Microfluidic Pore Model Study on Physical and Geomechanical Factors Influencing Fluid Flow Behavior in Porous Media

Shuang Cao
Louisiana State University and Agricultural and Mechanical College, scaocindy@gmail.com

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_dissertations

Part of the Geotechnical Engineering Commons

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_dissertations/4187

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Doctoral Dissertations by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
MICROFLUIDIC PORE MODEL STUDY ON PHYSICAL AND GEOMECHANICAL FACTORS INFLUENCING FLUID FLOW BEHAVIOR IN POROUS MEDIA

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Civil and Environmental Engineering

by:
Shuang Cao
B.Sc. China University of Petroleum-Beijing, 2011
M.Sc. University of Mississippi, 2013
May 2018
ACKNOWLEDGMENTS

I would like to express the deepest appreciation to my advisor, Dr. Jongwon Jung, who has offered me the precious opportunity for pursuing this Ph.D. degree as well as the mentorship, and support. Without his support, corrections, and guidance, this dissertation would not have been accomplished. I also want to appreciate my co-advisor, Dr. Shengli Chen, who continues supporting and helping me after Dr. Jung left LSU. Without his help, it would not be possible to finish this dissertation.

Besides, I would like to appreciate the help, support, and encouragement from my all other committee members, Dr. Mileva Radonjic and Dr. Clinton Willson for their guidance, cooperation, and great patience, which enhance the quality of my work and dissertation.

I also wish to acknowledge Dr. Jin-Woo Chio (School of Electrical Engineering and Computer Science, LSU), Dr. Junbong Jang (U.S. Geological Survey), and Dr. William Waite (U.S. Geological Survey) for their collaboration, help, and cooperation.

Furthermore, I would like to appreciate the help, and encouragement from my group mates (Jungyeon Jang, and Mohammad Jafari) and all friends (Ruijie Bian, Mengqiu Ye, and Shu Gao, etc.). Also, I am grateful to my parents, and parents-in-law for their endless support. Last but not least, I would like to thank my beloved husband, Hui Du, for his encouragement, support, and patience. You made this part of my life enjoyable and enriching.
# TABLE OF CONTENTS

ACKNOWLEDGMENTS ............................................................................................................. ii

ABSTRACT ............................................................................................................................... v

CHAPTER 1. INTRODUCTION ................................................................................................. 1
  1.1 Background and Motivation ......................................................................................... 1
  1.2 Research Objective ..................................................................................................... 3
  1.3 Overview of Dissertation ............................................................................................. 4
  1.4 References .................................................................................................................... 7

CHAPTER 2. LITERATURE REVIEW ......................................................................................... 9
  2.1 Engineering Applications of Fluid Flow in Porous Media .............................................. 9
  2.2 Fundamentals of Fluid Flow in Porous Media ............................................................... 11
  2.3 Fine Particles Influences of Fluid Flow in Porous Media ............................................ 16
  2.4 References .................................................................................................................... 31

CHAPTER 3. FLUID WETTING PROPERTIES INFLUENCES ON MULTIPHASE FLOW 
BEHAVIOR IN POROUS MEDIA ........................................................................................... 38
  3.1 Introduction .................................................................................................................. 38
  3.2 Literature Review ......................................................................................................... 39
  3.3 Experimental Method .................................................................................................. 46
  3.4 Results and Discussion ............................................................................................... 51
  3.5 Conclusion ................................................................................................................... 58
  3.6 References .................................................................................................................... 60

CHAPTER 4. PRESSURE AND TEMPERATURE EFFECTS ON MULTIPHASE FLOW 
BEHAVIOR IN POROUS MEDIA .......................................................................................... 66
  4.1 Introduction .................................................................................................................. 66
  4.2 Experimental Method .................................................................................................. 71
  4.3 Pore Network Model Simulation .................................................................................. 73
  4.4 Results ........................................................................................................................ 75
  4.5 Analyses and Discussion ............................................................................................. 80
  4.6 Conclusion ................................................................................................................... 84
  4.7 References .................................................................................................................... 85

CHAPTER 5. PORE FLUID CHEMISTRY RELATED GEOMECHANICAL FACTORS 
AFFECTED BY FINE-GRAINED MATERIALS ........................................................................ 91
  5.1 Introduction .................................................................................................................. 91
  5.2 Experimental Method .................................................................................................. 94
  5.3 Results and Discussion ............................................................................................... 97
  5.4 Conclusion ................................................................................................................... 112
  5.5 References .................................................................................................................... 114

CHAPTER 6. MECHANISM OF FINES CLOGGING IN POROUS MEDIA WITH SINGLE 
AND MULTIPHASE FLOW ................................................................................................. 117
ABSTRACT

Fluid flow in porous media is a subject of fundamental importance and relevant to numerous engineering applications. The comprehensive description of fluid interaction parameters containing wetting properties, fluid-fluid displacement ratio, and capillary pressure, are inevitably needed. Moreover, the fine-grained sediments’ response to various pore fluids and migration in porous media influences reservoir geomechanical properties and pore clogging is essential to a better understanding of fluids flow behavior.

This dissertation provides a detailed study of physical and geomechanical factors influencing fluids flow behavior in porous media. The two-dimensional micromodel tests have been conducted under a wide selection of fluids flow conditions. The experiments combined with pore network modeling are added to predict the fluid-fluid displacement ratio and capillary curves regarding different fluids. The fines’ geomechanical properties such as electrical sensitivity, compressibility, and hydraulic conductivity, together with pore plugging criteria are measured through various experiments including sedimentation, electrical sensitivity, and consolidation tests.

Results of this research show that increase in injection fluid velocity, viscosity, contact angle, and a decrease in fluid’s interfacial tension can result in higher viscosity and capillary numbers, which leads to an improvement of the fluid-fluid displacement ratio in porous media. Experiments with the subsequently conducted simulation corroborate a higher capillary pressure is expected with a decrease in contact angle and an increase in interfacial tension. Meanwhile, estimation of capillary pressure can be achieved with measured fluids’ wetting properties at different stress levels. Besides, the findings indicate that fine sediments’ geomechanical properties and clogging criteria can be altered due to fines’ response to distinct pore fluids. The
geomechanical properties of the different fine sediments also vary with pore fluid chemistry changes. And, fines clogging in porous media is observed under conditions of a lower pore throat width/fine size ratio, a higher fine concentration, a relatively higher flow rate, and the changed pore fluids. Additionally, the presence of a moving gas/liquid meniscus increases the fines clogging potential. In summary, an understanding of fluids’ physical and geomechanical properties, in addition to an identification of fines influences, can help to evaluate the performance of fluids flow in porous media.
CHAPTER 1. INTRODUCTION

This dissertation includes eight chapters. Except for the introduction (Chapter 1), literature review (Chapter 2), and conclusion (Chapter 8), other chapters are constructed using the technical paper format with the manuscript that has been published or will be submitted to peer-reviewed journals. Therefore, Chapter 3-7 are independent but relevant in this dissertation. Chapter 1 presents an overall background and motivation for the related research in this dissertation. In addition, the objective and an overview of each chapter are offered in this chapter. The detailed information is presented in each chapter.

1.1 Background and Motivation

Geologically, the reservoir, which is under a set of geological conditions, is a complex of pores, sediments, and fluids. Thus, fluids flow in porous media plays a significant role. The fluids flow in porous media is a subject of fundamental importance and is relevant to many engineering applications, for example, grouting for ground improvement, hydraulic fracturing, methane hydrate extraction, water flooding for hydrocarbon recovery, carbon dioxide (CO₂) sequestration, enhanced oil recovery, drill cuttings reinjection for solid site disposal, and construction of permeable reactive barriers for environmental remediation (Sandiford and Pye, 1964; Blokker, 2014; Bailey et al., 2000; Kosaric, 2001; Leveratto e al., 1996; Stepp et al., 1996; Tsouris et al., 2010; Xie and Economides, 2009). Therefore, a number of engineering events require a deeper exploration of fluids flow behavior within metabolic fluids and porous media conditions. The complexity of fluids and porous media condition is the challenge for different cases. Moreover, the intensive exploration of fluids flow in porous media related cases, such as the influences of fluid wetting properties, the capillarity changes at various back pressure, and mechanism of fine-grained materials (fines) clogging in single and multiphase flow, as well as fines migration and
clogging behaviors affected by pore fluids, have not been well understood. Hence, understanding the fluids flow behavior influenced by physical and geomechanical parameters of porous media within various subsurface conditions is needed. First, physical parameters of fluids affecting the wetting properties of porous media are critical. The physical factors of multiphase flow in porous media, including contact angle, surface tension, interfacial tension, and viscosity, which influence on capillary pressure, wettability, in particular for controlling fluids flow mobility by second fluid invading procedure need to be well explored. Second, the in-situ condition of fluids flow in porous media need to be well considered due to their particular temperature and pressure effects on fluids flow behavior in porous media. The temperature and pressure inflection can make drastic changes for fluids flow in porous media so that the capillary curve and relative permeability can be impacted immediately. Thirdly, the fine-grained materials (fines) exist in coarse-grained sediments, and forming interbeds between sediments can play an important role during fluids flow. The fluid refreshing or replacement coupling with these fine-grained materials can affect the overall sediment formation performance result in the geomechanical properties of formation change. Furthermore, the small fraction of fine particles migration through porous media involving multiphase flow become a significant consideration for reservoir performance. For some cases, the content of fines is even relatively small in porous media, fine particles still affect fluids volume expansion, changes in porosity, pore plugging, which generates many engineering problems such as sand production, low gas recovery efficiency, and borehole failure in gas production (Jung et al., 2012; Muecke, 1979; Fan et al., 1985; Herzig et al., 1970; Imdakm and Sahami, 1991; Khilar and Fogler, 1987; Mackie et al., 1987; Rege and Fogler, 1998; Sharma and Yortsos, 1987; Agbangla et al., 2012). In summary, understanding the principle of fluids flow behavior and fines migration with pore fluid in both single and
multiphase flow can be the good starting for solving those problems. A deeper and more comprehensive exploration of physical and geomechanical factors influencing fluids flow behavior in porous media is a pressing need.

1.2 Research Objective

The general aim of this research is exploring the numerous effects on fluids flow behavior in porous media. Several main factors that are considered as significantly influencing the fluids flow behavior in porous media are evaluated. The main concentrate of the research is understanding which and how these factors change the single and multiphase fluids flow behavior in the underground porous media. To successfully achieve the goal of this study, this research provides the exploration of physical and geomechanical factors influencing fluids flow behavior in porous media. Moreover, the fine particles effects on fluids flow behavior in porous media are emphasized. The changes of fines clogging behavior, pore fluid properties, fine particles electrical sensitivity, compressibility, as well as hydraulic conductivity, are discovered. Especially, this research includes various topic related implications in each chapter, such as geological carbon sequestration, oil-contaminated soil remediation, and fine-grained sediments related energy recovery. These implications can play a crucial role for a lot of engineering applications, such as geological carbon sequestration for short-term injection efficiency and the long-term capillary trapping and geological stability, soil improvement, contaminated soil remediation, mobility control for enhanced oil recovery (EOR), fines migration influences in hydrate-bearing sediments, and so on. Besides, this research investigates the advanced experimental tests analysis method for each particular test condition. The two-dimensional microfluidic model, which made of homogeneous pore-network patterns to form a two-
dimensional symmetrical pore-networks, were fabricated and utilized to achieve directly observing the experimental results.

1.3 Overview of Dissertation

The dissertation is organized in eight Chapters. The primary objective is to get a comprehensive understanding of influences of physical and geomechanical factors for multiphase flow behavior in porous media that is further discussed in the five paper-format chapters. The brief overviews of each chapter are list as follows.

Chapter 2 presents a general literature review and description of the aspects of influencing factors for multiphase flow behavior in porous media. First, the related engineering applications on multiphase flow in porous media are introduced. Then, the details of physical and geomechanical properties of fluids and porous media effects for mobility control, displacement efficiency in the subsurface reservoir, the geomechanical properties of fine-grained sediments, and the significant impacts related to fines migration in porous media, as well as the emphasis of fine responses to different pore fluids are explained.

Chapter 3 focuses on fluids influences for the wetting properties of porous media. Many types of fluids have been considered for oil-contaminated soil remediation thanks to their mobility control and flooding performance. The new type of injection fluid named biopolymer is intended in this research to understand the flow behavior of biopolymer solutions and biopolymer solutions-oil displacements in porous media. Five different biopolymer solution and influencing factors of fluid wettability, including contact angle, surface tension, interfacial tension, and viscosity that impacts on capillary pressure, biopolymer solution flow, and biopolymer solutions-oil displacement in porous media are explored.
Chapter 4 presents the temperature and pressure effects on fluid displacement efficiency, and capillary pressure curve changes. One of the most popular topics geological carbon sequestration (GCS), which relates to the short-term injection efficiency and the long-term capillary trapping and geological stability, are involved. This chapter intensively chooses and simulates the reservoir temperature and pressure for CO₂ and brine flow behavior to predict the CO₂ flow and CO₂-brine displacement efficiency in deep saline aquifers. This chapter also explores the pressure and temperature influencing injected fluid velocity and ionic strength impacts on invading patterns in multiphase flow implicated on geological CO₂ sequestration. Chapter 5 includes the description of various endmember fine materials sensitivity linked geomechanical factors properties, such as fines’ electrical sensitivity, compressibility, and hydraulic conductivity. The macroscopic impacts of pore fluids on fine sediments’ electrical sensitivity, compressibility, and hydraulic conductivity are explored in this chapter. It indicates the electrical sensitivity changes of fine grains due to pore fluid chemistry resulting alterations in fabric formation, compressibility, and hydraulic conductivity of a diverse suite of endmember fine materials. Since the fine-grained materials exist within sands, as well as forming interbeds between sediments layers are likely to impact the overall sediment formation performance (Jang et al., 2017), the related engineering events gas production from hydrate-bearing sediments in offshore and onshore are implicated. Chapter 6 show the research for studying the mechanism of fines clogging in porous media on single and multiphase flow. This chapter focuses on the mobilized fines or micro-particles, which can severely help understanding the influences of migration particles on bridging and clogging. Fines migration and clogging in porous media is a complex phenomenon but greatly related to the size of fine particle, host particle size, pore throat with, fines concentration, flow
rate, and invading fluid phase flow. The related industrial applications including filtration, water
and oil extraction, flow in biological system, the sand production, gas-driven fractures in
sediments, and gas production from hydrate-bearing sediments are implicated in this chapter.
The enhanced understanding of fines migration and clogging mechanism and its relation to the
parameters are discovered. This chapter presents a microfluidic model study utilizing the
artificial fine materials to explore the mechanism of fines clogging in porous media not only in
single but also in multiphase fluids flow including fine particles considering fine particle
concentration and the size ratio of the pore throat and fine particle. The influences of critical
ratios of the pore throat and fine particle, fine concentration, and invading fluid phase (gas) for
fines migration and clogging in porous media are well understood.
Chapter 7 emphasizes the pore fluids effects on nature endmember fines migrations and clogging
behavior in porous media. This chapter provides the study of the significant considerations for
various types of endmember fines migrating and clogging in coarse-grain sediments pores, and
reacting with different pore fluids. To evaluate fines migration and clogging behavior changes
with different pore fluids, two-dimensional micromodel experiments have been conducted on a
selection of pure fines, pore-fluids, and micromodel pore-throat sizes. Additionally, the tests in
this chapter have been run with and without an invading gas phase to test the significance of a
moving meniscus on fines mobility and clogging. The implication focuses on fines impacts in
course sandy sediments during gas hydrate production activities due to several methane
extraction processes that can alter the mobility and clogging potential of fines. For instance, the
fine particles influence may occur when pore-fluid chemistry shifts as pore-fluid brine freshen
due to pure water released from dissociating hydrate.
Finally, Chapter 8 summarizes this dissertation findings with some multiple conclusions. The research findings are expected to be of interest to geotechnical/geological/petroleum engineers and researchers who study or use experimental methods analyze different physical and geomechanical factors that influence multiphase flow behavior in porous media. The findings also can guide and applicate for a number of industrial applications or environmental processes.

1.4 References


CHAPTER 2. LITERATURE REVIEW

2.1 Engineering Applications of Fluid Flow in Porous Media

Fluids flow in porous media is described based on single-phase flow and fundamental factors of two-phase or multiphase flow behavior. Understanding the fluids flow behavior and the characteristics of different fluids wetting properties such as wettability, interfacial tension, fluid viscosity, fluid mobility, and fines migration in porous media can play a crucial role for enhancement of efficiency of engineering events.

Understanding fluids flow behavior in porous media influences many aspects in engineering applications. First, the engineering events related to fluids flow in porous media are resolving problems of contaminated soils and subsurface energy enhancement. For example, the modification of fluids using bio-chemical method can change the reservoir wetting influence, contact angle, fluids interfacial tension and viscosity, which can lead high efficacy of the results. Thus, water flooding by biopolymers or polymers has become a superior method for enhancing the oil recovery according to the laboratory and field tests (Sandiford and Pye, 1964; Blokker, 2014). Also, it has been considered for oil-contaminated soil remediation thanks to its mobility control and water flood performance (Bailey et al., 2000; Kosaric, 2001; Leveratto e al., 1996; Stepp et al., 1996).

Secondly, carbon-producing fossil fuels will continue to be the dominant energy resource for decades (Tsouris et al., 2010; Xie and Economides, 2009). Thus, more carbon dioxide (CO₂) is anticipated to be discharged into the atmosphere due to the continued increase in global energy demand. Geological CO₂ sequestration is a method to reduce CO₂, and deep saline aquifers are one of the most important categories due to their capacity for CO₂ storage. Therefore, understanding of two immiscible brine-CO₂ mobility and its saturation, including invading...
patterns in deep saline aquifers as CO$_2$ storage sites is required (White et al., 2005). Within understanding the multiphase flow theory, the prediction of CO$_2$ flow and CO$_2$-brine displacements in deep saline aquifers can be achieved. Furthermore, fine-grained materials ("fines") exist within sands, or forming interbeds between coarse grains layers play a critical role in many reservoirs. A lot of application can be seen in fields such as Geotechnical, Chemical, Environmental, and Petroleum Engineering. In detail, the fine particles exist in porous media is expected to affect ubiquitously on various events including filtration, water or oil extraction, flow in biological system, pore plugging, the sand production, and gas-driven fractures in sediments, as well as gas production from hydrate-bearing sediments (Sanderson et al., 2001; Sherard et al., 1984; Datta and Redner, 1998; Papamichos et al., 2001; MacDonald and Whitesides, 2002; Kampel and Goldsztein, 2008; Valdes and Santamarina, 2008; Shin and Santamarina, 2010; Jung et al., 2012). For example, gas production from hydrate-bearing sediments depends in part on geotechnical properties of fine-grained materials. And, the responses of fine-grained material to pore fluid chemistry changes could alter critical sediment characteristics during gas production activities (Jung et al., 2012). Moreover, the fine particles migration and clogging in porous media and involved with fluids flow in porous media is proved as a big challenging problem of both scientific and industrial importance (MacDonald and Whitesides, 2002, Kampel and Goldsztein 2008, Valdes and Santamarina, 2008).

The research in this dissertation can be implicated on most of these engineering applications, and understanding the physical and geomechanical parameter influencing fluids flow behavior in porous media is inherently needed for them.
2.2 Fundamentals of Fluid Flow in Porous Media

2.2.1 Porous media

The porous media properties are based on pore level, which needed to relate to the pore description, such as pore structure, porosity, permeability, tortuosity, connectivity, and pore characterizations (Bear, 1972; Dullien, 1992; Adler, 1992; Torquato, 2002; Chekired and Roubtsova, 2014). Known for the size, shape, and other characteristics of porous media are essential to the understudying of the various processes that occur in pours media. This research intends to study and discuss only the most physical and geomechanical relevant aspects of fluids flow in porous media, such pore structure, pore surface, characteristics of fluids flow in porous media, wettability, interactions between two-phase fluids flow, and geomechanical properties of porous media related fluids flow behaviors.

2.2.2 Pore structure

Pore structure varies due to how porous media contains voids dispersed in a solid matrix. The void space must be able to allow the fluid to permeate. Porous media can be considered to a system that the solid and void phases dispersed. The void phase is critical for fluids flow. Even the single pore medium, such as Ottawa sand, which could have the enormous pore size, shapes, and interconnections. Therefore, pore structure is often characterized based on fluids performances. The pores can be either interconnected to form a continuous phase or non-interconnected to form blind pores (Scheidegger, 1974). The interconnected pores are more important for which the transport of fluids and fines migration. The porous media, such as soil mass and different rock can be treated as a network of hosts. And those hosts forming the pore bodies which connect through pore throats. Two simple microscopic parameters pore host size and pore constriction size can characterize the pore structure geometrically. For nature pore
structure, it can be divided into three main types including intra-elemental pore space, intra-assemblage pore space, and trans-assemblage pore space (Collin and McGown, 1974; Mitchell, 1993). The intra-elemental pore spaces are made by particles which have singular shape. The intra-assemblage pore spaces and trans-assemblage are usually formed by different types of particles which have different shapes. Figure 2.1 illustrates the schematic representation of pore space types for nature sediments (Collin and McGown, 1974).

![Pore space types](image)

Figure 2.1 Schematic representation of pore space types for nature sediments (Collin and McGown, 1974).

To describe the pore structure easily, two kinds of packing of spherical particles are commonly used to describe the pore structure that is described as cubic packing and rhombohedral packing (Collins, 1990). The equilateral triangle and equilateral quadrilateral can simply represent these two pore structures for spherical host particles with a diameter equals to D. Figure 2.2 illustrates the most common types of packing of spherical particle and corresponding pore spaces

![Packing types](image)

Figure 2.2 Simple equilateral triangle (left) and equilateral quadrilateral (right) indicate the cubic and rhombohedral packings of spherical partials (grey color) and corresponding pore space (white color) (Collins, 1990; Liu and Masliyah, 1996).
In general, the pore body size of loosest spherical shape particles (simple cubic packing) is theoretically equal to 0.414 D with the highest pore throat size (o), while the pore body size of the densest spherical shape particles (cubic tetrahedral packing) is equal to 0.155 D with the lowest pore throat size (o).

2.2.3 Pore constriction size, porosity, void ratio, and permeability

Pore constrictions, also known as pore throats, are the narrowest segments of pores (Khilar and Fogler, 1998). It can be measured by some well-developed techniques. The most popular methods include mercury porosimetry and optical methods (Dullien, 1979; Biswas and Mukherjee, 1994). Table 2.1 shows a sample of pore throat size and host particle size for porous media such as sandstone. Base on pore throat and pore space, two important macroscopic parameters of porous media are created and called as porosity or void ratio and permeability.

Table 2.1 Pore throat size and host particle size of some sandstones (Dullien and Dhawan, 1974; Ioannidis and Chatzis, 1993; Lymberpolous and Payatakes, 1992)

<table>
<thead>
<tr>
<th>Sandstone</th>
<th>Pore throat size (μm)</th>
<th>Host particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berea</td>
<td>0.5-5.0</td>
<td>5-50</td>
</tr>
<tr>
<td>Boise</td>
<td>\</td>
<td>39-74</td>
</tr>
<tr>
<td>ST1</td>
<td>33-120</td>
<td>33-250</td>
</tr>
<tr>
<td>Bartseville</td>
<td>\</td>
<td>19-44</td>
</tr>
</tbody>
</table>

Porosity is the fraction of the total volume of porous media that occupied by void space. It also can be described as the void ratio. Void ratio is used in parallel with porosity that is defined as the ratio of the volume of voids to the total volume of the solid. Permeability is not only related to porosity/void ratio, but also to the shaped of pores and level of connectedness. It is the measurement of pore ability to allow fluids to pass through it. The permeability of porous medium is the proportionality constant in a local relationship between the pressure gradient and the flow velocity (Khilar and Fogler, 1998). It has been well described by Darcy’s law (Kamyabi, 2014). Darcy’s law indicates steady unidirectional flow in a uniform medium
revealed a proportionality between flow discharge rate and the applied pressure drop (Liu and Masliyah, 1996; Tiab and Donaldson, 2004). It is expressed as

\[ K = v \frac{\mu \Delta x}{\Delta p} \]  

(2.1)

where \( v \) is the superficial fluid flow rate, \( \mu \) is the dynamic viscosity of the fluid, \( \Delta p \) is the pressure drop across the porous media of thickness \( \Delta x \), and \( K \) is the intrinsic permeability of the porous media.

2.2.4 Characteristics of multiphase flow in porous media

The simple case of fluid flow in porous media is linear steady-state flow. It has been well described by Darcy’s law, which indicated that the primary elements of this subject had been well understood for 150 years (Kamyabi, 2014). However, multiphase flow through porous media is more complex and often involves the interactions of the various fluids with their interstitial surfaces. Therefore, a good understanding of the properties of fluids, pores, sediments, and multiphase fluid transport characteristics is desired. To maximize the understanding of multiphase flow in porous media, some essential characteristics of multiphase flow in porous media need to be well presented.

Wettability. The wettability is the ability of solid surface (pore surface) to reduce the surface tension (interfacial tension) of fluids in contact with that spreads over the surface and wets it (Donaldson and Alam, 2008). It is the relative adhesion of two fluids to a solid surface. The main characteristics of fluids in porous media are related to wettability, such as interfacial tension, contact angle, fluid-fluid displacement ability, and capillary pressure.

