$, in the x, y, and z directions, respectively. The remaining moments are zero (McClure et al., 2014).

The phase distribution is described by the phase indicator field, which is calculated as

$$\varphi = (\rho_n - \rho_w) / (\rho_n + \rho_w) \tag{3-10}$$

where ρ_n and ρ_w are the densities of the nonwetting phase and wetting phase fluids, respectively. φ takes a value of 1 for the non-wetting fluid and -1 for the wetting fluid. Within the interface zone, φ takes values between -1 and 1. The color gradient, $\mathbf{C}$, refers to the gradient of the phase indicator field, which is written as $\mathbf{C} = \nabla \varphi$.

To enhance the simulation efficiency, the D3Q7 (7 velocities in 3D space) lattice model was employed to track the mass transfer. The D3Q7 model recovers the mass continuity equation accurately because there is no stress tensor in mass transport (Ginzburg, 2005; Zheng et al., 2006). The discrete velocity space in the D3Q7 model matches the first seven vectors in the D3Q19 model (McClure et al., 2014). The recoloring step is used to separate fluids and maintain the phase interface, written as

$$\begin{aligned}
f_{nq}^* &= w_q \left[\rho_n (1 + \mathbf{e}_q \cdot \mathbf{u}) + \beta (\mathbf{e}_q \cdot \mathbf{n}) \rho_n \rho_w / (\rho_n + \rho_w) \right] & q = 0, 1, 2, \dots, 6 \\
f_{wq}^* &= w_q \left[\rho_w (1 + \mathbf{e}_q \cdot \mathbf{u}) - \beta (\mathbf{e}_q \cdot \mathbf{n}) \rho_n \rho_w / (\rho_n + \rho_w) \right] & q = 0, 1, 2, \dots, 6
\end{aligned} \tag{3-11}$$

where f_{nq}^* and f_{wq}^* are the density distributions for the non-wetting fluid and wetting fluid, respectively, in the q^{th} direction; $\mathbf{u}$ is the macroscopic velocity; β is the parameter that controls the interface width. After the recolor step, the fluid density, ρ_i , is updated in the D3Q7 model by

$$\rho_i(\mathbf{x}, t + \Delta t) = \sum_{q=0}^6 g_{iq}(\mathbf{x} - \mathbf{e}_q \Delta t, t) \quad i = w, n \quad (3-12)$$

The LB code used in this study has been validated in our previous papers (McClure et al., 2014; Fan et al., 2018; Fan et al., 2019; Fan et al., 2019). The initialization of fluid distribution at a given water saturation in the steady-state relative permeability simulation was obtained from the unsteady-state imbibition displacement process following the primary drainage process (Fan et al., 2018; Fan et al., 2019). The viscosity ratio of water to scCO₂ was set as 4:1 in this study (Chen and Zhang, 2009). The body force in the LB simulation was adjusted to obtain a Ca of 10^{-4} . The simulation took 20,000,000 LB time steps for the imbibition process and 1,500,000 LB time steps for a single point on the relative permeability curves.

3.2.5. Hybrid, multicore CPU/GPU parallel computing

LB simulations are demanding in computer memories and computing power (McClure et al. 2014). The required central processing unit (CPU) time by the LB model is estimated $10^4 - 10^5$ times higher than pore network models for a computational domain having the same dimensions (Vogel et al. 2005), which poses a significant challenge for the LB model in simulating large computational domains. As shown in Table 3-1, the largest 3D simulation domain in the literature had dimensions of 500^3 pixels, which was reconstructed from a Bentheimer sandstone (Wang et al. 2020). To increase the spatial scale of the LB multiphase flow simulation model, a hybrid, multi-core CPU/GPU parallel computing scheme was used in this study, where the GPU-accelerated implementation of momentum transport simulation was combined with CPU-based mass transport simulation using the Compute Unified Device Architecture parallel computing platform. The GPU parallel computing can accelerate the implementation of the LB model by one order of magnitude (Walsh et al. 2009, Bernaschi et al. 2010, McClure et al. 2010, Rinaldi et al. 2012). The mass transport simulation based on the D3Q7 model greatly reduced the memory and computing demands and was implemented on CPUs to maximize the usage of computing resources

(McClure et al. 2014). To improve the GPU parallel computing efficiency, the data structure was optimized by removing the interior solid nodes in the porous medium. In general, a real rock has a porosity lower than 30%. Excluding the interior solid nodes that are not adjacent to fluids nodes leads to a sparse data structure that significantly reduces the computing time (Chen et al. 2016). Furthermore, to enhance the implementation efficiency of the LB code, a kernel tuning technique was used, which included synchronizing, fusing, and coalescing of the LB methods (Chen et al. 2016). Synchronizing means doubling and flipping-flopping of two solution arrays to avoid race conditions in the streaming step. Fusing is to fuse the streaming and collision operators into one kernel to avoid the time-consuming multiple data reading and writing processes. Coalescing refers to the combination of multiple memory accesses into one transaction. The details can be found in one of our previous papers (Chen et al. 2016).

In addition, a morphological drainage process was used to replace the primary drainage process in the LB model in order to further enhance the computing speed. For a drainage process with a low Ca, direct simulation of a large-scale computational domain using the LB multiphase flow model can be time consuming. Even using the hybrid, multi-core CPU/GPU scheme in this work, the primary drainage process simulation for a domain having $800 \times 800 \times 600$ pixels can take 80 – 100 hours. A morphological drainage process can precisely resemble the primary drainage process with a low Ca (Wang et al. 2020). With this optimization, the time for simulating the primary drainage process in this study was reduced to 20 minutes. The parallel computing techniques described above greatly enhanced the performance of the hybrid, multi-core CPU/GPU scheme. The simulation was performed using 8 NVIDIA P100 GPUs. The lattice update rate is 12988 million lattice updates per second (MLUPS) and 103904 MLUPS in total.

3.3. Results and discussion

3.3.1. Variogram, covariance, and spatial correlation length of measured contact angles

Figure 3-2a illustrates a 2D cross section of the 3D reconstructed pore structure of the Bentheimer sandstone and distributions of water and scCO_2 after two drainage-imbibition cycles of core flooding. Based on the micro-CT images, the two-point correlation function method (Berryman and Blair, 1986; Berryman and Blair, 1987; Chen et al., 2009; Chen et al., 2009) was used to evaluate

the porosity and average pore size of the Bentheimer sandstone. The two-point correlation function, $S(\mathbf{r})$, is defined as $S(\mathbf{r}) = \langle g(\mathbf{x})g(\mathbf{x}+\mathbf{r}) \rangle$, where $\mathbf{x}$ is an arbitrary position in the micro-CT image and $\mathbf{x}+\mathbf{r}$ is another point separated by a distance of $\mathbf{r}$. The characteristic function, $g(\mathbf{x})$, is equal to 1 in the void region and 0 in the solid region. The function of $S(\mathbf{r})$ thus indicates the expectation that two points separated by a distance of $\mathbf{r}$ are both in the void space of the porous medium. The porosity of the Bentheimer sandstone, ϕ , is equal to $S(0)$. The average pore diameter, d , can be estimated using $d = -\phi/S'(\mathbf{0})$, where $S'(\mathbf{0})$ is the derivative of $S(\mathbf{r})$ at $\mathbf{r} = 0$, and the average particle diameter can be estimated as the separation distance at which S first reaches the stable value (Berryman and Blair, 1987). Figure 3-2b shows the two-point correlation function for the Bentheimer sandstone sample. Based on the image analysis, the porosity of the Bentheimer sandstone core was found as 25.3%, the average particle size was found as 80 pixels (132 μm), and the average pore diameter was found as 35 pixels (58 μm).

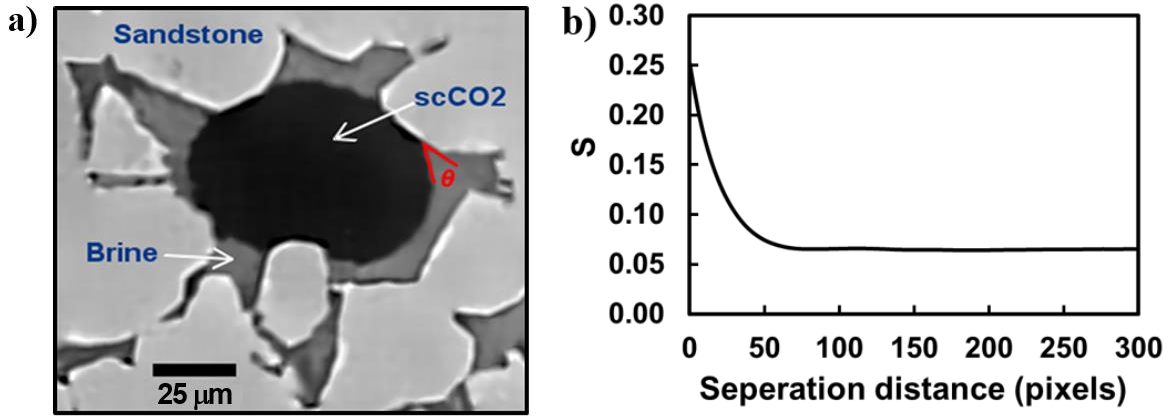


Figure 3 – 2. (a) The reconstructed 3D image is rotated so that the water/scCO₂ interface plane and water/solid interface plane are both perpendicular to the paper, which enables the measurement of the contact angle, θ . (b) Two-point correlation function for the Bentheimer sandstone sample based on analysis of the micro-CT images.

Three hundred CAs were measured after two drainage-imbibition cycles of core flooding based on the micro-CT images scanned on the Bentheimer sandstone core using the Angle Tool Package in the imageJ software (Dalton et al., 2018). The CAs were measured when the fluids were in the

equilibrium state, and the measurements considered the effects of sandstone surface roughness and pore size and shape. To identify the spatial correlation of surface wettability, variograms were calculated using the CT-measured CAs. **Figure 3-3a** illustrates the histogram of the CT-measured CAs after two drainage-imbibition cycles of core flooding. The measured CAs had a minimum value of 8.8°, a maximum value of 59.7°, a mean value of 29.2°, a median value of 28.1°, and a standard deviation of 9.1°. The wide range of the CT-measured CAs illustrated that the wettability distribution on the sandstone surface was highly heterogeneous. The mean value of the measured CAs was higher than the median value, which suggested that the CA distribution was right-skewed with a long tail on the right side. In addition, based on the definition, a CA value cannot be negative, which suggests that zero is the lower bound of its distribution. Therefore, a lognormal function was used to fit the measured CAs as shown in Figure 3-3a.

Figure 3-3b shows the variogram and covariance curves of the CT-measured CAs. The variogram

was calculated as
$$\gamma(|\mathbf{r}|) = \frac{1}{2N(|\mathbf{r}|)} \sum_{i=1}^{N(|\mathbf{r}|)} [\theta(\mathbf{x}_i) - \theta(\mathbf{x}_i + |\mathbf{r}|)]^2$$
 (Oliver and Webster, 2015),

where $|\mathbf{r}|$ is the spatial separation distance between two CT-measured CAs; $N(|\mathbf{r}|)$ is the total number of data pairs with the separation distance of $|\mathbf{r}|$. The covariance is calculated by $Cov(|\mathbf{r}|) = \sigma_\theta^2 - \gamma(|\mathbf{r}|)$, where σ_θ^2 is the variance of the CT-measured CAs (Oliver and Webster, 2015). Figure 3-3b clearly illustrates that there was a characteristic length associated with the variogram and covariance curves. When the separation distance was smaller than this characteristic length, the variogram increased whereas the covariance decreased with the separation distance increasing, which implies a decreasing similarity between two CAs separated by the separation distance. When the separation distance was larger than this characteristic length, the variogram and covariance reached stable values and did not vary significantly with the separation distance increasing. An exponential function was used to fit the data range in which the covariance declined, leading to a spatial correlation length of 71.4 pixel lengths, which suggested that statistically the covariance (i.e., similarity) between two CT-measured CA values reduced to e^{-1} (i.e., 36.8%) of the variance of the random field when the separation distance reached 71.4 pixel lengths. Unlike the work of AlRatrout et al. (2017), where the spatial correlation length of CA distribution in carbonates was found not larger than the average pore size, in the Bentheimer sandstone analyzed in this study the spatial correlation length of CA was more than two times the average pore size.

This was because the pore geometry, rock surface roughness, and mineralogy, all of which had an impact on the measured CA, were relatively more homogeneous in the Bentheimer sandstone than in carbonates, leading to a spatial correlation length of CA distribution that spans a scale over several pore diameters or larger. Therefore, in sandstone rocks, it is necessary to consider the impact of relatively long correlation lengths that span over several pore diameters on the multiphase flow properties, as illustrated in Table 3-2.

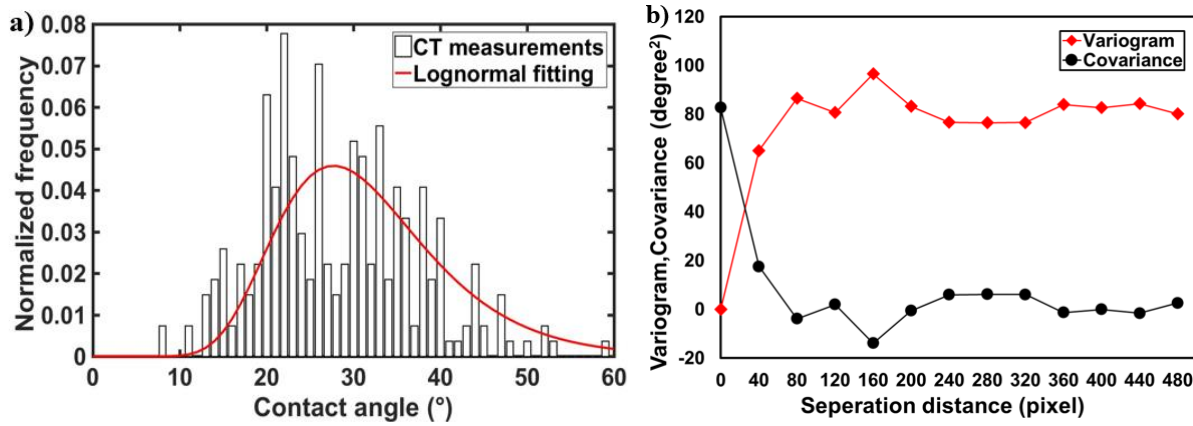


Figure 3 – 3. (a) Distribution of CT-measured CAs and the lognormal fitting. These CAs were measured in the Bentheimer sandstone after two cycles of core flooding experiments. (b) Variogram and covariance of the CT-measured CAs as a function of the separation distance.

3.3.2. *Effect of the standard deviation of contact angle*

Figure 3-4 demonstrates the impact of the CA standard deviation on fluid distribution at the pore scale. The CA correlation length was equal to the reference value (71 pixel lengths) in both scenarios, whereas the CA standard deviation in one scenario was reduced to 2° from the reference value (9°) and it was increased to 18° in the other scenario, as illustrated in the second row of Table 3-2. scCO_2 and water are shown in black and white, respectively, and the remaining region is the sandstone solid with the blue-to-red color gradient bar indicating the surface CAs. These 2D images are cross sections cut from the 3D fluid distributions simulated by the steady-state LB multiphase flow modeling. The water saturation was 0.55 in both scenarios, and the main flow direction was perpendicular to the 2D cross sections. When the CA standard deviation was raised to 18° , certain pore wall surfaces had CAs larger than 90° , indicating a CO_2 -wet surface, as shown

by the red circle in Figure 3-4b; in this case, the scCO₂ was able to overcome the capillary pressure resistance and move into the relatively small fissures and pore throats. In addition, it was clear that the enhanced CA standard deviation caused fluid redistribution in larger pores, as illustrated by the yellow circles; In this case, the scCO₂ ganglion was pulled toward the left side of the pore, as shown in the yellow circle in Figure 3-4b, because the left-side pore wall became more CO₂-wet. Note that the fluid distributions in both scenarios were simulated using the 3D LB multi-phase flow model with the same initial scCO₂/water distribution. It is clear that the difference in surface CA standard deviation led to different pore-scale fluid distributions during the steady-state two-phase flow process, which caused the variation in the relative permeability that was averaged over the entire computational domain.

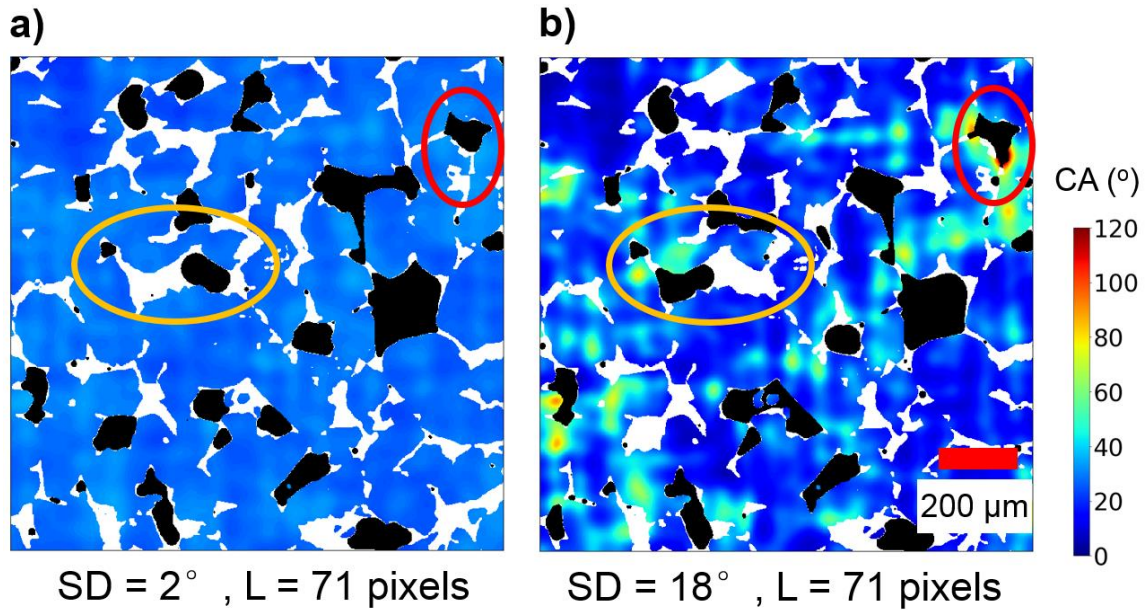


Figure 3 – 4. Distributions of scCO₂ (black) and water (white) in the pore space in the scenarios of (a) CA standard deviation = 2° and CA correlation length = 71 pixels, and (b) CA standard deviation = 18° and CA correlation length = 71 pixels. The remaining region is the sandstone solid with the blue-to-red color gradient bar indicating the surface CAs. These 2D images are cross sections cut from the 3D fluid distributions simulated by the steady-state LB multiphase flow modeling. The water saturation was 0.55 in both scenarios, and the main flow direction was perpendicular to the cross sections. In the figure legend, “SD” denotes the standard deviation of CA distribution.

The Corey model was used to fit the LB-simulated relative permeability curves, k_r , in order to quantitatively assess the role of the varying standard deviation and spatial correlation length of CA on k_r . The Corey model is a commonly used fitting model which assumes that the relation between k_r and the normalized water saturation follows a power law:

$$k_{rw} = k_{rw}^o S_w^{*N_w} \quad (3-13)$$

$$k_{ro} = k_{ro}^o (1 - S_w^*)^{N_o} \quad (3-14)$$

where k_{rw} is water relative permeability; k_{ro} is scCO₂ relative permeability; k_{rw}^o is the end-point relative permeability of water; k_{ro}^o is the end-point relative permeability of scCO₂; N_w is the power-law exponent for water relative permeability; N_o is the power-law exponent for scCO₂ relative permeability; S_w^* is the normalized water saturation defined as $S_w^* = \frac{S_w - S_{wir}}{1 - S_{wir} - S_{orw}}$, where S_w is water saturation, S_{wir} is irreducible water saturation, and S_{orw} is residual scCO₂ saturation.

Figure 3-5 illustrates the role of the varying standard deviation of CAs on the k_r curves. The scattered data points are relative permeabilities measured by the LB multiphase flow modeling, whereas the curves are the Corey model fitting. Rows 1, 2, and 3 represent the parameter values listed in the three rows in Table 3-2. In each row of the table 3-2, the standard deviation of CA increases from left to right, whereas the spatial correlation length of CA stays constant. Therefore, Figure 3-5 shows the impact of the varying standard deviation of CA on the k_r curves. It is observed that the standard deviation of surface CA affects the relative permeability of scCO₂, k_{ro} , more significantly than the relative permeability of water, k_{rw} . This was because, despite of the different standard deviations in CA, in all these simulation scenarios the average CA was the same and equal to 29°, which suggested that the Bentheimer sandstone surface was predominantly strongly water-wet. Therefore, in all these scenarios, water formed a relatively thin coating near the rock surfaces and flowed within this water layer. As a consequence, the connectivity and effective permeability of water depended primarily on the average CA of the entire rock surface and was relatively insensitive to the local heterogeneity (i.e., standard deviation) in the rock surface CA.

Conversely, scCO₂ flowed mainly in pore centers because the rock surface was strongly water-wet. A relatively large standard deviation in surface CA may cause a small part of local CA values larger than 90°, leading to a CO₂-wet surface locally. If these CO₂-wet surfaces occur in relatively small pores, they might noticeably increase the resistance to the overall scCO₂ flow and hence reduce the connectivity and effective permeability of the scCO₂ phase, which explains the more significant oscillations in the k_{ro} curves when the standard deviation of CA increased.

It is also observed that when water saturation approached zero and one, the variations in k_{rw} and k_{ro} were not noticeable when the standard deviation of CA changed. This was because when the water saturation was at 0.88, scCO₂ was at the residual saturation and immobilized, and it was actually single-phase flow of water that occurred in the pore space. Similarly, when the water saturation was at 0.12, water was at the irreducible saturation and immobilized, and the flow was single-phase flow of scCO₂ in the pore space. In either case, the flow in the pore space was approximately equivalent to single-phase flow and therefore there was no moving, dynamic interfaces between water and scCO₂. As a consequence, the heterogeneity (i.e., standard deviation) of CA on the rock surfaces had no impacts on k_{rw} and k_{ro} when the water saturation approached zero and one.

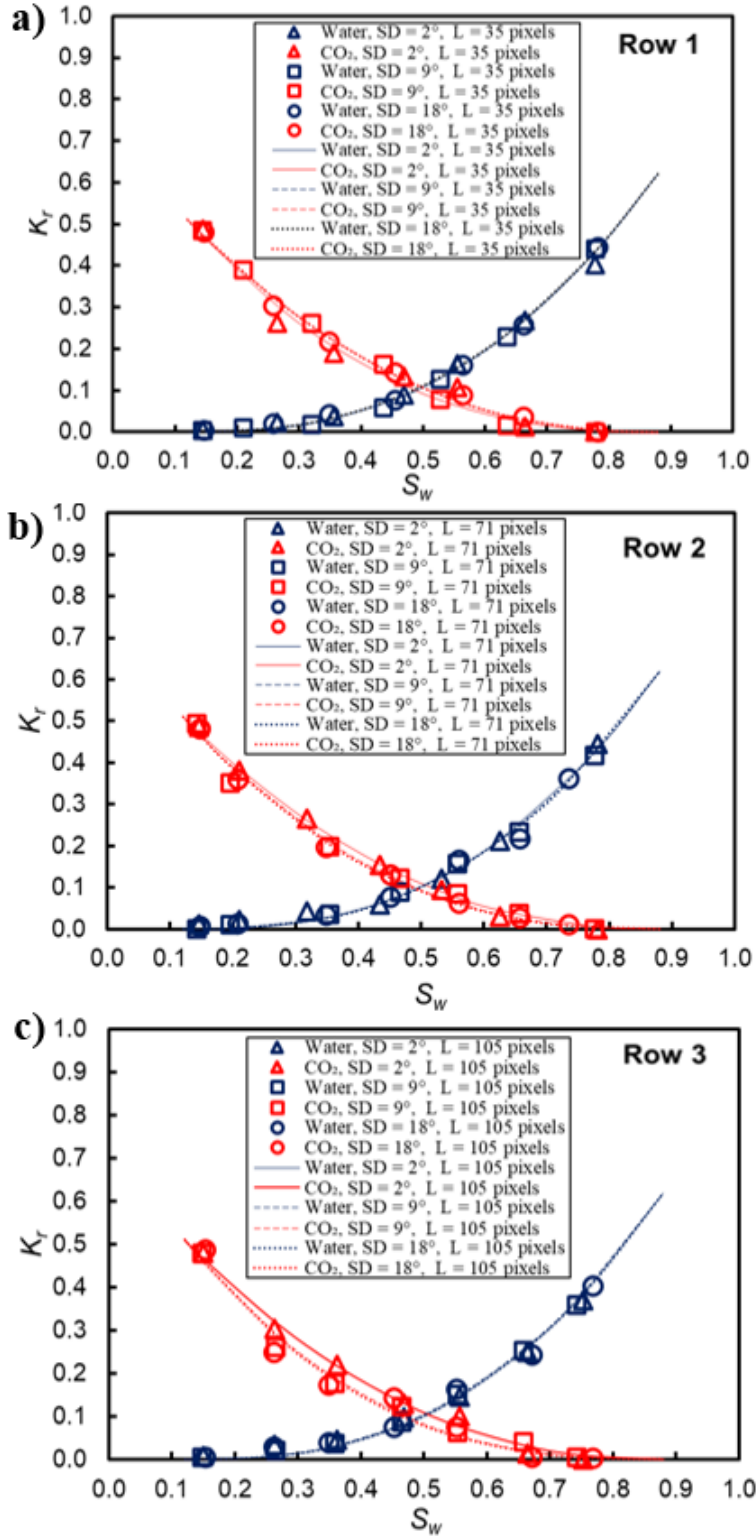


Figure 3 - 5. Relative permeability as a function of water saturation for the parameter values listed in (a) row 1, (b) row 2, and (c) row 3 of Table 3-2. The scattered data points are relative

permeabilities measured by the LB multiphase flow modeling, whereas the curves are the Corey model fitting. Rows 1, 2, and 3 represent the parameter values listed in the three rows in Table 3-2. In the figure legend, “SD” denotes the standard deviation of CA distribution.