Interfacial/surface tension. As introduced with wettability, when two immiscible fluids are in contact with the solid surface, the two fluids are separated by the interface. Interfacial tension is a property of two immiscible fluids, and it is the force that keeps the solid surface of one fluid
phase together with another fluid phase. It is similar to surface tension in that cohesive forces are involved (Donaldson and Alam, 2008). This property directly affects the fluids' behaviors in porous media that can cause capillary pressure and fluid saturation change. In general, the experimental methods can be used for measuring the interfacial tension. It includes the duNouy ring method (ASTM D1331, 2014), the Wilhelmy plate method (ASTM D1331, 2014), and pendant drop method (Donaldson and Pavelka, 1967).

Contact angle. When the interface exists between a liquid and solid, the angle between the surface of a liquid and the solid contact surface is defined as the contact angle (Volpe et al., 2006). It is the measurement of the wettability of the solid by liquids. In general, if the surface is hydrophilic (water-wet), the contact angle is less than 90°C. When the contact angle greater than 90°C, the solid surface is defined as hydrophobic (oil-wet). Also, if the contact angle is close to 90°C, the surface is considered as neutral-wet. It is important when the intensity of the fluid phases contact with solid substance need to be understood. In porous media, contact angle and interfacial tension are significant parameters for accessing the capillary pressure. To measure the contact angle, several standard experimental methods can be used based on measurement purposes which contain the static/dynamic sessile drop method (Volpe et al., 2006), the pendant drop method (Bhutani et al., 2013), and the Washburn’s equation capillary rise method (Washburn, 1921).

Viscosity. Viscosity is an important characteristic of fluid which is a measure of its resistance to deformation by shear stress or tensile stress (Symon, 1971). The fluid has no resistance to shear stress is defined as an ideal or inviscid fluid, such as the fluid is observed at very low temperatures. On the other hand, a fluid with relatively high viscosity may appear to be a solid. The fluids that usually appears in porous media can be observed as fresh water, brines,
hydrocarbon oils, and gases which have the various viscosities. A fluid with the high viscosity in porous media means that it has a higher resistance to flow. Understanding pore fluid viscosity can play an important role in estimating reservoir performance.

**Capillary pressure.** Capillary pressure in porous media is defined as the pressure difference between two immiscible fluids resulting from the interaction forces between fluids and solid. It is identified by Young–Laplace equation which is shown in equation 2.2 (Bear, 1972).

\[ P_c = \frac{2\sigma \cos \theta}{R} \]  

(2.2)

where the value of pore radius (R) depends on in-site geological conditions, \( \sigma \) is defined as interfacial tension, and \( \theta \) is defined as the contact angle of the liquid on the surface of the capillary. Measuring the capillary pressure and discovering the relationship between capillary pressure and fluid saturation in porous media is important for understanding the fluid distribution in reservoir and prediction of fluid-fluid displacement.

### 2.3 Fine Particles Influences of Fluid Flow in Porous Media

#### 2.3.1 Fine particles

Fines or fine particles are small particles present in porous media. The fine particles can be inorganic, organic, or biological. In Geotechnical Engineering, the fine particles exist in sediments can cause problems, such as internal and surface soil erosions, failure dams and roads (Aitchinson and Wood, 1965). Moreover, it is important to note the significance of fines influence for producing methane from hydrate-bearing reservoir sands. For gas hydrate production from hydrate-bearing sediments, the fines migration not only happens through reservoir sands, but also fines are attracted to, and collect on, interface between methane gas and fresh water flowing toward the production well (Jung et al., 2012). Mobilization of fine materials can severely affect the displacement performance of the porous media while subjected flooding
The consequences of the fines migration can be either adverse or beneficial for engineering application. For instance, a lot of research present the permeability reduction due to fines migration in porous media. Permeability is the ability of the fluid to flow through the porous media and it usually governed by pore size, specific surface, gradation, and fabric. Migratory fines clogging can lead permeability decline. Even fines clogging reduces reservoir permeability, recent research by Jung suggests a mechanism by which permeability may be enhanced over time as the certain clogs fracture in response to an increasing pressure differential across the clog (Jung et al., 2012).

By fines, here it means the small solid or solid-like particles exist in natural porous media. These fines are subjected as mobile or migratory particles. In this research, two characterizations of fines are discussed. The first aspect is the geometrical characterization of fines. The second aspect is the colloidal characterization of fines.

For geometrical characterization of fines, the shape and size play a significant role. Based on mineralogy, fines can be divided into two types, which are clay material and no-clay material. The clay material contains kaolinite, illite, montmorillonite, etc. The non-clay material includes quartz, feldspars, carbonates, muscovite, amorphous material, salts, as well as organic, and biological moieties (Khilar and Fogler, 1998). The largest of a dimension of fine varies from 0.1 to 20 μm. For instances, the biggest dimension of mobile fine in Berea sandstone is range from 0.1 to 5 μm (Khilar, 1981). The size of fine can be measured by means of a number of particles’ sizes. Moreover, the size of fine in a suspended state may be different from in a dry state.

Defining the sizes of these particles are difficult due to their irregular shape. In general, the shape of the clay fines can be described as platelets, blades, needles, and flacks. The fine sand particles,
as well as organic and biological fines, are not as irregular as the clay fines. None of the natural fines can be considered perfect spherical.

For colloidal characterization of fines, the physical size and the surface charge of fines are significant to know. The fine particles usually carry the surface changes which depend on how the fines are formed. For example, the physicochemical interaction between the fine particles and suspending solution can govern the surface electric charge. The most fines in solution carry a charge, and colloidal forces play a crucial role (Khilar and Fogler, 1998). The surface charge of fines can be determined to estimate the magnitude of colloidal forces. Therefore, the surface charge is directly related to the colloidally induced release of fines in porous media. It is an important characteristic of fines.

2.3.2 The statics of fine particles

**Total energy of interactions among fine particles.** For fine particles exist in the particulate medium and free to move within the pore space are defined as migratory fine. The migration of fines in porous media is the sequence of occurrences of release or detachment of fine particles, the motion of flow, and fines capture at pore sites or migration out of the porous media (Khilar and Fogler, 1998). Two major types of forces are important for the fine migration procedure, which includes colloidal and hydrodynamic.

The statics of fines migration procedure can be analyzed by the aggregation of colloidal force and hydrodynamic force. For colloidal force, it can be analyzed using potential energies of London-van der Waals attraction and electrical double layer repulsion. On the other hand, the hydrodynamic force of fluid flow subject the fine particles, such as flow velocity induced drag force. The total energy of interactions among fine particles and pore surface can represent the
level of force. The total interaction energy of the system including fine particle and pore surface can be defined as $V_T$ which can be expressed as:

$$V_T = V_{DLR} + V_{LVA} + V_{BR} + V_{AB} + V_{HR}$$  (2.3)

where $V_{DLR}$ is the double layer energy of interaction that gives rise to repulsive energy (Kar et al., 1973), $V_{LVA}$ is the van der Waals energy of interaction that contributes to the strength of the attachment energy (Hunter, 1989), $V_{BR}$ is the Born repulsive potential which results from the overlap of electron clouds as the particles approach the point of contact (Feke et al., 1984), $V_{AB}$ is the Acid-base interaction at solid-liquid interface that contributes substantially to the adhesion energy between two phases (Vrbanac and Berg, 1991), $V_{HR}$ is the energy potential due to hydrodynamic forces (Khilar and Fogler, 1998). The total interaction energy $V_T$ varies from negative values to positive values based on the relative magnitude of various contributions. Table 2.2 shows the magnitudes of various contributions to $V_T$ for the small particle condition at the low flow velocity which means the hydrodynamic potential can be primary minimum (Khilar and Fogler, 1998).

Table 2.2 Magnitudes of various contributions to $V_T$ at a particular condition (Khilar and Fogler, 1998).

<table>
<thead>
<tr>
<th>Energy of interaction</th>
<th>Magnitude (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{DLR}$</td>
<td>5.2-7.9 E-19</td>
</tr>
<tr>
<td>$V_{LVA}$</td>
<td>-9.9E-19</td>
</tr>
<tr>
<td>$V_{BR}$</td>
<td>7.4E-23</td>
</tr>
<tr>
<td>$V_{AB}$</td>
<td>-2.5E-20</td>
</tr>
<tr>
<td>$V_{HR}$</td>
<td>-2.1E-20</td>
</tr>
</tbody>
</table>

Table 2.2 presents that two major contributions to $V_T$ are London-van der Waals attraction and double layer repulsion. Therefore, a lot of researchers explain the colloidal system including fine particles considering the total energy of interaction between fine particles depending on two major contributions to $V_T$ (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). Figure
2.3 shows the repulsive and attractive forces as a function of the distance of separation. Figure 2.3 (a) indicates the van der Waals attraction $V_{LVD}$, double layer energy of interaction $V_{DLR}$, and the combination of the two opposite potentials as a function of distance from the surface of a spherical particle. The total interaction energy $V_T$ can be affected by many factors. The parameters such as particle size, distance of separation, salt concentration, hydrophobic interaction, density of the liquid, radius of pore, and so on can affect the total interaction energy $V_T$. For instance, the salt concentration is one important factor that directly affects the total interaction energy due to different contribution to London-van der Waals attraction and double layer repulsion. Figure 2.3 (b) shows an example of the qualitative variations of $V_T$ with distance of separation $h$ at three different salt concentrations (Khilar and Fogler, 1998). It illustrates that total interaction takes on large positive value when the salt concentration is relatively low.

Figure 2.3 Repulsive and attractive forces as a function of distance of separation. (a) The van der Waals attraction $V_{LVD}$, double layer energy of interaction $V_{DLR}$, and the combination of the two opposite potentials as a function of distance, (b) an example of the qualitative variations of total interaction energy $V_T$ with distance of separation at three different salt concentrations (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948; Khilar and Fogler, 1998).
Electrical interactions among fine particles. In general, the migratory fine particles occur in porous media can be composed of two major minerals which are silica SiO₂ and alumina Al₂O₃ (Khilar and Fogler, 1998). The particle can include clay particles such as kaolinite, illite, montmorillonite, and non-clay particles such silica silt and mica. The clay particles are most sensitive to pore fluids such as different salinity fluids due to high ion exchange capacity and specific surface. The existence of negative surface charge can general the diffuse electrical double layer on the clay particle surface in an aqueous suspension (Besra and Liu, 2007; Güven, 1992; Theng, 2012). The double layer thickness of clay particles can be changed while altering with pore fluid types or fluid properties such as pH and salinity. Figure 2.4 illustrates the structure of a diffuse electrical double layer at clay mineral surface (Besra and Liu, 2007).

Figure 2.4 Structure of a diffuse electrical double layer at clay mineral surface (Barbour and Yang, 1993).

The double layer (DDL) thickness of clay particles changes in various pore fluids. Changes in pore-fluid chemistry influences interaction between clay particles and affects the overall
behavior of fine particles (Barbour and Yang, 1993). Table 2.3 indicated the typical electrical double layer thickness of clay particles at different brine salinity (Israelachvili, 2007).

Table 2.3 Typical electrical double layer thickness of clay particles at different brine salinity (Israelachvili, 2007).

<table>
<thead>
<tr>
<th>Salinity (mg/L)</th>
<th>Double layer thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>~960</td>
</tr>
<tr>
<td>5E-9</td>
<td>0.92</td>
</tr>
<tr>
<td>1E-8</td>
<td>0.64</td>
</tr>
<tr>
<td>3.5E-8</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Fine particles fabric with electrical interactions. The electrical interactions among fine particles not only influences the electrical double layer thickness of fine particles but also affect fine particles fabric. The particles fabric refers to the geometric arrangement of particles (Holtz and Kovacs, 1981). The behavior of fine-grained materials depends much more on geological history and particle fabric (Lambe and Whitman, 1969). Figure 2.5 illustrates the common fabrics of granular and plate materials (van Olphen, 1991; Mitchell, 1993; Sogami and Ise, 1984; Jang et al., 2017).

![Figure 2.5 Common fabric of fine-grained materials. (a) Granular material (b) Plate material (van Olphen, 1991; Mitchell, 1993; Sogami and Ise, 1984; Jang et al., 2017).](image)
In general, the fine-grained material fabric can be changed by electrical interactions among fine particles. The granular material shows as loose fabric or dense fabric based on the electrical charge differences (Figure 2.5 (a)). For dense fabric of granular material, it presents as compacted and surrounded structures (Sogami and Ise, 1984; Jang et al., 2017). The plate shape material, especially clay material, the fabric can be changed by attractive and repulsive electrical interactions among particles. It can be dispersed fabric, or aggregated fabric, or flocculated fabric. In particular pore fluid, the negative charge of particles can attract positive ions to align them around the plate that leads particles to flocculate to form edge to face or edge to edge fabric, furthermore aggregate to form the face-to-face fabrics (Figure 2.5 (b)).

2.3.3 Pore fluid chemistry related geomechanical properties of fine particles

**Electrical sensitivity.** The pore fluid chemistry dependent fabric and volumetric strain are distinguishing characteristics of fine-grained sediments, so it is necessary to explore the behaviors of fine-grained sediments with different pore fluids (Jang et al., 2017; Santamarina et al., 2002; Mitchell and Soga 2005). Liquid limit is used to define the electrical sensitivity of fine-grained sediments with different pore fluids. Because liquid limits (LL) is related to geomechanical properties of remolded soils such as hydraulic conductivity and compressibility, which can emphasize the physical and engineering meaning of electrical sensitivity (Wroth and Wood, 1978; Carrier and Beckman, 1984; Sridharan and Nagaraj, 2000; Lee et al., 2005). The electrical sensitivity ($S_E$) is stated to capture in liquid limit (LL) changes with pore-fluid permittivity and electrical conductivity, van der Waals and double-layer effects (Jang and Santamarina, 2015). The liquid limits are obtained and contracted with different pore fluids such as deionized water, 2 M NaCl brine, and kerosene. Liquid limit and electrical sensitivity can be used for classifying fine grains according to their fluid-soil response. The liquid limits
determined with deionized water (LL\text{DW}), NaCl brine (LL\text{brine}), and kerosene (LL\text{ker}) are utilized to define the electrical sensitivity index (S_E) which is shown in equation 2.4.

\[
S_E = \sqrt{\left(\frac{LL_{\text{DW}}}{LL_{\text{brine}}} - 1\right)^2 + \left(\frac{LL_{\text{ker}}}{LL_{\text{brine}}} - 1\right)^2}
\]  

(2.4)

where S_E is equal to the distance from the origin at LL_{\text{ker}}/LL_{\text{brine}}=1.0 and LL_{\text{DW}}/LL_{\text{brine}}=1.0 to the data point (Jang and Santamarina, 2015). The ratios LL_{\text{DW}}/LL_{\text{brine}} and LL_{\text{DW}}/LL_{\text{ker}} are also corrected to account for differences in water versus kerosene unit weight (\gamma) through specific gravity (G) and the precipitation of excess salts during oven drying with brine concentration (c_{\text{brine}}). The correction equations are listed in equation 2.5 and 2.6 (Jang and Santamarina, 2015).

\[
\frac{LL_{\text{DW}}}{LL_{\text{brine}}}_{\text{corr}} = \frac{LL_{\text{DW}}}{LL_{\text{brine}}} \left(1 - \frac{c_{\text{brine}} LL_{\text{brine}}}{100}\right)
\]  

(2.5)

\[
\frac{LL_{\text{DW}}}{LL_{\text{ker}}}_{\text{corr}} = \frac{LL_{\text{DW}}}{LL_{\text{ker}}} G_{\text{ker}}
\]  

(2.6)

where the c_{\text{brine}} is the concentration of brine, and G_{\text{ker}} is the specific gravity of kerosene. Liquid limits are determined by experimental test method (Casagrande, 1958; Sowers et al., 1960; Sherwood and Ryley, 1970). The physical and engineering meaning of the liquid limit is retained in electrical sensitivity. The fine-grained materials can be classified as low, intermediate, or high electrical sensitivity so that the influences of pore fluid chemistry for fine-grained materials can be emphasized.

\textbf{Compressibility and hydraulic conductivity.} Hydraulic conductivity also called as the coefficient of permeability, and compressibility are two important fluid chemistry related geomechanical properties of fine-grained sediments. It is significant to know the magnitude and the rate of compression settlements to ensure the serviceability of formation structures related on a
compressible sediments layer (Cavalcante and Assis, 2002). As the pore fluid chemistry changes, the initial compressibility and hydraulic conductivity of sediments can be altered, which may cause the serious mechanical problems for entire formation. Many literatures show the influences of fine-grained materials response to different pore fluids in formation so that impacts the compressibility and permeability of reservoir sediments (Francisca et al., 2005; Jang and Santamarina, 2015; Mohan et al., 1993). For example, a lot of fine-grained materials are sensitive to pore-fluid chemistry, and swelling in reaction to pore brine while displaced by fresh water (Jang et al., 2017; Mohan et al., 1993). Therefore, understanding the compressibility and hydraulic conductivity changes of fine-grained sediments with different pore fluids are significant. The compressibility of fine-grained sediments can be achieved by consolidation process which is accompanied by a decrease in void ratio and the hydraulic conductivity (also called the coefficient of permeability). To measure the compressibility and hydraulic conductivity with different pore fluids, the consolidation test can be carried out on fine-grained materials saturated with different pore fluids (ASTM D-2435-02, 2002). The compression index (Cc) and recompression (Cr) represent the changes in void ratio due to stress changes. Based on the compression curves, the compression index, Cc, and recompression, Cr, are calculated by equation 2.7.

$$C_c \text{ or } C_r = \frac{e_{100kPa} - e_{1000kPa}}{\log_{10}(1000kPa/100kPa)} = e_{100kPa} - e_{1000kPa} \quad (2.7)$$

where $e_{100kPa}$ and $e_{1000kPa}$ are the void ratios at 100kPa and at 1000kPa vertical effective stress. Moreover, the consolidation process leads to decrease in the coefficient of permeability or hydraulic conductivity ($k$) so that can present the capacity of sediment to conduct pore fluid. The hydraulic conductivity ($k$) can be calculated according to the equation 2.8.

$$k = m_v \cdot C_v \cdot \gamma_f \quad (2.8)$$
where $m_v$ is defined as the coefficient of volume change, $C_v$ is called the coefficient of consolidation, and $\gamma_f$ is the unit weight of pore fluid.

2.3.4 Mechanisms of fine particles clogging at pore throat

The mobile or migratory particles through porous networks can have a significant effect on a variety of engineering events. Especially, researchers explore that particle entrapment can occur when filtration taken place, which is relevant to filter clogging and unclogging (Valdes and Santamarina, 2008). For example, the particle clogging may cause reduction of relative permeability and production efficiency decrease. The fine particles may also cause fluid volume expansion, changes in porosity, pore clogging, and low gas recovery efficiency in gas production (Jung et al., 2012). Therefore, the understanding mechanisms of fines clogging is a significant scientific and engineering challenge to maintain flow in transporting particles for some systems (Valdes, 2002). The permeating fluid with fine particles may experience electrical interactions that may lead aggregation and/or flocculation, forming groups and trapping even at large pore throats. The definition of clogging indicates the reduction in the effective area available for fluid flow. It is concluded as the macroscale effect of the microscale phenomenon of fines entrapment at pore throats (Valdes, 2002).

Recent low-cost devices and the optical microscopy ability allow the researchers to identify the mechanisms of clogging at pore-scale and monitor the clogging dynamics at pore throat.

Clogging is defined as the reduction in the effective area available for fluid flow. This definition is the macroscale effect of the microscale phenomenon of fines entrapment at pore throat (Valdes 2002). The mechanisms of clogging at pore throat are discussed as three main features which are sieving, bridging, and aggregation or blocking (Khilar and Fogler 1987; Bigno et al. 1994;
Oyeneyin et al. 1995; Khilar and Fogler 1998). Figure 2.6 illustrates three important mechanisms schematics that responsible for the clogging at pore throat.

![Figure 2.6 Main mechanisms of clogging at pore throat (Dressaire and Sauret, 2017).](image)

Sieving is one of the mechanisms involved for clogging, and sieving refers to the blockage of particle based on single particle size exclusion. Bridging is one possible clogging mechanism when particle size is smaller than the pore throat size that is depending on steric effects through the formation of an arch of particles cross the width of pore throat. The fluid flow and high particle concentration both generate bridge-like structure cross pore throat (Dressaire and Sauret, 2017). These two mechanisms only include steric effects, however, the aggregation or blocking occurs in the bulk of suspension. This mechanism may drive by short-range force such as van der Waals attraction and double layer repulsion that is only possible if the particles are close enough to each other (Dressaire and Sauret, 2017). The process of aggregation clogging thus results from a combination of hydrodynamic and colloid forces (Guo et al., 2012; Giglia and Straeffer, 2012).

2.3.5 Factors influencing fine particles migration and clogging in porous media

Several influence factors of fine migration and clogging in porous media are evaluated by different kinds of literature. It indicates the importance of the size of the fine particles, the pore throat size, the concentration of the suspension, and the flow rate, as well as the multiphase fluids, exist in porous media.
Pore/fine critical size ratio, fine concentration, and flow rate. Based on fines clogging mechanisms, parameters such as fine particle size, host size, porous throat size, superficial velocity of fluid, and particle concentration have been examined through experimental tests show important roles for fines migration process (Valdes and Santamarina, 2008; Muecke, 1979; Sakthivadivel and Einstein, 1970; Khilar and Fogler, 1998; Crist et al., 2005). They attempt to investigate the different mechanisms as well as provide some guidelines on fines migration. For instance, one of the experimental research on pore blocking/clogging mechanism in gravel packs illustrates that the high fluid flow rate is critical to fluid permeability, and the efficiency of fluid permeability is found to depend on the type of pore blocking mechanism (Bingo et al., 1994). In addition, many literatures investigate the pore throat size ($o$) and fine particles diameter ($d$) ratio effects for particles retention, which also called as critical size ratio ($o/d$), to predicted pore clogging or blocking (Sakthivadivel and Einstein, 1970; Muecke, 1979). Pore clogging mechanisms and the corresponding critical ratio ($o/d$) obtained from different literatures are summarized in Table 2.4 (Oyeneyin et al., 1995; Khilar and Fogler, 1998; Muecke, 1979; Bigno et al., 1994; Agbangla et al. 2012).

Table 2.4 Critical size ratio ($o/d$) and pore clogging mechanisms by literatures (Oyeneyin et al., 1995; Khilar and Fogler, 1998; Muecke, 1979; Bigno et al., 1994; Agbangla et al. 2012).

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Critical ratio: $o/d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instant clogging and size exclusion</td>
<td>$o/d&lt;1$</td>
</tr>
<tr>
<td>Instant bridging with particle migration</td>
<td>$o/d&lt;3$</td>
</tr>
<tr>
<td>Invasion and deposition with internal clogging</td>
<td>$3&lt;o/d&lt;10$</td>
</tr>
<tr>
<td>Clogging due to deposition and particle blocking</td>
<td>$10&lt;o/d&lt;25$</td>
</tr>
<tr>
<td>Particle deposition may or may not cause clogging occur</td>
<td>$25&lt;o/d&lt;100$</td>
</tr>
<tr>
<td>Flushing or no interaction</td>
<td>$o/d&gt;100$</td>
</tr>
</tbody>
</table>

Not only the critical size ratio ($o/d$) but also the fine particles concentration and flow rate are significant parameters for evaluating the condition of pore clogging. Table 2.5 shows the critical size ratio ($o/d$), suspension flow rate, and critical clogging particle concentration relationship by
literatures (Pandya et al., 1998). It explains that when the particle concentration is increased, many particles approach pore throat and cause clogging. Therefore, a higher critical size ratio (o/d) requires higher particle concentration to block pore throat. However, when flow rate raises, the clogging pore also can be unplugged (Pandya et al., 1998).

Table 2.5 Critical size ratio (o/d), suspension flow rate, and critical particle clogging concentration relationship by literatures (Pandya et al., 1998).

<table>
<thead>
<tr>
<th>Critical ratio: o/d</th>
<th>Flow rate $10^{-3}$ m$^3$/h</th>
<th>Critical particle clogging concentration(% v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5</td>
<td>7.2</td>
<td>0.35</td>
</tr>
<tr>
<td>27.5</td>
<td>7.2</td>
<td>1.75</td>
</tr>
<tr>
<td>40</td>
<td>7.2</td>
<td>9</td>
</tr>
<tr>
<td>75</td>
<td>7.2</td>
<td>10</td>
</tr>
<tr>
<td>17.5</td>
<td>9.2</td>
<td>0.875</td>
</tr>
</tbody>
</table>

Furthermore, some literatures suggest that at intermediate o/d, higher concentration results in rapid clogging, whereas low concentration results in flushing (Valdes, 2002). Moreover, the required critical particle clogging concentration increases as the size of fines decreases (Pandya et al., 1998). On the other hand, to analyze the flow rate effects on mobility of fine particles, pieces of literatures also present experimental tests show that fine particles are mobilized at all flow velocities of a chemically compatible, wetting fluid. Also, mechanical particle mobilization occurred when a critical flow velocity is exceeded, and they conclude that the extent of fluid permeability decline is a function of flow direction, and velocity, as well as porous media permeability and wettability (Gabriel and Inamdar, 1983).

**Fine particles migration in multiphase flow.** In multiphase flow, the fines migration is significantly influenced by the performance of fluids flow in porous media. For example, fine particles can affect fluids volume, change in porosity, and cause pore clogging, low gas recovery efficiency, as well as bore-hole failure in gas production. The naturally generated abundant fine particles, such as clay, silica, organic particles, and the other metal oxides, exist in porous media. (Valdes and Santamarina, 2008; Muecke, 1979; Sakthivadivel and Einstein, 1970; Khilar and
Fogler, 1998; Sauret et al., 2014; Bacchin et al., 2014; Agbangla et al., 2012). These fines and the behavior of migration in porous media are highly affected by pore fluids. Also, the interfacial tension between multi-phase fluids impacts the fines behavior while it migrates in porous media. Different fines are susceptible to different pore-fluids type and properties. For example, kaolinite, which is one of the clay material, exhibited extremely high affinity to the air-water (NaCl solution) interface at pH values below 7 (Wan and Tokunage, 2002). Moreover, fluids saturation in porous media affects the fines migration behavior. For instance, some researchers conducted two-phase (Non-polar/Polar oil and brine) experiments for fines migration in the core sample. The results conclude that the effluent particle concentrations from the core indicate that the rate and duration of fines release depend on the fluids saturating the core. (Sarkar and Sharma, 1990). It means the second or third fluid phase remaining in the pore throat can strongly influence particle mobility. After Muecke (1979) presented that the particle mobility in multiphase flow is effected by particle wettability and surface/interfacial forces, following studies have been conducted: (1) hydrophobic particles have move sorption on the air-water interface than hydrophilic particles (Wan and Willson, 1994; Crist et al., 2005); (2) while hydrophobic particles prefer to sorb on both air-water interface and glass-water interface, hydrophilic particles prefer to sorb on the downstream portion of air bubbles (Wan and Willson, 1994); and (3) when particle surfaces charge positive, more particles sorb on the gas-water interface (Wan and Tokunaga, 2002). However, the current understanding of particle migration in multiphase flow is not enough to explain many engineering problems such as the possible failure during gas production and the effect of migration particles on bridging and clogging.
2.4 References


Lymberopoulos, D.P., Payatakes, A.C., 1992; Derivation of topological, geometrical, and correlational properties of porous media from pore-chart analysis of serial section data. J. Colloid Interface Sci., 150(1), 61-81.


CHAPTER 3. FLUID WETTING PROPERTIES INFLUENCES ON MULTIPHASE FLOW BEHAVIOR IN POROUS MEDIA

3.1 Introduction

Wettability tells the preference of a solid to contact with one fluid rather than another fluid (Abdallah et al., 2007). To understand the multiphase flow in porous media, many of essential items related to wettability need to be well explicated, such as Darcy’s single-phase flow, reservoir wetting influence, contact angle, and fluids interfacial tension and viscosity. The wetting properties of porous media controls the distribution of the immiscible fluids by affecting the relative permeability. Modifying the fluid wettability is an effective method for improving the reservoir performance. However, many modification methods related to wetting properties of porous media for multiphase flow need the deeper information. For instance, instead of water, recently organic agents such as polymers, biopolymers, and surfactants have been developed for soil improvement and have demonstrated their abilities to improve the shear strength, stiffness, soil remediation, and erosion resistance of geomaterials. (Bate, et al., 2013; Briscoe and Klein, 2007; Cabalar and Canakci, 2005; Kang, et al., 2014; Kavazanjian Jr, et al., 2009; Martin, et al., 1996; Mitchell and Z., 1964; Nugent, et al., 2011; Yoshikawa, et al., 1993). However, the engineering behavior and characteristic for some of them have yet to be well recognized. As some literatures shown, this modified fluid with biopolymers such as polyacrylamide (PAM) and xanthan gum have provide a great effect in enhanced oil recovery (EOR) that improves water flooding performance (Hove, et al., 1990; Philips, et al., 1985; Pollock and Thorne., 1994). Thus, to improve the capacity of bio-chemical modified fluids such as biopolymer for oil-contaminated

*This chapter previously appeared as [Cao, S.C., Bate, B., Hu, J.W., Jung, J., Engineering behavior and characteristics of water-soluble polymers: implication on soil remediation and enhanced oil recovery. Sustainability 2016, 8, 205.].
soil remediation and enhanced oil recovery (EOR), we explored five different biopolymer solution and influencing factors of biopolymers wettability, including contact angle, surface tension, interfacial tension and viscosity that influences on capillary pressure, biopolymer solution flow, and biopolymer solutions-oil displacement in porous media. Additionally, the micromodel study was intended to understand the flow behavior of biopolymer solutions and biopolymer solutions–oil displacement in porous media.

3.2 Literature Review

3.2.1 Utilization of biopolymer in soil remediation and enhanced oil recovery

Soil contamination in urban and rural environments is usually caused by industrial activities, such as mining wastes, dumping and landfill settlement, or quarries (Meuser, 2010). Important characteristics and remediation techniques have been developed over the years to deal with soil contamination (Swartjes, 2011). Various technologies are under development for remediation of soils and sediments (Mulligan, 2003). For instance, soil remediation technologies, such as soil excavation, soil vapor extraction, bioremediation, and steam injection are basic methods used for soil remediation for years (Chai and Miura, 2004; Cho et al., 1997; Hall et al., 2001; Tse et al., 2001). Due to the limitation in soil excavation, including high cost and lack of available landfill sites (Chai and Miura, 2004; Cho et al., 1997; Hall et al., 2001; Tse et al., 2001; Mann et al., 1993), flushing and bioremediation methods that do not require the soil excavation have become more popular recently (Mulligan, 2003). For example, the surfactant flush has been used to improve the rate of soil remediation (Mulligan, 2003). Recently, more suitable eco-friendly soil remediation methods have been required. Thus, application of bio-surfactant and biopolymers could provide the sustainability because they are mainly obtained from plants containing eco-friendly properties (Khatami and O’Kelly, 2013; Lee et al., 2002; Rouse et al., 1996; Sabatini and
Biopolymer flushing was originally developed for petroleum recovery areas which, afterwards, had been used for the remediation of petroleum waste-contaminated sites (Jafvert, 1996; Jawitz et al., 1998; Lee et al., 2005; Mulligan et al., 2001). Biopolymers are biologically-available compounds that could be obtained using the basic principles of lowering the mobility ratio and increasing the capillary number of fluids (Lake et al., 2014; Hong et al., 2014). They aim to increase the viscosity and the mobility and to reduce the interfacial tension to enhance contamination recovery and accelerate contamination mobilization (Finch, 1991).

On the other hand, a large portion of the world’s oil reserves still has low permeability. Thus, enhanced oil recovery (EOR) technology has been used for exploitation (Moawad et al., 2007). Polymer solutions have been used to improve the water-flood performance in enhanced oil recovery (EOR) for 70 years (Sandiford and Pye, 1964). In general, two types of polymers could be applied to reservoir application, which are synthetic polymers and biopolymers (Moawad, et al., 2007; Jung et al., 2013; Jang et al., 2015). While synthetic polymers are not stable at high temperatures and high salinity, biopolymers are more stable, relatively (Moawad, et al., 2007). The basic principles of biopolymer flooding are to increase the viscous forces, control mobility as well as to reduce the interfacial tension in the reservoir for enhance oil recovery (Lake, 2008; Sorbie, 1991; Hong et al., 2015). Considering their lower cost and higher viscosity, the most widely-used biopolymers for enhanced oil recovery (EOR) application are Xanthan gum (Hove, et al., 1990; Philips et al., 1985; Pollock and Thorne, 1994), Pullulan (Cho, et al., 2001), Levan (Akit, et al., 1989), Curdlan (Canella, et al., 1988), Dextran (Kim and Fogler, 1999) and Scleroglucan (Sandford, 1979). However, better understanding of wettability of biopolymers including contact angle, surface tension, interfacial tension, and viscosity are required for both oil-contaminated soil remediation and enhanced oil recovery (EOR).
3.2.2 Capillary pressure

Wettability of mineral and interfacial tension between two fluids are key factors controlling the mobility of biopolymer solution, biopolymer solution-oil displacement and capillary pressure in porous media. Because of the differences in mineral surface wettability by biopolymer solution and oil, a capillary pressure difference (Pc) between these two phases must exceed in order for biopolymer solution to enter the pores in porous media. As described by the Young-Laplace equation (equation 3.1), capillary entry pressure of biopolymer solution into the original oil-filled pores is determined by the pore radius (R), the biopolymer solution-oil interfacial tension (σ) and the contact angle (θ) among biopolymer solution-oil-mineral surface (Bear, 1972).

\[
P_c = P_{biopolymer} - P_{oil} = \frac{2\sigma \cos \theta}{R}
\]

(3.1)

where the values of pore radius (R) are quite fixed depending on in-site geological conditions. However, both the biopolymer solution-oil interfacial tension (σ) and the contact angle (θ) among biopolymer solution-oil-mineral surface have not been well identified. Therefore, the biopolymer solution-oil interfacial tension (σ) and contact angle (θ) cause the great uncertainty to the predictions of biopolymer solution mobility, saturation and capillary entry pressure.

3.2.3 Biopolymers

Five different biopolymers are selected in this study that are popular in soil remediation and enhanced oil recovery: Chitosan (85% deacetylated power, Alfa Aesar), PEO (polyethylene oxide, Acros), Xanthan (Xanthan gum, Pfaltz&Bauer), SA (Alginic Acid Sodium Salt, MP Blommedicals), and PAA (polyacrylic acid, Polysciences) (Figure 3.1). The biopolymers are mixed with deionized (DI) water and biopolymer solutions are applied in this study (Table 3.1).
Figure 3.1 Biopolymer chemical composition structure (a) PAA (Polyacrylic acid) (~1,000,000 g/mol) (b) Chitosan (Chitosan, 85% deacetylated power), (c) PEO (Polyethylene oxide) (600,000 g/mol) (d) SA (Alginic Acid sodium salt), and (e) Xanthan (Xanthan gum).

Table 3.1 Biopolymer solutions and concentration.

<table>
<thead>
<tr>
<th>Biopolymer</th>
<th>PEO-1</th>
<th>PEO-10</th>
<th>SA-2</th>
<th>SA-20</th>
<th>Xanthan-2</th>
<th>PAA-2</th>
<th>Chitosan-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (g/L)</td>
<td>1</td>
<td>10</td>
<td>2</td>
<td>20</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Chitosan is obtained by deacetylating chitin which is the structural element in the exoskeleton of crustaceans and cell walls of fungi (Goosen, 1996; Woodmansey, 2002). Chitosan is one of agro-polymers which come from Biomass products (agro-resources). It is found in some mushrooms (zygote fungi) and the termite queen’s abdominal wall. And it is industrially came by partial and controlled chitin deacetylation (Peter MGPI, 2002). In general, the chitosan is characterized by its acetylation degree and molecular weight. Depending on the source, such as shrimp, crab, mushrooms), chitosan has molecular weight varying from 5,000 to 1,000,000 g.mol-1 and acetylation degrees from 2 to 60 % (Averous and Pollet, 2012). Also, Chitosan can be plasticized with glycerol to get thermoplastic material like plasticized starch (Epure et al., 2011). On the
other hand, Jiang et al., 2011 invested that removal of copper and nickel by the addition of the biodegradable chelating agent chitosan. The potential of derivative cross-linked chitosan is also evaluated as soil amendments for the remediation of metal contaminated land (Kamari, 2011). Polyethylene oxide (PEO) is produced through the interaction of ethylene oxide with water, ethylene glycol or ethylene glycol oligomers (Kahovec et al., 2002). It is a synthetic polyether that is with higher molecular weight polymers (molecular mass above 20,000 g/mol) and PEO refers to an oligomer or polymer of ethylene oxide. Polyethylene oxide (high-molecular weight polyethylene glycol) is synthesized by suspension polymerization. It is amphiphilic and soluble in water as well as in many organic solvents. On the other hand, PEO has medical uses function, such as many pharmaceutical products and lubricating eye drops. For EOR purpose, James and McLaren 1975 reported that for polyethylene oxide solution, the onset of elastic behavior at maximum stretch rates is of the 100 S-1 order and shear rated of 1000s-1 order, which can be used as a viscosity modifier for polymer flooding in EOR. Meanwhile, Nonionic surfactants such as nonionic surfactants which have polyethylene oxide (PEO) chains component can be the most favorable materials for soil remediation because of their intermediate sorption and low biotoxicity (Kim, 2012).

Xanthan gum is obtained from common allergens such as corn, wheat, dairy, and soy (Hove et al., 1990; Philips et al., 1985; Pollock and Thorne, 1994). SA is refined from brown seaweeds. Xanthan gum is a polysaccharide derived from the bacteria coat of Xanthomonas campestris (Barrére et al., 1986). It is commonly used as used as a food additive and rheology modifier (Davidson, 1980). And it is composed of pentasaccharide repeat units, which comprised glucose, mannose, and glucuronic acid in the molar ratio 2:2:1 (García-Ochoa et al., 2000). Furthermore, Xanthan can increase shear strength of a sand from 30 kPa to 190 kPa with only up to 5% (by
weight) addition (Cabalar and Canakci, 2005; Chen and Zhang 2013) using xanthan gum to stabilize mine tailings, the effect of biopolymer is building the bonding between mine tailing particles which could stabilize mine tailing. Also, a lot of research proved the EOR function. For instance, Heiri et al., 1991 developed correlations for the mobility of biopolymer in sandpacks. And Kolodziej 1988 flood in 100% oil saturated core to find Transport Mechanisms of Xanthan Biopolymer Solutions in Porous Media.

Sodium Alginate (SA) is a natural polysaccharide product (gum) extracted from brown seaweed that grows in cold water regions. This material can be soluble in cold and hot water with strong agitation and can thicken and bind. Also, Sodium Alginate is used in the food industry to increase viscosity and as an emulsifier. It has a wide use across the variety of industries including food, textile printing and pharmaceutical. Dental material utilizes, and it is both food and skin safe. For soil modification, Martin et al., 1996 explored application of SA technology in silty soil matrices to form impervious barriers, which showed that soil shear strength is increased by 50%.

PAA is the generic name for synthetic high molecular weight (~1,000,000 g/mol) polymers of acrylic acid which is produced from propene that is the byproduct of ethylene and gasoline productions (Orwoll, 1999). Polyacrylic acid and its derivatives are used in disposable diapers, ion exchange resins and adhesives. This polymer is one of the most abundantly used water-soluble anionic polyelectrolytes, e.g., dispersing agent, superabsorbent polymer, ion-exchange resin, etc. Furthermore, due to low toxicity, they are used as a food additive. For many applications, PAAs are used in a form of alkali metal or ammonium salts. Laumann et al., 2013 investigate the use of nanoremediation technique showed that polyacrylic acid coated nZVI (PAA-nZVI) is reduced in carbonate-containing porous media. However, the co-injection of
polyelectrolytes has been shown to increase the mobility of PAA-nZVI in carbonate-containing porous media. In addition, polyacrylic acid (PAA) can be used to stabilize nonparticles, which be able to propagate deep into the reservoir to assist oil displacement (Kanel et al., 2008).

3.2.4 Multiphase flow in porous media

In multiphase fluids flow, displacement ratios in porous media is determined by two dimensionless numbers (Lenormand, 1990; Lenormand et al., 1988) (Figure 3.2):

\[
Nm = \frac{\mu_{inv}}{\mu_{def}} \tag{3.2}
\]

\[
Nc = \frac{\mu_{inv}v}{\sigma \cos \theta} \tag{3.3}
\]

where viscosity number (Nm) is defined as the ratio of the injected fluid viscosity (\(\mu_{inv}\)) and the defensed fluid viscosity (\(\mu_{def}\)); in addition, capillary number (Nc) represents the ratio of viscous force over capillary force and is associated with the injected fluid velocity (\(v_{inv}\)), injected fluid viscosity (\(\mu_{inv}\)), the contact angle on mineral surface (\(\theta\)), and the interfacial tension between injected- and defensed- fluids (\(\sigma\)).

![Figure 3.2 Invading patterns of immiscible fluids in porous media. The displacement pattern of non-reactive flow in porous media is determined by the viscosity number (Nm) and capillary number (Nc) (Lenormand, 1990; Lenormand et al., 1988).](image-url)
These two dimensionless numbers govern three dominant regions with distinct displacement patterns and efficiencies (Figure 3.2): capillary fingering, viscous fingering, and stable displacement (Buchgraber, 2008; Daripa and Pasa., 2008; Lenormand, 1983).

3.3 Experimental Method

The bio-chemically modified fluids’ (Biopolymer& Water-Soluble Polymer) contact angle, interfacial tension, and viscosity are measured, also the biopolymer sweep efficiency using micromodel study is intended to understand the flow behavior of biopolymer solutions and biopolymer solutions-oil displacement in porous media for this research. Four tests are conducted that include contact angle measurement, interfacial tension measurement, viscosity measurement, and biopolymer sweep efficiency micromodel test.

3.3.1 Contact angle

The sessile drop technique is used to measure contact angle of biopolymer solution on silica surface. Smooth-fused pure silica plates (VWR Vista Vision – Cover Glasses, amorphous SiO2) are used as the substrates that represent Ottawa sand. Figure 3.3 shows the apparatus used in this research. Contact angles of different biopolymer solutions are measured both on silica plates submerged in decane (alkane hydrocarbon, anhydrous, ≥99%, C10H22) which are the main component consisting of natural oil and on the silica plates at atmospheric condition. The temperature is maintained constantly (24°C) at room temperature. To prepare the experiment, a silica plate is cleaned using ethanol (Malickrodt Baker, ACS reagent grad) and handled with gloved-hand. Each silica plate is not reused in order to avoid uncertainty from reaction history with decane and biopolymer solution. The droplet of biopolymer solution is foamed on the silica surface at atmospheric condition and contact angle is measured. In other tests, biopolymer is introduced into the decane-filled chamber and released on the silica plate that is placed in the
chamber (Figure 3.3b). The change in biopolymer droplet is monitored using high-resolution time-lapse photography (12.3 Megapixel, Nikon D90). The tests are repeated 3~4 times under same condition. Images of the droplets captured are used for measuring contact angle and analyzing with ImageJ (Figure 3.3b).

![Diagram of contact angle](image)

Figure 3.3 Contact angle of biopolymer solution; (a) schematic diagram of contact angle of biopolymer solution on silica surface, (b) biopolymer droplet on silica surface submerged in decane.

3.3.2 Interfacial tension

SensaDyne QC 6000 Surface Tensiometer is used to measure the surface tension of biopolymer solutions. This device can blow a nitrogen bubble using two probes with different radii into the liquid that generates the differential pressure. The dynamic surface tension can be calculated using equation 3.5 with consideration of both differential pressure measured and the calibration factor k supported by the device (Adamson and Gast, 1997).

\[ \Delta p = p_{\text{max}} - p_{\text{min}} \]  \hspace{1cm} (3.4)

\[ \sigma = k \times \Delta p \]  \hspace{1cm} (3.5)

where, \( \sigma \) is surface tension, \( k \) is calibration factor, \( \Delta p \) is a differential pressure between the maximum pressure \( p_{\text{max}} \) and the minimum pressure \( p_{\text{min}} \).

Additionally, interfacial tension was measured using a force Tensiometer (Sigma 703D) based on the Du Nouy ring method. In the Du Nouy ring method, the container including two fluids (decane and biopolymer solution) is prepared (note: the Du Nouy ring method may not give an
accurate value compared to the Wilhelmy plate method for viscoelastic water-soluble polymers). Decane is placed on the biopolymer solution due to its lower density. The platinum ring (with a diameter of 6 cm) is initially submerged into biopolymer solution and then raised to the decane phase forming a fluid meniscus. The meniscus tears from the ring and the maximum force required to support the ring is measured. The force measured is the interfacial tension between decane and the biopolymer solution.

3.3.3 Viscosity
The values of the biopolymer solutions viscosity are measured through the spindle rotation method using the Anton Paar MCR302 rheometer at room temperature and atmospheric pressure. Each solution is placed in Anton Paar MCR302 rheometer that controls shear rate at the range of 0.1 -to- 10 (1/s) and measured shear stress (Pa) at the same time. The values of viscosity are estimated using both shear rate and shear stress.

3.3.4 Micromodel test
The experimental configuration of this study is schematically shown in Figure 3.4. The silica micromodel is placed horizontally on a customized jack stage. A syringe (2.5 mL with 1/16 inch fitting) controlled by a precision syringe pump (Kats Scientific, NE-1010) is connected with the micromodel for biopolymer solution injection. To monitor the flow processes in the micromodel, a high-resolution camera (Nikon D7000, 16.2 Megapixels) with image and video- capturing function controlled by the computer is used. SA-20 and PAA-2 are not used in micromodel test due to excessively high viscosity.

The micromodel fabricated by Micronit Microfluidics BV is made of fused silica. Customized pore networks are etched on two symmetrically-patterned silica plates, which are then fused together to form a two-dimensional porous network.
Figure 3.4 Schematic design for micromodel setup (Note: Figure not drawn to scale)

Figure 3.5 Biopolymer solution-decane (or air) displacement using micromodel, (a) micromodel, (b) the injection of biopolymer solution into the decane-saturated micromodel.
The patterned area is $20 \times 10 \text{ mm}$, containing 576 discoid silica grains (590 μm in diameter and 1186 pore bodies). The pore throat is 20 μm deep and around 30 μm wide. Figure 3.5a shows the top view of the micromodel within a chip holder for protection and tubing connection.

3.3.5 Micromodel experimental procedure

The micromodel is firstly cleaned in a way of injecting 10 mL of absolute ethanol (Mallinckrodt Baker, ACS reagent grad) which is followed by 30mL of deionized (DI) water and then oven-dried at 120°C for 48 hours. After cleaning, the experimental system is assembled accordingly as illustrated in Figure 3.4. Two types of tests are conducted using micromodel. The first test is the biopolymer injection into air-filled micromodel at atmospheric condition. Biopolymer injection into micromodel is initiated at constant flow rate at the range of 0.7-to-70 μL/min. The injection continued until biopolymer percolated the micromodel. Additional one hundred pore volume (PV) of biopolymer is eventually injected into the micromodel after the biopolymer has percolated through the micromodel. The second test is the biopolymer injection into the decane-saturated micromodel. Small tubing chamber is placed between the micromodel and the syringe pump that is filled with biopolymer solution and decane (Figure 3.4). Decane always is placed on upper layer in this chamber considering the lower density than the biopolymer solutions. Thus, the micromodel is initially saturated with decane (Sigma-Aldrich, anhydrous, >99%) first. After that, biopolymer injection into the micromodel is initiated at constant flow rates at the range of 0.5-to-50 μL/min. Injection continued until no more decane is drained from the micromodel. Also, an additional one hundred pore volume (PV) of biopolymer is finally injected into the micromodel after the biopolymer has percolated through the micromodel. Additional injection of 100 PV is intended to clarify the displacement change after the percolation of fluid in micromodel.
Captured images and videos during such injection processes are used to compute the time-lapse biopolymer saturations and biopolymer-decane displacement ratios in the micromodel. Biopolymer saturation is defined as the ratio between the volume of biopolymer solution and the pore volume in micromodel obtained from biopolymer injection into air-filled micromodel test. Also, biopolymer-decane displacement ratio is defined as the ratio between the volume of biopolymer solution and the pore volume in micromodel obtained from biopolymer injection into decane-saturated micromodel test.

3.4 Results and Discussion

3.4.1 Result

Contact angle. Contact angles obtained using Image J are presented in Figure 3.6. The result shows that: (1) all biopolymer solutions used in this study represent hydrophilic on the silica surface at atmospheric condition and overall contact angles are within the range of 31.7° to 41.2° which is similar to deionized (DI) water (~39.1°); (2) contact angles on silica surface submerged in decane are higher than that at atmospheric condition. Even biopolymer solutions such as PEO-10, SA-20, Xanthan-2 including deionized (DI) water represent hydrophobic on silica surface in decane (> 90°); (3) while contact angles of PEO at atmospheric condition decrease in line with the increase in PEO concentration, but increase in decane with its concentration; and (4) contact angles of SA increased both at atmospheric condition and in decane with its concentration.

Surface/interfacial tension. Figure 3.7 shows the surface tensions and interfacial tensions measured. Figure 3.7 (a) shows that (1) PEO-1 and PEO-10 have lower surface tensions than deionized (DI) water; and (2) surface tensions of other biopolymer solutions used in this study (i.e., SA-2, SA-20, Chitosan-2, and Xanthan-2) are in the range of 74–81 (mN/m) and are slightly higher than deionized (DI) water (73 mN/m). Figure 3.7 (b) shows that (1) the interfacial
tensions among all fluids and decane are lower than its surface tension, and (2) the interfacial
tensions of all biopolymer solutions (25–39 mN/m) are lower than deionized (DI) water (51 mN/m).

**Figure 3.6** Contact angles of biopolymer solutions. (a) Contact angles on silica surface at atmospheric condition (b) contact angle on silica surface submerged in decane (DI: deionized water).