To accurately quantify the impact of the standard deviation of CA on the multiphase flow properties, the standard deviations between the Corey-model-fitted k_r curves were calculated as a function of water saturation and illustrated in **Figure 3-6a**. Specifically, the curve of “SD of k_{ro} with $L=35$ pixels” in Figure 3-6a was calculated based on the three Corey-model-fitted k_{ro} curves shown in Figure 3-5a, which were for the CA standard deviations of 2° , 8° , and 19° , separately; at a specific water saturation, the standard deviation between the three Corey-model-fitted k_{ro} values was calculated and then plotted as a function of water saturation. The same method was used to plot the other five curves in Figure 3-6a, which illustrates the impact of the varying CA standard deviation on the oscillation of the k_r curves. Figure 3-6a confirms that the variation (i.e., standard deviation) in the k_{ro} curves was more significant than that of the k_{rw} curves when the CA standard deviation changed from 2° to 9° and then 18° . Furthermore, it was confirmed that when the water saturation approached the two end points, the variation in the k_r curves was relatively small because the flow in the pore space was approximately equivalent to single-phase flow when the water saturation was near the two end points. In addition, it was clear that, when the CA standard deviation changed from 2° to 9° and then 18° , the variation in the k_r curves was more significant with a longer spatial correlation length. This observation suggested that, a longer spatial correlation length in CA distribution (105 pixel lengths) enhanced the influence of the increasing CA standard deviation on the k_r curves compared to shorter spatial correlation lengths (i.e., 35 and 71 pixel lengths). This finding is similar to a prior study (Chen et al., 2013) which showed that a large spatial correlation length in a Gaussian random field, associated with a large standard deviation of the random variable, led to the highest uncertainty in the system output.

To clearly illustrate the role of the spatial correlation length of CA when the standard deviation of CA varied, the standard deviations of the model-fitted relative permeability were averaged over the entire water saturation range (from 0.2 through 0.8) shown in Figure 3-6a and then plotted as a function of the corresponding correlation length, as illustrated in Figure 3-6b. Figure 3-6b confirms that the variation in the k_{ro} curves was more significant than that of the k_{rw} curves when the CA standard deviation increased from 2° to 9° and then 18° . Also, it was confirmed that a

longer spatial correlation length in CA distribution enhanced the influence of the increasing CA standard deviation on the k_r curves.

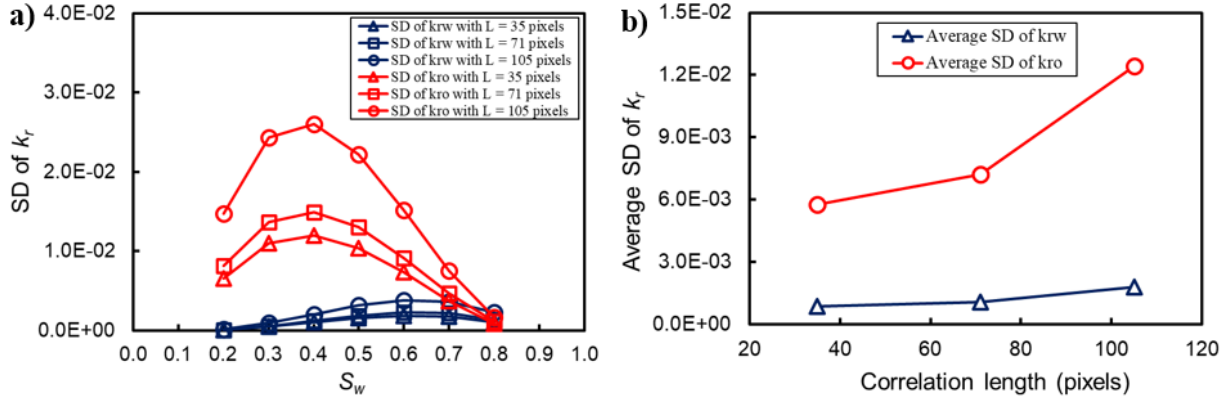


Figure 3 - 6. (a) Standard deviation between the Corey-model-fitted k_r values due to the variation in the standard deviation of CA as a function of water saturation. (b) Average standard deviation between the Corey-model-fitted k_r curves as a function of the spatial correlation length of CA distribution.

3.3.3. Effect of the spatial correlation length of contact angle

Figure 3-7 demonstrates the impact of the CA's spatial correlation length on fluid distribution at the pore scale. The CA standard deviation was equal to the reference value (9°) in both scenarios, whereas the CA's spatial correlation length in one scenario was reduced to 35 pixel lengths from the reference value (71 pixel lengths) and it was increased to 105 pixel lengths in the other scenario, as described in the second column of Table 3-2. The water saturation was 0.55 in both scenarios, and the main flow direction was perpendicular to these 2D cross sections. Because of the relatively low CA standard deviation (9°), the rock surface CAs in both scenarios were primarily close to their average value (29°) and thus all smaller than 90° . It was noticeable that the spatial distribution of CA had a spotted pattern in Figure 3-7a due to its shorter CA correlation length. Conversely, Figure 3-7b illustrated a longer similarity length with respect to the CA spatial distribution, because of its longer CA correlation length. The longer CA correlation length can cause most of

the inner wall area in a pore to become less water wet, thereby attracting a significant amount of scCO₂ to move into this pore, as demonstrated by the red circle in Figure 3-7b.

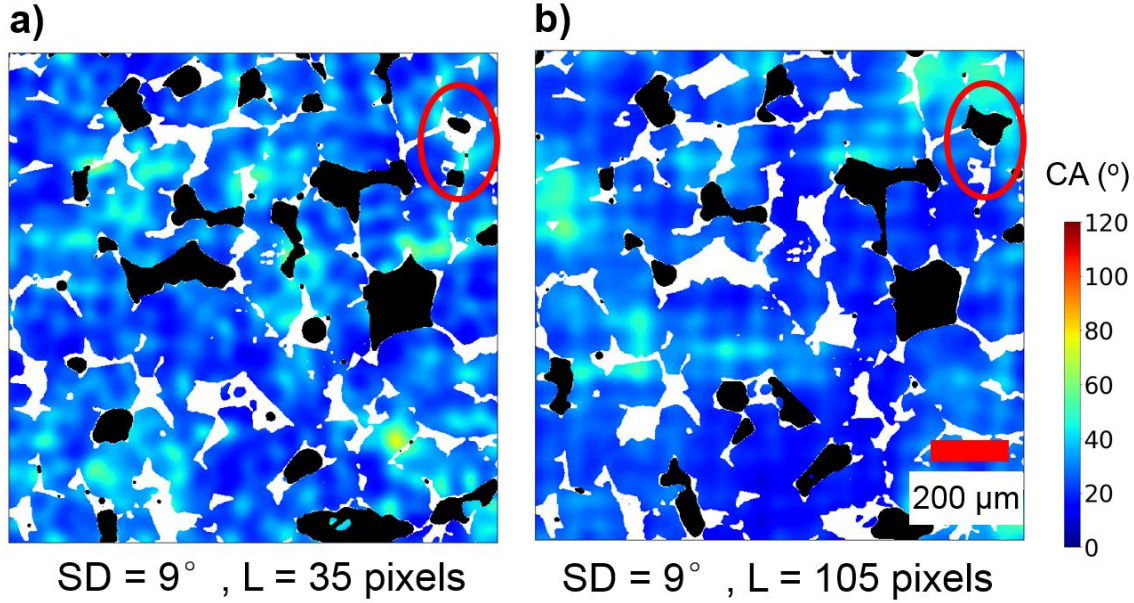


Figure 3 - 7. Distributions of scCO₂ (black) and water (white) in the pore space in the scenarios of (a) CA standard deviation = 9° and CA correlation length = 35 pixels, and (b) CA standard deviation = 9° and CA correlation length = 105 pixels. The remaining region is the sandstone solid with the blue-to-red color gradient bar indicating the surface CAs. These 2D images are cross sections cut from the 3D fluid distributions simulated by the steady-state LB multiphase flow modeling. The water saturation was 0.55 in both scenarios, and the main flow direction was perpendicular to the cross sections. In the figure legend, “SD” denotes the standard deviation of CA distribution.

Figure 3-8 illustrates the role of the varying spatial correlation length of CA on the k_r curves. Similarly, the scattered data points are relative permeabilities measured by the LB multiphase flow modeling, whereas the curves are the Corey model fitting. Columns 1, 2, and 3 represent the parameter values listed in the three columns in Table 3-2. In each column of Table 3-2, the spatial correlation length of CA distribution increases from top to bottom, whereas the standard deviation of CA stays constant. Therefore, Figure 3-8 demonstrates the impact of the varying spatial correlation length of CA distribution on the k_r curves. It is observed that the spatial correlation

length of CA distribution affected k_{ro} more significantly than k_{rw} , which is similar to the finding observed in Figure 3-5. It is also observed that when water saturation approached zero and one, the variations in k_{rw} and k_{ro} were not noticeable when the spatial correlation length of CA distribution changed. This can be explained using the same rationale that when the pore fluid distribution approached the irreducible water saturation or the residual scCO_2 saturation, the flow in the pore space was approximately equivalent to single-phase flow and therefore there was no moving interfaces between water and scCO_2 ; as a consequence, the increasing spatial correlation length of CA distribution had no impacts on the k_{rw} and k_{ro} curves.

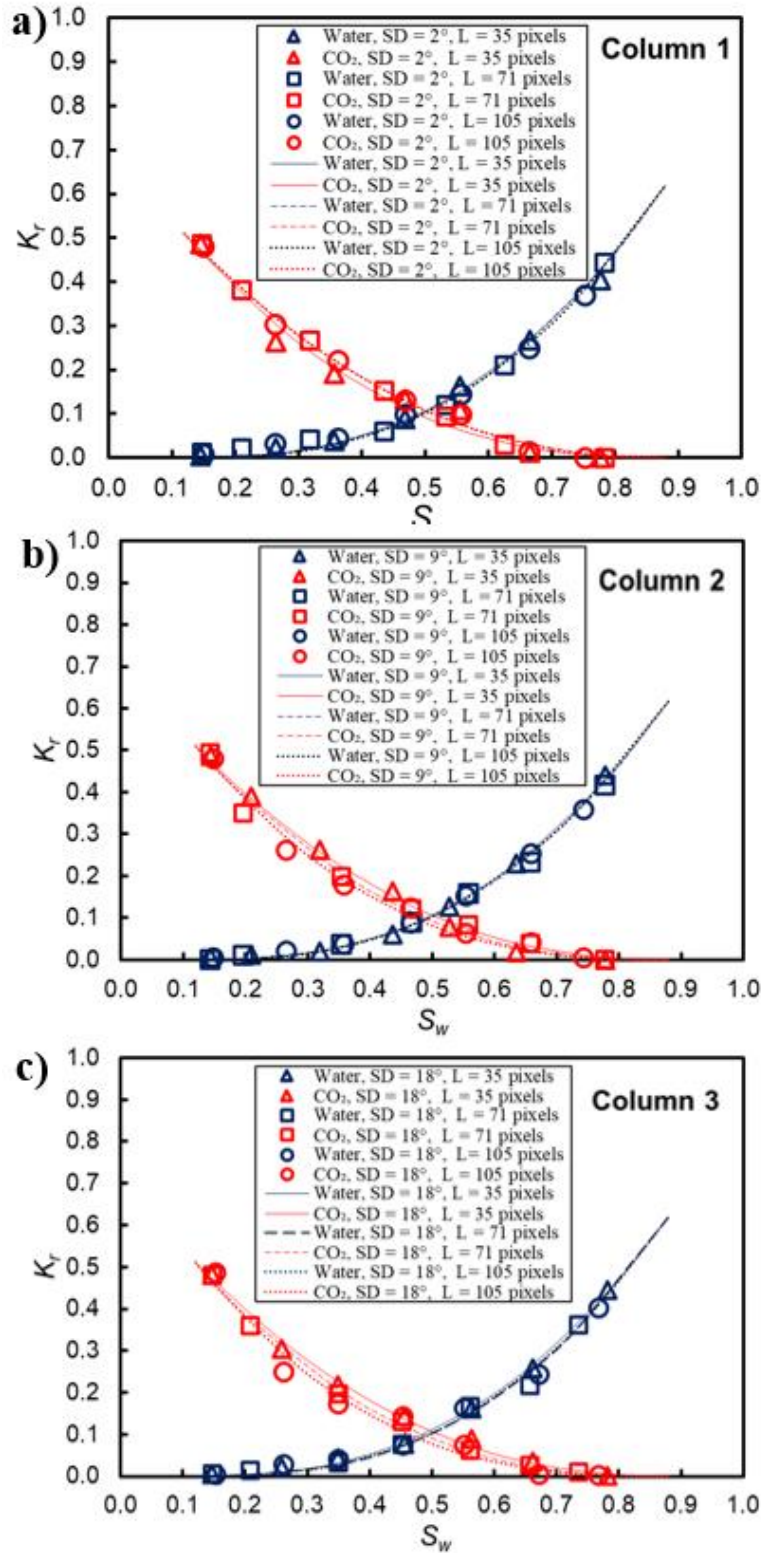


Figure 3 - 8. Relative permeability as a function of water saturation for the parameter values listed in (a) column 1, (b) column 2, and (c) column 3 of Table 3-2. The scattered data points are relative

permeabilities measured by the LB multiphase flow modeling, whereas the curves are the Corey model fitting. Columns 1, 2, and 3 represent the parameter values listed in the three columns in Table 3-2. In the figure legends, “SD” denotes the standard deviation of CA distribution.

To accurately quantify the impact of the spatial correlation length of CA distribution on the multiphase flow properties, the standard deviations between the Corey-model-fitted k_r curves were calculated as a function of water saturation and illustrated in **Figure 3-9a**. Specifically, the curve of “SD of k_{ro} with SD of CA=2°” in Figure 3-9a was calculated based on the three Corey-model-fitted k_{ro} curves shown in Figure 3-8a, which were for the spatial correlation lengths of 35, 71, and 105 pixels, separately; at a specific water saturation, the standard deviation between the three Corey-model-fitted k_{ro} values was calculated and then plotted as a function of water saturation. The same method was used to plot the other five curves in Figure 3-9a, which illustrates the impact of the varying spatial correlation length of CA distribution on the oscillation of the k_r curves. Figure 3-9a confirms that the variation (i.e., standard deviation) in the k_{ro} curves was more significant than that of the k_{rw} curves when the spatial correlation length of CA distribution changed from 35 to 71 and then 105 pixels. It was also confirmed that when the water saturation approached the two end points, the variation in the k_r curves was relatively small because the flow in the pore space was approximately single-phase flow when the water saturation was near the two end points. In addition, it was clear that, when the spatial correlation length of CA distribution changed from 35 to 71 and then 105 pixels, the variation in the k_r curves was more significant with a larger standard deviation of CA. This observation suggested that, a larger standard deviation of CA (i.e., 18°) enhanced the influence of the increasing correlation length of CA on the k_r curves compared to the smaller standard deviations of CA (i.e., 2° and 9°). This finding, associated with the observation from Figure 3-6, implies that a relatively large standard deviation of rock surface CA, combined with a relatively long spatial correlation length of CA distribution, will lead to relatively large variations in the k_r curves of the rock.

In Figure 3-9a, the standard deviations between the model-fitted relative permeability were averaged over the entire water saturation range (from 0.2 through 0.8) and then plotted as a function of the corresponding standard deviation of CA, as illustrated in Figure 3-9b. Figure 3-9b confirms that the variation in the k_{ro} curves was more significant than that of the k_{rw} curves when

the spatial correlation length of CA distribution increased from 35 to 71 and then 105 pixels. Also, it was confirmed that a larger standard deviation of CA enhanced the influence of the increasing correlation length of CA distribution on the k_r curves.

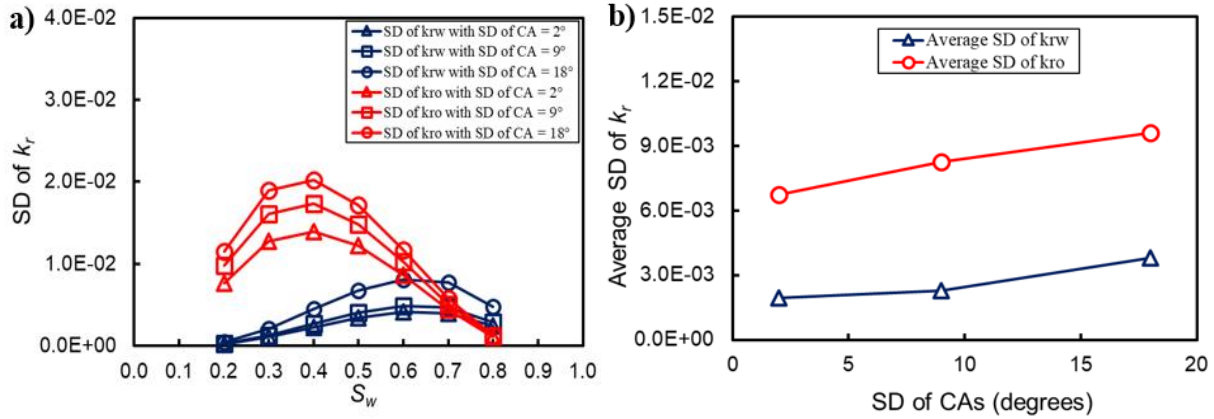


Figure 3 - 9. (a) Standard deviation between the Corey-model-fitted k_r values due to the variation in the spatial correlation length of CA distribution as a function of water saturation. (b) Average standard deviation between the Corey-model-fitted k_r curves as a function of the standard deviation of CA.

3.4. Conclusion

In this study, we conducted in-situ measurements of surface CAs in a Bentheimer sandstone after scCO_2 flooding using micro-CT scanning, and found that the pore-scale CA distribution on rock surfaces followed a log-normal distribution associated with a spatial correlation length. Based on the statistical information measured from the CT scanning, a Gaussian random field was used to model surface CA distributions that have desired standard deviations and spatial correlation lengths. The standard deviation and correlation length of CA distribution were then adjusted within a certain range of values for comprehensive sensitivity analyses to study their combined effects on the multiphase flow properties in the porous medium, which was simulated using the LB multiphase flow modeling. The LB model was accelerated using hybrid, multicore CPU/GPU parallel computing to overcome the challenges in simulating multiphase flow in a large 3D domain having $800 \times 800 \times 600$ pixels. The simulation results showed that even with the same initial fluid distribution, the changes in the statistical properties of surface CA distribution led to noticeably

different pore-scale fluid distributions in the steady-state two-phase flow process, which consequently caused the variation in the macroscopic relative permeability. The surface wettability heterogeneity (i.e., standard deviation of surface CA) had a lesser effect on the relative permeability of the wetting fluid but a more noticeable impact on the relative permeability of the non-wetting fluid. The Corey model was used to fit the LB-simulated relative permeability of water and scCO₂, and the fitting results illustrated that the variations in the relative permeability curves for both water and scCO₂ increased as the standard deviation and spatial correlation length of CA increased. These findings suggested that a relatively large standard deviation of rock surface CA, combined with a relatively long spatial correlation length of CA distribution, led to relatively large variations in the relative permeability curves of the rock. This study illustrated that it was not sufficient to only use spatially-averaged CA to describe the role of rock surface wettability on the multiphase flow properties in a 3D porous medium. Instead, the impacts of both standard deviation and spatial correlation length of surface CA must be accounted for.

To the best of our knowledge, this is the first study that explored the spatial correlation lengths associated with CA distributions on sandstone surfaces and comprehensively investigated the roles of both spatial variation and correlation length of CA on multiphase flow properties in 3D porous media. In this study, the spatial correlation length of surface CA in a Bentheimer sandstone sample was found at least two times larger than the average pore size. This was because the pore geometry and rock surface roughness and mineralogy, all of which have an impact on the measured CAs, were relatively homogeneous in the sandstone, leading to a spatial correlation length of CA distribution that spans a scale over several pore diameters. This finding suggested the necessity to account for the impact of relatively long correlation lengths that span over several pore diameters on the multiphase flow properties in 3D porous media. Additionally, the LB multiphase flow model, optimized by state-of-the-art multicore CPU/GPU parallel computing, proved to be a powerful tool in the study of the interplays and combined effects of the spatial variation and correlation length of surface CA, because in practice it is extremely challenging to fabricate 3D porous media that have desired and well-controlled surface wettability properties for laboratory experiments.

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Nomenclature

$\mathbf{C}$	color gradient
$\mathbf{C}_Y$	covariance matrix
Cov	covariance of CAs
c	lattice speed
c_Y	correlation function
D_i	side length of computing domain in the i direction
d	average pore diameter
$\mathbf{e}_q$	lattice velocity vector in the q direction
f_q	particle-distribution function in the q direction
f_{nq}^*	mass transport distribution of non-wetting phase in the q direction
f_{wq}^*	mass transport distribution of wetting phase in the q direction
g	characteristic function in two-point correlation function
j_i	fluid momentum in the i direction
k_r	relative permeability
k_{r0}	scCO ₂ relative permeability
k_{r0}^o	end-point relative permeability of scCO ₂
k_{rw}	water relative permeability
k_{rw}^o	end-point relative permeability of water
$\mathbf{L}$	lower triangular matrix in Cholesky decomposition

L	correlation lengths
L_i	correlation lengths in the i direction
m_i	moments in the i direction
m_i^{eq}	equilibrium moments in the i direction
M_{iq}	transform matrix
M_{iq}^*	inverse of M_{iq}
$\mathbf{n}$	unit normal vector of the color gradient
n_i	component of unit normal vector of the color gradient in the i direction
N	number of data points
N_o	Corey non-wetting phase exponent
N_w	Corey wetting phase exponent
$\mathbf{r}$	separation distance
S	two-point correlation function
S_{orw}	residual saturation of non-wetting phase
S_w	wetting phase saturation
S_w^*	normalized wetting phase saturation
S_{wir}	irreducible saturation of wetting phase
t	time
Δt	time step
$\mathbf{u}$	fluid velocity
w_q	weights for D3Q7 model
$\mathbf{x}$	location
x_i	coordinate of location $\mathbf{x}$ in the i direction
$\mathbf{Y}$	log CA field
Y	logarithm of CA
$\mathbf{y}$	location
y_i	coordinate of location $\mathbf{y}$ in the i direction
α	a parameter that linearly related to the interfacial tension
β	a parameter that controls the width of the interface
ϕ	porosity
φ	phase field indicator

γ	variogram
Λ	relaxation coefficient
λ	eigenvalue of correlation function
μ_Y	mean of logarithm of contact angle
μ_θ	mean of contact angle
θ	contact angle
ρ_{nw}	fluid density of non-wetting phase
ρ_w	fluid density of wetting phase
σ_Y	standard deviation of logarithm of contact angle
σ_θ	standard deviation of contact angle
ω	positive root of the characteristic equation
ξ_n	independent zero-meaned Gaussian random variables with unit variance
ψ	eigenfunction of correlation function

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Chapter 4. Role of heterogeneous surface wettability on immiscible displacement, capillary pressure, and relative permeability in a CO₂-brine-rock system

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Abstract

Surface wettability is one of the major factors that regulate immiscible fluid displacement in porous media. However, the role of pore-scale wettability heterogeneity on immiscible displacement is rarely investigated. This study investigated the impact of pore-scale wettability heterogeneity on immiscible two-fluid displacement and the resulting macroscopic constitutive relations, including the capillary pressure-water saturation curve and relative permeability curves. A digital rock model was extracted from X-ray micro-computed tomography (micro-CT) images of a Bentheimer sandstone. Heterogeneous surface wettability fields were constructed based on the standard deviation and spatial correlation length of static contact angles measured from the micro-CT images. A graphics processing unit-accelerated lattice Boltzmann model was employed to simulate the immiscible displacement processes through the primary drainage, imbibition, and second drainage stages in a CO₂-brine-rock system. Supercritical CO₂ (scCO₂) and water distributions at certain water saturations were extracted from the displacement process and then used to simulate steady-state relative permeability curves. We found that pore-scale surface wettability heterogeneity caused noticeable local scCO₂ and water redistribution under less water-wet conditions at the pore scale. At the continuum scale, the capillary pressure-water saturation curve under the heterogeneous wetting condition was overall similar to that under the homogeneous wetting condition. This is because the impact of local wettability heterogeneity on the large-scale capillary pressure-water saturation curve was statistically averaged out at the entire-sample scale. The only difference was that heterogeneous wettability led to a negative entry pressure at the primary drainage stage under the intermediate-wet condition, which was caused by local, scCO₂-wet surfaces. The impact of pore-scale wettability heterogeneity was more noticeable on the relative permeability curves. Particularly, the variation of the scCO₂ relative permeability

curve in the heterogeneous wettability scenario was more significant than that in the homogenous wettability scenario. This suggests that pore-scale wettability heterogeneity enhances the coalescence and snap-off behaviors of scCO₂ blobs, which consequently leads to more significant variations of scCO₂ relative permeability at the larger scale. This is the first study that systematically investigated the role of pore-scale contact angle heterogeneity on larger-scale capillary pressure curves and relative permeability associated with immiscible two-fluid flow in complicated, three-dimensional porous media. The findings from this study will have significant implications to numerous engineered and natural processes that involve multiphase flow in porous media, such as geological CO₂ sequestration, hydrocarbon recovery, and contaminated soil remediation.

Key words: geological CO₂ sequestration, immiscible displacement, wettability heterogeneity, *Pc-Sw* curve, relative permeability

4.1. Introduction

Mitigation of the global climate change has become an urgent and pressing challenge of our time. Reduction and prevention of emissions of CO₂, a major greenhouse gas, into the atmosphere has been gaining increasing attention in recent decades. Geological carbon sequestration (GCS) has proven a viable solution to mitigating CO₂ emissions while allowing continued large-scale consumptions of fossil fuel energy (Michael et al., 2010). Subsurface saline aquifers have been considered ideal geological formations for GCS due to their extensive distribution and vast storage capacity, which was estimated to be 320 – 10,000 gigatons of CO₂ across the world (Bachu, 2002). After the emplacement of CO₂ in a deep saline aquifer, the CO₂ exists in the supercritical phase if the temperature is higher than 31°C and pressure is higher than 1,000 psi (Chen et al., 2013). The supercritical CO₂ (scCO₂) migrates upward due to buoyancy and then spreads horizontally when it reaches the impermeable cap rock (Sathaye et al., 2014; Emami-Meybodi et al., 2015; Guo et al., 2021). It is critical to understand and predict the migration of scCO₂ in saline aquifers to ensure the long-term security of GCS (Chang et al., 2020).

The migration of injected scCO_2 in saline aquifers can be modeled as an immiscible displacement process, which is regulated by the pore geometry, fluid properties, and rock surface wettability (Tanino and Blunt, 2013). The surface wettability of a porous medium is usually characterized as the static contact angle (CA), the distribution of which on rock surfaces can be homogeneous or heterogeneous. In general, water is referred to as the wetting-phase fluid because its CA is usually smaller than 90 degrees, whereas another fluid (e.g., scCO_2 or oil) is referred to as the nonwetting-phase fluid (Fan et al., 2019). The impact of homogeneous wettability on multiphase flow in porous media has been intensively studied (Pan et al., 2004; Li et al., 2005; Boek et al., 2017; Leclaire et al., 2017). However, studies on rock samples strongly suggested that the surface wettability in a natural rock is heterogeneous (Morrow, 1975; Bradford and Leij, 1995; Hwang et al., 2006; Rucker et al., 2019; Arshadi et al., 2020; Guo et al., 2020). Previous studies usually modeled heterogeneous surface wettability as a mixture of two types of surfaces, with one being water-wet and the other being oil-wet. The heterogeneous surface wettability model can be further classified as fractional wettability and mixed wettability, depending on whether the distribution of surface wettability is a function of pore size. A fractional wettability model assumes that the distribution of wetting surfaces is independent of the pore size, whereas a mixed wettability model assumes that rock surfaces in small pores are water-wet and rock surfaces in large pores are oil-wet (Valvatne and Blunt, 2004; Skauge et al., 2007). The overall wettability of a porous medium is usually modified by changing the ratio between the wetting and non-wetting surfaces for a fractional wettability model and the extent of surface property alteration for a mixed wettability model (Zhao et al., 2018; Chang et al., 2020).

Recently published studies on in-situ measurements of surface wettability suggested that the surface wettability of a natural rock can cover a wide range of CAs rather than only two CAs (Saraji et al., 2013; Andrew et al., 2014; Alhammadi et al., 2017; Mutailipu et al., 2017; AlRatrout et al., 2018; Arshadi et al., 2020; Guo et al., 2020; Liu et al., 2020). Our previous work (Guo et al., 2020) modeled the heterogeneous surface wettability in a sandstone sample as a Gaussian random field with a spatial correlation length based on in-situ CA measurements using X-ray micro-computed tomography (micro-CT). To adequately leverage the power of pore-scale numerical simulation of multiphase flow in porous media, it is critical to accurately describe and incorporate the detailed surface wettability information into the model (Akai et al., 2019).

Constitutive relations, such as the capillary pressure-water saturation (P_c - S_w) relationship and relative permeability, are critical inputs for continuum-scale simulations of multiphase flow in porous media. The role of pore-scale wettability heterogeneity on the macroscopic constitutive relations has attracted significant attention. Previous studies have intensively investigated the displacement mechanisms under different wetting conditions (Zhao et al., 2016;Hu et al., 2017) and the effect of surface wettability on capillary pressure and relative permeability (Hwang et al., 2006;Landry et al., 2014;Zhao et al., 2018;Bakhshian and Hosseini, 2019;Chang et al., 2020;Nemer et al., 2020). In the studies on fractional wettability, the physical model for fractional-wet porous media were constructed by mixing sands having different wettability (Bradford and Leij, 1995;Hwang et al., 2006), mixing beads having designed wettability (Murison et al., 2014;Hiller et al., 2019), and mapping surface wettability fields to digital rock models (Bakhshian and Hosseini, 2019). It was observed that an increasing fraction of non-wetting surface led to increasing wetting-phase relative permeability and decreasing non-wetting-phase relative permeability (Bradford and Leij, 1995;Hwang et al., 2006). However, the impact of fractional wettability on capillary pressure is more complicated. In an oil-water or CO_2 -water system, it was observed that increased fraction of non-wetting sand reduces the capillary pressure in both the primary drainage and imbibition curves (Bradford and Leij, 1995;Hwang et al., 2006). In an air-water system, Hwang's results showed that there was no noticeable relationship between the fraction of non-wetting surface and capillary pressure (Hwang et al., 2006). Studies using beads with designed wettability patterns showed that the spatial correlation length also had an impact on capillary pressure; particularly, a smaller spatial correlation length enhanced the hysteresis in the P_c - S_w curves (Murison et al., 2014;Hiller et al., 2019).

A mixed wettability model assumes that the oil-wet surfaces were caused by the contact with oil. Mixed-wet porous media were typically constructed using the surface aging method, which altered water-wet surfaces using non-wetting fluids (Masalmeh, 2002;Tanino and Blunt, 2013;Chang et al., 2020;Qin et al., 2020). The impact of mixed wettability on relative permeability varied, which depended on the extent of surface property alteration. It was observed that mixed wettability decreased oil relative permeability and increased water relative permeability (Zou and Armstrong, 2019;Nemer et al., 2020). The influence of mixed wettability on oil relative permeability was more significant than on water relative permeability. The impact on water relative permeability was small and sometimes negligible (Landry et al., 2014). In the imbibition stage under the mixed-wet

condition, a non-monotonic relation between the initial oil saturation and remaining oil saturation was observed (Tanino and Blunt, 2013). Mixed wettability can also cause preferential non-wetting flow paths (Chang et al., 2020).

In the laboratory, it is challenging to construct a rock sample having desired heterogeneous surface wettability and to investigate displacement dynamics at the pore scale. Therefore, pore-scale simulation, such as the lattice Boltzmann (LB) method, has become a powerful tool to unravel the role of pore-scale wettability heterogeneity on large-scale displacement dynamics (Berg et al., 2013; Andrew et al., 2015; Nemer et al., 2020). The LB method also has advantages in incorporating complex physicochemical properties, such as surface wettability, solubility, and phase separation, compared to traditional computational fluid dynamics models (Shi and Tang, 2018; Zhao et al., 2018; Guo et al., 2020; McClure et al., 2021). In addition, the rapid development of graphics processing unit (GPU)-based parallel computing technologies makes the LB method an efficient numerical scheme in simulating large-scale multiphase flow in porous media (McClure et al., 2010; McClure et al., 2014; Xue and Roy, 2021).

Although many studies have been conducted to investigate immiscible two-fluid displacements in porous media, there is still a lack of fundamental understanding of immiscible displacements under heterogeneous wettability conditions. This study investigated the impact of pore-scale surface wettability heterogeneity, which has a wide range of CA distribution, on the immiscible displacement process in a Bentheimer sandstone. The heterogeneous wettability fields were generated based on the CA variance and spatial correlation length measured from X-ray micro-CT images of a Bentheimer sandstone, which were then imported into a LB multiphase flow model as rock surface properties. The goal of this study is to investigate the role of pore-scale surface wettability heterogeneity on large-scale immiscible displacement dynamics, which has extensive applications in many geo-energy and hydrogeological systems associated with multiphase flow in complicated porous media (Chen and Ewing, 1997; Hewitt, 2008; Feng et al., 2021; Li et al., 2022).

4.2. *Materials and methods*

4.2.1. *LB method for multiphase flow modeling*

The color-gradient LB multiphase flow model was used in this study for numerical simulation of immiscible two-phase displacement in the sandstone and calculations of the P_c - S_w curves and relative permeability. The LB method has proven an efficient tool to simulating multiphase flow in complex 3D porous media (McClure et al., 2014;Guo et al., 2020), and the LB model used in this study has been validated and published in our previous studies (Fan et al., 2019;Fan et al., 2020;Guo et al., 2020). In our LB model, the momentum equation is simulated using the D3Q19 lattice structure, which means there are 19 velocity directions in the 3D space. The discrete velocity vectors in D3Q19 are:

$$\begin{cases} (0,0,0) & \text{for } q = 0 \\ (\pm 1, 0, 0) & \text{for } q = 1, 2 \\ (0, \pm 1, 0) & \text{for } q = 3, 4 \\ (0, 0, \pm 1) & \text{for } q = 5, 6 \\ (\pm 1, \pm 1, 0) & \text{for } q = 7, 8, 9, 10 \\ (\pm 1, 0, \pm 1) & \text{for } q = 11, 12, 13, 14 \\ (0, \pm 1, \pm 1) & \text{for } q = 15, 16, 17, 18 \end{cases} \quad (4-1)$$

In order to reduce the computing costs, the mass transfer equation was simulated using a D3Q7 lattice structure (McClure et al., 2014). The corresponding velocity vectors in D3Q7 are the first seven vectors in Equation 1. The mass distributions for the wetting fluid and non-wetting fluid are constructed using their densities, ρ^w and ρ^n , and the velocity, $\mathbf{u}$:

$$\begin{aligned} g_q^w &= w_q \left[\rho^w (1 + \mathbf{e}_q \cdot \mathbf{u}) + \beta (\mathbf{e}_q \cdot \mathbf{n}) \rho^n \rho^w / (\rho^n + \rho^w) \right] & q = 0, 1, 2, \dots, 6 \\ g_q^n &= w_q \left[\rho^n (1 + \mathbf{e}_q \cdot \mathbf{u}) - \beta (\mathbf{e}_q \cdot \mathbf{n}) \rho^n \rho^w / (\rho^n + \rho^w) \right] & q = 0, 1, 2, \dots, 6 \end{aligned} \quad (4-2)$$

where weights w_q are $1/3$ for $q = 0$ and $1/9$ for $q = 1, 2, \dots, 6$, and $\mathbf{n}$ is the unit vector normal to the fluid-fluid interface. The superscripts w and n refer to the wetting fluid and nonwetting fluid, respectively.

The fluid densities are then calculated as:

$$\rho^i(\mathbf{x}, t + \Delta t) = \sum_{q=0}^6 g_q^i(\mathbf{x} - \mathbf{e}_q \Delta t, t) \quad i = w, n \quad (4-3)$$

In the multi-relaxation-time approach, the collision process is simulated in the moment space. The transformation between moments, $\mathbf{m}$, and the distribution function, $\mathbf{f}$, are written as:

$$\mathbf{m} = \mathbf{M} \cdot \mathbf{f}, \mathbf{f} = \mathbf{M}^{-1} \cdot \mathbf{m} \quad (4-4)$$

where $\mathbf{M}$ is the transformation matrix, and $\mathbf{M}^{-1}$ is the inverse of $\mathbf{M}$.

The particle distribution evolution equation is written as:

$$f_q(\mathbf{x} + \mathbf{e}_q \Delta t, t + \Delta t) - f_q(\mathbf{x}, t) = \sum_{i=0}^{Q-1} M_{qi}^{-1} \Lambda_i (m_i^{eq} - m_i) \quad q = 0, 1, 2, \dots, 18 \quad (4-5)$$

where $f_q(\mathbf{x}, t)$ is the particle distribution function at location $\mathbf{x}$ and time t travelling in the q^{th} direction; $f_q(\mathbf{x} + \mathbf{e}_q \Delta t, t + \Delta t)$ is the particle distribution function at the adjacent lattice node after each streaming step in the q^{th} direction; Λ_i is the i^{th} relaxation rate of moment m_i toward its corresponding equilibrium value, m_i^{eq} .

To simulate the interfacial tension, additional terms are incorporated into the non-zero equilibrium moments:

$$\begin{aligned} m_1^{eq} &= (j_x^2 + j_y^2 + j_z^2) + \alpha |\mathbf{C}| \\ m_9^{eq} &= (2j_x^2 - j_y^2 - j_z^2) + \alpha \frac{|\mathbf{C}|}{2} (2n_x^2 - n_y^2 - n_z^2) \\ m_{11}^{eq} &= (j_y^2 - j_z^2) + \alpha \frac{|\mathbf{C}|}{2} (n_y^2 - n_z^2) \\ m_{13}^{eq} &= j_x j_y + \alpha \frac{|\mathbf{C}|}{2} n_x n_y \\ m_{14}^{eq} &= j_y j_z + \alpha \frac{|\mathbf{C}|}{2} n_y n_z \\ m_{15}^{eq} &= j_x j_z + \alpha \frac{|\mathbf{C}|}{2} n_x n_z \end{aligned} \quad (4-6)$$

where j_x, j_y , and j_z are fluid momentums in the x, y, and z directions, respectively; α is the parameter to adjust the interfacial tension; $\mathbf{C}$ is the color gradient; n_x, n_y , and n_z are the components of the unit norm vector, $\mathbf{n}$, in the x, y, and z directions, respectively.

In the LB simulation of immiscible two-fluid displacement, a buffer layer with a thickness of six lattice units (lus) was placed at both ends of the rock in the main flow direction. The buffer layer at the inlet was set as scCO₂ whereas the buffer layer at the outlet was set as water. The viscosity ratio of water to scCO₂ was set as 4:1 (Chen and Zhang, 2009). The pressure boundary condition was applied at the inlet and outlet, and the no-slip boundary condition was applied at rock surfaces. The rock was initially saturated with water. We gradually changed the pressure difference between the two ends of the rock sample to let the system go through the primary drainage (PD), imbibition

(IM), and secondary drainage (SD) stages. The capillary pressure (i.e., pressure difference between the non-wetting fluid and wetting fluid) and water saturation in the sample were recorded when the flow reached a steady state at each pressure difference. At each water saturation, scCO_2 and water distribution in the three-dimensional (3D) pore space was extracted and then used as the initial condition to simulate the steady-state relative permeability curves. In the simulation of relative permeability, fluid flow was driven by applying a constant external body force with a periodic boundary condition in the main flow direction, which aimed to maintain a constant water saturation in the domain and to mimic fractional flow experiments typically used to measure relative permeability in the laboratory (Fan et al., 2019). To address the high demand of computing costs associated with the LB method, a hybrid, multicore central processing unit (CPU)/GPU parallel computing acceleration algorithm was employed in the implementation of the LB modeling (McClure et al., 2014; Chen et al., 2016).

4.2.2. Generation of heterogeneous surface wettability

The wettability of a rock surface can be characterized using the static CA measured on the sandstone surface. In our previous study (Guo et al., 2020), we conducted in-situ measurements of static CAs on the rock surfaces in a Bentheimer sandstone based on high-resolution X-ray micro-CT scanning (Wang et al., 2022). The measurements showed that the surface CA distribution follows a lognormal distribution and can be modeled as a Gaussian random field with a spatial correlation length. The log wettability field, $\mathbf{Y}$, is defined as $\mathbf{Y} = \log(\boldsymbol{\theta})$, where $\boldsymbol{\theta}$ is the CA random field. The mean and variance of $\boldsymbol{\theta}$ are related to the mean and variance of $\mathbf{Y}$ by $\mu_{\theta} = e^{\mu_Y + \sigma_Y^2/2}$ and $\sigma_{\theta}^2 = (e^{\sigma_Y^2} - 1) \cdot e^{2\mu_Y + \sigma_Y^2}$, respectively (Chen and Zeng, 2015). The correlation function of the log wettability field between points $\mathbf{x}$ and $\mathbf{y}$ in the 3D space, $c_Y(\mathbf{x}, \mathbf{y})$, is calculated as $c_Y(\mathbf{x}, \mathbf{y}) = \sigma_Y^2 \exp[-(|x_1 - y_1|/L_1 + |x_2 - y_2|/L_2 + |x_3 - y_3|/L_3)]$, where L_1 , L_2 , and L_3 are the correlation lengths in the three principal directions (Guo et al., 2020).

We used the Karhunen-Loève expansion (KLE) method to efficiently generate the heterogeneous wettability field on rock surfaces, which reduces the time and computer memories required compared to other methods that directly generate 3D random fields (Zhang and Lu, 2004). In the KLE method, the correlation function of the log wettability field, $c_Y(\mathbf{x}, \mathbf{y})$, is decomposed in the form of eigenvalues and eigenfunctions:

$$c_Y(\mathbf{x}, \mathbf{y}) = \sum_{n=1}^{\infty} \lambda_n \psi_n(\mathbf{x}) \psi_n(\mathbf{y}) \quad (4-7)$$

where λ_n and $\psi_n(\mathbf{x})$ are the n^{th} eigenvalue and eigenfunction, respectively.

The wettability fields are then generated using the KLE method:

$$\mathbf{Y}(\mathbf{x}) = \langle \mathbf{Y}(\mathbf{x}) \rangle + \sum_{n=1}^{\infty} \xi_n \sqrt{\lambda_n} \psi_n(\mathbf{x}) \quad (4-8)$$

where ξ_n are independent zero-mean Gaussian random variables having a unit variance. In practice, finite terms in the KLE method are employed to approximate the desired random fields (Chen et al., 2013). The details of this method were given in (Zhang and Lu, 2004; Guo et al., 2020). In the next step, the surface wettability of the sandstone is constructed by mapping the generated wettability field onto the surface of the Bentheimer sandstone.

4.2.3. Rock models with heterogeneous surface wettability

The 3D digital rock model in this study has dimensions of $240 \times 240 \times 240$ pixels, with a micro-CT resolution of $6.67 \mu\text{m}$ per pixel length. The porosity of the rock is 26%. Iglaue et al. (2015) classified the rock surface wettability in a CO_2 -water-rock system into 7 types based on the value of the static surface CA: completely water-wet (i.e., a CA of 0°), strongly water-wet (0° - 50°), weakly water-wet (50° - 70°), intermediate wet (70° - 110°), weakly CO_2 -wet (110° - 130°), strongly CO_2 -wet (130° - 180°), and completely CO_2 -wet (180°). In this study, we used this classification to characterize the wetting conditions of rocks. In a saline aquifer, the sandstone is usually water-wet or intermediate wet. Therefore, we only generated heterogeneous strongly water-wet (SWW), weakly water-wet (WWW), and intermediate wet (IW) fields having mean CAs of 25° , 60° , and 90° , respectively. The standard deviation and correlation length of the CA distributions were 9° , and $118.6 \mu\text{m}$, respectively, which were measured in the Beithermer sandstone core after two drainage-imbibition cycles of core flooding experiments using in-situ X-ray micro-CT (Guo et al., 2020). The generated heterogeneous wettability fields were then projected onto the rock surfaces on the Bentheimer rock, as shown in **Figure 4-1**. We then conducted LB multiphase flow modeling in all of the three rock models to simulate the immiscible two-phase displacement processes that included the PD, IM, and SD stages.

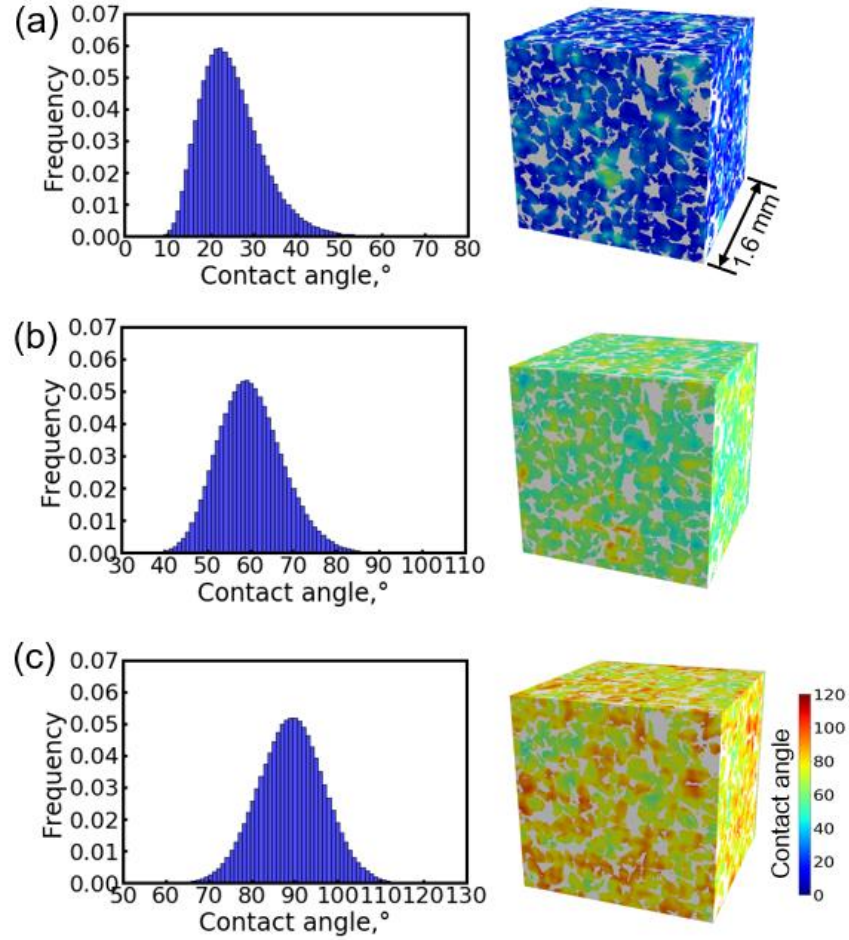


Figure 4 - 1. CA distributions of generated heterogeneous wettability fields and corresponding rock models under (a) SWW, (b) WWW, and (c) IW conditions. In the rock models, the pore space is white, and the solid is rendered with a color bar ranging from blue (water-wet) to red (CO₂-wet) that represents the range of CA values.