**Figure 3.7** Surface- and interfacial tensions of biopolymer solutions. (a) Surface tensions of biopolymer solutions. (b) Interfacial tensions between biopolymer solution-decane.

**Viscosity.** Figure 3.8 shows that (1) while biopolymer solutions such as PEO-1, SA-2, and Chitosan-2 have similar viscosity to deionized (DI) water, the rest of them (PEO-10, SA-20, PAA-2, Xanthan-2) have higher viscosities than deionized (DI) water; (2) while viscosities of PAA-2 and Xanthan-2 decrease in line with the increase of shear rate that represent non-
Newtonian fluids, the rest of them have relatively constant viscosities; and (3) the viscosities of both SA and PEO increase in line with their concentration.

![Figure 3.8 Shear rate effect on viscosity of biopolymer solution. (a) Viscosity of Xanthan-2, PAA-2, and SA-20. (b) Viscosity of SA-2, PEO-1, PEO-10, Chitosan-2, and deionized (DI) water.](image)

**Fluid-fluid displacement ratio.** Figure 3.9 shows that (1) biopolymer saturation (biopolymer-air displacement) was obviously increased in line with the increase in injection rate, which agrees with previous study by Kuo et al. (2011); (2) the pore saturations of SA-2 and PEO-1, according to injection rate, have a similar pattern with deionized (DI) water; (3) the pore saturation of Xanthan-2 and PEO-10 are higher than others, including SA-2, PEO-1, and deionized (DI) water at the same injection rate; and (4) at higher injection rate (>0.1 mL/s), the pore saturations of all fluids are relatively high (>90%).

Figure 3.5(b) shows the snapshot of biopolymer injection into the initially decane-saturated micromodel. With this image, the biopolymer–decane displacement ratio was obtained. In this case, the injected biopolymer solution percolates through the micromodel within 2.0 s. While additional 100 pore volume (PV) biopolymer solution is injected into the micromodel after percolation (>2.0 s), distribution of residual decane remains unchanged. Biopolymer solution injection was controlled at constant flow rates (from 0.5 μL/min to ~70 μL/min) during the tests.
Figure 3.9 Effects of biopolymer injection rate on pore saturation of biopolymer solutions on a logarithmic scale. The pore saturation generally increases with the injection rate of biopolymer solution.

Figure 3.10 shows that: (1) biopolymer–decane displacement was obviously increased in line with the increase in the injection rate, which also agrees with previous study; (2) at a higher injection rate (>0.1 mL/s), the biopolymer–decane displacements of all fluids are relatively high (>90%); and (3) the biopolymer–decane displacement ratios with SA-2, PEO-10 and chistosan are immensely high even at a lower injection rate (~0.00002 mL/min).

Figure 3.10 Effects of biopolymer injection rate on biopolymer solution–decane displacement ratios on a logarithmic scale. The displacement ratio was generally increased with the injection rate of the biopolymer solution.
3.4.2 Analyses and discussion

**Viscous number (Nm) and Capillary number (Nc).**Nm and Nc values of each test in this study are calculated based on equation 3.2 and 3.3, respectively. Injection velocity of biopolymer solution $v_{inv}$ is computed using the injection rate divided by the cross-sectional pore area (20μm×30μm) of the micromodel. For example, an injection rate of 10 μL/min in this study corresponds to the injection velocity of 104.16 cm/min. Figure 3.11 and 3.12 show the Nc and Nm values in our experiments, which are also relevant to field conditions, located at the transition region among the invading patterns represented by Lenormand (1990). Within this region, while the changes of Nm do not show any clear tendency in this study (Figure 3.11-a and 3.12-a), biopolymer solution-decane displacement ratio (or biopolymer saturation) is clearly increased with Nc (Figure 3.110-b and 3.12-b). This finding also agrees with previous pore network simulation results (Ferer et al., 2002). Thus, increasing Nc value is recommended to increase the biopolymer solution-decane displacement ratio (or biopolymer saturation). Nc is proportional to injection velocity $v_{inv}$, injected biopolymer solution viscosity $\mu_{inv}$ and contact angle on the mineral surface $\theta$, but inversely proportional to the interfacial tension $\sigma$. The following techniques which increase Nc values are recommended for biopolymer solution injection into the porous media for oil contaminated-soil remediation and enhanced oil recovery: (1) increasing the biopolymer solution injection velocity [Note. while excessively increasing velocity may cause potential plugging problem or others in the field, however, this study focuses on relations between injection velocity and displacement efficiency in the laboratory]; (2) increasing the viscosity of biopolymer solutions by adding more biopolymer; and (3) increasing contact angle and decreasing interfacial tension (or surface tension) controlling the concentration of biopolymer solution [Note. Preliminary results show the proportional changes of viscosity,
contact angle and interfacial with the concentration of biopolymer solutions]. Conversely, any event that decreases the Nc value will impede the biopolymer solution injection efficiency for oil contaminated-soil remediation and enhanced oil recovery.

Figure 3.11 Pore saturation of biopolymers at various Nc and Nm conditions. (a) The experimental conditions are within the transition region of the log(Nc)-log(Nm) plot. (b) Pore saturation of biopolymers generally increases along with the log(Nc).

Figure 3.12 Biopolymer–decane displacement ratios at various Nc and Nm conditions. (a) The experimental conditions are within the transition region of the log(Nc)-log(Nm) plot. (b) The biopolymer–decane displacement generally increases along with the log(Nc).

Effects of effective stress on capillary pressure. The capillary pressure curve is inherently dependent on pore-scale characteristics, including pore connectivity, size distribution, and gas–fluid–mineral contact properties in the manifestations of contact angle, interfacial tension (or
surface tension), and hysteresis. To prove the effect of pore size distribution on the capillarity development during biopolymer solution–decane displacement, the following analysis is conducted to identify the influential factors and their interrelation. Capillary pressure as a function of effective stress \( p' \), sediment compressibility \( e_{\text{1kpa}} \), pore structure \( S_s \), \( \alpha \sigma_x \), pressure-dependent surface tension \( \sigma \), and contact angle \( \theta \) are expressed (equations (3.6) and (3.7)) (Espinoza and Santamarina, 2010).

\[
P_c^* = \psi \frac{S_x \rho \sigma \cos \theta}{e_{\text{1kpa}} - C_c \log \frac{p'}{1\text{KPa}}}
\]

\[
\psi = \frac{4}{k10^{a \sigma_x}}
\]

where \( p' \) is the effective stress of sediments that are defined with a depth and unit weight of soil, \( C_c \) is the compressive index of sediments, \( e_{\text{1kpa}} \) is the void ration of sediments at 1kPa effective stress, \( S_s \) is the specific surface, \( \rho \) is the density of mineral, \( k \) is the geometric factor between 6 and 12, \( \sigma_x \) is the standard deviation of pore size distribution, \( \alpha \) is the factor of standard deviation, \( \sigma \) is the interfacial tension, and \( \theta \) is the contact angle.

Table 3.2 Soil properties in relationship between capillary pressure and effective stress (Espinoza and Santamarina, 2010; Burland, 1990; Lambe and Whitman, 1969; Mitchell and soga; 2005; Santamarina et al., 2001; Skempton, 1970).

<table>
<thead>
<tr>
<th>Soil Properties</th>
<th>Sand</th>
<th>Silt</th>
<th>Kaolinite</th>
<th>Illite</th>
<th>Montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_s ) (m²/g)</td>
<td>0.044</td>
<td>0.045–1.0</td>
<td>10.0–20.0</td>
<td>65–100</td>
<td>300–780</td>
</tr>
<tr>
<td>( \rho_{\text{particle}} ) (t/m³)</td>
<td>2.655–2.659</td>
<td>2.798</td>
<td>2.65</td>
<td>2.6–2.9</td>
<td>2.35</td>
</tr>
<tr>
<td>( \rho_{\text{bulk}} ) (t/m³)</td>
<td>1.586–2.083</td>
<td>1.3</td>
<td>7.69</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( e_{\text{100}} ) (at 100 Kpa)</td>
<td>0.35–0.85</td>
<td>0.6–0.8</td>
<td>0.9–1.1</td>
<td>2.0–3.0</td>
<td>2.5–4.0</td>
</tr>
<tr>
<td>( C_c )</td>
<td>&lt;0.02</td>
<td>0.02–0.09</td>
<td>0.2–0.4</td>
<td>0.5–1.1</td>
<td>1.0–2.0</td>
</tr>
</tbody>
</table>

In general, the factor \( \psi = 4/ k10^{a \sigma_x} \) is in the range of 0.04 to 0.08 (Espinoza and Santamarina, 2010). Table 3.2 shows soil properties of sand, silt, kaolinite, illite, and montmorillonite. For example, considering various effective stress conditions, the capillary pressure for each biopolymer solution to inject into silt sediments can be interpreted using both surface tension and
contact angle measured in this study and the soil properties in Table 3.2. The results show that capillary pressure was increased with applied effective stress (Figure 3.13).

![Figure 3.13 Capillary pressure caused by different biopolymers into silt sediments as function of effective stress.](image)

It also shows that PEO-10 causes smallest capillary pressure, while Chitosan-2 causes the largest capillary pressure. Furthermore, higher capillary pressures are expected with (1) higher density minerals, (2) increase in the effective stress of sediments p’ that can be increased with the depth of sediments, (3) higher specific surface of mineral Ss, like clay materials, (4) higher compressive index Cc material, like clay, and (5) lower void ratio at 1kPa effective stress e1kpa.

### 3.5 Conclusion

The biopolymer solutions such as Chitosan, PEO, Xanthan, SA and PAA are tested to identify the contact angle, surface tension, interfacial tension and viscosity. Flow characteristic has been studied using micromodel. The implications from the test results with regard to soil remediation and enhanced oil recovery are discussed below.

In the air, overall contact angles of all biopolymer solutions on silica surface are within the range of 31.7° to 41.2°, which is similar to deionized (DI) water (39.1°). Contact angles on silica surface submerged in decane are higher than those at atmospheric condition and biopolymer
solutions such as PEO-10, SA-20 and Xanthan-2 including deionized (DI) water (94.5°), even represent hydrophobic in decane. Overall, contact angles of all biopolymer solutions on silica surface submerged in decane are within the range of 76.1° to 102.6°. Within the given range of contact angles, the effect of contact angles on flow behavior in porous media would be minor comparing to fluid injection rate.

While PEO-1 and PEO-10 solutions have lower surface tensions than deionized (DI) water, the rest of them (i.e., SA-2, SA-20, Chitosan-2, PAA-2, and Xanthan-2) have higher surface tensions than deionized (DI) water. Overall surface tensions are within the small range of 62 mN/m to 81mN/m. Thus, the influence of surface tension for capillary pressure (Pc) and capillary number (Nc) is significant and more obvious than contact angle (θ).

The viscosities of PAA-2 and Xanthan-2 have higher values than deionized (DI) water, which causes biopolymer solution–decane (or air) displacements to increase. Biopolymers have lower viscosities effect on less biopolymer solution–decane (or air) displacement at the same flow rates. Additionally, the viscosities of PAA-2 and Xanthan-2 solutions are highly dependent on shear rate. Therefore, it is important to properly determine the shear rate (that is, in turn, injection rate) in order to design soil remediation process and calculate the efficiency.

The biopolymer solution–decane (or air) displacement ratio was increased with the capillary number Nc, while its dependency on the viscosity number Nm remains unclear. The capillary number Nc in microscopic multiphase flow is different from that of the macroscopic flow, which is also associated with length scale, saturation history, and relative permeability. However, the biopolymer solution–decane (or air) displacement ratio was clearly increased with the increase in flow rate. Low flow rate results in low levels of displacement ratio, but the displacement ratio is
higher for biopolymer solutions than deionized (DI) water. Thus, biopolymer injection would possibly lead to cost-efficient high flow rates.

In high-pressure reservoirs, the capillarity at the early stage is relatively lower, which is attributable to both increased contact angle and decreased interfacial tension. Within the function of effective stress of capillary pressure, estimation of capillary pressure can be achieved with measured interfacial tension and contact angle of fluids at different effective stress levels. In this research, the capillary pressure for each biopolymer has been estimated in silt sediments at different effective stress levels. Compared with all biopolymers, PEO-10 could result in the smallest capillary pressure at the same effective stress level compared with other biopolymers. On the contrary, Chitosan-2 leads to the largest capillary pressure. Furthermore, higher capillary pressure can be expected within (1) a decrease in contact angle θ, such as PEO-1 and PEO-10; (2) an increase in surface tension σ, like SA-2 and SA-20; (3) a higher density mineral; (4) an increase in effective stress of sediments p’ that can be increased with the depth of sediments; (5) a higher specific surface of mineral Ss, like clay materials; (6) a higher compressive index Cc material, like clay; and (7) lower void ratio at 1kPa effective stress.

3.6 References


CHAPTER 4. PRESSURE AND TEMPERATURE EFFECTS ON MULTIPHASE FLOW BEHAVIOR IN POROUS MEDIA

4.1 Introduction

The multiphase flow behavior of fluids through porous media, among others, depends on the reservoir in-site properties of the fluids mixtures. The detailed knowledge of the properties of fluids involved in subsurface condition is necessary for successful implementation of all multiphase flow related events. Recently, geological carbon sequestration (GCS) is recommended considering of high potential and effectiveness for reducing atmospheric carbon dioxide (CO₂). Moreover, geological carbon sequestration (GCS) is desired to inject and store a large amount of CO₂ in places like the deep saline aquifers, depleted oil or gas reservoirs, and deep ocean sediments (Benson and Surles, 2006; Li et al., 2009; White et al., 2005). Therefore, the understanding of two immiscible brine-CO₂ mobility and their saturation condition including invading patterns in deep saline aquifers is necessary. This research intensively chooses the supercritical CO₂ to replace brine resulting in predicting CO₂ displacement efficiency in deep saline aquifers.

As the world energy demand has increased, more atmospheric CO₂ has been discharged. In order to reduce atmospheric CO₂, geological CO₂ sequestration is required to reduce atmospheric CO₂. The competence of geological carbon sequestration relies on the short-term injection efficiency and the long-term capillary trapping and geological stability. As a prospective method to alleviate CO₂ emission into the atmosphere, geological carbon sequestration (GCS) is desired to store large amount of CO₂ in places like the deep saline aquifers, depleted oil or gas reservoirs,


66
and deep ocean sediments (Benson and Surles, 2006; Li et al., 2009; White et al., 2005;). Among those potential sites, deep saline aquifers are the most important due to their capacity for CO₂ storage (IPCC, 2005). Overall, the key questions arising from various stages of the carbon sequestration process are different, i.e., potentials of reservoir instability, and intense of seismic events during initial injection phase, as well as trapping, mineralization, brine imbibition, and cap rock behaviors in long term (Gaus, 2010; Zoback and Gorelick, 2012a; Zoback and Gorelick, 2012b; Juanes et al., 2012).

The prediction of CO₂ flow and CO₂-brine displacement in deep saline aquifers largely relies on the relation between capillary pressure (Pₖ) and water saturation (Sₘ) under reservoir conditions (Bachu, et al., 2007; Bennion and Bachu, 2008; Benson and Cole, 2008). This Pₖ-Sₘ relationship is usually termed as capillary pressure curve, soil water characteristic curve, or water retention curve. The two most popular models to describe the capillary pressure curve are:

**Brooks-Corey (Brooks and Corey, 1964):**

\[ P_c = P_0 \left( \frac{S_w - S_r}{1 - S_r} \right)^m \]  

(4.1)

**van Genuchten (van Genuchten, 1980):**

\[ P_c = P_0 \left[ \left( \frac{S_w - S_r}{1 - S_r} \right)^{-1/m} - 1 \right]^{1-m} \]  

(4.2)

where \( P_0 \) is a reference capillarity which reflects the entry pressure value, \( S_r \) is the residual water saturation, and \( m \) is a fitting parameter that captures the sensitivity of the capillarity change in response to saturation change. The capillary pressure curves for CO₂ and brine at reservoir pressure and temperature conditions have been measured in the laboratory (Krevor et al., 2011; Pentland et al., 2011; Pini et al., 2012; Plug and Bruining, 2007; Tokunaga, et al., 2013). The capillary pressure \( P_c \) is often determined by measuring the contact angle and the interfacial tension at various pressure-temperature conditions relevant to GCS (Bikkina, 2011; Chiquet et
al., 2007; Dickson et al., 2006; Jung and Wan, 2012; Kim et al., 2012; Chalbaud et al., 2009; Aggelopoulos et al., 2010; Bachu and Bennion, 2009; Shah et al., 2008; Duchateau et al., 2012). However, both mineral wettability (Bikkina, 2011; Chiquet et al., 2007; Dickson et al., 2006; Jung and Wan, 2012) and interfacial tension (Chiquet et al., 2007; Chalbaud et al., 2009; Bach and Bennion, 2009) are subject to change during CO$_2$ injection, leading to alternations in the capillary pressure curve and the CO$_2$-brine displacement patterns.

The overall effectiveness of the short-term CO$_2$ injection into brine-saturated reservoirs, without considering mineral dissolution and precipitation, is inherently governed by two dimensionless numbers N$_m$ and N$_c$ (Lenormand et al., 1998; Lenormand, 1990):

Viscosity number: $N_m = \frac{\mu_{\text{inv}}}{\mu_{\text{def}}}$ (4.3)

Capillary number: $N_c = \frac{\mu_{\text{inv}} v_{\text{inv}}}{\sigma \cos \theta}$ (4.4)

where N$_m$ is defined as the ratio of the injected fluid viscosity $\mu_{\text{inv}}$ and the defensed fluid viscosity $\mu_{\text{def}}$, N$_c$ depicts the ratio of viscous force over capillary force and is associated with injected fluid velocity $v_{\text{inv}}$, injected fluid viscosity $\mu_{\text{inv}}$, the contact angle on mineral surface $\theta$, and the interfacial tension between injected- and defensed-fluids $\sigma$. These two dimensionless numbers govern three dominant regions with distinct displacement patterns and efficiencies (Figure 4.1): capillary fingering, viscous fingering, and stable displacement (Lenormand et al., 1983; Daripa and Pasa, 2008; Buchgraber, 2008). Among these regions which affect to N$_m$ and N$_c$ values, contact angle (Jung and Wan, 2012; Bikkina, 2011; Kim et al., 2012; Wang et al., 2012; Dickson et al., 2006), viscosity of fluids (Fenghour et al., 1988), and interfacial tension (Chiquet et al., 2007; Shah, et al., 2008; White et al., 2005; Li et al., 2009; Benson et al., 2007; Chalbaud et al., 2009) in geological CO$_2$ sequestration have been studied (Bachu and Bennion, 2009).
Figure 4.1 Invading patterns of immiscible fluids in porous media. The displacement pattern of non-reactive flow in porous media is governed by the viscosity number $N_m$ and the capillary number $N_c$ (Lenormand, 1990; Lenormand et al., 1988).

The studies show that the pressure and temperature effects for these parameters is proved to have an important role for fluids transporting in porous media. For instance, interfacial tension between supercritical CO$_2$ (scCO$_2$) and brine in geological CO$_2$ sequestration varies within a small range of about 20-35 mN/m (White et al., 2005; Li et al., 2009; Benson et al., 2007; Chalbaud et al., 2009). However, the viscosity of CO$_2$ dramatically decreases with increased pressure, but slightly increases with increased temperature (Sih and Foster, 2008; Ozbek, 2010). Moreover, as pressure increases from 0.1MPa to 7.3MPa at 40°C, the viscosity of CO$_2$ decreases from 0.00027 Pa·s to 0.000076 Pa·s. The viscosity of CO$_2$ at 25°C, 5.5MPa and 40°C, 5.6Mpa are 0.000088 Pa·s and 0.00011 Pa·s, respectively (Sih and Foster, 2008). Also, the viscosity of brine decreases with increased temperature (i.e., 1.41 Pa·s at 25.5°C and 0.974 Pa·s at 40°C with the same 4.4M NaCl brine), but rarely remains constant by pressure in a range of 0.1~15.9MPa (Ozbek, 2010). For contact angle, while previous brine contact angle results on silica surface have large discrepancies, all results have shown that scCO$_2$ reacting on silica surface, altering the wettability of the surface that causes contact angles increase in geological CO$_2$ sequestration (Jung and Wan, 2012; Sih and Foster, 2008; Bachu and Bennion, 2009). For example, Jung and
Wan (2012) explores that equilibrium de-ionized water contact angles on silica surface increases up to $17.6^\circ \pm 2.0^\circ$ and 5.0 M NaCl brine contact angle increases up to $19.6^\circ \pm 2.1^\circ$ in geological CO$_2$ sequestration (Jung and Wan, 2012). Furthermore, injecting scCO$_2$ velocity also imparts the largest uncertainty on the prediction of invading patterns in deep saline aquifers for geological CO$_2$ sequestration.

Overall, the key questions arising from various stages of the carbon sequestration process are different, i.e., potentials of reservoir instability, intense of seismic events during initial injection phase, as well as trapping, mineralization, brine imbibition, and caprock behaviors in long term (Gaus, 2010; Zoback and Gorelick, 2012a; Zoback and Gorelick, 2012b; Juanes et al., 2012).

This study, however, explores the short-term injection of scCO$_2$ into saline aquifers and the long-term brine imbibition processes, with emphases on scCO$_2$-brine displacement patterns, the capillary pressure curve, and relative permeability. We utilize transparent engineered silica micromodels to directly visualize the scCO$_2$-brine displacement processes at pore-scale under conditions relevant to geological CO$_2$ sequestration. We also use 2D pore network modeling of two immiscible fluids as a complementary approach to investigate the impacts of pore size statistics and the differences in flow properties during the brine drainage and imbibition processes. Note that we herein focus on scCO$_2$-brine displacement patterns and efficiencies in relatively short periods, during which mineral dissolution and chemical reactions between pore fluids and porous matrix become negligible and also the scCO$_2$-brine are treated as immiscible since mutual solubility is important only at the scCO$_2$ flood front. Also note that phenomena observed in this study are not readily expected in the field, due to their differences in scale and complexity among many other factors, e.g., the CO$_2$-brine displacement stability is heavily impacted by the length scale, gravitation, and capillarity (Berg and Ott, 2012). However, this
study does reveal and investigate two essential parameters, i.e., salinity and pore size
distribution, which strongly affect the CO$_2$-brine displacement process in both microscopic and
macroscopic flows through porous media.

4.2 Experimental Method

4.2.1 Apparatus and materials.

The experimental configuration of this study is schematically shown in Figure 4.2 (a). The silica
micromodel is placed horizontally on a customized jack stage. A stainless steel syringe (KD
scientific, 2.5 mL with 1/16 inch Swagelok fitting) controlled by a precision syringe pump (Kats
Scientific, NE-1010) is connected with the micromodel for brine injection. The other end of the
micromodel is connected to an ISCO pump (Teledyne ISCO) for scCO$_2$ injection and a constant
pressure (8 MPa). Pressure transducer monitors the change of pressure during tests. The CO$_2$
(Airgas, 99.99%) is saturated with sodium chloride brine (0, 1, and 5 M concentrations) at 8.0
MPa and 45±1°C before the injection. To monitor the flow processes in the micromodel, a high-
resolution camera (Nikon D7000, 16.2 Megapixels) is used with image and video capture
function controlled by a computer. The micromodel and tubes are contained within an insulated
enclosure, heated with a heating gun and a heating light, which are controlled with PID
temperature controllers (Cole Parmer, EW-89000-10) with T-type thermocouples (Omega).

4.2.2 High-pressure micromodel.

The micromodels fabricated by Micronit Microfluidics BV are made out of fused silica.
Customized pore networks are etched on two symmetrically patterned silica plates, which are
then fused together to form a two-dimensional porous network. The patterned area is 20 × 10
mm, containing 576 discoid silica grains (590 μm in diameter and 1186 pore bodies). The pore
throat is 20 μm deep and around 30 μm wide. Figure 4.2 (b) shows the top view of the micromodel within a chip holder for protection and tubing connection.

Figure 4.2 Configuration of the scCO$_2$–brine displacement experiments using a high-pressure micromodel. (a) Schematic diagram of the experimental set-up. (b) The high-pressure micromodel chip.

4.2.3 Experimental procedure.

The micromodel is firstly cleaned by injecting 5 mL of absolute ethanol (Mallinckrodt Baker, ACS reagent grad), followed by 30mL of deionized (DI) water, and then oven-dried at 120°C for 48 hours. After the cleaning, the experimental system is assembled accordingly as shown in Figure 4.2 (a). All components connected with the micromodel including valves and transparent
tubing are kept inside of the thermal insulation enclosure. The temperature within the enclosure is maintained at 45±1°C throughout the experiments by the temperature controller. To begin each injection test, the micromodel is initially saturated with brine (0, 1, or 5 Molar of NaCl) and pressurized to 8 MPa using ISCO pump. The whole system is then held at 45°C for 24 hours to reach thermal equilibrium. After that, brine drainage is initiated by injecting scCO$_2$ into the micromodel at constant flow rates, i.e., 5.21, 10.42, 52.08, 104.17, 208.33, 312.50, and 416.67 cm/min. Table 4.1 lists the experimental tests input parameters at three different salinity of brine saturated conditions within varied CO$_2$ injection velocity. The injection continues until no more brine is drained from the micromodel. An additional one hundred pore volume (PV) of scCO$_2$ is eventually injected into the micromodel after the scCO$_2$ has percolated through the micromodel. Captured images and videos during these injection processes are eventually used to compute the time-lapse CO$_2$ saturations or scCO$_2$-brine displacement ratios in the micromodel.