4.2.4. Corey model for fitting relative permeability curves

The Corey model was used to fit the LB-simulated water and scCO₂ relative permeabilities, which assumes that the relationship between relative permeabilities and normalized water saturations follows a power law:

$$k_{rw} = k_{rw}^o S_w^{*N_w} \quad (4-9)$$

$$k_{rg} = k_{rg}^o S_w^{*N_g} \quad (4-10)$$

where k_{rw} and k_{rw}^o are water relative permeability and end-point water relative permeability, respectively; k_{rg} and k_{rg}^o are scCO₂ relative permeability and end-point scCO₂ relative permeability, respectively; N_w and N_g are the power-law exponents for water and scCO₂ relative permeability curves, respectively. S_w^* is the normalized water saturation defined as $S_w^* = (S_w - S_{wir}) / (1 - S_{wir} - S_{grw})$, where S_w is water saturation, S_{wir} is irreducible water saturation, and S_{grw} is residual scCO₂ saturation.

4.3. Results and discussion

4.3.1. Pore-scale scCO₂ and water distribution

The pore geometry, rock surface wettability, and saturation history determine the scCO₂ and water distribution at the pore scale. Wettability is the competition between scCO₂ and water to adhere to rock surfaces (Nemer et al., 2020). Pore-scale heterogeneity of rock surface wettability can cause redistribution of scCO₂ and water in the pore space. **Figures 4-2, 4-3, and 4-4** demonstrate pore-scale scCO₂ and water distribution under different wetting conditions in the PD, IM, and SD stages. To better demonstrate the surface wettability heterogeneity, pore-scale surface wettability distributions were illustrated in Figures 4-2, 4-3, and 4-4 using the color bars that indicated the distribution of surface CAs.

Under the SWW and WWW conditions, the shape and distribution of scCO₂ blobs were determined primarily by the pore geometry. The scCO₂ blobs were more likely to reside on the less water-wet surfaces. As shown in Figure 4-2, the distribution of scCO₂ under the SWW condition in the PD and SD stages were almost identical, whereas the distribution of scCO₂ in the IM stages was slightly different from that in the PD and SD stages. In intermediate-sized and large-sized pores, as indicated by the red ellipse and rectangle, respectively, the saturation and shape of scCO₂ blobs were similar among the three displacement stages, whereas in small pores the difference can be identified observed. In the SWW heterogeneous wettability scenario, all CAs were less than 90° with an average CA of 25°. This indicated that in this scenario the scCO₂ always had lower affinity to rock surfaces compared to water.

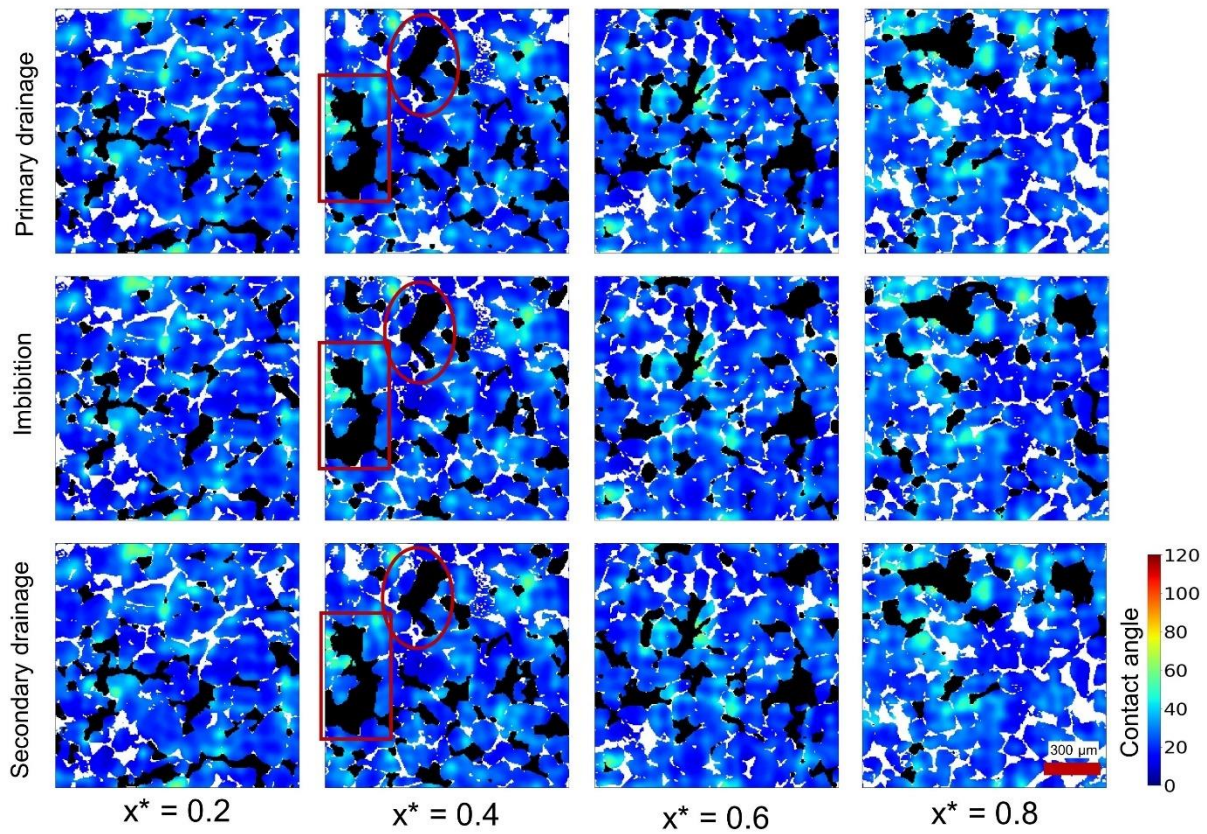


Figure 4 - 2. Pore-scale scCO₂ and water distribution at various dimensionless distances, x^* , under the SWW condition with a water saturation of 0.5 in the Bentheimer sandstone. The scCO₂ is marked in black and water is marked in white. Sandstone is demonstrated with a color bar ranging from blue to red which indicate the distribution of surface CA values. The red ellipse and rectangle mark the scCO₂ distributions in intermediate and large pores, respectively.

Figure 4-3 demonstrates the distribution of scCO₂ under the WWV condition with an average CA of 60°. Larger CAs led to weaker affinity of water to rock surfaces compared to the SWW condition, which resulted in enhanced CO₂ mobility. This was confirmed by the noticeable CO₂ saturation changes in intermediate- and large-sized pores among the PD, IM, and SD stages, which suggested that the scCO₂ blobs were able to move through small pore throats and thus were not trapped in intermediate- and large-sized pores. This was further confirmed by **Figure 4-4**, where rock surfaces were under the IW condition. It was noticeable that in this scenario the scCO₂ saturation variations in intermediate- and large-sized pores were significant, which suggested that

the rock surfaces were neutral-wet, leading to reduced capillary barriers and consequently enhanced mobility for both fluids.

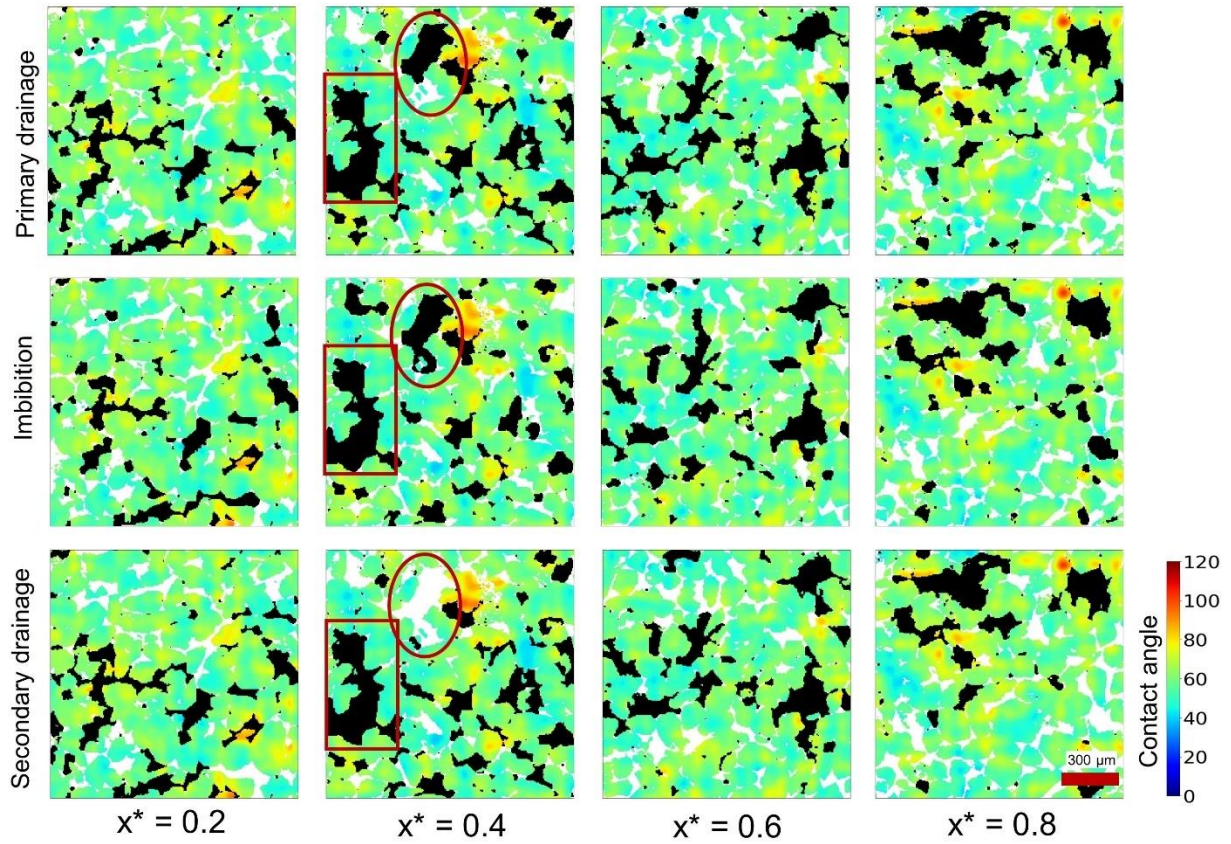


Figure 4 - 3. Pore-scale scCO_2 and water distribution at various dimensionless distances under the WWW condition with a water saturation of 0.5 in the Bentheimer sandstone.

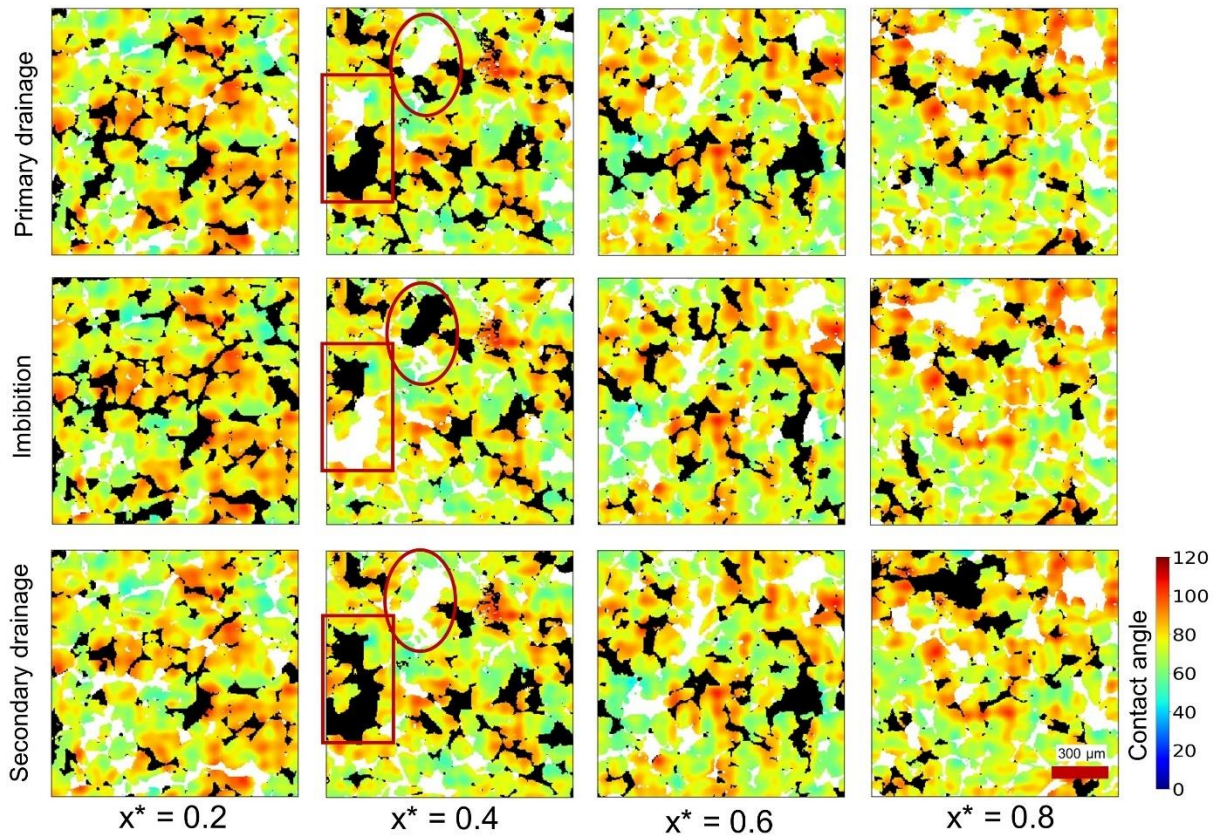


Figure 4 - 4. Pore-scale scCO₂ and water distribution at various dimensionless distances under the IW condition with a water saturation of 0.5 in the Bentheimer sandstone.

Slice-averaged water saturation against the dimensionless distance, x^* , were plotted to elucidate the impact of rock surface wettability on the scCO₂ distribution in the longitudinal (i.e., main flow) direction. **Figure 4-5** illustrates the water saturation distributions under the SWW, WWW, and IW scenarios, and the overall water saturation was 0.5 for all these scenarios. It is noticeable that the water saturation profiles were similar between the PD, IM, and SP stages under the SWW and WWW conditions, which suggested that scCO₂, the non-wetting fluid, was trapped in large- and intermediate-sized pores under the SWW and WWW conditions due to the capillary barrier pressures in small pores and throats, leading to reduced mobility of scCO₂ and consequently small variations of local fluid saturations. Conversely, under the IW condition, the capillary barrier pressures associated with small pores and throats were mitigated due to the neutral CAs on rock surfaces, resulting in enhanced scCO₂ mobility throughout the entire sample and consequently

different water saturation profiles between the PD, IM, and SD stages. This suggested that surface wettability played a more noticeable role on pore- and large-scale fluid distributions under the IW condition compared to the SWW and WWW conditions. These observations were consistent with the pore-scale fluid distributions shown in Figures 4-2, 4-3, 4-4. Note that during the PD, IM, and SD stages, the left end of the core (i.e., $x^*=0$) was connected to a scCO₂ reservoir whereas the right end (i.e., $x^*=1$) was connected to a water reservoir, which explains why the water saturation was equal to zero at the left end and equal to one at the right end.

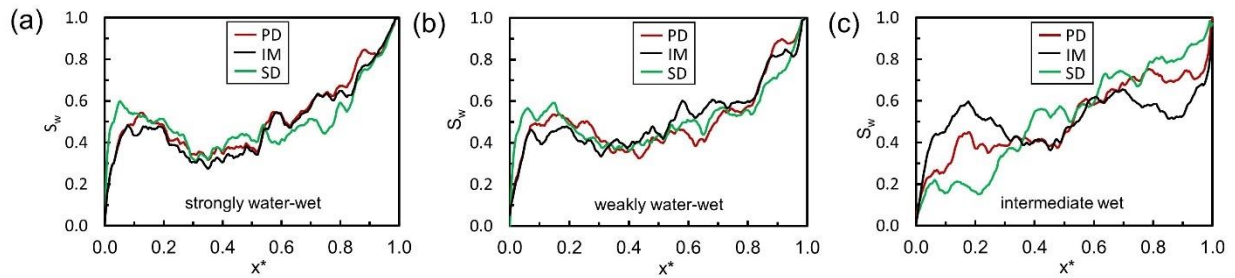


Figure 4 - 5. Water saturation profile along the main flow direction under (a) SWW condition, (b) WWW condition, and (c) IW condition.

4.3.2. Capillary pressure

The relation between capillary pressure and water saturation, commonly characterized as the P_c - S_w curve, is a fundamental constitutive equation for predicting CO₂ migration and capillary trapping (Tokunaga et al., 2013). The factors regulating the P_c - S_w curve including pore structure, rock surface wettability, and saturation history (Bakhshian and Hosseini, 2019). In this work, the P_c - S_w curve under the SWW, WWW, and IW conditions were numerically simulated using the LB multiphase flow model. During the two-phase displacement, the pressure difference between the inlet and outlet was gradually increased or decreased, leading to varying capillary pressure in the drainage-imbibition-drainage process. The simulation time at each pressure difference was adequately long to allow the scCO₂-brine-rock system to reach a steady state.

Figure 4-6 illustrates the P_c - S_w curves for both homogeneous and heterogeneous surface wettability under the SWW, WWW, and IW conditions. In the homogeneous scenario, the surface CA was a constant over the entire rock surface and equal to the average surface CA in the

heterogeneous scenario. Figures 4-6a, 4-6b, and 4-6c show that the P_c - S_w curves for homogeneous and heterogeneous surface wettability were almost identical. This suggests although pore-scale heterogeneity induced local redistribution of $scCO_2$ and water blobs, it had almost no effect on the large-scale P_c - S_w curve which was an average property of the entire sample. In other words, the local variations of $scCO_2$ and water distribution caused by surface wettability heterogeneity were statistically averaged out at the entire-sample scale. One noticeable difference between the homogeneous and heterogeneous scenarios can be found under the IW condition as shown in Figure 4-6c, where the entry capillary pressure of the PD section was zero for the homogeneous scenario whereas it was negative for the heterogeneous scenario. This was because under the IW condition and heterogeneous surface wettability a large fraction of rock surfaces had CAs larger than 90 degrees, leading to local, CO_2 -wet surfaces at these areas; consequently, $scCO_2$ can migrate into the rock spontaneously, leading to a negative entry capillary pressure. In practice, a negative entry capillary pressure has significant influences on field-scale CO_2 migration and distribution in a saline aquifer (Singh et al., 2021).

Figure 4-6d demonstrates the comparison of the P_c - S_w curves between the SWW, WWW, and IW conditions in rock samples having heterogeneous surface wettability. When surface wettability changed from SWW to IW sequentially, the P_c - S_w curves shifted in the left and downward directions, leading to a lower capillary pressure at the same water saturation, a lower irreducible water saturation at the end of the PD stage, and a higher residual CO_2 saturation at the end of the IM stage.

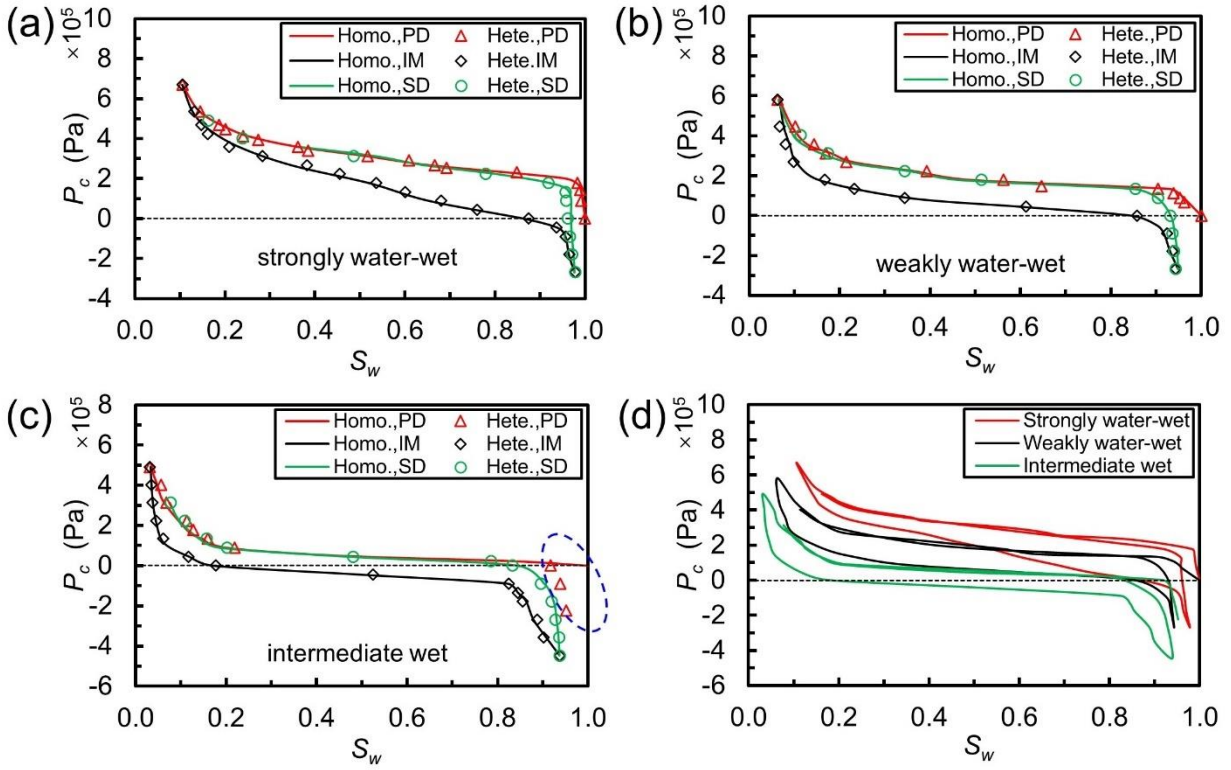


Figure 4 - 6. Comparison of P_c - S_w curves between homogeneous and heterogeneous wettability distributions under (a) SWW, (b) WWW, and (c) IW conditions. (d) Comparison of P_c - S_w curves under heterogeneous SWW, WWW, and IW conditions.

4.3.3. Relative permeability

The relative permeabilities under homogeneous and heterogeneous wetting conditions were also simulated. The capillary number in these simulations was 10^{-5} , which suggested that the interfacial force dominated the transport of the two fluids (Fan et al., 2019). **Figure 4-7** illustrates the relative permeability curves under heterogeneous rock surface wettability and the SWW, WWW, and IW conditions. When the system moved from the PD stage into the IM stage, the relative permeability of scCO₂ decreased whereas the relative permeability of water increased. In other words, the relative permeability curves rotated in the counterclockwise direction. This was because in the PD stage, scCO₂ was injected into the rock, leading to enhanced connectivity of scCO₂ in the pore space, especially through small pore throats, which was favorable for the relative permeability of scCO₂ and unfavorable for the relative permeability of water. In the IM stage, water returned into the rock, leading to enhanced connectivity of water and disconnected scCO₂ blobs trapped in big

pores, which enhanced the relative permeability of water and decreased the relative permeability of scCO₂. Based on the same mechanism, when the system moved from the IM stage into the SD stage, the relative permeability of water decreased whereas the relative permeability of scCO₂ increased (i.e., the relative permeability curves rotated in the clockwise direction). These phenomena can be clearly observed under the IW condition (i.e., Figure 4-7c) because the average rock surface CA in this case was 90 degrees, leading to enhanced mobility for both fluids. Conversely, under the SWW (i.e., Figure 4-7a) and WWW (i.e., Figure 4-7b) conditions these variations were not as noticeable as under the IW condition, because the water-wet rock surfaces limited the mobility of both fluids, which was confirmed in Figures 4-2 and 4-3. These findings showed that the relative permeability can be influenced by the saturation history.

In addition, it was observed that in all of these wettability conditions (i.e., Figures 4-7a, 4-7b, and 4-7c) the variation of the scCO₂ relative permeability curves between the PD, IM, and SD stages was more significant than that of the water relative permeability curves. This was because the viscosity of scCO₂ was 25% of water viscosity (Chen and Zhang, 2009). During the PD and SD stages, a low-viscosity fluid (i.e., scCO₂) was forced to displace a high-viscosity fluid (i.e., water), leading to scCO₂ coalescence and finger-shaped displacement fronts, thereby noticeably enhancing the connectivity and consequently the relative permeability of scCO₂. During the IM stage, scCO₂ was subject to snap-off due to its lower viscosity compared to water, leading to isolated scCO₂ blobs trapped in large pores, which significantly reduced the connectivity and consequently the relative permeability of scCO₂. Therefore, the variation of the scCO₂ relative permeability curves was more noticeable than water when the system went through the PD, IM, and SD stages.

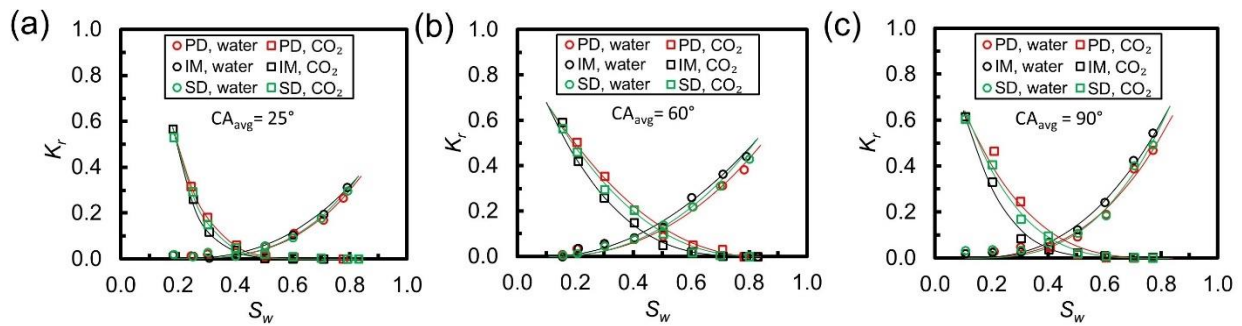


Figure 4 - 7. Relative permeabilities for water and scCO₂ under heterogeneous (a) SWW, (b) WWW and (c) IW conditions. The scatter data points are LB-simulated relative permeabilities, whereas the solid lines are fitted relative permeability curves using the Corey model.

Figure 4-8 illustrates the relative permeability curves under homogeneous rock surface wettability and the SWW, WWW, and IW conditions. The overall evolution pattern of the relative permeability curves was similar to that in the heterogeneous wettability scenario when the system went through the PD, IM, and SD stages. However, it can be observed that the variation of the scCO₂ relative permeability curves between the PD, IM, and SD stages was less than that in the heterogeneous wettability scenario, especially under the WWW and IW conditions. This suggests that pore-scale CA heterogeneity enhances the coalescence and snap-off behaviors of scCO₂ blobs, as described before, which consequently leads to more significant variations of scCO₂ relative permeability at the larger scale.

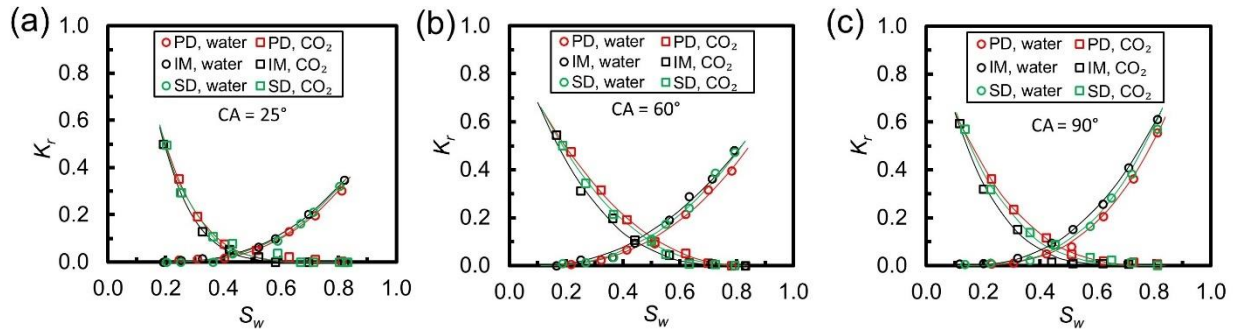


Figure 4 - 8. Relative permeabilities for water and scCO₂ under homogeneous (a) SWW, (b) WWW and (c) IW conditions. The scatter data points are LB-simulated relative permeabilities, whereas the solid lines are fitted relative permeability curves using the Corey model.

To quantify the role of surface wettability heterogeneity on relative permeability, the standard deviations between the Corey-model-fitted relative permeabilities were calculated. Specifically, the relative permeabilities in the water saturation range between 0.2 and 0.8 were used. At each water saturation, the relative permeability values from the PD, IM, and SD relative permeability curves were extracted and then the standard deviation of these three values was calculated. The

average standard deviation over the entire water saturation domain was calculated, which indicates the variation between the PD, IM, and SD relative permeability curves. **Figure 4-9** illustrates the average standard deviations for the water and scCO₂ relative permeability curves under the three surface wettability conditions. It is clear that under the WWW and IW conditions the average standard deviations of the scCO₂ relative permeability curves between the PD, IM, and SD stages in the heterogeneous wettability scenario were noticeably higher than those in the homogeneous wettability scenario, which confirms the observations in Figures 4-8, and 4--9. In addition, it is clear that the average standard deviations of the scCO₂ relative permeability curves between the PD, IM, and SD stages were always higher than those for water in both the homogeneous and heterogeneous wettability scenarios, which is also consistent with the observations in Figures 4-8, and 4--9.

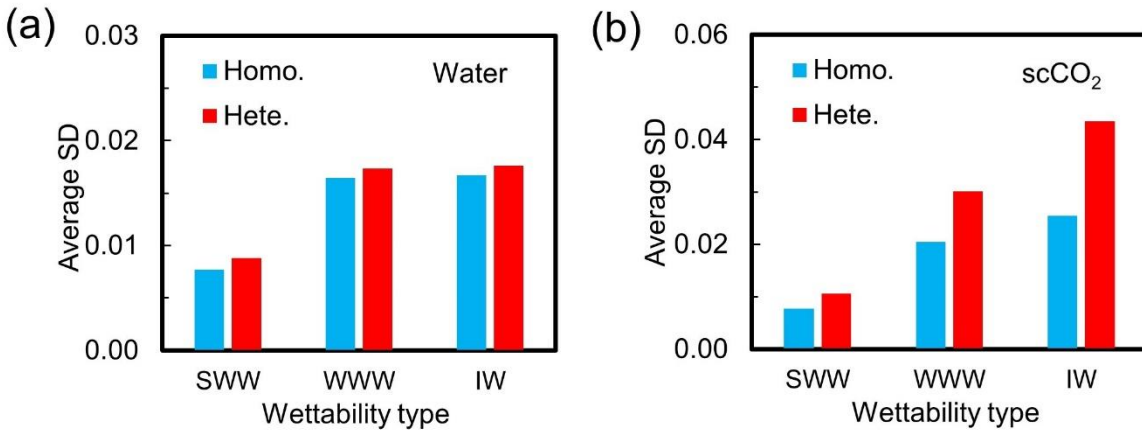


Figure 4 - 9. Average standard deviations (SDs) of relative permeability curves for water (a) and scCO₂ (b) under the SWW, WWW, and IW conditions.

4.4. Summary and conclusion

Surface wettability is one of the major factors that regulate immiscible two-phase displacements in porous media. This study modeled heterogeneous surface wettability in a Bentheimer sandstone sample of which the 3D pore structure information was obtained using X-ray micro-CT scanning. The pore-scale, heterogeneous surface wettability fields were generated using Gaussian random fields based on the mean, standard deviation, and spatial correlation length obtained from in-situ

measurements of CAs in the micro-CT images. The immiscible two-phase displacements were simulated using a LB multiphase flow simulator which was accelerated with a hybrid, multicore CPU/GPU parallel computing algorithm. The simulation results indicated that pore-scale heterogeneity of rock surface wettability caused noticeable redistribution of fluids at the pore scale. Particularly, when the CO₂-water-rock system switched from the SWW condition to IW condition, scCO₂ blobs tended to reside in regions having relatively large CAs. The wettability heterogeneity coupled with different saturation histories (i.e., PD, IM, and SD stages) enhanced the variations in pore-scale scCO₂ and water distribution, especially under the IW condition.

Pore-scale surface wettability heterogeneity influences the P_c - S_w curves, which characterize the macroscopic properties in immiscible two-phase displacements. Under the heterogeneous IW condition, the entry pressure of the PD stage was negative, whereas it was zero under the homogeneous IW condition. The negative entry pressure in the heterogeneous CA scenario was caused by local, CO₂-wet rock surfaces, which has critical implications to large-scale geological CO₂ sequestration. In other stages (i.e., IM and SD), the P_c - S_w curves were almost identical between the homogeneous and heterogeneous wetting conditions. The finding suggested that the local effects of surface wettability heterogeneity on the P_c - S_w curve were averaged out at the entire-sample scale.

The relative permeability curves were affected by the saturation history under both homogeneous and heterogeneous wetting conditions. The imbibition process increased the relative permeability of water and decreased the relative permeability of scCO₂, compared to the drainage process. Under the SWW condition, the effects of pore-scale wettability heterogeneity on the relative permeability curves were not noticeable. Under heterogeneous WWW and IW conditions, the variation of the scCO₂ relative permeability curve was more significant than that in the homogenous wettability scenario. This is because pore-scale wettability heterogeneity enhances the coalescence and snap-off behaviors of scCO₂ blobs when the system goes through the PD, IM, and SD stages, thereby leading to more significant variations of scCO₂ relative permeability curves at the larger scale.

This study demonstrated the effects of pore-scale surface wettability heterogeneity on microscopic fluid distribution, macroscopic P_c - S_w relationship and relative permeability. The findings advanced our understanding of the role of pore-scale wettability heterogeneity on immiscible two-

phase displacement in complicated 3D porous media, which has a wide range of applications in many natural and engineered processes such as geological carbon storage, contaminated soil remediation, flow control in micro-chips, and advanced manufacturing.

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Chapter 5. A Novel Experimental Study on Density-driven Instability and Convective Dissolution in Porous Media

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Abstract

Geological carbon dioxide (CO₂) sequestration (GCS) in deep saline aquifers is a promising solution to mitigating the impact of anthropogenic CO₂ emissions on global climate change. Dissolution of CO₂ in brine is a primary mechanism to ensure the long-term security of GCS. CO₂ dissolved in formation water increases the solution density and thus can lead to miscible density-driven downward convection, which is favorable for GCS because it significantly accelerates the sequestration process. Onset of density-driven instability and onset of convective dissolution are two critical events in the transition process from a diffusion-dominated regime to a convection-dominated regime. Experimental studies on miscible density-driven convection have been extremely limited due to the challenges associated with the measurement of in situ solute concentration, which prevents us from obtaining advanced understanding of this important hydrogeological process. In the laboratory, we developed an empirical correlation between transmitted visible light intensity and in situ solute concentration, which featured the primary novelty of this study and enabled direct measurements of solute concentrations in the spatial and temporal domains and consequently the mass flux across the top interface. Based on the novel and well-controlled experimental techniques, we measured the critical Rayleigh-Darcy number and critical times for the onset of density-driven instability and convective dissolution. This is the first study to determine these critical system parameters using experimental methods. In practice, the determination of the critical time for the onset of convective dissolution has important applications in field-scale GCS projects because it marks a crucial moment when the overall dissolved CO₂ mass flux starts to accelerate due to density-driven downward convection. The findings from this experimental study also have practical applications in many other engineered and natural processes,

such as geothermal convection, heat transfer due to subsurface nuclear waste disposal, and variable-density groundwater flow.

Keywords: geological CO₂ sequestration, convective dissolution, density-driven instability, characteristic time, experimental study

5.1. *Introduction*

When a layer of viscous fluid is confined between two horizontal boundaries and heated from below, the fluid near the bottom boundary expands, leading to reduced density and a net buoyancy force in the opposite direction of the gravity. When the temperature difference between the top and bottom boundaries exceeds a certain threshold, the system becomes unstable and the denser fluid near the top boundary penetrates downward, resulting in density-driven downward convection. This process is referred to as the Rayleigh-Bénard convection and was first studied by Rayleigh (1) and Jeffreys (2, 3). If a porous medium saturated with a fluid is heated at the bottom boundary, similar instability can occur in the porous medium, which was first studied by Horton and Rogers (4) and Lapwood (5) and is referred to as the Rayleigh-Darcy or Horton-Rogers-Lapwood instability.

In addition to temperature gradients, fluid density variation can also be caused by solute transport. One example is geological carbon sequestration (GCS), which is permanent disposal of CO₂ in geological formations and has been considered a promising solution to reduce continuous CO₂ buildup in the atmosphere. Geological formations for CO₂ injection include deep coal beds, depleted oil and gas reservoirs, deep-sea sediments, and deep saline aquifers (6-13). Specifically, saline aquifers are permeable porous media filled with non-potable water and usually covered by low-permeability cap rocks at the top boundary. Saline aquifers are preferable for GCS because they have the highest storage capacity globally (7). The Sleipner Field project in Norway is one of the first commercial GCS projects within saline aquifers, which stores one million tons of CO₂ per year (14). In the U.S., several field CO₂ injection projects in saline aquifers have been conducted at the pilot and demonstration scales (15). GCS has been considered the only viable technology to mitigate CO₂ emissions while allowing continued large-scale use of fossil fuels (8).

When CO₂ is injected into deep saline aquifers with a pressure higher than 73.8 bar and temperature higher than 31.0 °C, it exists in the supercritical phase. Injected supercritical CO₂ (scCO₂) migrates upward due to the buoyancy until it is stopped by the low-permeability cap rock. Meanwhile, scCO₂ dissolves in brine. Brine saturated with dissolved CO₂ has a density increase around 10 kg/m³ (10, 14, 16). Increased brine density near the scCO₂-brine interface can cause miscible density-driven downward convection, which is favorable for improving the long-term security of CO₂ storage. This CO₂ trapping mechanism is referred to as convective mixing (14) or convective dissolution (17). Convective dissolution drives dissolved CO₂ away from the scCO₂-brine interface, which accelerates subsequent scCO₂ dissolution and thus facilitates the overall mass transfer rate from scCO₂ to brine. In a previous pore-scale study (16), we confirmed that CO₂ mass transfer by means of convective mixing is significantly faster than that driven by pure molecular diffusion. Sathaye et al. (18) used geophysical and geochemical data to show that convective mixing in the Bravo Dome, a large natural CO₂ field in New Mexico, led to a CO₂ mass flux of 0.1 g/(m²y). This work provided field evidence of convective mixing. In contrast, the convective CO₂ mass flux at the Sleipner Field was estimated as high as 20 kg/(m²y) due to its much higher formation permeability than the Bravo Dome (17).

There are several critical system parameters that regulate the behaviors of miscible density-driven downward convection. The first is the Rayleigh-Darcy number (Ra), which is a dimensionless number that describes the ratio of gravitational instability to molecular diffusion. Density-driven instability and convective dissolution can only occur when Ra exceeds a certain minimum value, which is referred to as the critical Ra number, Ra_{cr}. When Ra is higher than Ra_{cr}, the next question is how long it takes to trigger density-driven instability and convective dissolution. The onset of density-driven instability refers to rapid developments of local velocities, especially at penetration fronts. In this stage, however, the total mass flux across the top boundary is still dominated by molecular diffusion. The onset of convective dissolution marks the moment when the overall mass transfer switches from a diffusion-dominated process to a convection-dominated process, which is usually associated with an increase of the overall mass flux across the top boundary. Due to the challenges associated with laboratory experiments, existing studies on Ra_{cr} and the critical times of triggering density-driven instability and convective dissolution relied heavily on stability analysis (9, 10, 19-33) and direct numerical simulations (14, 20, 34-39).

Some laboratory experiments have been conducted to study miscible density-drive convection. Typical experimental methods include pressure-volume-temperature (PVT) cells (40-43) and Hele-Shaw cells (17, 44, 45). PVT cells allow for assessment of CO₂ dissolution flux by measuring the pressure decay. However, most PVT cells do not provide direct observations of convection dynamics. Hele-Shaw cells provide direct visualization of convective dissolution dynamics by using transparent panels. Some experiments combined these two types of cells to come up with a PVT-Hele-Shaw cell, which allowed for direct observations of CO₂ dissolution in brine under reservoir conditions (46). In these previous experimental studies, however, dissolved CO₂ mass fluxes were in general measured indirectly. For example, the CO₂ dissolution rate was usually inferred by monitoring the amount of CO₂, or the analogue fluid, remaining in the cells, which can be calculated using the pressure, volume, and temperature of CO₂ in PVT cells (46) or the interface position in Hele-Shaw cells (17). Liyanage et al. (2019) used X-ray computed tomography technologies to investigate density-driven convection in a methanol-ethylene-glycol (MEG)/water system (47). In their study, dissolved MEG distribution within the porous medium was determined using CT scanning. However, the dissolved MEG mass flux was still indirectly measured using the amount of undissolved MEG in the system. In summary, no prior experiments were able to determine Ra_{cr} and the critical times for triggering density-driven instability and convective dissolution due to the challenges associated with direct measurements of in situ solute concentrations. Given the critical role of convective dissolution in GCS, investigations and measurements of these critical system parameters using well-controlled experimental methods are necessary.

In this study, we developed a novel experimental setup, which allowed for both direct laboratory observations of density-driven convection and quantitative measurements of spatial-temporal distributions of solute concentrations in porous media. To the best of our knowledge, this is the first study to determine Ra_{cr} and the relevant critical times using well-controlled laboratory experiments. In practice, the determination of the critical time for triggering convective dissolution has important applications in field-scale GCS projects because it marks a crucial moment when the overall dissolved CO₂ mass flux starts to increase, which has important implications to the long-term security of CO₂ storage. The findings from this experimental study also have practical applications in many other engineered and natural processes, such as geothermal convection, heat transfer due to subsurface nuclear waste disposal, and variable-density groundwater flow.

5.2. Theories and mathematical model

Density-driven instability and convective dissolution of CO₂ in a deep saline aquifer can be modeled in a homogeneous and isotropic porous medium. The Boussinesq approximation is adopted to assume that the CO₂ concentration affects only the body force term (Chen et al., 2013). The fluid flow and mass transfer in this system are governed by the following equations (Chen et al., 2013):

$$\frac{\mu}{k} \mathbf{u} = -\nabla p + \rho g \mathbf{e}_y \quad (5-1)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (5-2)$$

$$\phi \frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C = \phi D \nabla^2 C \quad (5-3)$$

$$\rho = \rho_0 (1 + \beta C) \quad (5-4)$$

where μ is fluid dynamic viscosity; k is porous medium permeability; $\mathbf{u}$ is Darcy velocity vector; p is fluid pressure; ρ is fluid density; g is gravitational acceleration; $\mathbf{e}_y$ is the unit vector in vertical direction; C is dissolved CO₂ concentration; ϕ is porous medium porosity; D is the effective diffusivity of dissolved CO₂ in the porous medium; ρ_0 is the density of pure water; β is expansion coefficient and equal to 0.001 m³/kg, which indicates that a dissolved CO₂ concentration of 1 kg/m³ will increase the solution density by 0.1% (i.e., 1 kg/m³). Particularly, **Equation 5-1** is the momentum equation. **Equation 5-2** is the mass continuity equation. **Equation 5-3** is the advection-diffusion equation that describes mass transfer of dissolved CO₂ in the porous medium. **Equation 5-4** is the constitutive relationship between solution density and dissolved CO₂ concentration.

The characteristic parameters are $L_c = H$, $u_c = \phi D / H$, $C_c = C_0$, $p_c = \mu \phi D / k$, and $t_c = H^2 / D$, where H is the depth of the porous medium in the sand box; C_0 is the saturated CO₂ concentration in the solution. The dimensionless variables are then defined as $x^* = x / L_c$, $y^* = y / L_c$, $\mathbf{u}^* = \mathbf{u} / u_c$,

$C^* = C / C_c$, $p^* = p / p_c$, and $t^* = t / t_c$. After normalization, Equations. 5-1~4 can be re-written in the dimensionless form:

$$\mathbf{u}^* = -\nabla p^* + Ra C^* \mathbf{e}_y \quad (5-5)$$

$$\nabla \cdot \mathbf{u}^* = 0 \quad (5-6)$$

$$\frac{\partial C^*}{\partial t^*} + \mathbf{u}^* \cdot \nabla C^* = \nabla^2 C^* \quad (5-7)$$

where Ra in **Equation 5-5** is a dimensionless number that characterizes the ratio of gravitational instability to molecular diffusion, which is written as $Ra = \Delta \rho g k H / (\rho_0 \phi \nu D)$, where $\Delta \rho$ is the density difference between CO₂-saturated solution and pure water, which is calculated as $\Delta \rho = \rho_0 \beta C_0$. This suggests that the maximum solution density increase, $\Delta \rho$, is 10 kg/m³ because the dissolved CO₂ concentration in the saturation state, C_0 , is 10 kg/m³ (Chen et al., 2013). According to Equations 5-5~7, Ra is the controlling factor that regulates the convective dissolution dynamics. The higher the value of Ra, the more likely that density-driven instability and convective dissolution will be triggered at a later time.

5.3. *Experimental methods and materials*

The experiments were carried out in a 0.8 m × 0.8 m × 0.018 m (height × width × thickness) quasi-two-dimensional (2D) sand box fabricated with transparent acrylic panels, which enabled direct observation of the transport processes in the porous medium. The size of the sand box was larger than those in the literature (17, 46-48), which aimed to allow density-driven, MEG-rich fingers to fully develop. The sand in the box was initially saturated with pure water. MEG and pure water were mixed to mimic a solution saturated with dissolved CO₂, which was then injected into the top fluid reservoir slowly to trigger density-driven downward flow velocity and convective dissolution. A porous mesh sheet was placed on the top of the sediment bed to prevent sand particle movement and to ensure that mass transfer was diffusion dominated in the early stage. Overlying the porous mesh sheet was an impermeable panel, which aimed to eliminate the impact of fluid flow when the MEG solution was injected into the top fluid reservoir. After the reservoir was filled

with the MEG solution, the impermeable panel was removed to allow MEG to migrate into the sand box through molecular diffusion. **Figure 5-1A** illustrates the experimental setup.

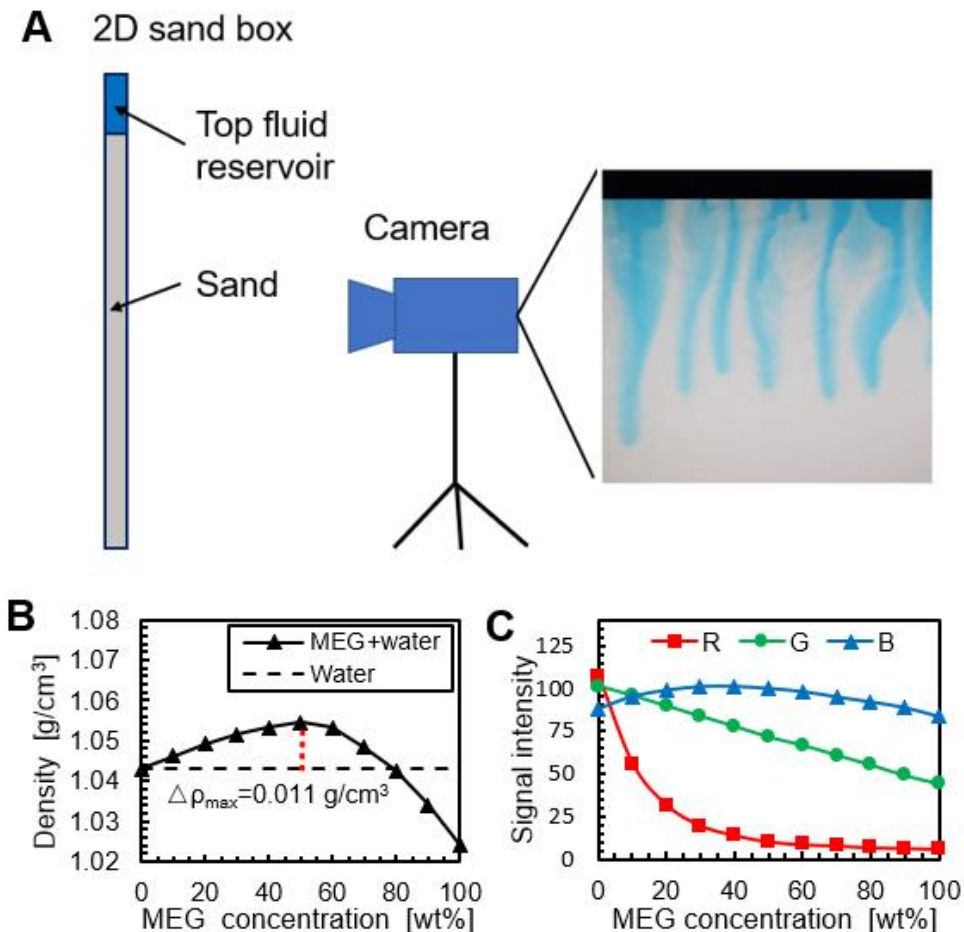


Figure 5 - 1. (A) Schematic plot of the experimental setup. (B) Density of MEG-water solution as a function of MEG mass concentration. (C) Color intensity for the red, green, and blue channels as a function of MEG mass concentration. A linear relationship between green channel intensity and MEG mass concentration was observed.