Table 4.1 Summary of experimental conditions for scCO$_2$-brine displacement processes

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity of the brine [M]</td>
<td>0</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Pressure, P [MPa]</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Temperature, T [°C]</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Contact angle, $\theta$ [°]</td>
<td>40.7</td>
<td>52</td>
<td>62.6</td>
</tr>
<tr>
<td>Interfacial tension, $\gamma$ [mN/m]</td>
<td>28.5</td>
<td>33.1</td>
<td>45.7</td>
</tr>
<tr>
<td>CO$<em>2$ viscosity, $\mu</em>{CO2}$ [µPa·s]</td>
<td>23.7</td>
<td>23.7</td>
<td>23.7</td>
</tr>
<tr>
<td>Brine viscosity, $\mu_{Brine}$ [µPa·s]</td>
<td>596</td>
<td>1061.5</td>
<td>1099</td>
</tr>
</tbody>
</table>

(a) Jung and Wan, 2012, (b) Adjusted from 0 to 5 M NaCl by interpreted interfacial tension based on Bachu and Bennion, 2009, (c) Fenghour et al., 1998, (d) Mao and Duan, 2009.

4.3 Pore Network Model Simulation

Pore-scale modeling is becoming an invaluable tool in reservoir management, contaminant clean-up, and secure carbon dioxide storage (Blunt et al., 2013). Recent development in pore network modeling considers more sophisticated network structures and flow physics, and thus, greatly enhanced its predictive power on multiphase flow dynamics (Blunt et al., 2002; Øren et
al., 1998; Patzek, 2001; Piri and Blunt, 2005; Hammond and Unsal, 2012; Joekar-Niasar et al., 2009). The appropriate pore network simulation tool was selected by non-commercial ready-coded package provide by Georgia Institute of Technology (Dai and Santamarina, 2013). This simulation package uses a 2D lattice consisting of cylindrical tubes with identical length but varying radii to represent the pore structure of porous media (Dai and Santamarina, 2013). The tube radii follow a lognormal distribution with mean $\mu(\ln r/\mu m) = 1$ and standard deviation $\sigma(\ln r/\mu m) = 0.4$. In total 4028 tubes are randomly generated following the desired distribution to construct a $50 \times 50$ square network. This network has a tube connectivity $cn = 4$, which defines the number of tubes connected at one node and inherently captures the connectivity of each pore with its neighboring pores. The node itself is assumed to have no volume based on Fatt’s model (Fatt, 1956). Also note that computed hydraulic properties from a 3D network with $cn = 6$ lie between the results from 2D networks with $cn = 6$ and $cn = 8$ (Patzek, 2001). The model follows the methodology documented with details by Aker (1996) to simulate the flow of two immiscible fluids through a lattice pore network. The flow in each tube of the network is characterized by the Hagen-Poiseuille equation, with the consideration of CO$_2$-brine interfaces, i.e., the pipe flow needs to conquer additional capillarity in tubes having CO$_2$-brine menisci. Both CO$_2$ and brine are assumed incompressible, so that volume conservation (i.e., the inlet flow volume equals the outlet flow volume) applies to all nodes of the network. Thus, each node with an unknown nodal pressure in the network associates with an independent linear equation of volume conservation. By solving these linear equations as a matrix, it resolves all nodal pressures of the network, and further use them to compute the flow velocity in each tube of the network. The simulation starts with a fully brine-saturated net-work. The procedure starts with scCO$_2$ invading at a certain rate from the left boundary of the network to displace the brine
within the network. The assumption is made that only one tube is invaded by CO$_2$ in each time step and this process continues until no more brine drainage occurs at the right boundary of the network. This quasi-static simulation decouples viscous and capillary flows which occur simultaneously in reality. To consider the effect of trapping, the brine is assumed remains within the tube if both ends of the tube have been exposed to CO$_2$, i.e., the tight trapping algorithm. Additionally, the simulation package follows the method in Dai and Santamarina (2013) so that the capillary pressure curve is computed for increasing capillarity at the CO$_2$ invasion front as the brine drainage progresses in the network (see also Joekar-Niasar et al., 2008 for computing this curve using pore network modeling). Table 4.2 lists the simulation parameters at four different background pressure and temperature conditions.

Table 4.2 Input parameters used for the pore network model simulations of scCO$_2$-brine displacement processes

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity of the brine [M]</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Pressure, P [MPa]</td>
<td>0.1</td>
<td>5</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>Temperature, T [°C]</td>
<td>25</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Contact angle $\theta$ [°]</td>
<td>35</td>
<td>36</td>
<td>52</td>
<td>56</td>
</tr>
<tr>
<td>Interfacial tension $\gamma$ [mN/m]</td>
<td>74.4</td>
<td>51</td>
<td>33.1</td>
<td>30.1</td>
</tr>
<tr>
<td>CO$<em>2$ viscosity, $\mu</em>{CO_2}$ [µPa·s]</td>
<td>15.02</td>
<td>17.24</td>
<td>23.7</td>
<td>47.42</td>
</tr>
<tr>
<td>Brine viscosity, $\mu_{Brine}$ [µPa·s]</td>
<td>1549</td>
<td>1051</td>
<td>1061.5</td>
<td>1072</td>
</tr>
</tbody>
</table>

(a) Jung and Wan, 2012, (b) Adjusted from 0 to 5 M NaCl by interpreted interfacial tension based on Bachu and Bennion, 2009, (c) Fenghour et al., 1998, (d) Mao and Duan, 2009.

4.4 Results

4.4.1 scCO$_2$-brine displacement ratios

Figure 4.3 shows a few snapshots of scCO$_2$ injections at 208.33 cm/min into the initially brine (5 M NaCl) saturated micromodel. With these images, we obtain the time-lapse scCO$_2$ saturations and scCO$_2$-brine displacement ratios. In this case, the injected scCO$_2$ percolates through the micromodel within 1.5 seconds. While additional 100 pore volume (PV) scCO$_2$ is injected into
the micromodel after percolation (>1.5 sec), the distribution of residual brine remains unchanged. Note that some processes associated with the flow of the wetting phase forming thin films are very slow and may eventually change the displacement patterns but beyond the time and length scales accessible to the experiments.

Figure 4.3 Experimental results of snapshots for scCO$_2$ injection into the brine-saturated micromodel at background pressure $P_b = 8$ MPa and temperature $T = 45$ °C. The salinity of the NaCl brine in this test is 5 M. The displacement ratio at this condition is 50.34%.

The scCO$_2$ injection is controlled at constant rates (from 5.21 cm/min to ~ 416.67 cm/min) during the tests. Figure 4.4 (a) shows the representative images taken at the end of each test using 5 M NaCl brine at different scCO$_2$ injection rates. Results show the overall scCO$_2$-brine displacement ratio increases with the injection flow velocity. This displacement ratio can increase from 20.24% under 5.21 cm/min injection rate up to 63.49% under 312.50 cm/min injection. This trend agrees with the pore network simulation results (Figure 4.4b and 4.4c) and previous study by Kuo et al., 2011. The dependency of the displacement ratio on the injection flow velocity applies to different salinity conditions, e.g., 0, 1, and 5 M NaCl brine in this study. However, the displacement ratio under identical injection rates decrease with increased brine salinity (Figure 4.5).
Figure 4.4 Effects of injection flow velocity on the displacement ratio (Disp. ratio): the displacement ratio generally increases with the flow velocity of injected scCO$_2$. (a) The micromodel is initially saturated by 5M NaCl and then displaced by scCO$_2$ at various flow velocity under $P_b = 8$ MPa and $T = 45$ °C in experiments. (b) The simulation is performed using the network under conditions of Case 2 and Case 3 in Table 2. (c) scCO$_2$-brine displacement patterns and increasing displacement ratios with increasing scCO$_2$ injection flow velocity under conditions of Case 3 in simulation.

(fig. cont'd.)
Figure 4.5 Salinity effects on the scCO$_2$-brine displacement ratio: experimental results show the displacement ratio increases with injection flow velocity but decreases with brine salinity.

4.4.2 Capillary pressure curves

The computed capillary pressure curves at four different pressure-temperature conditions (Table 4.2) using the pore network modeling are shown in Figure 4.6. To better compare the results, the capillarity term is expressed in a relative form ($P_c - P_b$), where $P_c$ is the apparent capillary pressure.
during scCO₂ invasion; Pᵦ is the background pressure, i.e., the initial network pressure and Pᵦ = 0.1, 5, 8, and 12 MPa for the four cases respectively (note: we show the apparent capillarity versus brine saturation Pₑ-Sₑ_brine relations in the right upper inset of Figure 4.6). These capillary pressure curves are further fitted using the van Genuchten model (equation 4.2, with the best fitting parameters listed in the left lower inset table in Figure 4.6).

![Graph showing computed water retention curves at various background pressures Pᵦ](image)

Figure 4.6 Computed water retention curves at various background pressures Pᵦ (refer to Table 4.2 for details). With increasing pressure Pᵦ, the relative entry pressure P₀ decreases but the curve slope increases (note: the slope is inversely proportional to the m-value). The inset table shows the best fitting parameter values using the van Genuchten model (equation 4.2). This simulation result implies that at higher pressure conditions, massive brine discharge starts to occur at relatively lower injection pressure of scCO₂ and the change in capillarity is more sensitive to the change in scCO₂ saturation (i.e., increasing in ∂Pₑ/∂Sₑ_brine).

Results show that the entry pressure P₀ decreases with increasing background pressure (Figure 4.6). This is consistent with previous experimental study that the entry pressure P₀ decreases with increasing reservoir pressure within the range from atmospheric pressure to 12 MPa due to increased contact angle and decreased interfacial tension (Tokunaga et al., 2013). Also, the m-value, which reflects the sensitivity of capillarity increase over saturation change ΔPₑ/ΔSₑ_brine.
decreases with the increasing reservoir pressure; this implies that the capillarity increases faster as scCO$_2$ injection progresses in reservoirs with higher pressures. Therefore, when scCO$_2$ saturation in the reservoir exceeds approximately 20% (i.e., $S_{\text{brine}} < ~0.8$), the injection pressure should be raised faster in order to overcome the capillarity in reservoirs with higher pressures.

4.5 Analyses and Discussion

4.5.1 Hysteresis of relative permeability during drainage and imbibition

One of the most important properties in multiphase flow through porous media is relative permeability. It is conclusive that the relative permeability does not purely depend on phase saturation but exhibits hysteresis during the drainage and imbibition processes, mainly because the differences in the contact angle and the nonwetting phase trapping between drainage and imbibition (De Gennes et al., 2004; Mohanty et al., 1987). Figure 4.7 shows the relative scCO$_2$ permeability during the drainage (scCO$_2$ injection into brine-saturated network) and the imbibition (brine injection into scCO$_2$-saturated network) processes. The relative permeability of scCO$_2$ during imbibition is lower than that during drainage. As scCO$_2$ emerges from a water-wet pore throat into a brine-saturated pore space, the interfacial forces and the momentum of the moving scCO$_2$ clusters may cause the separation of non-wetting phase scCO$_2$ at narrow pore throats. This ‘snap-off’ leads to isolated scCO$_2$ clusters (see the inset of Figure 4.7). Such ‘snap-off’ phenomena have been observed in oil imbibition experiments (Roof, 1970) and 3D X-ray computed microtomography (Berg et al., 2013). Aside from this, narrower pore throats which have higher capillary suction that can both draw preferential flow of the wetting phase toward and ‘shut-off’ the non-wetting phase flow at these tiny pore throats. Additionally, any reduction of the pressure in the non-wetting phase, such as during Haines jumps, will result in re-imbibition of the wetting phase to ‘shut-off’ the non-wetting phase flow, progressively from the
smallest pores toward larger ones (see the inset of Figure 4.7) (Hildenbrand et al., 2002). Therefore, the narrower pore throats play an important role in the non-wetting phase trapping and hysteresis in relative permeability.

![Figure 4.7 Hysteresis of relative permeability of scCO₂ during drainage and imbibition processes. Network model simulation results on hysteresis of relative permeability of scCO₂. Results are obtained using the network (μ₂/μ₃ = 1, σ₂/μ₃ = 0.4). Two major mechanisms of causing lower relative permeability of scCO₂ during the imbibition process are the ‘snap-off’ of nonwetting phase to form isolated clusters and imbibition/re-imbibition caused ‘shut-off’ of small pore throats, as illustrated by the insets. Complete hysteresis curves of relative scCO₂ permeability provide both the maximum scCO₂ saturation S_{scCO₂}^{max} during drainage and the residual scCO₂ content S_r during imbibition, which respectively reflect the best achievable injection efficiency (short-term performance) and the utmost capillary trapping (long-term performance) for geological carbon storage. However, it is worth mentioning here that the mass transfer besides displacement patterns between CO₂ and brine is important in the field and in a longer time scale. Mutual solubility caused mass transfer (i.e., CO₂ dissolves into brine and vice versa) can lead to water evaporation and diminished brine displacement by CO₂, transiting from residual trapping to solubility trapping (Berg et al., 2013).
4.5.2 scCO₂-brine displacement as function of Nc and Nm

The Nm and Nc values of each tests in this study are calculated based on equation 4.3 and 4.4 respectively. The CO₂ injecting velocity \( v_{\text{inv}} \) is computed using the injection flow velocity divided by the cross-sectional pore area of the micromodel. In this case, an injection rate of 20 \( \mu L/min \) corresponds to an injecting velocity of 208.33 cm/min.

Figure 4.8 (a) shows that the Nc and Nm values in the experiments, which are also relevant to field conditions, locate at the transition region among the invading patterns represented by Lenormand (Lenormand, 1990). Within this region, the scCO₂-brine displacement ratio clearly increases with Nc (Figure 4.8(b)); yet, its dependency on Nm is not always consistent (Figure 4.8 (c)). This finding also conceptually agrees with previous pore network simulation results (Ferer et al., 2002). Thus, increasing the Nc value is desired to increase the scCO₂-brine displacement ratio, i.e., the CO₂ injection efficiency. Since Nc is proportional to the injecting velocity \( v_{\text{inv}} \), the injected CO₂ viscosity \( \mu_{\text{inv}} \), and the contact angle on the mineral surface \( \theta \), but inversely proportional to the interfacial tension \( \sigma \), the following techniques which increase Nc values are favored for optimizing CO₂ injection into saline aquifers: (1) increasing the CO₂ injection velocity; (2) increasing the CO₂ viscosity by adding viscosifiers, or alkaline particles/polymers to on one hand increase its viscosity and on the other hand naturalize pore fluid to slow down mineral dissolution and thus improve long-term geological stability; and (3) increasing contact angle and decreasing interfacial tension using for instance surfactants (Kim and Santamarina, 2014). Conversely, any event that decreases the Nc value, such as salt precipitation and salinity increase, will impede the CO₂ injection efficiency.
Figure 4.8 Displacement ratios at various Nc and Nm conditions in experiments. (a) The experimental conditions are within the transition region of the log(Nc)-log(Nm) plot. Brine drainage rates in the range of 5.21 cm/min ~ 416.67 cm/min, ionic strengths (0M, 1M, 5M NaCl brine), and pressure (8MPa) are controlled at 45 °C. (b) The scCO₂-brine displacement ratio generally increases with the log(Nc). (c) The displacement ratio shows no evident dependency on the log(Nm) value.

It is not already evident from existing (to authors’ best) knowledge that how the immiscible displacement stability diagrams (Lenormand, 1990) evolve for scCO₂ injection into brine saturated porous media, primarily due to mutual solubility, even at microscopic flow regime.

Additionally, the capillary number Nc is inherently a dimensionless ratio of viscous and capillary forces. Yet, microscopic multiphase flow has a different description of the capillary number Nc from that of the macroscopic flow which also depends on length scale, saturation history, and relative permeability (Berg, et al., 2013; Hilfer and Øren, 1996; Øren et al., 1998). In particular,
capillary forces dominate on the microscopic scale; while the viscous and gravity forces
dominate the macroscopic scale.

4.6 Conclusion

Conclusions obtained from micromodel study are following; scCO$_2$ injection into a brine-
saturated porous medium will gradually displace the brine and eventually percolate through the
medium. Subsequent injection under identical conditions does not further drain the brine out of
the medium. In this study, the distributions of scCO$_2$ and brine within the micromodel remain
unchanged even after an additional 100 pore volumes of scCO$_2$ is injected after the scCO$_2$
percolating through the medium. Thus, the efficiency of CO$_2$ injection into saline aquifers is
largely constrained by percolation. Also note, however, that some processes associated with the
flow of the wetting phase forming thin films, which may eventually change the displacement
patterns, are extremely slow and beyond the time and length scales accessible to these
experiments.

The scCO$_2$-brine displacement ratio increases with the injection rate (validated in this
experimental study up to 416.67 cm/min). This trend applies to various salinity conditions, i.e.,
0, 1, and 5 M NaCl. However, higher brine salinity decreases the overall displacement ratio
because of altered contact properties and displacement patterns.

The scCO$_2$-brine displacement ratio increases with the capillary number Nc, while its
dependency on the viscosity number Nm is not clear. The capillary number Nc in microscopic
multiphase flow is different from that of the macroscopic flow which also associated with length
scale, saturation history, and relative permeability. Upscaling using the Leverett-J function and
the characteristic lengths of micro- and macro-scopic flows remains challenging to address
anisotropy in really natural reservoir systems.
Also, conclusions obtained from pore network study are following: in high pressure reservoirs, the capillarity at entry period is relatively lower as a result of both increased contact angle and decreased interfacial tension. As brine drainage progresses, however, the capillary pressure increases much faster in these reservoirs particularly when scCO₂ saturation exceeds ~20% (i.e., $S_{\text{brine}} < ~0.8$). Therefore, high injection efficiency in high pressure reservoirs exists only in the early stages of scCO₂ injection.

The relative permeability of scCO₂ during imbibition is lower than that during drainage, primarily due to the trapping of scCO₂, particularly at narrower pore throats where the snap-off of the non-wetting phase and the shut-off by the wetting phase occur. Computed relative permeability hysteresis provides both the maximum scCO₂ saturation $S_{\text{max}}$ during drainage and the residual scCO₂ content $S_{\text{scCO₂}}^{r}$ during imbibition, which inherently are the CO₂ injection and the utmost capillary trapping efficiencies of geological carbon storage. Therefore, saline reservoir rocks with widely-distributed pore sizes are better sites for geological carbon sequestration.

All observations obtained through both micromodel and pore network simulation studies in this study remain valid in microscopic flow regime. It is not evident that mutual solubility and upscaling may readily expand the injection efficiency results of this study to reservoirs; yet, the effects of salinity and pore size distribution on the CO₂-brine displacement process remain pertinent in both microscopic and macroscopic flows through porous media.

4.7 References


Bachu, S., Bennion, B., 2009. Interfacial tension between co2, freshwater, and brine in the range of pressure from (2 to 27) mpa, temperature from (20 to 125) °c, and water salinity from (0 to 334 000) mg•l-1. J. Chem. Eng., 54(3), 765–775.


Fatt, I., 1956. The network model of porous media i. capillary pressure characteristics. Trans. AIME, 207 (7), 144 – 159.


Patzek, T.W., 2001. Verification of a complete pore network simulator of drainage and imbibition. SPE J., 6(02), 144-156.


CHAPTER 5. PORE FLUID CHEMISTRYRELATED GEOMECHANICAL FACTORS AFFECTED BY FINE-GRAINED MATERIALS

5.1 Introduction

Regarding fluids flow in subsurface condition, fine-grained materials (fines) exist within coarse sediments, as well as forming interbeds between coarse grains layers can play a crucial role for reservoir performance with pore fluids flow. These fines are likely to affect the overall sediment formation performance, especially for the geomechanical response of formation sediments. These fines can contribute to either impairment or enhancement of the geomechanical performance of formation, which is primarily affected by fine materials compositions and pore fluid properties. Therefore, exploring the fine material sensitivity linked to geomechanical parameters such as compressibility (Sridharan and Nagaraj, 2000), permeability (Carrier and Beckman, 1984), and strength of reservoir sentiments are necessary (Quirk and Schofield, 1955; Bolt, 1956; Olson and Mesri, 1970; Sridharan and Rao, 1973; Moore and Mitchell, 1974; Fernandez Quingly, 1985; Di Maio and Fenelli, 1994; Chen et al., 2000). On the other hand, the pore fluids exist in sediments including fresh water, saline water, crude oil, and natural gas are important under subsurface condition due to their reaction with nature coarse sediments as well as fine-grained materials. Since the pore fluids exchanges existing in sediments can be applicable to many engineering events such as enhanced oil recovery, geological CO2 sequestration, and soil contamination remediation, it is necessary to understand the physical and geomechanical instability of sediments with pore fluids exchanges.

Fine-grained materials (fines) refer to the small size of sediments including silts and clay. In general, the fine is defined as the particle size smaller than 75µm (ASTM D2487, 2011).

Comparison between coarse and fine-grained materials, one of the boundaries to separate them is described based on whether the gravitational force dominates or electrical force dominates.
In most of the cases, the pore fluid chemistry change plays more effective role on the behavior of the fine-grained materials compared with coarse sediments. Due to surficial electrical charges of fine materials, the fluid can adsorb onto the fines in accordance with the fluid’s and fine surface’s electrical properties. Depend on different fluids regarding to different fine materials, the surficial charges are various. For instance, the pore fluid like brine can adsorb onto fines due to the counter ions adsorb onto the charged surface so that the electrostatic repulsion among particles can be decreased. However, the high ionic content of brine can also offset the fine’s surficial charge, reducing the extent to which each fine particle can surround itself with bound layers of fluid (Jang and Santamarina, 2015). Compared with deionized water (DW), the net surface charge of each particle can push charged particle away which causes a dispersed fabric among particles. Also, deionized water (DW) does not offset the fine’s surface charge so that additional layer of water can become bound around each particle. It means the higher possibility of enhancing the interparticle spacing and the effective of fines inflation. As long as the injecting or exchanging fluid procedure happens, the fines can either swell or shrink (Francisca et al., 2005). Thus, there is a potential for changing the flow pathways and the overall permeability of the host sentiments (Konno et al., 2015). Not all fines exhibit the same sensitivity to pore-water chemistry. To effectively predict the extent to what pore fluid alters the properties of fines, a quantitative description of sensitivity is generated and linked to geomechanical parameters of interest.

Jang and Santamarina, 2015 developed the electrical sensitivity index \( (S_E) \) to address the fines reaction ability with pore fluid chemistry change. To inform the electrical sensitivity, liquid limit (LL), which relates to geomechanical properties of remolded soils such as hydraulic conductivity and compressibility, is used for defining the electrical sensitivity (Wroth and Wood, 1978;
Carrier and Beckman, 1984; Sridharan and Nagaraj, 2000; Lee et al., 2005; Jang et al., 2017). The electrical sensitivity index \( (S_E) \) is expressed as:

\[
S_E = \sqrt{\left(\frac{LL_{DW}}{LL_{brine}} - 1\right)^2 + \left(\frac{LL_{kero}}{LL_{brine}} - 1\right)^2}
\]  

where liquid limit (LL) usually indicates the water content for which a sediment transitions from a plastic state to a liquid state. Here, it is required to be corrected liquid limits to account for weight of pore fluids (Jang and Santamarina, 2015). \( LL_{DW} \), \( LL_{brine} \), and \( LL_{DW} \) are defined as liquid limits measured in the presence of deionized water, NaCl brine (2 M concentration), and kerosene. The electrical sensitivity index \( (S_E) \) is used to identify the level of fines to fluid sensitivity. It is divided into three ranges which called as the low electrical sensitivity \( (S_E<0.4) \), the intermediate electrical sensitivity \( (0.4\leq S_E \leq 1) \), and the high electrical sensitivity \( (S_E>1) \). In addition, the soil property called plasticity index \( (PI=LL-PL) \), in term of plastic limit (PL) and liquid limit (LL), is also used to describe the fine sediments’ electrical sensitivity. Because plastic limit (PL), which is used to distinguish silts from clays, can represent the water content range required for soil to transition from a semi-solid state to plastic state, and it is related to interactions among particles and pore fluid (ASTM D2487, 2011). A higher plasticity index \( (PI) \) of soil often possess excess or unbalanced electrical charges on their surface (Lambe and Whitman, 1969; Santamarina et al., 2001). Moreover, the unbalanced surface charge can make fines susceptible to electrical interactions that control the arrangement of fine particles (van Olphen, 1977; Mitchell and Soga, 2005). As long as the pore fluid chemistry changes with fine particles, the geomechanical response at formation sediments can be altered. Potential damages of formation may occur due to compressibility decrease or permeability reduction. Therefore, the
compressibility and permeability dependence on the electrical sensitivity of sediments need to be explored.

In a summary, changes in fluid’s and fine surface’s electrical properties can alter the sediment deposition or sedimentation (Lambe and Whitman, 1969; Bennett and Hulbert, 1986; Pierre and Ma, 1999; Palomino and Santamarina, 2005), also, the pore fluid chemistry changes can have significant impacts on in situ fine sediment properties such as permeability, strength, and compressibility (Quirk and Schofield, 1955; Bolt, 1956; Olson and Mesri, 1970; Sridharan and Rao, 1973). Therefore, this research here provides the study of the electrical sensitivity of fine grains to link pore fluid chemistry changes to alterations in fines fabric and geomechanical properties of endmember soils. The quantitative description of the sensitivity of fine materials is generated and linked to geomechanical parameters of interest.

**5.2 Experimental Method**

**5.2.1 Materials**

A wide range of fine-grained materials is selected to understand the influences of material properties and physical morphologies. The selected endmember materials are covered by the most compositions of onshore, offshore, and marine sediments that include silica silt (SiO$_2$), mica (muscovite), diatoms (siliceous microfossils), calcium carbonate (CaCO$_3$), kaolinite, illite, and bentonite (primarily montmorillonite) (Table 5.1) (Bahk et al., 2013; Anderson et al., 2014; Sun and Turchyn, 2014; Egawa et al., 2015; Wiemer et al. 2017). Silica silt has a similar grain size to the three clay mineral endmembers, but has different electrical sensitivity. Bentonite is a combination of montmorillonite and ash, which is treated as swelling clay in many application. Diatoms has extremely porous internal structures that can cause problems with standard index property measurements (Tanaka and Locat, 1999). Organic calcium carbonate is one of the
important compositions in the form of microfossils. The pore fluids utilized in this research contain deionized water (DW), sodium chloride (NaCl) brine (2 M concentrations), and kerosene. The kerosene is picked as the representative fluid for a non-polar and low permittivity fluid required for characterizing electrical sensitivity (Jang and Santamarina, 2015).

5.2.2 Electrical sensitivity

The electrical sensitivity tests were conducted by cone penetrometer test. This test assesses alterations in electrical interactions between fines which is implemented by measuring the liquid limit (LL) of materials in different fluids. The measured liquid limit of materials for deionized water, 2 M brine, and kerosene are defined as $LL_{DW}$, $LL_{brine}$, and $LL_{ke}$ (Table 5.1). A cone penetrometer (BS 1377) was utilized for measuring liquid limit (LL). The electrical sensitivity index ($SE$) is calculated based on equation 5.1. To inform the electrical sensitivity characterization, physical properties such as hydraulic conductivity and compressibility of remolded endmember materials are estimated by consolidation test (Sridharan and Nagaraj, 2000; Lee et al., 2005).

5.2.3 Sedimentation test

Sedimentation tests were used for evaluating the dependence of pore fluid chemistry for different inter-particle arrangements and particle segregation (Pierre and Ma, 1999; Palomino and Santamarina, 2005). First, the endmember particles were prepared at oven-dries (80°C) condition. Second, the specimens’ weights were measured out to create a loose-packed (maximum void ratio) fabric in an acrylic mold so that the same in the mold has a diameter and height both equal to 25.4 mm. Then, the specimen was respectively mixed and stabilized for more than 12 hours with three different fluids (DW, brine, and kerosene) to a final height of 152.4 mm (six times the original sediment height). To remove the air among particles, the
cylinder was vacuumed to remove existing air. Third, the cylinder was covered and shaken for one minute and immediate left to settle undisturbed. The depositional interface height \((H_1)\) and the accumulated sediment interface height \((H_2)\) were measured as a function of time \((t)\) until the both interfaces locations stabilized. Figure 5.1 shows the schematic of sedimentation tests with height measurements observation.

Figure 5.1 Schematic of sedimentation tests with height measurement observation for the different type of soil responses. (a) Uniform sedimentation response in which mainly all particles fell together with a sharp interface at the depositional height \((H_1)\). (b) Segregated sedimentation response in which the sediment segregated into the lower layer \((H_2)\) containing the largest accumulated sediment, the middle layer containing smaller particles extending to the depositional height \((H_1)\), and the top layer with the colloidal suspension containing the finest particles (Pierre and Ma, 1999).

5.2.4 Consolidation test

The one-dimensional consolidation test was conducted on all endmember fine materials with three different pore fluids (DW, brine, and kerosene) by 2.5-inch consolidometer (Geotac) according to the specification of ASTM D-2435-02. The incremental loading consolidation method was used to evaluate the saturated endmember fine material’s compressibility and hydraulic conductivity with different pore fluids (DW, brine, and kerosene). With measured
liquid limit (LL) for each endmember fine material, the fluid content was decided at 1.2LL. Figure 5.2 shows the schematic of experimental test setup. The sample was oven-dried (80°C), then, mixed with three pore fluids respectively (DW, 2 M brine, and kerosene) and stabilized for 24 hours prior to be placed in a rigid consolidation ring of 19.05 mm height and 63.5 mm diameter. The specimen was fully submerged with corresponding pore fluid during the consolidation test.

This experiment result was evaluated based on specified geomechanical parameters changes to emphasize the fines material impacted by different pore fluids (DW, brine, and kerosene), such as the hydraulic conductivity (k) changes, the coefficient of consolidation (Cv) changes, and the compression index (Cc and Cr) variations (Terzaghi, 1943). The coefficient of consolidation (Cv) was calculated by Taylor’s procedure in addition to the coefficient of volume change (mv). Then, the hydraulic conductivity (k) was calculated based on the unit weight of pore fluids (γf).

5.3 Results and Discussion

5.3.1 Material physical properties and fluid sensitivity

The endmember fine materials properties and fluid sensitivity are listed in Table 5.1. It includes the specific gravity (Gs), the specific surface (Ss), the particle size (D50), sedimentation test dry weight (W) at loose pack condition, the liquid limit for three different pore fluids (LLDW, LLbrine, Llkero).
and LLker, plastic limit (PLdw), plastic index (PIdw), and the electrical sensitivity (Se), as well as electrical sensitivity classification. Moreover, based on plasticity level and electrical sensitivity index, the electrical sensitivity of each material is plotted in Figure 5.3. Table 5.1 indicates the mica and illite have the relatively large particle size (D50>15). The silica silt, diatoms, and CaCO3 have the intermediate particle size (5< D50 < 15), while kaolinite and bentonite have the small particle size (D50 < 5).

Table 5.1 Endmember fine material properties and electrical sensitivity: physical and index properties.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sediment</th>
<th>Gs (1)</th>
<th>Ss [m²/g] (2)</th>
<th>D50 [μm] (2)</th>
<th>W [g]</th>
<th>Liquid limit</th>
<th>PLdw</th>
<th>PLbrine</th>
<th>PLker</th>
<th>PIdw</th>
<th>PIbrine</th>
<th>PIker</th>
<th>Electrical sensitivity soil classification (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Silica</td>
<td>2.65</td>
<td>0.2</td>
<td>10.5 (1)</td>
<td>9.13</td>
<td>31</td>
<td>31</td>
<td>36</td>
<td>30</td>
<td>1</td>
<td>LI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Mica</td>
<td>2.82</td>
<td>4.2</td>
<td>17 (1)</td>
<td>3.59</td>
<td>94</td>
<td>81</td>
<td>110</td>
<td>80</td>
<td>14</td>
<td>HI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CaCO3</td>
<td>2.73</td>
<td>0.2</td>
<td>8 (1)</td>
<td>9.87</td>
<td>25</td>
<td>23</td>
<td>31</td>
<td>17</td>
<td>8</td>
<td>NI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Diatoms</td>
<td>2.23</td>
<td>98</td>
<td>10 (1)</td>
<td>2.90</td>
<td>119</td>
<td>111</td>
<td>140</td>
<td>98</td>
<td>21</td>
<td>HI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Kaolinite</td>
<td>2.68</td>
<td>24</td>
<td>4</td>
<td>5.57</td>
<td>77</td>
<td>55</td>
<td>83</td>
<td>38</td>
<td>39</td>
<td>II</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Illite</td>
<td>2.71</td>
<td>29</td>
<td>20</td>
<td>10.49</td>
<td>56</td>
<td>52</td>
<td>59</td>
<td>32</td>
<td>24</td>
<td>IL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Bentonite</td>
<td>2.53</td>
<td>579</td>
<td>&lt; 2 (1)</td>
<td>9.71</td>
<td>288</td>
<td>126</td>
<td>65</td>
<td>54</td>
<td>234</td>
<td>HH</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) Density measured by gas pycnometer, 2) data from manufacturer, 3) Santamarina et al., 2002, 4) indicating no (N), low (L), intermediate (I), or high (H) plasticity fine grains of low (L), intermediate (I), or high (H) electrical sensitivity, 5) Arnott, 1965.

Figure 5.3 Endmember fine material classification based on electrical sensitivity and plasticity.
Based on data provided by Figure 5.3, the endmember fine materials can be classified into low electrical sensitivity (L), intermediate electrical sensitivity (I), and high electrical sensitivity (H). For plasticity of fine sediments, they are considered to have no (N), low (L), intermediate (I), or high (H) plasticity (Table 5.1). Mica and diatoms have the higher liquid limit (LL) compared with kaolinite and illite, but it indicates that they have less plasticity index (PI=LL-PL) than illite and kaolinite (Table 5.1). So mica and diatoms are considered has high plasticity (H) in the tested materials (Figure 5.3). Kaolinite and illite are classified as intermediate plasticity (I). Silica is considered has low plasticity (L). CaCO$_3$ shows no plasticity (N) while bentonite expresses the high plasticity (H). On the other side, silica, CaCO$_3$, diatoms, and mica, are considered to have an intermediate electrical sensitivity (I) due to sensitivity to electrical permittivity changes (LL$_{ker}$/LL$_{brine}$), but similarities between the DW and brine liquid limit (LL$_{DW}$/LL$_{brine}$) (Table 5.1). These four fine sediments express a smaller sensitivity to ionic concentration (brine) than to permittivity (kerosene). Because of small particle size and large excess surface charge, bentonite shows strong responses to both ionic concentration (brine) and permittivity (kerosene) changes in the pore fluid chemistry. So it is treated to have the highest electrical sensitivity (H) of the tested fine sediments. In the same way, kaolinite shows the intermediate electrical sensitivity (I) while illite is classified to have a low electrical sensitivity (L) (Figure 5.3). The electrical sensitivity of fine material classification is also shown in figure 5.3.

5.3.2 Sedimentation test

**Sedimentation behaviors of clay fine sediments.** Figure 5.4 indicates the sedimentation test results for clay materials including kaolinite, illite, and bentonite. Kaolinite (Figure 5.4 (a)) and bentonite (Figure 5.4 (c)) demonstrate the uniform settlement pattern, while illite (Figure 5.4 (b))
indicates the segregated sedimentation. Because the depositional interface ($H_1$) and accumulated interface ($H_2$) in segregated sedimentation are not as clearly defined as the interfaces in uniform sedimentation.

Figure 5.4 Sedimentation test interface height measurements with time for clay materials. The initial height of each dry and loose-packed specimen is 25.4mm. Inset images illustrate the example of each specimen in deionized water, 2 M brine, and kerosene. (a) Kaolinite, (b) illite, and (c) bentonite.

In the case of kaolinite (Figure 5.4 (a)), particles flocculate in DW, and the flocculated particles settle rapidly due to the edge-to-face cluster. This phenomenon requires less electrical interaction time compared with forming the face-to-face cluster in brine (Palomino and Santamarina, 2005). Thus, the depositional height decreases fast in DW. For bentonite (Figure 5.4 (c)), it is concluded as the highly electrically-sensitive material, the diffusive double layer (DDL) controlled electrical repulsive interactions among particles are strong in DW which reduces particle packing and settle, and the depositional interface does not fall. However, the DDL thickness shrinks with increased ionic concentration (2 M brine) which allows bentonite to approach closer so that the settling rate become fast. The segregated sedimentation behavior is discovered for illite in this
research (Figure 5.4 (b)). It behaves similarly with silica here which shows the depositional interface (H₁) and accumulated interface (H₂) in DW and brine are not as clearly defined. It can be explained by uneven grain size range. The large particles are controlled by falling gravity and the small particles are controlled by electrical interaction. With the larger particles falling gravimetrically, the smaller particles form DDL and remain suspended. For kerosene cases, the three clay sediments (kaolinite, illite, and bentonite) also demonstrate the flocculated fabric due to the unbalanced charges on the particle surface (Figure 5.4). The settlement time is fast compared to other fluids. The only special phenomenon happens in illite and bentonite. Due to strong DDL effect for illite and bentonite (Figure 5.4 (b) and (c)), the final depositional height (H₁) in kerosene is relatively lower compared within DW and brine.

**Sedimentation behaviors of Non-clay fine sediments.** Figure 5.5 shows the sedimentation test results for non-clay materials which contain silica, mica, diatoms, and CaCO₃. Silica (Figure 5.5 (a)), mica (Figure 5.5 (b)), and diatoms (Figure 5.5 (c)) demonstrate the segregated sedimentation while the CaCO₃ (Figure 5.5 (d)) expresses the uniform sedimentation. Silica and diatoms show similar sedimentation behavior (Figure 5.5 (a) and (c)). In DW and brine, they are influenced by two main effect parameters in this test including gravity and electrical interactions. The large particles are controlled by falling gravity. The small particles are controlled by electrical interaction so that particles form DDL near particle surfaces. Compared with DW, the increased brine concentration (2 M brine) brings more ions, which allows a greater fraction of the small particles to move closer to large particles and reduces the DDL thickness, so the larger cluster can form and become heavy, and the depositional interface (H₁) falling rate is increased. Thus, the observation shows quickly clears up the supernatant
liquid above the depositional interface in brine. Moreover, the increased participation in settling with brine increases the overall height of the accumulation interface \( (H_2) \) in DW.

The mica particles (Figure 5.5 (b)) in the cloudy supernatant behave similarly with silica and diatoms. The high ionic concentration brine makes cloudy supernatant above depositional interface fades faster compared with DW. However, the depositional interface settles slowly in brine, which is different from silica and diatoms. Because the increased ion concentration (2 M brine) slows the falling rate of mica particles. In detail, mica particles in DW can form the edge-to-face cluster which requires less electrical interaction time compared with forming face-to face cluster in brine (Palomino and Santamarina, 2005).

The \( \text{CaCO}_3 \) (Figure 5.5 (d)) represents the uniform sedimentation behavior due to clear interface between sediment and supernatant. In addition, the sedimentation pattern does not indicate big differences between DW and brine. The settling rate and final depositional height \( (H_1) \) are similar in both DW and brine. It means that \( \text{CaCO}_3 \) relies on the particle arrangement by electrical interactions among particles in DW and brine is not distinct.

All four fine sediments (Silica, mica, diatoms, and \( \text{CaCO}_3 \)) in non-polar fluid kerosene present the flocculated fabric due to the unbalanced charges on the particle surface, also, the settlement time is fast compared to other fluids (Figure 5.5).
Figure 5.5 Sedimentation test interface height measurements with time for non-clay materials. The initial height of each dry and loose-packed specimen is 25.4mm. Inset images illustrate the example of each specimen in deionized water, 2 M brine, and kerosene. (a) Silica, (b) mica, and (c) diatoms demonstrate segregated sedimentation. (d) CaCO₃ demonstrates uniform sedimentation.
**Electrical sensitivity and sedimentation.** Figure 5.6 illustrates the endmember fines’ sedimentation responses to three different pore fluids (DW, 2 M-brine, and kerosene). Compared with their initial dry height (25.4mm) at loose condition, the lower sensitivity fine materials such as diatoms, silica, and mica in DW and brine have lower accumulated sedimentation height ($H_2<25.4\text{mm}$). They all indicate segregated sedimentation pattern that shows not only separated smaller particles suspend in the colloidal suspension but also larger particles settle fast into accumulated sediment layer. The presence of ionic concentration (2 M brine) reduces the fraction of smaller particles that remain suspended. Thus, the sediment height is lower in DW compared within brine. For these three materials, the non-polar fluid kerosene presents the higher sediment height with flocculated fabric due to the unbalanced charges on the particle surface. Similar to silica, diatoms, and mica, the observations also show the highest sediment height for CaCO$_3$ and kaolinite in kerosene. In the cases of CaCO$_3$ and kaolinite, the final sedimentation heights in DW and brine are similar due to evenly particle sizes. On the contrary, the 2:1 clay materials such as illite and bentonite have the reversed pattern that indicates the descending order of final sediment height in DW, brine, and kerosene. The reason can be concluded as the DDL effect on 2:1 clay materials, so it indicates the higher sediment height in DW and the lower sediment height in kerosene.

The rate of sedimentation interface movement is various for different pore fluids. Figure 5.7 indicates the endmember fine materials’ falling time ($t_{50}$) dependence on electrical sensitivity. For all seven materials, the kerosene presents the fastest settlement among three pore fluids (DW, brine, and kerosene). Except bentonite and diatoms, other materials present the quicker settlement rate in brine compared with DW. The sign of dependence for electrical sensitivity
index is not captured. It only shows the fine sediments can behave significantly differently in three pore fluids.

Figure 5.6 Sedimentation behavior dependence on electrical sensitivity. The initial height of each dry and loose-packed specimen is 25.4mm. If cloudiness obscures the depositional interface height (silica, mica, and diatoms in DW), the accumulated fine sediment interface is used instead of the depositional interface.

Figure 5.7 Falling-time ($t_{50}$) dependence on electrical sensitivity. $t_{50}$ represents when the measurable interface moves half its total travel distance. If cloudiness obscures the depositional interface height (silica, mica, and diatoms in DW), the accumulated fine sediment interface is used instead of the depositional interface.
5.3.3 Consolidation test

Consolidation behavior. The influence of pore fluid chemistry on the swelling, compressibility, and hydraulic conductivity parameters of endmember fine materials are explored by consolidation test. Figure 5.8 shows the consolidation results for non-clay material including silica, mica, CaCO$_3$, and diatoms. The non-clay materials show similar trend for initial void ratio which indicating the kerosene can lead the highest initial void ratio. Due to electrical interaction on surface of particles, brine cause higher initial void ratio for silica and diatoms compared with DW. Moreover, three clay materials (kaolinite, illite, and bentonite) consolidation results are indicated in Figure 5.9. Due to swelling ability of bentonite, it shows distinct high initial void ratio in DW.

Figure 5.8 Non-clay material consolidation test results in deionized water, 2 M brine, and kerosene. (a) Silica silt, (b) mica, (c) CaCO$_3$, and (d) diatoms.
Figure 5.9 Clay material consolidation test results in deionized water, 2 M brine, and kerosene. (a) Kaolinite, (b) illite, and (c) bentonite.

**Electrical sensitivity and compressibility.** The compression indices for endmember materials are discovered with different pore fluids (DW, brine, and kerosene) by consolidation tests. These indices represent the changes in void ratio due to effective stress changes. Based on the compression curves (Figure 5.8 and Figure 5.9), the compression index, $C_c$, and recompression, $C_r$, are calculated by equation 5.2.

$$C_c \text{ or } C_r = \frac{e_{100kPa} - e_{1000kPa}}{\log_{10}(1000kPa/100kPa)} = e_{100kPa} - e_{1000kPa} \tag{5.2}$$

where $e_{100kPa}$ and $e_{1000kPa}$ are the void ratios at 100kPa and at 1000kPa vertical effective stress, respectively. Table 5.2 indicates the data of compression index and recompression index for all endmember fine materials. Swelling clay bentonite presents the highest compression index and recompression index in DW and brine compared with other materials.

**Table 5.2 Compression and recompression indices of endmember fine materials**

<table>
<thead>
<tr>
<th>No.</th>
<th>Sediment</th>
<th>Compression index $C_c$</th>
<th>Recompression index $C_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DW</td>
<td>2 M brine</td>
</tr>
<tr>
<td>1</td>
<td>Silica</td>
<td>0.055</td>
<td>0.094</td>
</tr>
<tr>
<td>2</td>
<td>Mica</td>
<td>0.75</td>
<td>0.86</td>
</tr>
<tr>
<td>3</td>
<td>CaCO$_3$</td>
<td>0.138</td>
<td>0.098</td>
</tr>
<tr>
<td>4</td>
<td>Diatoms</td>
<td>0.39</td>
<td>0.54</td>
</tr>
<tr>
<td>5</td>
<td>Kaolinite</td>
<td>0.54</td>
<td>0.39</td>
</tr>
<tr>
<td>6</td>
<td>Illite</td>
<td>0.39</td>
<td>0.352</td>
</tr>
<tr>
<td>7</td>
<td>Bentonite</td>
<td>2.8</td>
<td>1.12</td>
</tr>
</tbody>
</table>
In addition, the compressibility index dependence on electrical sensitivity is plotted in Figure 5.10. The trend is similar to the final height of sedimentation (Figure 5.6). The result enhances that the fine sediments’ compressibility dependents on pore fluid for the remolded sample, also, the pore fluid chemistry influences the fabric and initial void ratio for the remodeled fine sediment (Burland, 1990; Sridharan and Nagaraj, 2000; Cerato and Lutenegger, 2004; Hong et al., 2010).

The low to intermedium electrical sensitivity materials (i.e., illite, silica, mica, and diatoms) with segregated sedimentation result in DW can be concluded as less compressibility in DW with lower compressibility index compared within brine (Figure 5.10 yellow shaded region). That is because the smaller particles in DW can remain in suspension and float in the free pore space without attracting by larger particles while in the compression test. However, the brine allows a greater fraction of the small particles to move closer to large particles so that the compressibility can be enhanced. In kerosene, these particles present the flocculated fabric due to the unbalanced charges on the particle surfaces. Also, smaller particles are expected to settle along with the larger particles and existing in pore space of larger particles so that the compressibility in kerosene is highest among three pore fluids.

On the contrary, the high to intermedium electrical sensitivity materials including kaolinite, bentonite, and CaCO$_3$ in DW present the higher compressibility compared within brine due to DDL effects (Figure 5.10 blue shaded region). The brine solution reduces the DDL thickness of clay material, so, the particles are closer, and the compressibility is reduced. Besides, kaolinite and CaCO$_3$ in kerosene also show the flocculated fabric so that the compressibility is highest among three pore fluids. However, the high electrical sensitivity material, bentonite, is
significantly affected by DDL. Therefore, the descending order of compressibility of bentonite is DW, brine, and kerosene.

Figure 5.10 Compressibility index dependence on electrical sensitivity. (a) Compression index $C_c$, and (b) recompression index $C_r$.

In general, the results show clear compressibility difference among seven endmember fine materials (Figure 5.10). Illite, diatoms, and mica present the relatively high compressibility regardless pore fluids influences. Because the platy particle morphology (illite and mica) and special internal structure (diatoms), the high compressibility can be developed by inter-particle electrical forces and weight forces.

**Coefficient of consolidation.** The coefficient of consolidation ($C_v$) based on Taylor’s method is plotted as a function of vertical consolidation stress in Figure 5.11.

The results show the almost constant coefficient of consolidation while increasing the vertical stress for non-clay materials (Silica, mica, diatoms, and CaCO$_3$). Moreover, the values of coefficient of consolidation for non-clay materials are kept similar even in three different pore fluids (DW, 2 M brine, and kerosene). However, the clay materials (kaolinite, illite, and bentonite) present the big various compared with non-clay materials. Due to pore fluid effects, kaolinite and illite show the increases of coefficient of consolidation ($C_v$) with an increase in
vertical consolidation stress in DW and 2 M brine. Also, illite indicates higher coefficient of consolidation ($C_V$) value in DW compared within brine. On the other side, bentonite expresses the reversed result compared with kaolinite and illite. The coefficient of consolidation ($C_V$) decreases with an increase in vertical stress for both DW and brine because of its swelling ability. Due to DDL effect, the value of coefficient of consolidation ($C_V$) for bentonite is smaller in brine compared within DW. For non-polar fluid kerosene, the values of seven endmember fine materials’ coefficient of consolidation ($C_V$) are similar and constant, which means the influence of pore fluid kerosene for the coefficient of consolidation ($C_V$) is small for all endmember materials.

![Figure 5.11 Coefficient of consolidation as function of vertical consolidation stress for endmember fine materials with different pore fluids (DW, brine, and kerosene).](image)

**Hydraulic conductivity.** The hydraulic conductivity, $k$, values of endmember materials are plotted versus vertical consolidation stress with different pore fluids (DW, brine, and kerosene) in Figure 5.12. The consolidation process is accompanied by a decrease in void ratio so that leads to a decrease in the hydraulic conductivity ($k$). The hydraulic conductivity ($k$) represents the capacity of fine sediment to conduct pore fluid which depends on the fluid content and pore fluid pressure. It can be calculated according to the equation 5.3.
\[ k = m_v \cdot C_v \cdot \gamma_f \]  \hspace{1cm} (5.3)

where \( m_v \) is defined as the coefficient of volume change, \( C_v \) is called the coefficient of consolidation, and \( \gamma_f \) is the unit weight of pore fluid.

Figure 5.12 illustrates the expected trend of decreasing hydraulic conductivity with increasing vertical stress for all endmember fine materials. The polar fluids (DW and brine) hydraulic conductivity differences between non-clay materials (silica, mica, diatoms, and CaCO\(_3\)) and clay material (kaolinite, illite, and bentonite) are clear. The result shows high hydraulic conductivity for non-clay materials (silica, mica, diatoms, and CaCO\(_3\)) and relative low hydraulic conductivity for clay materials (kaolinite, illite, and bentonite). In the case of bentonite, it is strongly affected by DDL so that a higher hydraulic conductivity value is presented in brine than in DW. Similar to the coefficient of consolidation value, non-polar fluid kerosene indicates the low influences of hydraulic conductivity for all endmember materials.