The density of a MEG-water solution can be either higher or lower than pure water, which depends on the MEG mass concentration in the solution (17, 47). In this work, we used MEG having a 60 wt% ethylene-glycol content. Figure 5-1B illustrates the measured MEG solution density as a function of MEG concentration. It was clear that the MEG solution density increased

approximately linearly with the MEG mass concentration, and it reached the maximum when the MEG concentration was 50%. In addition, at a MEG concentration of 50%, the MEG solution density was higher than water by 11 kg/m^3 , which is approximately equal to the density increase in CO_2 -saturated solution (14). This implies that the maximum increased gravitational acceleration due to the dissolved MEG, calculated as $\Delta\rho g/\rho_0$, was around 0.1 m/s^2 , which is the same as that in a CO_2 -saturated solution. Therefore, in the experiments we placed a MEG solution having a 50% MEG mass concentration in the top fluid reservoir as an analogue of CO_2 -saturated solution at the top boundary, and thus in the porous medium the MEG mass concentration was in the range of 0-50%. By doing this, we ensured a quasi-linear relationship between MEG solution density and MEG mass concentration, as shown in Figure 5-1B.

The porous media in the sand box were constructed using silica sand with uniform size distributions. **Table 5-1** illustrates the sand and relevant properties. In this study, Ra ranged from 481 to 7959, which was within the relevant range associated with field-scale saline aquifers (47).

Table 5 - 1. Parameters on the experiments

Sand mesh size	Average grain size (μm)	Permeability ($\times 10^{-12} \text{ m}^2$)	Porosity	Ra
#12-20	1144	49.00	0.325	7959
#16-30	768	29.90	0.345	4723
#20-40	499	15.00	0.369	2404
#40-70	285	5.37	0.357	944
#50-80	250	4.38	0.416	481

The MEG solution, which was placed in the top fluid reservoir and had an initial mass concentration of 50%, was dyed with a passive blue tracer. We then used high-speed high-resolution digital cameras to calibrate the relationship between MEG mass concentration and intensities of the red, green, and blue color signals transmitted through the porous medium, as shown in Figure 5-1C. Particularly, the panel light source was placed behind the 2D sand box, and the digital cameras were placed at the front side to analyze the visible light signals that were transmitted through the sand box. It was observed that the intensities of the transmitted red and green visible light signals decreased with an increasing MEG mass concentration, because a higher

MEG concentration absorbed more red and green visible light signals, allowing less red and green light going through the sand box. We used the transmitted green light signal from the digital images to infer the MEG mass concentration because of the linear relationship between them. Because the transmitted green light intensity on each individual pixel can be obtained using digital image analysis, the MEG mass concentration at the same pixel can be calculated, which enabled us to obtain the MEG concentration distribution over the entire 2D domain. The distribution of the dimensionless concentration, C^* , can be obtained by normalizing the MEG concentration distribution with the initial MEG concentration in the top fluid reservoir. The signal intensity-MEG concentration correlation shown in Figure 5-1C was measured before each experiment to mitigate the influence of a possible background light change. Correlating the transmitted visible light intensity with in-situ MEG concentration features the primary novelty in this experimental study, which enables direct characterization of MEG distributions in the spatial and temporal domains using digital image analysis and is critical for tracking the mass flux across the top interface in density-driven convective mixing.

5.4. *Results and discussion*

5.4.1. *Overview of density-driven instability and convective dissolution in the experiments*

The transition from diffusion-dominated transport processes to convection-dominated transport processes in the experiments can be classified into three stages, which were the diffusive regime, velocity-growth regime, and flux-growth regime. In the diffusive regime, MEG mass transfer was controlled primarily by molecular diffusion. With the development of density difference across the top interface (i.e., reservoir-sand boundary), the onset of density-driven instability led to local convective mass transfer at the penetration front. The characteristic time for the onset of density-driven instability, t_{cr1} , was defined as the time when the peak downward velocity grew to a level that was one order of magnitude higher than the diffusion-regulated characteristic velocity; this characteristic time marked the end of the diffusive regime and the beginning of the velocity-growth regime. However, despite the initiation of local convective mass transfer at MEG-rich fingers, in the velocity-growth regime the overall MEG mass transfer from the top fluid reservoir to the underlying porous medium was still dominated primarily by molecular diffusion. Therefore, the

overall MEG mass flux continuously decayed at early times because mass transferred into the underlying porous medium diminished the concentration gradient across the interface, which hampered diffusive mass transfer. At a later time, MEG-rich fingers were adequately developed, and consequently the mass flux contributed by convection started to dominate over the mass flux contributed by pure molecular diffusion. At this point, the total MEG mass flux started to increase. The time when the total MEG mass flux started to increase was the characteristic time for the onset of convective dissolution, t_{cr2} , which marked the end of the velocity-growth regime and the beginning of the flux-growth regime.

Our experimental study focused on these three regimes, which formed a transition stage from diffusion-dominated to convection-dominated transport process, which has not been systematically investigated in previous experimental studies. Figure 5-2 illustrates the development of density-driven instability and convective dissolution under two Ra numbers, 481 and 4723.

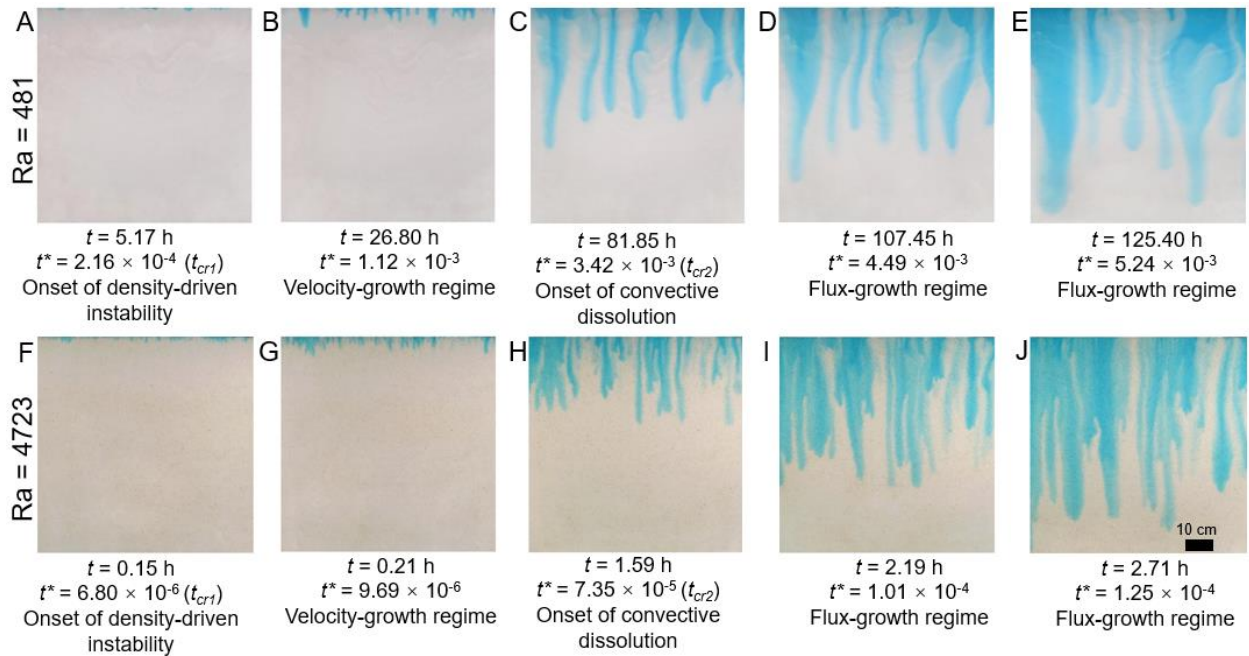


Figure 5 - 2. Development of density-driven instability and convective dissolution for Ra = 481 (A-E) and Ra=4723 (F-J). The blue fingers indicate density-driven downward penetration of MEG-rich solution.

In the diffusive regime, the transport of dissolved MEG from the top interface to the underlying porous medium was purely caused by molecular diffusion. Figures 5-2A and 5-2F are the images at the end of the diffusive regime for $Ra = 481$ and $Ra = 4723$, respectively. In this regime, MEG-water solution formed a stable dense layer beneath the top interface.

In our experiments, the velocity-growth regime was defined as the stage in which the peak downward velocity started to grow exponentially whereas the overall mass transfer rate was still dominated by pure molecular diffusion. Specifically, the onset of the velocity-growth regime was considered as the onset of density-driven instability. The determination of the onset time for density-driven instability, t_{cr1} , will be discussed in Section 4.5. After the onset of density-driven instability, the system entered the velocity-growth regime, in which MEG-rich fingers started to develop and grow at the top boundary whereas the overall mass transfer rate across the boundary was still dominated by molecular diffusion. Therefore, the velocity-growth regime was a stage in which local downward velocities developed rapidly due to the density difference whereas the total mass transfer across the top boundary was still dominated by molecular diffusion.

With the MEG-rich fingers penetrating downward continuously, convective dissolution started to dominate the overall mass transfer of MEG across the top boundary. The onset of the flux-growth regime was considered as the onset of convective dissolution, which indicated a turning point when the overall mass flux started to increase. The convective dissolution patterns for the onset of the flux-growth regime are shown in Figures 5-2C and 5-2H for $Ra = 481$ and 4723 , respectively. The determination of the onset time for convective dissolution, t_{cr2} , will be discussed in Section 4.5. During the flux-growth regime, MEG-rich fingers started to interact with each other, resulting in complicated transport processes such as finger coalescence and splitting as shown in Figures 5-2D, 5-2E, 5-2I, and 5-2J.

5.4.2. Peak downward velocity

Our previous numerical studies (14, 16) on miscible density-driven convection showed that the peak downward velocity occurs at the penetration front. Therefore, we used digital image tracking methods (49) to find the downward velocities on the MEG-rich penetration front, and the maximum downward velocity on the penetration front was the peak downward velocity. Figure 5-

3 illustrates the dimensionless peak downward velocity as a function of dimensionless time under various Ra numbers. The dimensionless peak downward velocity is defined as $u_{\max}^* = u_{\max} / u_c$, where $u_{\max}$ is the peak downward velocity (m/s) and u_c is the characteristic velocity (m/s) which has been defined previously. The dimensionless time is defined as $t^* = t/t_c$, where t is the experimental time (s) and t_c is the characteristic time (s) which has been defined previously. This result demonstrated that under a higher Ra number the peak downward velocity reached its maximum value in the temporal domain earlier, and the magnitude of its maximum value was higher.

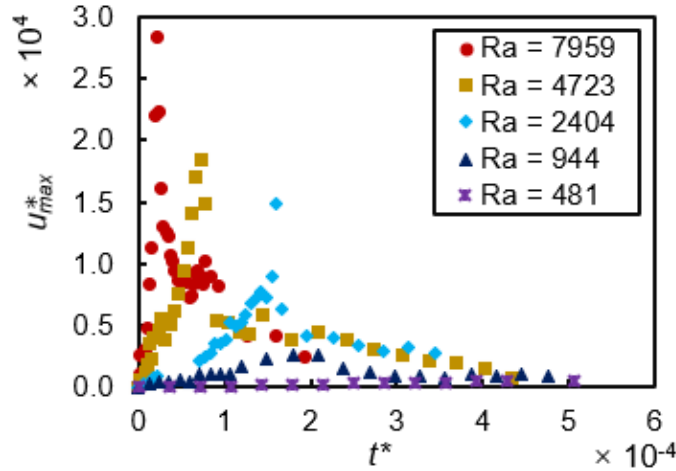


Figure 5 - 3. Normalized peak downward velocity as a function of dimensionless time.

Figure 5-3 demonstrates that the evolutions of the peak downward velocities in the experiments showed a non-monotonic mode, which was caused by a competing process between the convection of dissolved MEG and transverse dispersion. Transverse dispersion not only affected the pattern and time scale of convective dissolution (50), but also affected the local dynamics of the fingers (51). The growth of the peak downward velocity followed an exponential mode. During the downward penetration process, transverse dispersion decreased the concentration gradient across the finger front and thus reduced the density difference, which hampered the development of the downward convection. After the peak downward velocity reached its maximum value, it gradually decreased to a relatively low level. In some cases, the later-time peak downward velocity can approach zero under an extremely high Ra, as observed in our experiments.

Whether the peak downward velocity approached zero at a later time depended on the Ra number. In high Ra number scenarios, the front fingers were slim and penetrated downward rapidly. For example, in the case of $Ra = 7959$ convection played a dominant role, which led to a sharp transverse concentration gradient. Because the fingers were slim, the transverse dispersion diminished the concentration gradient rapidly and caused the slim fingers to stop penetrating downward before they reached the bottom of the sand box. The peak downward velocity approached to zero when the dimensionless time reached 2.5×10^{-4} , as shown in Figure 5-3. In a low Ra number scenario, however, the penetration fronts were relatively thick compared to the high Ra number scenarios. In these low Ra scenarios, the peak downward velocity decreased at a later time and did not approach zero. In the flux-growth regime, new MEG-rich fingers constantly formed at the interfaces and they followed the preferential flow paths of the previous fingers, leading to an increasing mass flux across the interface.

5.4.3. Critical Ra

Theoretical analyses found that no instability is possible with $Ra < 32.5$ in thin layers of porous media and the onset of density-driven instability is independent of the porous medium thickness when Ra is greater than 75 (25). The numerical study of Chen et al. (2013) found that $Ra_{cr} = 250$ in a homogeneous and isotropic aquifer (14). Due to the challenge in measuring the in situ concentration, spatial distribution, and flow velocity of dissolved CO_2 in the laboratory, there were no existing experimental data in determining the Ra_{cr} in the laboratory. This study is the first one to use well-controlled laboratory experiments to quantify the value of the Ra_{cr} in porous media.

Based on our previous numerical study (14), when density-driven instability is triggered, the peak downward velocity grows exponentially with time. Therefore, exponential functions were used to fit the peak downward velocities in the increasing stage shown in Figure 5-3. Figure 5-4A demonstrates the natural logarithm of the dimensionless peak downward velocity as a function of the dimensionless time, as well as the data fitting lines. The linear correlations shown in Figure 5-4A confirm that in the early stage of the instability development. Therefore, the slopes of the linear relationships in Figure 5-4A are the growth rates of the peak downward velocities. Figure 5-4B illustrates the velocity growth rate as a function of Ra. It is clear that the growth rate

decreased approximately linearly with the decrease of Ra. When the growth rate approached zero, the corresponding Ra was considered as the Ra_{cr} , which was found to be 259 in this experiment.

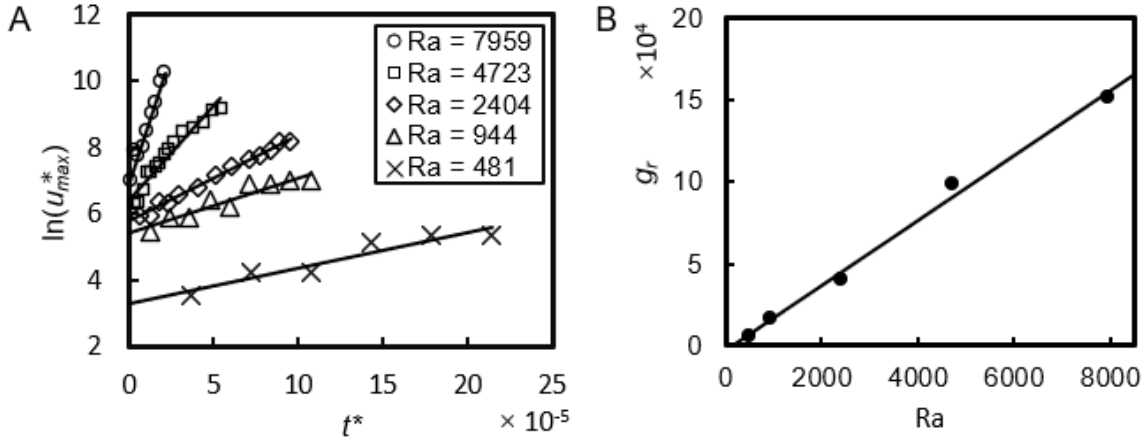


Figure 5 - 4. (A) Natural logarithm of dimensionless peak downward velocity as a function of dimensionless time. (B) Growth rate of peak downward velocity as a function of Ra. The intersection of the extrapolation line with the x axis corresponds to $Ra = 259$, which is the Ra_{cr} .

5.4.4. Mass transfer rate

Figure 5-5A illustrates the spatial distribution of normalized MEG mass concentration, C^* , over the 2D porous medium under $Ra = 481$ and $t^* = 4.12 \times 10^{-3}$. As described before, the local MEG concentration was determined using the transmitted green light intensity at the same pixel based on the signal intensity-MEG concentration relationship shown in Figure 5-1B. Using this digital image analysis technique, the MEG concentration distribution over the entire 2D porous medium can be determined, based on which the total MEG mass transferred across the top interface can be calculated by integrating the MEG concentration over the entire 2D domain. Correlating transmitted visible light intensity with in-situ MEG concentration features the primary novelty of this experimental study, which enables direct characterization of MEG distributions in the spatial and temporal domains. The MEG mass flux ($\text{kg}/(\text{m}^2 \cdot \text{s})$), defined as MEG mass transferred across a unit interfacial area per unit time, was calculated as the total MEG mass increment in the porous medium over two consecutive measurement times normalized by the total interfacial area and the time increment.

Figures 5-5B~5F demonstrate the MEG mass flux as a function of dimensionless time under various Ra numbers. It is clear that the evolution of MEG mass flux was non-monotonic, which decreased first and then increased. This was due to a competing process between diffusive mass transfer and convective mass transfer. In the early stages (i.e., diffusive regime and velocity-growth regime), MEG mass transfer from the top fluid reservoir to the underlying porous medium was dominated primarily by molecular diffusion. Although the onset of density-driven instability led to local convective mass transfer at the penetration front, the mass flux at the interface was still dominated primarily by molecular diffusion. The MEG mass transported into the porous medium reduced the concentration gradient across the top interface, which hampered the mass flux contributed by pure molecular diffusion. This explained the continuous decay of MEG mass flux in the early stages. At a later time, MEG-rich fingers were adequately developed, and consequently the mass flux contributed by convection started to dominate over the mass flux contributed by molecular diffusion. At this point, the total MEG mass flux started to increase even the mass flux contributed by pure molecular diffusion was continuously diminished. The time when the total MEG mass flux started to increase, which were marked by the blue dash lines in Figures 5-5B~5F, was the characteristic time for the onset of the flux-growth regime (i.e., convective dissolution).

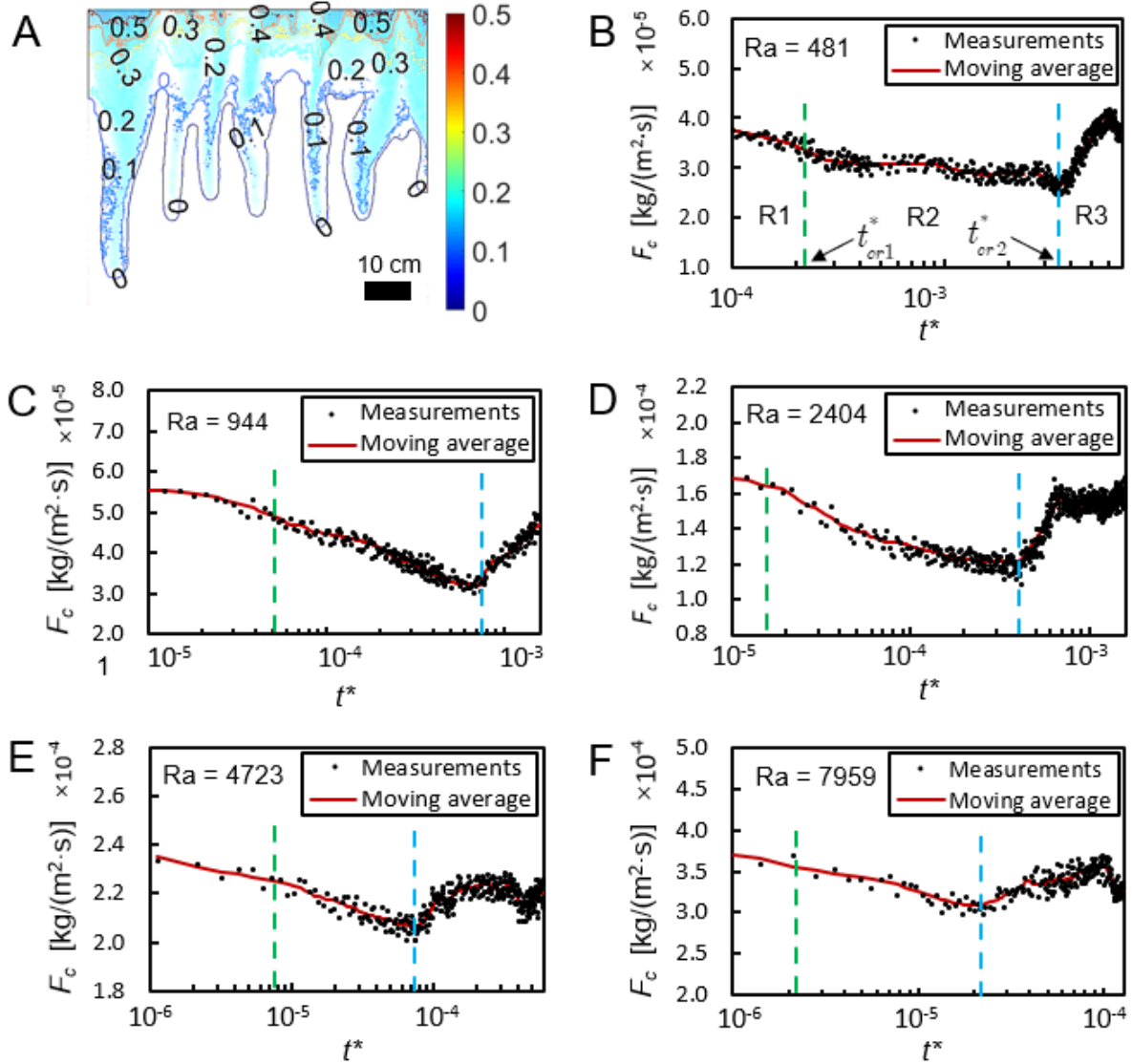


Figure 5 - 5. (A) Spatial distribution of normalized MEG concentration in the 2D sand box, and MEG mass flux across the top boundary as a function of dimensionless time for (B) $Ra = 481$, (C) 944, (D) 2404, (E) 4723, and (F) 7959. The green dash line indicates the dimensionless onset time for density-driven instability, t_{cr1}^* . The blue dash line indicates the dimensionless onset time for convective dissolution, t_{cr2}^* . The two onset times divide the transition stage into three regimes, which are the diffusive regime (R1), velocity-growth regime (R2), and flux growth regime (R3).

The ratio of convective mass flux to diffusive mass flux can be described using the Sherwood number (Sh), a dimensionless number defined as $Sh = F_c / (\phi \Delta C D / H)$, where the value of MEG mass

flux, F_c , was calculated as the average over the entire temporal domain, and ΔC was the difference between the MEG concentration in the top fluid reservoir (i.e., C_0) and MEG concentration in pure water (i.e., zero). Figure 5-6 illustrates that the experimental measurements showed a power-law correlation between Sh and Ra , written as $Sh \propto Ra^{0.95}$, which was consistent with previous experimental studies (17, 47). This suggested that a higher Ra number led to a higher MEG mass transfer rate across the top boundary caused by convective mass transport.

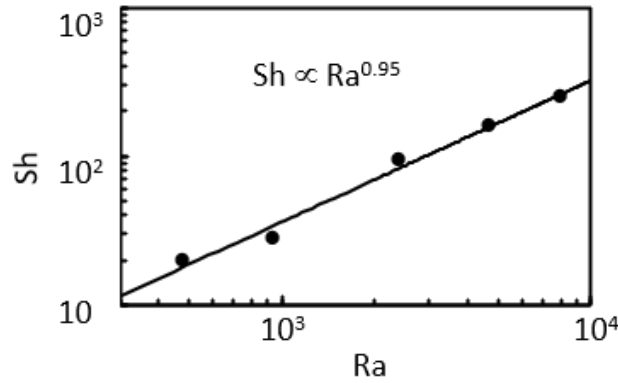


Figure 5 - 6. Power-law relationship between Sh and Ra observed in the experiments.