Figure 5.12 Endmember fine materials’ hydraulic conductivity as function of vertical consolidation stress with different pore fluids (DW, brine, and kerosene).
5.4 Conclusion

The responses of endmember fine particles to pore fluid chemistry and stress changes with different pore fluids are investigated in this research to provide a particular information on how each type of fine materials behaves in the primarily coarse-grained sediments, as well as forming interbeds between coarse-grained layers in reservoir. A set of experimental tests is conducted to evaluate the dependence of fine sediments’ geomechanical properties such as compressibility and hydraulic conductivity on pore fluid chemistry. The experimental tests include electrical sensitivity measurements, a set of sedimentation tests, and consolidation tests. The fabric changes of fine sediments with different pore fluid chemistry are investigated by measuring index property of electrical sensitivity with the liquid limits. The geomechanical behavior variations in the sedimentation and consolidation according to the pore fluid chemistry are discovered by analyzing the depositional behavior, compressibility, and hydraulic conductivity of each fine material. Overall, the following conclusions can be made:

The pore fluid chemistry affects the sedimentation behavior of fine materials. Because of electrical interaction between fine particles, the different fabric can be observed based on different pore fluids. Two types of sedimentation behaviors among these fine materials are discovered, which are segregated sedimentation and uniform sedimentation. The low electrical sensitivity fine sediments with enough small fraction of particle size, such as silica, mica, and diatoms are significantly affected by electrical forces. Water freshen or DW can enhance electrical repulsion among particles so that hinders settlement and causes segregation. In addition, the high electrical sensitivity fine sediments such as bentonite and kaolinite can rearrange particles into a loose fabric in fresh water (DW) compared within brine. The non-polar
fluid kerosene presents the flocculated fabric for all fine sediments due to the unbalanced charges on the particle surface.

The electrical interaction controls not only fine particles fabric but also compressibility and hydraulic conductivity of fine materials. The fine sediments contain gravimetrically controlled large particles mixed with electrically controlled small particles can be more compressible in brine than in fresh water. With fresh water or DW, low sensitivity fine materials contain silica, mica, and diatoms can maintain fabric and keep the similar hydraulic conductivity compared within brine, but the overall sediment compressibility can decrease than in brine. The relatively high electrical sensitivity sediments such as bentonite and kaolinite can be rearranged in to a higher void ratio condition with fresh water or DW, which is more susceptible to recompression and hydraulic conductivity due to the fabric built by DDL. The non-polar fluid kerosene presents high compressibility for all fine materials except bentonite. Kerosene expresses rarely influences on hydraulic conductivity for non-clay fine materials. But it indicates the significantly enhanced hydraulic conductivity for clay fine materials due to the flocculated fabric.

The findings of this research can be implicated when nature sediments are disturbed by human activities such as pore fluid replacement, depressurization of formation, groundwater production, and gas production. The pore fluid chemistry can affect the fabric of particles. Furthermore, the invading pore fluid replacement changes pore fluid chemistry thereby alters the initial fabric of sediments. Therefore, the geomechanical properties such as compressibility and hydraulic conductivity can be changed. The high electrical sensitivity materials such as bentonite can be significantly affected due to the disturbed fabric. Moreover, a decrease in effective stress can be observed for the sediments containing bentonite during the water freshen due to DDL thickness raising and pore fluid pressure increase. On the other hand, when water freshen happens in
sediments containing enough fraction of silica silt, or mica, or other low electrical sensitivity fines, the sediment’s compressibility in brine would change toward to a lower compressibility in deionized water so that the raising of effective stress can be observed.

5.5 References


CHAPTER 6. MECHANISM OF FINES CLOGGING IN POROUS MEDIA
WITH SINGLE AND MULTIPHASE FLOW

6.1 Introduction

The fine particles migration in porous media is expected to effect on industrial applications of filtration (Sherard et al., 1984; Datta and Redner, 1998), water and oil extraction (Muecke, 1979; Gruesbeck and Collins, 1982), flow in biological system (Sanderson et al., 2001), the sand production (Papamichos et al., 2001), the pore clogging (MacDonald and Whitesides, 2002; Kampel and Goldsztein, 2008; Valdes and Santamarina, 2008), gas-driven fractures in sediments (Shin and Santamarina, 2010), and gas production from hydrate-bearing sediments (Jung et al., 2012).

Previous laboratory experiments have been developed using two-dimensional microfluidic pore models and three-dimensional porous sediment models to understand the migration of fine particles and its impacts on bridging or/and clogging for a single-phase flow in porous media (Herzing et al., 1970; Fan et al., 1985; Khilar and Fogler, 1987; Mackie et al., 1987; Sharma and Yortsos, 1987; Rege and Fogler, 1988; Imdakm and Sahami, 1991; Valdes, 2002; Agbangla et al., 2012; Jung et al., 2012). In those models, a host particle size (D), a fine particle size (d), and a pore throat size (o) have been identified as the main parameters affecting the migration and behavior of fine particles in porous media (Figure 6.1). The experimental results show that two critical size ratios (i.e., o/d and D/d) significantly influence the three distinct cases of fine particle behaviors, which are named as migration of fine particles without interaction, bridging formation, and clogging formation in pore throats (Figure 6.1). The size ratio of the pore throat and fine particles (o/d) has the most direct impact on the determination of three cases that is affected by the density of natural sediments and the size of fine particles.
Figure 6.1 Porous media including fine particles. Sizes of fine particle (d), host particle (D), and pore throat (o). Fine migrations, bridging and clogging are determined by two critical size ratios (D/d and o/d) (Khilar and Fogler, 1987; Bigno et al., 1994; Oyeneyin et al., 1995; Khilar and Fogler, 1998).

The size ratio of the host to fine particles (D/d) in three-dimensional sediments influences on the behavior of fine particles in porous media. Previous studies have observed three distinct cases.

First, a single particle with a diameter (d) can easily migrate through a porous medium when o/d is greater than 1.67 with water flow (Bigno et al., 1994; Oyeneyin et al., 1995; Khilar and Fogler, 1998) (Figure 6.1 (1)). On the contrary, when o/d is smaller than 1.67, clogging can be observed in the pore throat even with a few particles (Bigno et al., 1994; Oyeneyin et al., 1995; Khilar and Fogler, 1998) (Figure 6.1 (3)). Second, when a pore throat-particle size ratio (o/d) is between 1.67 and 100, a number of migrating particles can form bridging at the pore throat that illustrates the particle entrapment by particle interactions at the pore throat larger than the diameter of single particle (Valdes, 2002) (Figure 6.1(2)). Thirdly, when the pore throat (o) is much larger than the diameter of a single particle (o/d >100), no interaction among particles is expected so that neither clogging nor bridging can occur.
Bridging and clogging by fine particles in porous media are influences not only by the two critical size ratios (i.e., D/d and o/d) but also the concentration of fine particles, as well as the flow rate (Muecke, 1979; Bigno et al., 1994; Oyeneyin et al., 1995; Valdes, 2002, Agbangla et al., 2012). Figure 6.2 shows that the flow rate required to form clogging increases as the concentration of fine particles decreases (Muecke, 1979; Bigno et al., 1994; Agbangla et al. 2012).

Figure 6.2 Boundary between clogging and non-clogging by the pore throat to fine particle size ratio (o/d), fluid flow rate, and fine particle concentration. (Pandya et al., 1998; Agbangla et al., 2012).

While a higher concentration results in rapid clogging in the intermediate size ratio of the pore throat and fine particle (1.67< o/d < 100), flushing occurs in a low concentration of fine particles without clogging (Muecke, 1979; Valdes, 2002). For example, when o/d = 2.5, bridging is initiated at 15% fine particle concentration, while no-bridging occurs at less than 15% fine particle concentration (Muecke, 1979). Furthermore, Pandya et al. (1998) presented that the clogging required higher fine particle concentration with the decreased fine particle size through experiments using glass beads and latex particles, which was consistent with other studies (Pandya et al., 1998; Agbangla et al., 2012). On the other hand, Bigno et al. (1994) showed the decrease of fluid flow rate with the increase of fine particle concentration in gravel packs due to
bridging and clogging. In other words, the result shows a low fluid flow rate requires higher fine particle concentrations to form clogging. It can be concluded that clogging easily occurs with lower fine particle concentrations at a higher fluid flow rate, but an extreme high fluid flow rate prevents fine particles forming bridging or clogging due to disruptions by pressure distributes or flow reversals (Bigno et al., 1994).

A multiphase flow is defined as a flow of two or more fluids with different states of phases (i.e., gas or liquid). In a multiphase flow, even a low fine particle concentration can influence the behavior of sediments and fluids that results on volume expansion of pore fluid, change in porosity, sand production, low gas recovery efficiency, and bore-hole failure in gas production (Jain and Juanes, 2009). For instance, it has been known that the gas-driven fracturing could develop from hydrate-bearing sediments even composed of small fine fractions due to the clogging in pores by the accumulated fine particles (Jung et al., 2012). Furthermore, fine particle tend to move only if the fluid is wetting them as mobile. It has been observed that the surface wettability of host particles and the interfacial tension between multi-phase fluids impact the migration of fine particles in porous media. Hydrophobic fine particles tend to accumulate on the water-gas interface compared to hydrophilic fine particles (Wan and Wilson, 1994; Crist et al., 2005). On the other hand, when the surface charge of the host particles is positive, more fine particles tend to accumulate on the water-gas interface (Wan et al., 2001; Wan and Tokunaga, 2002).

In general, Bridging and clogging in the porous media caused by the migration of fine particles are important processes that depend on the concentration of fine particles, the flow rate, the pore throat to fine particle size ratio, and the surface wettability of particles, as well as fluids interfacial tension. However, the initiating mechanism of bridging and clogging in a multiphase
flow has not been fully understood. In addition, typical methods of measuring the relative permeability of a flow in porous media and a possible mechanical failure of sediments due to bridging or clogging may not be sufficient in explaining the initiating mechanism of bridging and clogging. Therefore, to better understand the mechanism and its relation to the aforementioned parameters, a microfluidic apparatus has been developed in this study. This chapter presents a microfluidic model study to explore the mechanism of single and multi-phase fluids flow in porous media including fine particles considering fine particle concentration and the size ratio of the pore throat and fine particle. The aim is to parametrically study bridging and clogging to understand the influence of the critical ratios for the pore throat and fine particle.

6.2 Experimental Study

6.2.1. Apparatus and materials

A schematic diagram of the experimental setup used in this study is provided in Figure 6.3 (a). The microfluidic model was fabricated and placed horizontally on a microscope (Figure 6.3 (b)). It was connected to a precision syringe pump (Kats Scientific, NE-1010) which was used to inject mobile fine particles with deionized water (DW) into the microfluidic model. The other port of microfluidic model was connected to another pump (Teledyne ISCO) that was used to inject CO\textsubscript{2} into the microfluidic model. The commercial CO\textsubscript{2} cylinder (Airgas, 99.99%) was connected to the ISCO pump. The CO\textsubscript{2} pressure was maintained at 10 kPa ± 1 kPa and room temperature (25 ± 1 °C) by a pressure regulator and the ISCO pump. A filter was connected with the microfluidic model in order to prevent fine particles from migrating into the pressure regulator and the ISCO pump. Injected fluids including fine particles (0.5%~50% fine particle concentration) were prepared with deionized water (DW) and spherical traceable polystyrene latex particles (19.2 μm diameter). In order to view the pore-network of the microfluidic model,
the microscope was used with function of capturing images and videos. Figure 3 (c) illustrates the top image (plan view) of the microfluidic model and pore-network that allows clearer observations of mobile particles and particle migration.

Figure 6.3 Micromodel test experimental setup. (a) Schematic diagram of the experimental setup, (b) Image of the microfluidic pore model, (c) Image of the top (plain view) of one of the developed microfluidic pore models.
6.2.2 Microfluidic pore model

The microfluidic models were fabricated using standard photolithography followed by a soft lithography. They were made of homogeneous pore-network patterns to form a two-dimensional symmetrical pore-networks. The material of the microfluidic models was polydimethylsiloxane (PDMS) (MacDonald and Whitesides, 2002). A homogeneous two-dimensional pore-network had a patterned area of 2 cm × 1 cm, composing of 152 grains (1190 μm diameter). The pore throat depth or the height of the microfluidic channel was set to 100 μm, and the pore throat
width of microfluidic models varied 700 μm, 300 μm, 100 μm, and 50 μm. The microfluidic channel surface has an average contact angle of 76.95°.

6.2.3 Fine particles

Polystyrene latex particles (MAGSPHERE INC) were used to represent the fine particles in both single-phase and multiphase flow experiments. The average diameter of the particles is 19.2 μm and the specific gravity is 1.0 ~1.05 g/ml. The concentrations of the fine particles in deionized water (DW) were controlled at 0.5%, 1%, 2%, 5%, 10%, and 50% by weight.

6.2.4 Experimental procedure

The microfluidic models were cleaned before tests by injecting 5 ml of ethanol (70%) (Mallinckodt Baker, ACS reagent grade) followed by 30 ml of deionized water (DW), then dried at room temperature (25°C ± 1 °C) for 72 hours. After the cleaning step, the microfluidic model was assembled in the experimental system. All components including valves, filter, transparent tubing, pressure transducer (Omegadyne INC), and pressure regulator (Swagelok INC) were connected with the microfluidic model, which was maintained at room temperature (25°±1 °C) (Figure. 6.3). The microfluidic model was saturated with DW including fine particles (19.2 μm, Polystyrene Latex, MAGSPHERE INC) suspension (i.e., 0.5%, 1%, 2%, 5%, 10%, and 50% by weight) using the syringe pump (Kats Scientific, NE-1010) and the pressure in system gradually increased up to 10 kPa ± 1 kPa using the pressure regulator and ISCO pump with CO₂ (Teledyne ISCO). Then, fine particle migration was initiated using the syringe pump while keeping constant 10 kPa ± 1 kPa by the ISCO pump with CO₂ injection into the microfluidic model. Flow rate (50 μl/min) was controlled using the syringe pump. At the same time, a camera took a video clip and pictures during and after fine particle drainage process. Images captured from the video clip were used to analyze the particle migration and clogging in the microfluidic model.
6.3 Results and Discussion

6.3.1. Single phase flow in microfluidic pore models

Pore throat to fine particle size ratio (o/d). Figure 6.4 shows snapshots of DW injection with fine particles (d=19.2 μm) into the micromodel at different pore throat sizes (o=50 μm to 700 μm). The o/d ratio was 2.6~36.4. The flow rate of water was controlled to be 50 μl/min and the concentration of fine particles in DW was 2%. The injected water with fine particles percolated through the microfluidic model within 1 s. Figure 6.4 shows the overall distribution of residual water with fine particles in the microfluidic model. Neither bridging nor clogging was observed in microfluidic models at the given conditions (d = 19.2 μm, o = 50 to 700 μm, flow rate =50 μl/min, concentration = 2%).

As shown in Figure 6.2, migration and clogging of fine particles in a single-phase flow depend on geometric parameters including the size of fine particles, the pore throat size, and fluidic parameters including the flow rate and the fine particle concentration. Particularly at a given intermediate o/d ratio (1.67< o/d <100), bridging and clogging can easily occur with the increase in the particle concentration (Muecke, 1979; Bigno et al., 1994; Oyeneyin et al., 1995; Valdes, 2002; Agbangla et al., 2012). In addition to the published data in Figure 6.2, the results obtained in this study provide the insight at a relatively higher flow rate (50 μl/min) than previous studies that fine particles with 2% concentration can migrate in the pore throat without bridge or clogging at the various o/d ratios (o/d = 2.6~36.4).
Figure 6.4 Snapshots of DW injection with fine particles (d = 19.2 μm) into microfluidic models that have different pore throat sizes (o = 50 to 700 μm) at P = 10 kPa ± 1 kPa. The flow rate of injected DW with fine particles is 50 μl/min and fine particle concentration is 2%. (a) o/d = 36.4, (b) o/d = 15.6, (c) o/d = 5.2, (d) o/d = 2.6.

Fine particle concentration. Figure 6.5 shows DW injection with different concentrations of fine particles (0.5%, 1%, 2%, 5%, 10%, 50% by weight) into the micromodels that had the same pore throat size (o = 50 μm). All particles have the same average size of 19.2 μm. The o/d ratio was 2.6. The flow rate of injected DW with fine particles was kept constant at 50 μl/min to study the effect of concentration of fine particles on bridging or clogging.
Figure 6.5 Snapshots of DW injection with various fine particle concentrations (d = 19.2 μm, 0.5%~50%) into the microfluidic model (o = 50 μm) at the pressure P = 10 kPa ± 1 kPa. The flow rate of injected DW is 50 μl/min. Fine particle concentrations by weight are: (a) 0.5%, (b) 1%, (c) 2%, (d) 5%, (e) 10%, (f) 50%.

Figure 6.5 shows the overall distribution of residual water with fine particles remain without bridging or clogging in the microfluidic model at lower fine particle concentrations (0.5%~2%) that has consistency with the results obtained using the microfluidic models with various o/d ratio. The bridging was observed at 5% fine particle concentration (Figure 6.5(d)), while partial or multi-particle clogging in the microfluidic pore model was detected at 10% fine particle concentration. In addition, obvious clogging in the microfluidic pore model was observed at 50% fine particles concentration.

Data in Figure 6.6 with additional data obtained in this study show that a higher fine particle concentration (> 5%) is required to form clogging in pore throat at o/d = 2.5 and a lower fluid flow rate (50 μl/min) in a single-phase fluid flow. Furthermore, in a single-phase fluid flow, the results clarify that clogging can occur easily at a higher flow rate, a higher concentration, and a
smaller pore throat and fine particle size ratio (o/d) like previous studies (Pandya et al., 1998; Agbangla et al., 2012).

Figure 6.6 Modified boundary between clogging and non-clogging by the pore throat size-fine size ratio (o/d), fluid flow rate, and particle concentration by adding the results including single- and multiphase flow (inside red square) obtained in this study (concentration 0.5% ~ 50%, o/d = 2.5, flow rate = 50 μl/min, P = 10 kPa ± 1 kPa). (Oyeneyin et al., 1995; Khilar and Fogler, 1998; Pandya et al., 1998; Agbangla et al., 2012)

6.3.2 Multiphase flow in microfluidic pore models

Fine particle migration, bridging and clogging in a multiphase flow. Figure 6.7 shows the migration of fine particles in a multiphase flow system. Figure 6.7(a) illustrates the outcome after completion of DW injection including 2% fine particles (d = 19.2 μm, o = 50 μm). The micromodel was filled with DW including 2% fines (Figure 6.7(a)). Then, CO₂ was injected into the DW-saturated micromodel. The local concentration of fine particles in micromodel increased with CO₂ injection, which caused clogging by fine particles (Figures 6.7(b) and 6.7(c)). Fine particles were observed migrating along the water-CO₂ interface, which also increased the local concentration of fine particles in micromodel (Figures 6.7(d), 6.7(e), and 6.7(f)). And, more clogging in pore throats were observed as the concentration of fine particles raised (Figures 6.7(b), 6.7(c), 6.7(d), 6.7(e), and 6.7(f)). With given condition (o/d = 2.6, 2% fine particle
concentration, and a flow rate of 50 μm/min), fine particles were able to migrate without
clogging in a single-phase flow. However, CO₂ injection into the water-saturated micromodel
containing fine particles caused clogging due to fine particle concentrations increasing in the
pores.

Fine particles migration could locally change the pore geometry by moving the host particles in
natural sediments due to high pressure caused by clogging in a multiphase flow (Jung et al.,
2012). When the fluid (i.e., CO₂ or other gas) pressure exceeds the total stress of sediments, the
host particles move and in turn initiate a fracture in the system. As a result, findings of this study
such as fine particles migrating along the water-gas interface that locally increase fine particle
concentration and subsequently cause clogging in the pore throat can explain gas-driven
fracturing in hydrate-bearing sediments containing fine particles during gas production (Jung et
al., 2012).

Figure 6.7 Fine particles migration in multiphase flow. (a) The migration of fine particles in
single-phase flow, (b) and (c) the clogging by the increased particle concentration in pore throat,
(d) the migration of fine particles along with the water-CO₂ interface, (e) and (f) the increased
fine particles concentration in pores and clogging in pore throats (red line represents water-CO₂
interface).
Fine particle accumulation along the water-CO$_2$ interface. Figure 6.8 shows two representative images obtained after CO$_2$ injection into the water-saturated micromodel (o=700 µm and 50 µm). When CO$_2$ was injected into the initially water-saturated micromodel, fine particles accumulated along the water-CO$_2$ interface and migrated together (Figure 6.8), which caused the increase in fine particle concentration (Figures 6.8(d), 6.8(e), and 6.8(f)). Once fine particles start to accumulate along the water-CO$_2$ interface, more mobile fine particles accumulate easily to the periphery of existing fine particles along the interface. Such observation is consistent with a previous study (Kim and Berg, 2000).

Figure 6.8 Snapshots of CO$_2$ injection into the water-saturated microfluidic pore models including fine particles (d = 19.2 µm, 2% concentration) at the pressure P = 10 kPa ± 1 kPa. The flow rate of injected CO$_2$ is 50 µl/min. (a) Pore throat size o = 700 µm, (b) o = 50 µm.

Literature studies show that the hydrophobic particles tend to accumulate on both water-air interface and water-solid interface (Wan and Wilson, 1994; Crist et al., 2005), and the hydrophilic particles tend to accumulate on the downstream portion at air bubbles (Wan and Wilson, 1994; Wan and Tokunaga, 2002). Therefore, the polystyrene latex particles used in this study were assessed close to hydrophobic causing the fine particles easily to accumulate along water-CO$_2$ interface. It implies that in-situ sandy sediments having hydrophilic surfaces could accumulate on the downstream portion of the water-gas interface but oil contaminated hydrophobic particles could accumulate along the water-gas interface.
Fine particle concentration. Figure 6.9 shows snapshots of CO$_2$ injection into the water-saturated micromodels. Each micromodel with the same pore throat size ($o = 50 \, \mu m$) includes different fine particle concentrations (i.e., 0.5%, 1%, 2%, 5%, 10%, and 50%). The gas flow rate was also set to 50 $\mu l/min$. For the range of 0.5% to 1% fine particle concentrations at both single and multiphase flow condition, fine particles migrated along the interface without clogging (Figures 6.5(a) and 6.5(b), Figures 6.9(a) and 6.9(b)). No clogging was observed in a single-phase flow in the concentration range between 2% and 10% (Figures 6.5(c), 6.5(d), and 6.5(e)), but the number of fine particles accumulated at the water-CO$_2$ interface increased in a multiphase flow that caused the clogging in pores (Figures 6.9(c), 6.9(d), and 6.9(e)). For 50% fine particle concentration, a large number of fine particles were injected in the pores, which caused clogging (Figure 6.5(f) and Figure 6.9(f)).
6.6 Conclusions

The behaviors of fine particles in porous media largely divided by these regions: the fine migration, bridging, and clogging that are affected by pore throat and fine particle size ratio, fine particle concentration, and flow rate. Neither clogging nor bridging was observed at a higher pore throat to fine particle size ratio, while clogging occurred at a lower pore throat and fine particle size ratio even with a few fine particles. However, all published data are scattered. Thus, it is not clear to explore exact boundaries between clogging (or bridging) and non-clogging. Also, all previous studies have focused on only single-phase fluid flow. Thus, we have gathered all previous data, presented them together in one figure to explore the effects of pore throat and fine particle size ratio, fine concentration, and flow rate on boundaries, added more experimental results at lower single-phase fluid flow rates, and explored the effects of multi-phase fluids flow on boundaries between clogging and non-clogging.

Single-phase flow experiments were conducted at flow rates lower than what was used in previously reported studies. Bridging or clogging was observed at lower o/d ratios, higher fine particle concentrations, and higher flow rates. The results obtained in this study show that a lower flow rate requires a higher fine particle concentration to form the clogging or bridging. Furthermore, results from multiphase flow experiments show that fine particles accumulate along the water-gas (CO₂) interface and migrate together, which in turn causes bridging or clogging easily to occur in pores. In other words, bridging or clogging in multi-phase fluids flow can be more expected at fine particles accumulate along the water-gas (CO₂) interface, the fine concentration in pores increases, bridging or clogging in pore throat occurs, which is similar to single fluid system. On the other side, bridging and clogging in multi-phase fluids flow can more easily occur than in single phase fluid flow due to the fines migration along the gas-water
interface that also causes the fine particle concentration increase in porous media. This implies that while a lower flow rate can prevent clogging in pores during single-phase fluid flow, however, clogging can be occurred even in the lower flow rate in multi-phase fluids flow. These observations imply that a multiphase flow during gas production in hydrate-bearing sediments and geological CO₂ sequestration could easily form bridging and/or clogging, in which the permeability of porous media decreases even clogging has not been occurred in the same conditions with a single-phase flow such as gas production from oil-reservoir and soil remediation in oil contaminant sites. Therefore, the permeability of porous media in petroleum engineering applications should be estimated by considering relatively easy bridging and clogging in pores in a multiphase flow compared to a single-phase flow. Also, this work further suggests that additional studies in various conditions are desired using the demonstrated microfluidic pore model approach.