5.4.5. Critical times

The experimental results described above indicate that there were two characteristic times that triggered density-driven instability and convective dissolution sequentially. Particularly, the characteristic time for the onset of density-driven instability (i.e., onset of the velocity-growth regime) was defined as the time when the peak downward velocity grew to a level one order of magnitude higher than the diffusion-regulated characteristic velocity; this characteristic time marked the end of the diffusive regime and the beginning of the velocity-growth regime. At a later time, MEG-rich fingers were adequately developed, and consequently the mass flux contributed by convection started to dominate over the mass flux contributed by pure molecular diffusion. At this point, the total MEG mass flux started to increase, as shown in Figures 5-5B~5F. The time when the total MEG mass flux started to increase is the characteristic time for the onset of convective dissolution (i.e., onset of the flux-growth regime), which marked the end of the velocity-growth regime and the beginning of the flux-growth regime.

The first characteristic time, t_{cr1} , which triggered the onset of density-driven instability, was determined using the following equation based on our experimental measurements:

$$u_{\max} = u_c \exp(g_r t) \quad (5-8)$$

Particularly, the value of the velocity growth rate, g_r , was known based on the measurements shown in **Figure 5-4A**. Based on **Equation 8**, t_{cr1} was the t value that gave $u_{\max} = 10u_c$, which was the time when the peak downward velocity grew to a level one order of magnitude higher than the diffusion-regulated characteristic velocity. This characteristic time marked the initiation of convective fluid flow caused by the solution density difference across the top interface. It should be noted that t_{cr1} is usually too short to directly measure in laboratory experiments (Mojtaba et al., 2014; Newell et al., 2018; Shi et al., 2018; Mahmoodpour et al., 2019). Therefore, in this study we calculated t_{cr1} using Equation 8, which was based on the extrapolation in the temporal domain.

The measured t_{cr1} values and the corresponding sand permeability values were used to fit the following empirical correlation based on the formulation found in our previous numerical study (Chen et al., 2013):

$$t_{cr1} = C_1 \frac{(\mu\phi)^2 D}{(g\Delta\rho k)^2} \quad (5-9)$$

Figure 7A illustrates that data fitting based on the laboratory experimental data found $C_1 = 53.1$. Xu et al. (2006) (Xu et al., 2006) found $C_1 = 75.2$ using linear stability analysis with periodic-wave perturbations. Slim and Ramakrishnan (2010) (Slim and Ramakrishnan, 2010) found $C_1 = 47.9$ using linear stability analysis with infinitesimal perturbations. Chen et al. (2013) (Chen et al., 2013) found $C_1 = 61.1$ using direct numerical simulations. Our study is the first one to measure the value of C_1 using well-controlled laboratory experiments.

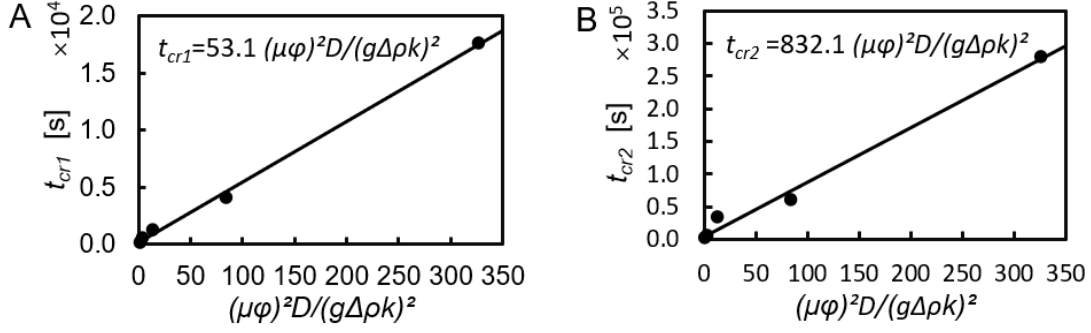


Figure 5 - 7. Critical times for the onset of (A) density-driven instability, and (B) convective dissolution as a function of $(\mu\phi)^2 D / (g\Delta\rho k)^2$.

Based on data fitting using the experimental measurements, the following empirical correlation was found for t_{cr2} :

$$t_{cr2} = C_2 \frac{(\mu\phi)^2 D}{(g\Delta\rho k)^2} \quad [10]$$

Figure 5-7B illustrate the data fitting of the experiment data using Equation 10, and the value of C_2 was found as 832.1. Emami-Meybodi et al. (2015) reviewed previous numerical simulation studies and showed that the value of C_2 ranged from 500 to 5619 (Emami-Meybodi et al., 2015). Our study is the first one to experimentally measure the value of C_2 in the laboratory.

5.5. Conclusion and implications

Convective dissolution is a major mechanism that accelerates the dissolution of injected CO_2 in saline aquifers, which enhances the long-term security of GCS. After the injection of CO_2 , the dissolution process goes through a transition stage from diffusion-dominated to convection-dominated regimes. The critical Rayleigh-Darcy number for the onset of density-driven instability and the critical times for the onset of density-driven instability and convective dissolution are critical system parameters that have the capability in predicting the convective dissolution process. In this study, we experimentally investigated the flow and mass transport processes in a 2D sand box that evolved from a diffusion-dominated regime to a convection-dominated regime. In the laboratory we found a linear relationship between MEG mass concentration and transmitted green

light intensity, which features a primary novelty of this experiment study. Using this novel experimental technique, we were able to accurately measure the spatial distribution of dissolved MEG concentration across the 2D domain. Based on the laboratory measurements of peak downward velocity and spatial-temporal distributions of dissolved MEG, the critical Rayleigh-Darcy number and the critical times for the onset of density-driven instability and convective dissolution were determined. This is the first study to measure these critical system parameters using well-controlled laboratory experiments.

We found that Ra has a significant impact on the convective dissolution pattern. The MEG-rich fingers were relatively thick for a low Ra whereas they were relative slim for a high Ra . The peak downward velocity after the onset of density-driven instability was measured, which followed an exponential growth mode. The critical Ra was estimated as 259. The empirical formula for calculating the critical time for the onset of density-driven instability was found as $t_{cr1} = 53.1(\mu\phi)^2D/(g\Delta\rho k)^2$ based on laboratory data fitting. The empirical formula for calculating the critical time for the onset of convective dissolution was determined as $t_{cr2} = 832.1(\mu\phi)^2D/(g\Delta\rho k)^2$ by fitting laboratory data. The empirical correlation between average MEG mass flux and Ra was found as $Sh \propto Ra^{0.95}$. This work is the first study to determine the empirical correlations for these two critical times using laboratory experiments. In practice, the determination of the second critical time (i.e., t_{cr2}) has important applications in field-scale GCS projects because it marks a crucial moment when the overall dissolved CO_2 mass flux starts to accelerate due to density-driven downward convection.

This study used novel and well-controlled experimental techniques to study miscible density-driven convection in porous media, which has critical implications to the basic science because it is a fundamental subsurface hydrology phenomenon. The findings and empirical correlations obtained from this experimental study also have practical applications in many other engineered and natural processes, such as geothermal convection, heat transfer due to subsurface nuclear waste disposal, and variable-density groundwater flow.

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Chapter 6. Using Novel 3D Printing to Study the Role of Permeability Heterogeneity on Miscible Density-driven Convection in Porous Media

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Abstract

Density-driven convection is ubiquitous in natural and industrial processes. Experimental investigations on density-driven convection in heterogeneous porous media are limited due to challenges in constructing heterogeneous porous media. A three-dimensional (3D) fluidics platform was proposed and assisted with 3D printing technology porous media with complex permeability heterogeneity can be efficiently constructed. In the experiments, methanol-ethylene-glycol (MEG), was used as surrogate fluid to CO₂. The heterogeneous porous media was placed in a transparent box allowing visual observation. Density-driven convection in porous media with different correlation lengths were investigated. Results showed that permeability structure controlled the migration of MEG-rich water with fingering and channeling mechanism. Permeability heterogeneity caused noticeable uncertainty in total transferred MEG mass and the uncertainty increases with correlation length of porous media. A larger correlation length also led to more total transferred MEG mass. The findings have practical significance in evaluating the time scale of dissolution trapping of geological carbon storage in deep saline aquifers. The 3D fluidics provide deterministic controls over pore structure and permeability heterogeneity structure in 3D spaces, which may transform the research on multiphase flow in porous media.

Key words: density-driven flow, porous media, permeability heterogeneity, 3D printing, geological carbon sequestration

6.1. Introduction

Porous media are ubiquitous in natural and industrial processes, where complex fluids flow, mass transfer and chemical reactions occur (Fredd and Fogler, 1998;Dudukovic et al., 2021). Density-driven convection in a porous medium is one common phenomenon of mass transfer which finds

wide applications in solute transport in ground water (Simmons et al., 2001), intrusion in coastal aquifers (Kopsiaftis et al., 2009), nuclear waste disposal (Neretnieks and Winberg-Wang, 2019). In recent decades density-driven convection in porous media obtained renewed attention in the context of geological carbon sequestration (GCS) because solubility trapping is one principal trapping mechanism of GCS, which could be greatly enhanced by density-driven convection (Chen et al., 2013).

Deep saline aquifers are considered promising formations for long-term CO₂ storage because of its vast storage capacity. After injected into formations, CO₂ migrates upwards due to buoyancy and pools beneath an impermeable cap rock. The accumulation of CO₂ has a risk of leaking into the atmosphere. Dissolution of CO₂ into brine increases the brine density, which results in an unstable density stratification of denser CO₂-brine solution over lighter brine. Density-driven convection will occur under certain conditions (Chen et al., 2013). The enhanced dissolution of CO₂ into brine by density-driven convection favors the long-term safety of GCS (Yang and Gu, 2006).

Density-driven convection in porous media was first studied by Horton and Rogers (1945) and Lapwood (1948), which is commonly referred to as the Rayleigh-Darcy convection or Horton-Rogers-Lapwood convection. Rayleigh-Darcy convection in homogeneous porous media has been intensively studied (Ennis-King and Paterson, 2005; Farajzadeh et al., 2007; Neufeld et al., 2010; Slim and Ramakrishnan, 2010; Slim et al., 2013; Emami-Meybodi et al., 2015; Shi et al., 2018; Mahmoodpour et al., 2019; Tang et al., 2019). Critical Rayleigh number, Ra, for instability, onset time for instability and convective dissolution, mass transfer rate at CO₂-brine interface are critical parameters for describing the convective dissolution process. Critical Ra for instability was determined by theoretical analysis (Slim and Ramakrishnan, 2010) and direct simulation (Chen et al., 2013) and experiment (Guo et al., 2021). Numerous simulations and experiments were conducted to determine the onset time of convective dissolution (Riaz et al., 2006; Farajzadeh et al., 2007; Pau et al., 2010; Liyanage et al., 2019). The mass transfer rate was estimated by direct numerical simulations and experiments (Neufeld et al., 2010; Slim et al., 2013; Slim, 2014; Newell et al., 2018; Mahmoodpour et al., 2019). A systematic understanding on density-driven convection in homogeneous porous media has been established.

The permeability of natural formations is commonly heterogeneous, and convective dissolution in heterogeneous porous media is different from that in homogeneous porous media (Wang et al., 2021). It is needed to develop a fundamental understanding of the role of permeability heterogeneity on density-driven convection in porous media. Rayleigh-Darcy convection in heterogeneous porous media was studied by multiple direct numerical simulations (Farajzadeh et al., 2011; Cheng et al., 2012; Ranganathan et al., 2012; Chen et al., 2013; Kong and Saar, 2013; Li et al., 2020). Due to the challenge in constructing heterogeneous porous media, limited experimental studies on density-driven convection in heterogeneous porous media were carried out compared to studies in homogeneous porous media. In the limited experimental studies, heterogeneous porous media constructed in a laboratory were commonly layered or block wise sand packs. Agartan et al. (2015) experimentally investigated the effects of geologic heterogeneity on convective mixing on layered and block-wise sand packs in a transparent 2D water box and found that low-permeability zones can significantly hinder the magnitude of convection. Taheri et al. (2018) established heterogeneous porous media by placing scattered barriers to sands inside a Hele-Shaw cell and investigated the convective mixing process. Agartan et al. (2020) investigated the effect of heterogeneous low-permeability layer on the density-driven convection in sand packs. Amarasinghe et al. (2021) studied the density-driven convection in layered sand packs. Wang et al. (2021) built sand packs and investigated the impact of permeability heterogeneity on spatiotemporal variations in the convection mixing process by magnetic resonance imaging. Bharath and Flynn (2021) investigated density-driven convection in sand packs with inclined permeability jump. These studies advanced our understanding of density-driven flow in heterogeneous porous media with simple heterogeneity structure.

The CO₂ dissolution rate is controlled by distribution of permeability in a porous medium (Kong and Saar, 2013). Significant challenges exist in constructing heterogeneous porous media with complex permeability heterogeneity structure. In previous studies fabricating a porous medium by randomly packing sand grains or beads, there was limited controls on the permeability structure. The 3D printing technology has a promising potential in fabricating porous media with desired microscopic structures (Almetwally and Jabbari, 2021; Dudukovic et al., 2021). This work presented an efficient 3D printing-based method to construct heterogeneous porous media with designed heterogeneity structure. We used it to investigate density-driven convection in

heterogeneous porous media. The investigation focused on the effect of spatial correlation of permeability fields on the density-driven convection at early stages.

6.2. Materials and methodology

6.2.1. Generation of heterogeneous permeability fields

A heterogeneous porous medium in this work is modeled as a heterogeneous permeability field. The permeability of geological formations commonly followed a log-normal distribution. The corresponding log permeability field is defined as $Y = \log(k)$, where k is permeability. The mean and variance of the log permeability field can be calculated by solving the equations $\mu_k = e^{\mu_Y + \sigma_Y^2/2}$ and $\sigma_k^2 = (e^{\sigma_Y^2} - 1) \cdot e^{2\mu_Y + \sigma_Y^2}$. An exponential kernel was used in the covariance function, which is defined as $c_Y(\mathbf{x}, \mathbf{y}) = \sigma_Y^2 \exp[-(|x_1 - y_1|/L_1 + |x_2 - y_2|/L_2)]$, where L_1 , and L_2 are the correlation lengths in principal directions, $\mathbf{x}$ and $\mathbf{y}$ are coordinates of points.

A Cholesky decomposition-based method is used to generate the log permeability field Y (Chen and Zeng, 2015). The symmetric and positive definite covariance matrix can be decomposed to a lower triangular matrix and an upper triangular matrix, $C_Y = LL^T$. A Gaussian white noise field is generated, $\xi \sim N(\mu_\xi = 0, \sigma_\xi = 1)$. The log permeability field can be calculated by $Y = \mu_Y + L\xi$.

6.2.2. Construction of heterogeneous permeability fields using 3D-printed sediment blocks

Figure 6-1a illustrates a realization of a heterogeneous permeability field, which was generated using the method described in Section 6.2.1. A threshold method was used to convert the continuously distributed permeability field into a discrete, binary permeability field to allow for convenient construction of such a heterogeneous porous medium in the laboratory using 3D printing. The value and number of thresholds are selected to match the permeability and the number of 3D printed blocks. In this work, the threshold was the mean of the permeability field. Particularly, the 3D printer deposited photocurable acrylic resin and wax layer by layer, which is ideal for printing 3D objects with fine features. The resin was transparent and used to fabricate the spherical particles, whereas the wax was used as the supporting material during the 3D printing

process. In the post-processing stage, the wax was heated up, melted, and removed from the pore spaces between spherical particles, which allowed the delicate features and complex internal cavities to be thoroughly cleaned without damage. In this study, we used 3D printing to fabricate two types of “digital sediment” blocks to construct the binary heterogeneous permeability field, as shown in Figure 6-1b. The first type of sediment block was packed with uniform grain particles having diameter of 2 mm, whereas the second type was packed with uniform grain particles having diameter of 3 mm. Both types of sediment blocks were 3D-printed with a spatial resolution of 13 μm and had overall dimensions of 2 cm $\times$ 2 cm $\times$ 2 cm. Particularly, the gray area in Figure 6-2b indicates the high-permeability region, which was constructed using the 3D-printed sediment blocks having 3 mm grain diameter, whereas the yellow area is the low-permeability region and was constructed using the sediment blocks having 2 mm grain diameter. **Table 6-1** summarizes the laboratory-measured properties of these 3D-printed sediment blocks.

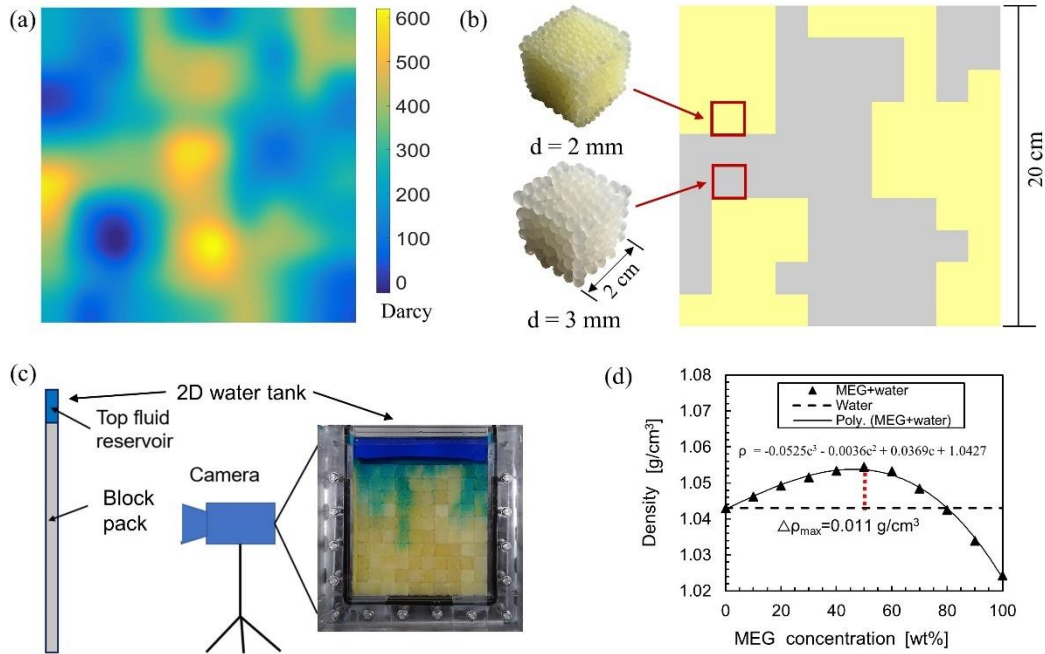


Figure 6 - 1. (a) An exemplar realization of heterogeneous porous media. (b) Discrete heterogeneous porous media converted from (a) with a threshold method and 3D-printed elementary porous blocks. The elementary blocks comprised of randomly distributed spheres with the same diameter. (c) Experimental setup. (d) Density of methanol-ethylene-glycol (MEG)-water

solution against MEG weight concentration. The data points are experimental data, and the solid line is the fitted relation function between MEG-water solution and MEG weight concentration.

Table 6 - 1. Properties of 3D-printed porous blocks used in the experiments.

Block type	Grain diameter d (mm)	Permeability k ($\times 10^{-12}$ m ²)	Porosity ϕ (-)
#d2	2	95.01	0.419
#d3	3	526.42	0.442

6.2.3. Laboratory experiment

A fluid reservoir was placed at the top of the 2D sand box; an analogous fluid was placed in the fluid reservoir to trigger miscible density-driven downward convection that penetrated into the underlying 3D-printed porous medium. Analogous fluids have commonly been used to mimic density-driven convection caused by dissolved CO₂ in saline aquifers (Neufeld et al., 2010; Liyanage et al., 2019). In this work, a mixture of 40% mass fraction of methanol and 60% mass fraction of ethylene glycol formed the methanol ethylene glycol (MEG) fluid, which was then mixed with water to surrogate a CO₂-saturated brine solution. Although the density of MEG is lower than water, the density of a MEG-water solution can be higher than water, depending on the mass concentration of MEG in the solution. Figure 6-1c illustrates the laboratory-measured MEG-water solution density as a function MEG mass concentration. It can be observed that the MEG solution density increased approximately linearly with the MEG mass concentration, and it reached the maximum when the MEG mass concentration was 50%. In addition, at a MEG mass concentration of 50%, the MEG solution density was higher than water by 11 kg/m³, which is approximately equal to the density increase in a CO₂-saturated brine solution (Chen et al., 2013). This implies that the maximum increased gravitational acceleration due to the dissolved MEG, calculated as $\Delta \rho g / \rho_0$, is around 0.1 m/s², which is the same as that in a CO₂-saturated brine solution. Therefore, similar to a previous study (Guo et al., 2021), we placed a MEG-water solution having a 50% MEG mass concentration in the fluid reservoir as an analogue of CO₂-saturated brine solution at the top boundary.

Figure 6-1d demonstrates the laboratory experiment setup. The two-dimensional (2D) sand box was fabricated using of transparent acrylic panels, allowing direct visual observation of miscible density-driven convection processes. The porous medium was constructed by stacking 10×10 3D-printed sediment blocks, leading to total dimensions of $20 \text{ cm} \times 20 \text{ cm} \times 2 \text{ cm}$ (i.e., height $\times$ width $\times$ thickness). The porous medium was placed within the sand box; the transparent resin used to 3D print the grain particles also allowed direct observations of density-driven convection within the pore spaces. A mechanical stress was applied to ensure adequate contact between the porous medium and the front and rear panels of the sand box, thereby eliminating preferential flows between the panels and the surfaces of the porous medium.

The Rayleigh number, Ra , is a dimensionless number to characterize the ratio of gravitational instability to diffusive transport. In this paper, Ra is defined as $Ra = \Delta\rho g \bar{k}_v H / (\rho_0 \phi \nu D)$, where $\Delta\rho$ is the density difference between the MEG-water solution in the top fluid reservoir and water (kg/m^3); g is gravitational acceleration (m/s^2); $\bar{k}_v$ is the average vertical permeability of the porous medium (m^2); H is the characteristic length, which is the height of the porous medium (m); ρ_0 is the density of water (kg/m^3); ϕ is the porous medium porosity; ν is the kinematic viscosity of water (m^2/s); D is the effective diffusivity of MEG in the porous medium (m^2/s). The average vertical permeability, $\bar{k}_v$, was calculated using reservoir simulation. Particularly, a pressure difference was imposed on the top and bottom boundaries of the heterogeneous permeability field, and no-flow conditions were applied at the left and right boundaries. The simulated overall flow rate in the vertical direction, along with the imposed pressure gradient, was used to calculate the effective (i.e., average) vertical permeability of the entire porous medium, $\bar{k}_v$, based on the Darcy's law.

The 3D-printed sediment blocks in the sand box were fully saturated with water before the experiment. The MEG-water solution was then slowly injected into the top fluid reservoir. Overlying the 3D-printed sediment blocks was an impermeable film, which eliminated the impact of fluid flow when the MEG-water solution was injected into the top fluid reservoir. After the fluid reservoir was filled, the impermeable film was removed to allow MEG to migrate into the underlying sediment blocks via molecular diffusion and density-driven convection. In order to visualize the migration of MEG into the sand box, a blue dye was mixed in the MEG-water solution as a tracer. The dye was chemically stable and did not adsorb onto the surfaces of resin grains

within the 3D-printed sediment blocks. A high-speed high-resolution digital camera and two panel light sources were placed at the front side of the sand box to take pictures, which had a pixel resolution much smaller than the pore size of the porous medium. The penetration front of the MEG-rich solution was tracked using digital image processing (Guo et al., 2021).

In this study, two spatial correlation lengths, 2 cm and 4 cm, were used to build the heterogeneous permeability fields. For each correlation length, eight realizations of the random permeability fields were generated in order to satisfy the ergodicity requirement. Therefore, we constructed in total 16 heterogeneous porous media using the 3D-printed sediment blocks, and conducted the miscible density-driven convection experiment for 16 times.

6.2.4. Calculation of mass flux across the top boundary

The MEG mass transferred from the top fluid reservoir into the underlying porous medium was calculated using digital image processing based on mass balance. During the process of miscible density-driven convection, the penetration front movement was adequately slow. In addition, the local convective flow enhanced the dispersion coefficient for solute transport. These two processes suggested that MEG was adequately mixed behind the penetration front, leading to homogeneous solute concentration behind the penetration front (Chen and Zeng, 2015). Therefore, the MEG concentration as a function of time can be calculated as: $C(t) = V_r C_0 / (V_r + \sum \phi_{ij} V_{p,ij})$, where V_r is the volume of top fluid reservoir, C_0 is the initial MEG mass concentration in the top fluid reservoir, ϕ_{ij} and $V_{p,ij}$ are the porosity and volume of pixel (i, j) , respectively. Particularly, pixel (i, j) presents all porous medium pixels behind the penetration front (i.e., the porous medium region that the penetration front has swept), which were determined by tracking the penetration front boundary using digital imaging processing. $V_{p,ij}$ is calculated as the pixel area multiplied by the porous medium thickness (i.e., 2 cm). The total MEG mass within the porous medium at time t can be calculated as: $M(t) = C(t) \cdot \sum (\phi_{ij} V_{p,ij})$. The MEG mass flux ($\text{kg}/(\text{m}^2\text{s})$), defined as MEG mass transferred across a unit interfacial area of the top boundary per unit time, is calculated as the total MEG mass increment in the porous medium over two consecutive measurement times normalized by the total interfacial area and the time increment.

6.3. Results and discussions

6.3.1. Development of density-driven convection

Figure 6-2 illustrates the temporal evolutions of MEG downward penetration caused by miscible density-driven convection in 3D-printed heterogeneous permeability fields. The onset of instability and density-driven convection pattern were affected by permeability heterogeneity. Particularly, the onset of instability occurred in high-permeability regions (i.e., sediment blocks having 3-mm grain diameter). At the time scale of 1 min, MEG-rich fingers had developed to a noticeable extent, and after that these density-driven fingers developed preferentially following the high-permeability regions. Previous studies showed that after the onset of gravitational instability, three mechanisms control the convective mixing process, which are dispersion, channeling, and fingering (Farajzadeh et al., 2011; Ranganathan et al., 2012; Chen et al., 2013). Figure 6-2 demonstrated that the density-driven downward convection in this study was controlled primarily by channeling due to the relatively high Ra and heterogeneous permeability structure. Particularly, at later times (i.e., time scales of 5 min and 10 min) MEG-rich fingers developed preferentially following the high-permeability blocks in both experiments, whereas the low-permeability blocks acted as barriers which hindered the downward penetration of the MEG-rich fingers.

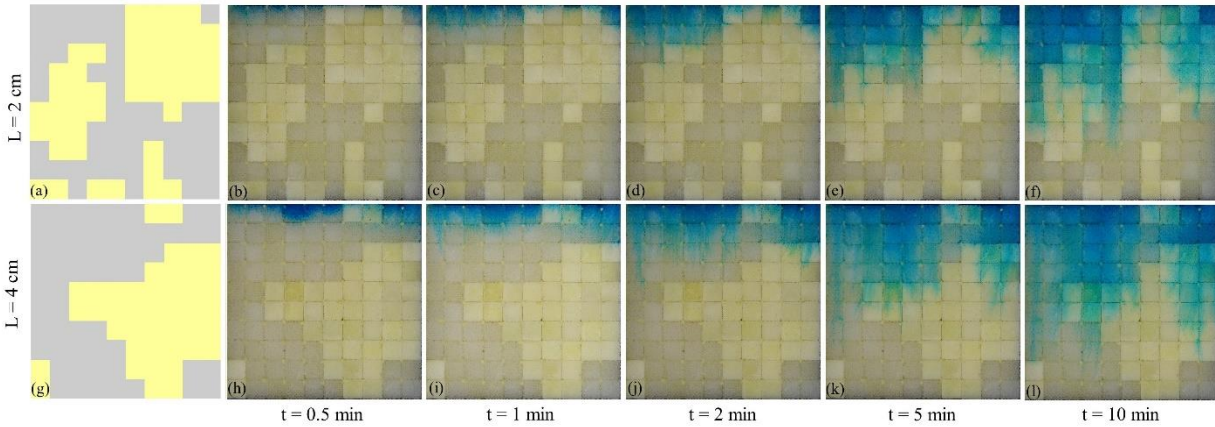


Figure 6 - 2. Evolution of early-stage density-driven convection in heterogeneous permeability fields. The photos in the top row demonstrate the experiment in a heterogeneous permeability field with a spatial correlation length of 2 cm, whereas the photos in the bottom row demonstrate the

experiment in a heterogeneous permeability field with a spatial correlation length of 4 cm. The gray region was constructed using 3D-printed sediment blocks with grain diameter of 3 mm, whereas the yellow region was constructed using 3D-printed sediment blocks with grain diameter of 2 mm.

6.3.2. *Mass flux across the top boundary*

Figure 6-3 illustrates the development of the penetration front in the 3D-printed porous media, as well as MEG mass flux and total transferred MEG mass across the top medium boundary as a function of time. The effect of permeability heterogeneity on the penetration front development was noticeably observed. The MEG-rich solution front preferentially developed along the high-permeability 3D-printed sediment blocks.

The development of the miscible density-driven convection process can be characterized into five regimes, which are the diffusive regime, velocity-growth regime, flux-growth regime, quasi-steady regime, and shutdown regime (Mahmoodpour et al., 2019). The MEG mass transfer is dominated primarily by molecular diffusion in the diffusive and velocity-growth regimes. The overall MEG mass flux across the top boundary of the 3D-printed porous medium continuously decays at early times because the MEG mass transferred into the underlying porous medium diminishes the concentration gradient across the penetration front, which hampers the diffusive mass transfer. At a later time, the mass flux contributed by convection starts to dominate over the mass flux contributed by pure molecular diffusion. At this point, the total MEG mass flux starts to increase. The time when the total MEG mass flux starts to increase marks the end of the velocity-growth regime and the beginning of the flux-growth regime, which is then followed by the quasi-steady regime and shutdown regime. Figure 6-3 illustrates that the onset of the flux-growth regime occurred approximately after eight minutes in both experiments.

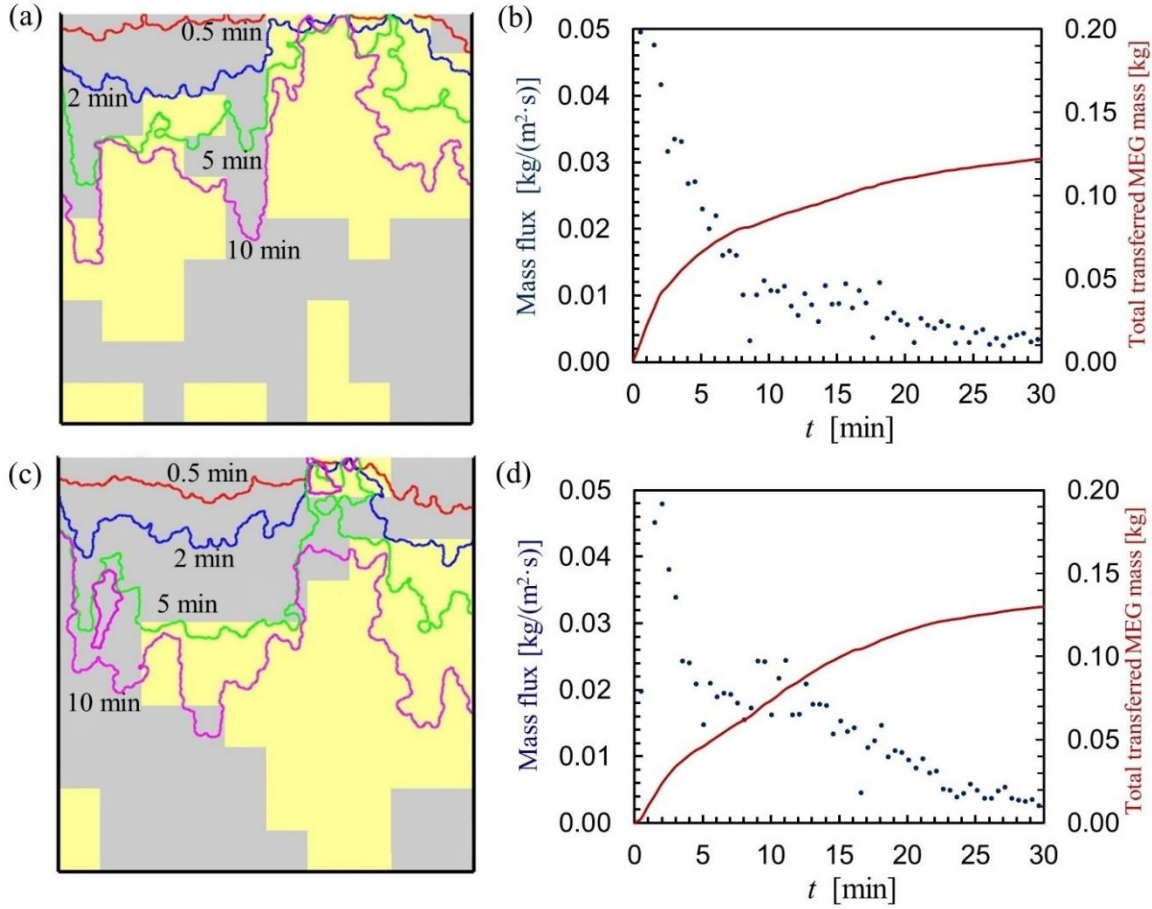


Figure 6 - 3. (a) Density-driven penetration fronts at 0.5 min, 2 min, 5 min, and 10 min, and (b) mass flux and accumulated mass of MEG across the top boundary as a function of time in a heterogeneous permeability field having a spatial correlation length of 2 cm. The white region is constructed using 3D-printed sediment blocks with grain diameter of 3 mm, whereas the gray region is constructed using 3D-printed sediment blocks having grain diameter of 2 mm. (c) Density-driven penetration fronts at 0.5 min, 2 min, 5 min, and 10 min, and (d) mass flux and accumulated mass of MEG across the top boundary as a function of time in a heterogeneous permeability field having a spatial correlation length of 4 cm.

6.3.3. Uncertainty in mass transfer flux

Figure 6-3 demonstrates only one realization of the heterogeneous permeability field for each spatial correlation length. As described previously, in order to meet the ergodicity requirement, eight realizations of the random permeability field for each correlation length were generated and

3D printed; we then conducted the miscible density-driven convection experiment on each of the realization. **Figure 6-4A** and **6-4B** illustrate the total transferred MEG mass amounts against time and average vertical permeability measured in these experiments, as well as the means and standard deviations. The result showed that the average MEG mass transfer rate was similar for both spatial correlation lengths. In other words, the mean total transferred MEG mass across the top boundary at the same experimental time was similar in both scenarios. However, for the correlation length of 4 cm, the collective behavior of the measured mass-time curves showed a more scattered pattern, leading to a wider envelope in comparison to the correlation of 2 cm. This indicates that a larger spatial correlation length in a heterogeneous permeability field causes a higher uncertainty on the total transferred MEG mass into the porous medium.

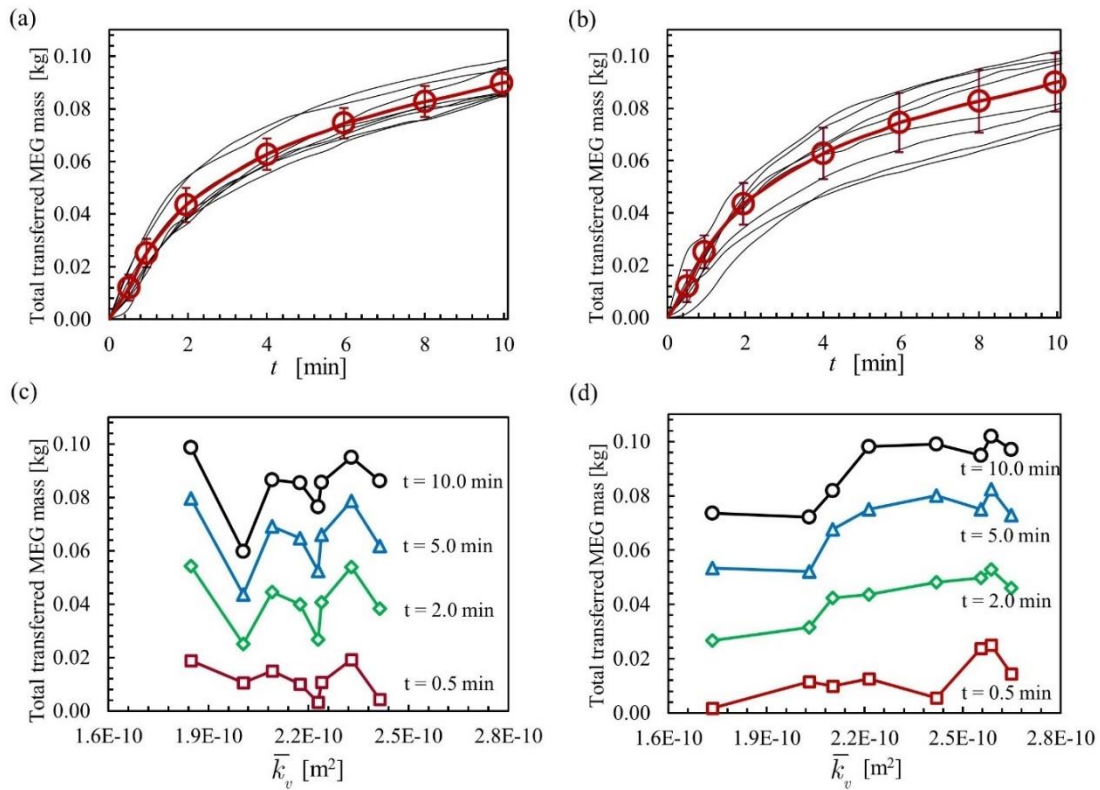


Figure 6 - 4. (a) Total transferred MEG mass across the top boundary of a heterogeneous permeability field having a spatial correlation length of 2 cm against time, (b) total transferred MEG mass across the top boundary of a heterogeneous permeability field having a spatial correlation length of 4 cm against time. Each black curve is the experimental measurement

obtained from a specific realization of heterogeneous permeability field. The red curve and error bars indicate the average and standard deviations. (c) Total transferred MEG mass across the top boundary of a heterogeneous permeability field having a spatial correlation length of 2 cm as a function of average vertical permeability, and (d) total transferred MEG mass across the top boundary of a heterogeneous permeability field having a spatial correlation length of 4 cm as a function of average vertical permeability.

Figure 6-4c and 6-4d demonstrate the relation between total transferred MEG mass and $\bar{k}_v$. Total transferred MEG mass has no noticeable correlation with $\bar{k}_v$ in porous media with correlation length of 2 cm, whereas total transferred MEG mass slightly increases as $\bar{k}_v$ increases in porous media with correlation length of 4 cm. The early-stage MEG mass transfer rate is controlled by permeability close to the top surface of the porous media. The heterogeneity structure of porous media with correlation length of 2 cm is more complex than that of porous media with correlation length of 4 cm. This finding suggests that the $\bar{k}_v$ of the entire porous media with larger correlation length can better represent the effective permeability close to top surface of porous media.

6.4. *Summary and conclusions*

We proposed a three-dimensional (3D) printing-based method to build heterogeneous porous media to investigate density-driven convection in porous media in the context of geological carbon storage. Porous media with desired heterogeneity structure could be established efficiently by stacking 3D-printed elementary porous blocks. We investigated the density-driven convection pattern at early stages. The results suggested that in high-permeability porous media with strong heterogeneity density-driven convection was controlled by fingering and channeling. The average total transferred MEG mass of porous media with the same mean permeability and different correlation lengths were the same. The correlation length caused noticeable uncertainties in total transferred MEG mass and the uncertainty increased as correlation length increased. In porous media with correlation length of 4 cm the total transferred MEG mass slightly increased as average vertical permeability increased, whereas there was no noticeable correlation between the total transferred MEG mass and average vertical permeability in porous media with correlation length

of 2 cm. This is the first experimental study on density-driven convection in heterogeneous porous media with well-controlled heterogeneity. We envision this innovative well-controlled porous media constructing method as an extension to conventional research on convection in heterogeneous porous media and can be further extended to a broad range of fluid flow in porous media. The 3D fluidics provide deterministic controls over pore structure and permeability heterogeneity structure in 3D spaces, which may transform the research on multiphase flow in porous media.

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Chapter 7. Conclusions and Future Work

7.1. Conclusions

In this dissertation, the migration of CO₂ in saline aquifers was investigated at both a pore scale and a continuum scale. The investigation focused on the role of heterogeneity of wettability and permeability on the migration of CO₂ in a CO₂-brine-rock system. In-situ measurements of wettability were conducted on a Bentheimer sandstone after CO₂ flooding. A new heterogeneity model was proposed. LBM-based simulations were conducted to study the impact of wettability heterogeneity on multiphase flow in porous media. At a continuum scale, a novel experimental setup was proposed to determine critical variables of the density-driven convection in homogeneous porous media. To further investigate the role of permeability heterogeneity, a 3D-print technology-based method was proposed to construct porous media with designed heterogeneity patterns. The findings extended existing theory and advanced our understanding on critical processes. The conclusions can be drawn as follow:

1. In-situ measurements of wettability confirmed that wettability of a natural rock was heterogeneous at a subpore scale. The wettability measured as static contact angles followed a lognormal distribution. The correlation length of the wettability of the Bentheimer sandstone is approximately the order of the average pore size.
2. Wettability heterogeneity has noticeable impact on the relative permeability under wetting conditions with the same average wettability. Higher wettability (i.e., higher standard deviation and higher correlation length) can cause increased variation in relative permeability of both CO₂ and brine.
3. Pore-scale surface wettability heterogeneity influences the P_c - S_w curves, which characterizes the macroscopic properties in immiscible two-phase displacements. Under the heterogeneous IW condition, the entry pressure of the PD stage was negative, whereas it was zero under the homogeneous IW condition. The negative entry pressure in the heterogeneous CA scenario was caused by CO₂-wet rock surfaces, which has critical implications to structural trapping of geological CO₂ sequestration. In other stages (i.e., IM and SD), the P_c - S_w curves were almost identical between the homogeneous and heterogeneous wetting conditions. The finding suggested that the effects of surface wettability heterogeneity on the P_c - S_w curve were averaged out at the entire-sample scale.

4. The relative permeability curves were affected by the saturation history under both homogeneous and heterogeneous wetting conditions. The imbibition process increased the relative permeability of water and decreased the relative permeability of scCO₂, compared to the drainage process. Under the SWW condition, the effects of pore-scale wettability heterogeneity on the relative permeability curves were not noticeable. Under heterogeneous WWW and IW conditions, the variation of the scCO₂ relative permeability curve was more significant than that in the homogenous wettability scenario. This is because pore-scale wettability heterogeneity enhances the coalescence and snap-off behaviors of scCO₂ blobs when the system goes through the PD, IM, and SD stages, thereby leading to more significant variations of scCO₂ relative permeability curves at a larger scale.
5. This study demonstrated the effects of pore-scale surface wettability heterogeneity on microscopic fluid distribution, relative permeability and macroscopic P_c - S_w relation. Compared to SWW condition, the wettability heterogeneity can cause noticeable redistribution of CO₂ and brine for different displacement path under IW condition. Accordingly, the variation in the relative permeabilities under IW condition is larger than that under SWW condition. The P_c - S_w relations under heterogeneous wetting condition is close to those under homogeneous wetting condition. This is because that the effects of wettability heterogeneity were averaged out through the entire rock. The difference from homogeneous wetting condition is that for heterogeneous IW condition, the entry pressure is negative, while that for homogeneous IW condition is zero.
6. We found that Ra has a significant impact on the convective dissolution pattern. The MEG-rich fingers were relatively thick for a low Ra whereas they were relative slim for a high Ra . The peak downward velocity after the onset of density-driven instability was measured, which followed an exponential growth mode. The critical Ra was estimated as 259. The empirical formula for calculating the critical time for the onset of density-driven instability was found as $t_{cr1} = 53.1(\mu\phi)^2D/(g\Delta\rho k)^2$ based on laboratory data fitting. The empirical formula for calculating the critical time for the onset of convective dissolution was determined as $t_{cr2} = 832.1(\mu\phi)^2D/(g\Delta\rho k)^2$ by fitting laboratory data. The empirical correlation between average MEG mass flux and Ra was found as $Sh \propto Ra^{0.95}$. This work is the first study to determine the empirical correlations for these two critical times using

laboratory experiments. In practice, the determination of the second critical time (i.e., t_{cr2}) has practical significations in field-scale GCS projects.

7. We investigated the density-driven convection pattern at the early stage. The permeability structure has strong control over the onset of instability and convection. The density-driven instability occurred at the interfaces with high permeability. The density-driven convection was controlled by fingering and channeling. MEG-rich water preferentially migrated along high-permeability channels. Convection in low-permeability regions right beneath the top boundary of porous media was hindered by the upward flow caused by downward fingers in the nearby high-permeability regions. The average dissolution rates for porous media with the same mean permeability and different correlation lengths were the same. The correlation length caused noticeable uncertainties in the dissolution rates and the uncertainty increased with increasing correlation length.

7.2. *Future work*

The work in this dissertation advanced our understanding on the wettability of a natural rock and the role of heterogeneous wettability on the multiphase flow in a rock. This work also provided experimental evidence for the determination of critical parameters in density-driven flow in porous media. However, there still exist some work, which needs to be further investigated in the future.

1. The in-situ wettability measurements of a rock are difficult because distribution of CO_2 /brine are uncontrollable. The limited in-situ measurements of wettability are not enough to describe the entire wettability of a natural rock. Employing innovative technology to measure subpore scale wettability will be needed in the future investigation on characterizing wetting conditions of complex porous media.
2. The computational resources needed in the pore scale simulation are too large. Although the LBPM code used in this dissertation is very powerful, comprehensive simulations on the displacement process through all desired parameter range are still too time-consuming. Integrating innovative hardware acceleration technology is a promising way to advance pore-scale simulations.
3. Density-driven flow was investigated in a quasi-2D box where the convection is different from the flow in a 3D space. The distribution of CO_2 was averaged in the third dimension,

which limits our ability to obtain information inside the porous media. High-resolution nondestructive detecting technologies will be needed to advance the studies on multiphase flow in porous media.

4. The resolution of 3D printing technology is limited. It is difficult to print porous media with average grain sizes less than 1 mm. Using 3D printing technology with higher resolution to print porous media with finer pore structure will be the next work.

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The role of the spatial heterogeneity and correlation length of surface wettability on two-phase flow in a CO₂-water-rock system

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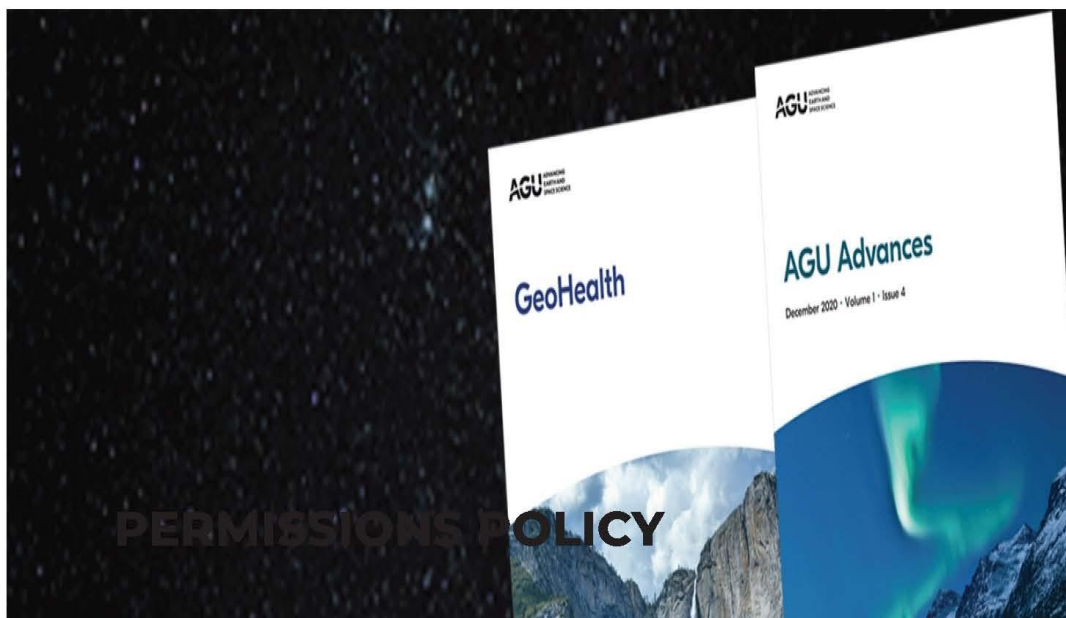
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