6.7 References


CHAPTER 7. PORE SIZE AND FLUID CHEMISTRY INFLUENCING NATURE ENDMEMBER FINES MIGRATION AND CLOGGING IN POROUS MEDIA

7.1 Introduction

Fines migration in porous media can cause challenging problems of both scientific and industrial importance. The consequences of the migration of fines in porous media can be either beneficial or adverse (Papamichos et al., 2001; Sherard et al., 1984; Datta and Redner, 1998; Shin and Santamarina, 2010; Sanderson et al., 2001). Fine-grained sediments, or “fines,” exist nearly ubiquitously in natural sediments, even in predominantly coarse-grained sediments hosting gas hydrates that are widely prospected in offshore and onshore sediments (Takahashi et al., 2003; Anderson et al., 2011). Therefore, the fine-grained materials (fine particles or fines) exists within these sand sediments, as well as forming interbeds between hydrate-bearing layers, can play a crucial role during gas hydrate production activities. These fines can affect the overall sediment formation performance and gas production efficiency (Shin and Santamarina, 2010; Jung et al., 2012). During methane extraction, several processes can alter the mobility and clogging potential of fines: (1) fluid flow as the formation is depressurized to release methane from the hydrate; (2) pore-fluid chemistry shifts as pore-fluid brine freshens due to released pure water from the dissociating hydrate; (3) the presence of a moving gas/water interface as gas evolves from the dissociating hydrate and moves through the reservoir toward the production well. This study focuses on the exploration of the significant considerations for different types of fines migrating and clogging in coarse-grained sediment pores and reacting with different pore fluids during gas production. The responses of various fine-grained particles to pore-fluid chemistry can cause significant consequences during pore-water freshening and gas production, such as leading the particular gas migration path or pore space reduction in these coarse-grained sediments.
7.1.1 Effect of pore throat/fine size and fine concentration on fines migration behavior

Fine-grained particles (fines) refer to small particles with a diameter of less than 75 µm (ASTM D2487-11, 2011). Under subsurface conditions, the migratory fine particles are usually kaolinite, montmorillonite, illite, mica, and quartz. These fine particles act as an agent that may reduce permeability and increase sensitivity to saline fluids. The effective size and concentration of migratory fines are regarded as the primary important factors dictating the clogging potential of fines in porous media.

The behavior of fines migration in porous media is affected by not only the size of fine itself but also pore body size and pore throat size. The size and skeleton of pores have been identified as the main parameters influencing the migration behavior of fine particles. To simplify the relationship between pore throat size and fine size during fines migration, the host grain size (D), fine particle size (d), and pore throat size (o) have been defined in this study. Based on these parameters, two critical size ratios including the pore throat-to-fine particle size ratio (o/d) and host particle-to-fine particle size ratio (D/d) are identified to describe the effects of the four distinct cases of fine particle migration behavior in porous media. Several studies have demonstrated that the two critical size ratios (i.e., o/d and D/d) can significantly influence the four distinct cases of fine particle migration behavior in porous media, which are shown in Figure 7.1 (Bingno et al., 1994; Oyeneyin et al., 1995; Khilar and fogler, 1998; Dressaire and Sauret, 2017). The four distinct cases also involve the primary mechanisms of fine migration and clogging at the pore throat, which are known as piping, bridging, clogging (blocking), and sieving (no invasion).
Figure 7.1 Main mechanisms of fine migrating and clogging at pore throat that classified based on critical size ratios (D/d, o/d). (Host particle size (D), fine particle size (d), and a pore throat size (o)) (Bingno et al., 1994; Oyeneyin et al., 1995; Khilar and Fogler, 1998; Dressaire and Sauret, 2017).

Various macroscale experimental studies have investigated fines migration through porous media (Bingno et al., 1994; Oyeneyin et al., 1995; Khilar and Fogler, 1998; Dressaire and Sauret, 2017).

When the o/d ratio is between 1.67 and 100, as long as a number of migrating particles reach the pore throat, more migrating particles can form a bridge, which demonstrates particle entrapment by particle interactions at the pore throat (1.67 < o/d < 100) (Figure 7.1) (Valdes, 2002; Bingno, et al., 1994; Oyeneyin, et al., 1995; Khilar and Fogler, 1998). However, when the pore throat size (o) is much larger than the diameter of a single particle (o/d > 100), no interaction or piping among the particles is expected, thus, neither clogging nor bridging would occur at the pore throat. On the other hand, when the o/d ratio is smaller than 1.67, clogging or blocking can easily occur at the pore throat even with a single or few particles (Bingno et al., 1994; Oyeneyin, et al., 1995; Khilar and Fogler, 1998).

The concentration of fines can also be a crucial parameter in determining migration or clogging. In general, a small fine concentration does not cause clogging; however, clogging or plugging
can occur at a higher fine concentration. The critical clogging concentration is used to describe the criticality for clogging and non-clogging in this study. The fine critical clogging concentration is defined as the concentration at which pore clogging or plugging occurs. It is described as the ratio of fine content to fluid content, which can be calculated based on weight or volume. For example, a study (Pandya et al., 1998) found that the fine critical clogging concentration is strongly dependent on the D/d ratio. The experimental result showed that the fine critical clogging concentration increases from 0.35% (v/v) to 9% (v/v) when the D/d ratio rises from 12 to 40 (Bhuniya, 1996; Pandya et al., 1998). However, a higher concentration of fines might not strongly increase the probability of fines clogging the pore throat at a higher critical o/d ratio. In other words, even if a low concentration of fines is present in a small pore throat, clogging or bridging can occur. In addition, at a high concentration of fines in a relatively large pore throat, the probability of clogging or blocking can be low (Gruesbeck and Collins, 1982).

7.1.2 Effect of pore-fluid chemistry on fines migration behavior

Most common fine particles, such as clay, have a high plasticity index that represents a higher water/fluid content range required for transition from a liquid state to a semi-solid state (ASTM D4318-17, 2017). This characteristic may be attributed to interactions among particles and the pore water/fluid. Most migratory fines, such as clay minerals, are more pliable and have a high plasticity index due to the electrical interactions among particles and the pore fluid (Jang et al., 2017). Therefore, a new fine classification method based on the sensitivity to pore-fluid chemistry has been introduced to address fine related engineering problems (Jang and Santamarina, 2015). This method combines the liquid limits obtained with electrically contrasting pore fluids, which are defined as soil electrical sensitivity. A soil’s electrical sensitivity is described in terms of its liquid limits measured with deionized water (DW), 2 M
brine, and kerosene (Jang and Santamarina, 2015). Knowledge of the electrical sensitivity of various fines can enhance the understanding of the interactions among particles under different pore-fluid conditions.

Electrical sensitivity can be implicated in many science and engineering applications. For example, during gas hydration production, the pore-fluid exchange occurs during pore-water freshening while the hydrate dissociates. The literature shows that the dissociation of 1m³ of hydrate-bearing sediment with 80% hydrate saturation would mix 0.22m³ of fresh water into the existing pore fluid brine (Jang et al., 2017). This means the salt concentration is reduced to 25% of the original salt concentration. The reduction in salt concentration can directly affect the existing fine particles in sediments. Therefore, the electrical sensitivity of fines is a significant parameter for evaluating the behavior of fines in porous media.

Furthermore, excess or unbalanced surface electrical charges are often associated with fine particles owing to isomorphous substitution, surface disassociation, and structural disorder and defects (Lambe and Whiteman et al., 1969; Santamarina et al., 2001). Consequently, these fines are sensitive to electrical interparticle interactions, which also dominate the arrangement of fine particles (Jang et al., 2017; Santamarina et al., 2011; Mitchell and Soga, 2005; Sogami and Ise, 1984; McBride and Baveye, 2002). This easily affects the behavior of fine migration in the pores of coarse sediments. For example, fine migration behavior-related parameters such as quantity of fines in the fluid, fine cluster size/shape, and fine fabric can be changed under different pore fluid conditions. Therefore, the migration and clogging behavior of fines may be directly affected in porous media.

The electrical interactions of fine particles can affect the particle fabric due to the primary attractive and repulsive forces between fine particles. The two major contribution forces are
London-van der Waals attraction and double layer repulsion (Sogami and Ise, 1984; McBride and Baveye, 2002). Parameters such as particle size, the distance of separation, and salt concentration are susceptible to these two major forces. For example, when fine particles are in DW, the net surface charge of each particle can push the charged particle away, which is known as the diffusive double layer (DDL). This can cause a dispersed fabric pattern among particles. On the other hand, the brine solution can cause counter ions to adsorb onto the charged surface so that the electrostatic repulsion among particles is decreased in a lower void ratio. As a result, counter ions in the brine solution continue to be attracted to the spaces among particles. Moreover, the particular shape of fine particles can result in various particle interactions and fabrics in different pore fluids, leading to distinct fines or fine cluster migration behaviors in porous media.

Figure 7.2 illustrates the attractive and repulsive electrical interactions among two types of particles with net surface charges under different pore fluid. For platy particles, such as kaolinite and illite, the negative charge of the particles will attract positive ions to align them surround the plate particle. In addition, the brine solution results in an attractive electrical interactions that cause platy particles to flocculate and form face-to-face fabrics, which are different from edge-to-face fabrics in DW.
7.1.3 Fine migration in porous media for single and multiphase fluid flow

Previous laboratory experiments have been conducted to understand the migration of fine particles, bridging, and clogging through porous media under single-phase fluid flow conditions (Herzing, et al., 1970; Fan, et al., 1985; Khilar and Fogler, 1987; Mackie, et al., 1987; Sharma and Yortsos; 1987, Rege and Fogler, 1988; Imdakm and Sahami, 1991; Valdes, 2002; Agbangla et al., 2012; Jung et al., 2012). However, the effect of migration particles on bridging and clogging is poorly understood under multiphase flow condition, and there is no universal theory can adequately describe fine migration behavior in porous media. Therefore, it is important to elucidate fine migration in porous media under multiphase flow condition.

Some studies have indicated that in addition to mechanical bridging, particle wettability and interfacial forces can affect particle migration behavior when multi-fluids phases are presented under multiphase flow condition (Muecke, 1979). The observation indicates that fines only move
in the phase that wets fines can immerse in and move on. Moreover, fines can easily migrate only when the fluid phase is sufficiently mobile to carry the fines. In other words, localized pressure disturbances caused by a multiphase flow can keep the fines agitated, which would reduce the chance of bridging at the pore throat (Muecke, 1979). On the other hand, the fines can localize at the interface between two fluids and follow the interface contour until reaching a region of low velocity and low permeability, such as a region where pore clogging or blocking already occurred. Fine particles tend to remain at the interface where they are most stable (Ivanov et al., 1986). In addition, in a region involving the interface between a wetting (i.e., water) and non-wetting phase (i.e., gas), particles in a weaker wettability phase would first migrate to the interface and then move from the interface to a stronger wettability phase (Civan, 1996). Figure 7.3 shows particle retention at solid-fluid and fluid-fluid interfaces in multiphase systems (Civan, 1994). Particles are transferred between two fluid phases, and the fine particles prefer to accumulate along the interface between the two fluid phases.

Figure 7.3 Particle retention at solid-fluid and fluid-fluid interfaces in the multiphase systems (Muecke, 1979; Civan, 1994; reprinted from U.S. Department of Energy).
7.2 Experimental Method

7.2.1 Apparatus and materials

Fine Materials. Pure fine particles were selected as endmembers to illustrate the effect of pore-fluid over the different ranges of electrical sensitivities, particle shapes, and sizes of the different fine particles in different geological reservoirs. Furthermore, the fine particles were classified into two types: clay and non-clay. To determine the role of endmember fines in migration and clogging at the pore throat, different fine particles were examined in this study, including silica silt, mica, calcium carbonate (CaCO₃), diatoms, kaolinite, illite, and bentonite (primarily made of montmorillonite). Table 7.1 shows the properties of endmember fine particles, which included a broad range of fines in porous media. For example, the clay mineral bentonite is affected by the DDL thickness due to its small particle size and large excess surface charge, and it shows a strong response to fluid permittivity, conductivity, and ionic concentration. Moreover, it has high sensitivity to pore-fluid chemistry because of the higher sensitivity to ionic concentration and permittivity. On the other hand, the non-clay minerals containing silica silt, mica, diatoms, and CaCO₃ are considered to have intermediate electrical sensitivity due to a higher sensitivity to electrical permittivity changes and similar sensitivity to DW and brine liquid (Table 7.1).

Pore fluids. The pore fluids used in this study included DW, sodium chloride (NaCl) brine (2 M), and kerosene. These three fluids are the most common fluids for representing subsurface pore fluids. Moreover, a low permittivity fluid (kerosene) was used for characterizing the electrical sensitivity difference between fines in DW and brine (Jang and Santamarina, 2015). Electrical sensitivity tests were performed with each fluid to evaluate the changes in electrical interactions between fines in response to fluid permittivity and conductivity (Jang and Santamarina, 2015).
Table 7.1 shows the properties of endmember fine particles. The concentrations (w/w%) of these fines in each pore fluid were maintained at 0.1%, 0.2%, 0.5%, 1%, 2%, 5%, and 10%.

Table 7.1 Material description: physical and index properties (Arnott, 1965)

<table>
<thead>
<tr>
<th>No.</th>
<th>Sediment</th>
<th>Specific gravity $G_s$</th>
<th>Median particle size $D_{50}$ [µm]</th>
<th>Liquid limit $LL_{DW}$</th>
<th>$LL_{brine}$</th>
<th>$LL_{ker}$</th>
<th>Electrical sensitivity soil classification$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Silica silt</td>
<td>2.65$^2$</td>
<td>10.5$^2$</td>
<td>31</td>
<td>31</td>
<td>36</td>
<td>LI</td>
</tr>
<tr>
<td>2</td>
<td>Mica</td>
<td>2.82$^2$</td>
<td>17$^2$</td>
<td>94</td>
<td>81</td>
<td>110</td>
<td>HI</td>
</tr>
<tr>
<td>3</td>
<td>CaCO$_3$</td>
<td>2.73</td>
<td>8$^2$</td>
<td>25</td>
<td>23</td>
<td>31</td>
<td>NI</td>
</tr>
<tr>
<td>4</td>
<td>Diatoms</td>
<td>2.23</td>
<td>10$^2$</td>
<td>119</td>
<td>111</td>
<td>140</td>
<td>HI</td>
</tr>
<tr>
<td>5</td>
<td>Kaolin</td>
<td>2.68</td>
<td>4</td>
<td>77</td>
<td>55</td>
<td>83</td>
<td>II</td>
</tr>
<tr>
<td>6</td>
<td>Illite</td>
<td>2.71</td>
<td>20</td>
<td>56</td>
<td>52</td>
<td>59</td>
<td>IL</td>
</tr>
<tr>
<td>7</td>
<td>Bentonite</td>
<td>2.53</td>
<td>$&lt; 2^4$</td>
<td>288</td>
<td>126</td>
<td>65</td>
<td>HH</td>
</tr>
</tbody>
</table>

$^1$Density analysis by gas pycnometer, $^2$data from manufacturer, $^3$indicating no (N), low (L), intermediate (I), or high (H) plasticity fine grains of low (L), intermediate (I), or high (H) electrical sensitivity, $^4$approximated value from literature (Arnott, 1965).

**Microfluidic pore model.** The microfluidic pore models were fabricated using standard photolithography followed by soft lithography. The material of the microfluidic pore model was polydimethylsiloxane (PDMS) bonded to a glass slide (MacDonald and Whitesides, 2002). They consisted of homogeneous pore network patterns to form a two-dimensional and two-symmetry pore network. The homogeneous two-dimensional pore-network had a patterned area of 2 cm × 1 cm, consisting of different grains sizes (D) to simulate different pore throat sizes (o) (Figure 7.4 (b)). The pore throat depth or height of the microfluidic channel was 100 µm, and the pore throat width (o) of the microfluidic pore models was varied between 10 µm, 20 µm, 40 µm, 60 µm, and 100 µm with sizes ranging from 10 µm to 100 µm to form a random pore throat pattern.

**Supplementary capillary tubes.** Since the microfluidic pore model only allows an observation from above (plane view) to assess fine migration and clogging behavior in the porous media, capillary tubes (inner diameter (ID) = 1/16 inch) (chemical-resistant PVC; McMaster-Carr) were used to assess fine migration with different fluids from the side. Therefore, an accurate
assessment of fine migration behavior with fluid meniscus can be performed with the side-view images of the capillary tube.

7.2.2 Experimental setup of the micromodel/tubing test

**Microfluidic pore model setup and experimental procedure.** The schematic experimental setup of the micromodel used in this study is shown in Figure 7.4 (a). The microfluidic pore model was placed horizontally on a microscope (Olympus IX51-LWD 4X/0.1) and connected to a syringe that was controlled with a precision syringe pump (NE-1010; Kats Scientific). The other port of the microfluidic pore model was connected to another syringe pump (Teledyne ISCO) that was used to inject gas (CO$_2$) into the microfluidic pore model channel. A commercial CO$_2$ cylinder (99.99%; Airgas) was connected to the ISCO pump. CO$_2$ pressure was maintained at 10 ± 1 kPa by a pressure regulator and the ISCO pump at room temperature (25 ± 1 °C). A filter was connected to the microfluidic pore model to prevent fine particles from migrating into the pressure regulator and the ISCO pump. The injected fluids (DW, brine, and kerosene) including fine particles (0.1~10% fine particle concentration) were prepared in the syringe. To view the pore network of the microfluidic pore model, the microscope was used to capture images and videos (Figure 7.4). Figure 7.4(b) shows the top image (plane view) of the microfluidic pore model and pore network, which allowed a clear observation of mobile particles and their migration. The microfluidic pore models were fabricated and cleaned before tests by injecting 5 ml of absolute ethanol (ACS reagent grade; Mallinckrodt Baker) followed by 30 ml of DW. Then, they were dried at room temperature (25 ± 1 °C) for 72 h. After cleaning, it was assembled in the experimental system. All components including the valves, filter, transparent tubing, pressure transducer (Omegadyne INC), and pressure regulator (Swagelok INC) were connected to the microfluidic model.
First, the microfluidic model was saturated by injecting fluid with fine particle suspension using a syringe pump (NE-1010; Kats Scientific). Then, the pressure in the system was gradually increased up to 10 ± 1 kPa using a pressure regulator and ISCO pump (Teledyne ISCO). While the system was maintained at a constant pressure (10 ± 1 kPa) and temperature (25 ± 1 °C), the syringe pump withdrew fine particles at a constant flow rate (50 μl/min), which addressed the typical pulsation problem of a syringe pump. The migrating fine particles were withdrawn by the syringe pump with different fine particle concentrations (i.e., 0.1%, 0.5%, 1%, 2%, 5%, and 10% by weight). At the same time, digital images and video clips were captured during and after the experiment. The migration and clogging of fines in the micromodel were analyzed using the available optical images and videos.

(a)

Figure 7.4 Micromodel and tubing test experimental setup. (a) Schematic diagram of the experimental setup, (b) image of the microfluidic model and top (plane view) of the microfluidic model.

(fig. cont’d)
Supplementary capillary tubing setup and experimental procedure. To examine fine migration behavior and the fines with fluid meniscus from the side, a supplementary capillary tubing system was added. This supplementary tubing system can provide a transparent observation from the side so that the meniscus behavior of the fluid can be easily evaluated. In addition, this tubing system is more applicable for kerosene because kerosene has a high viscosity and lower transparency. Moreover, the migration behavior of fine particles cannot be clearly observed through the microfluidic pore model because of the high gravitational difference between fine particles and kerosene. The schematic of the experimental setup of the tubes used in this study is shown in Figure 7.4 (a). Instead of the microfluidic pore model, a 1/16 inch (ID) tube (chemical-resistant PVC; McMaster-Carr) was placed horizontally in front of a camera with image and video capture function. Other parts of the system were assembled in a similar manner to that in the micromodel experiment. The pressure was maintained at 10 ± 1 kPa at room temperature (25 ± 1 °C). The injected fluid (kerosene) including fine particles was prepared in the syringe. Instead of capturing the top-view image/video of fines migrating in the tubes, the side-view
optical image/video was obtained to evaluate the results. The experimental procedure was similar to that in the micromodel experiment.

7.3 Results and Discussion

7.3.1 Effect of Pore-fluid chemistry on endmember fine particle migration and clogging in porous media

Endmember fine particles including silica silt, mica, diatoms, CaCO$_3$, kaolinite, illite, and bentonite were evaluated in the micromodel with DW, brine, and kerosene. Owing to pore-fluid chemistry differences, various endmember fine particles had specific cluster behaviors. The differences in fine clogging behavior and meniscus effects among DW, brine, and kerosene were apparent.

Effect of pore fluids on fine clogging due to the attractive and repulsive electrical interactions among particles. Figure 7.5 shows the images of the effect of pore fluids on fine clogging in DW and 2 M brine with 0.5% (w/w%) silica silt. The injected DW or brine with fine particles percolated through the microfluidic pore model within 1 s. Additional fluid with fines was injected into the microfluidic pore model for full saturation after percolation (> 1 s). The result demonstrated the even distribution of silica particles in DW (Figure 7.5 (a)). Neither bridging nor clogging was observed in the micromodel with DW under the given condition (pore throat = 60 μm, flow rate = 50 μl/min, fine particle concentration = 0.5%). However, with the same concentration of silica and flow condition (pore throat = 60 μm, flow rate = 50 μl/min, fine particle concentration = 0.5%) in 2 M brine solution, the distribution was uneven with several silica clusters (Figure 7.5 (b)). In addition, silica fines clogged the pore throat (Figure 7.5, red circles).
Figure 7.5 Snapshots of DW and 2 M brine injection with silica fines (0.5% concentration) into the micromodel (o = 60 μm, P = 10 ± 1 kPa). (a) No clogging occurs with 0.5% silica for DW, (b) several clogging (red circles) pore throats observed with 0.5% silica for 2 M brine.

Figure 7.6 shows the experimental data on silica in two pore fluids (DW and 2 M brine), which indicated the boundary between clogging and non-clogging according to pore throat size ratio and fine particle concentration. The results revealed that water can easily cause clogging compared with brine with the same pore structure and fine concentration of silica.

Figure 7.6 Boundaries between clogging and non-clogging for silica with fine/pore throat size ratio and fine particle concentration in different pore fluids (DW and 2 M brine). (Dots represent the experimental data, lower left part in the figure represents non-clogging area while higher right part in the figure represents clogging area).

The experimental data demonstrated the influence of pore-fluid chemistry on silica silts. The brine solution can cause counter ions to adsorb onto the charged surface, thus decreasing the
Electrostatic repulsion between silica fines and resulting in a lower void ratio. As a result, counter ions in the brine solution would continue to be attracted to the spaces among particles to form clusters. Furthermore, the enhancement of the silica cluster size can cause easy clogging or bridging at the pore throat.

**Effect of pore fluids on fines clogging due to particle fabric.** Pore-fluid chemistry could affect the arrangement or “fabric” of fine particles due to the unbalanced surface charge, especially for platy-shaped fine particles such as kaolinite and illite. Figure 7.7 shows the critical clogging concentrations of illite in two different pore fluids (DW and 2 M brine).

Figure 7.7 Snapshots of illite with DW and 2 M brine injection into micromodel (o = 60 μm, P = 10 ± 1 kPa) at different fine concentrations. (a) The illite critical clogging concentration is observed at 0.2% in DW, (b) the illite clogging occurs at 0.5% concentration in 2 M brine, which shows a higher critical clogging concentration compared within DW.

With the same pore structure and flow condition (pore throat = 60 μm, flow rate = 50 μl/min), the critical clogging concentration of illite was higher in brine (0.5%, Figure 7.7 (b)) compared with DW (0.2%, Figure 7.7 (a)). This finding indicated that if the amount of illite fines is the
same between different pore fluids, the possibility of clogging would be lower in brine compared with DW.

The presence of brine could change the fraction of these platy specimens (i.e., illite and kaolinite), causing these platy fines to flocculate and form face-to-face fabrics, which are different from edge-to-face fabrics in DW (Jang et al., 2017). The change in fabric causes a reduction in platy fine (i.e., illite and kaolinite) cluster size; thus, a higher critical clogging concentration is required in the brine solution. Figure 7.8 shows the experimental data of fine particles (i.e., illite and kaolinite) with differences in the clogging boundary because of the particle fabric.

Figure 7.8 Boundaries between clogging and non-clogging for illite and kaolinite with fine/pore throat size ratio and fine particle concentration in different pore fluids (DW and 2M brine) (Dots represent the experimental data, lower left part in the figure represents non-clogging area while higher right part in the figure represents clogging area). (a) Data of kaolinite, (b) data of illite.

The fine/pore throat size ratio and fine particle concentration in two pore fluids (DW and 2 M brine) demonstrated the boundary between clogging and non-clogging. Kaolinite (Figure 7.8 (a)) and illite (Figure 7.8 (b)) exhibited a similar behavior of fine migration and clogging in the porous media, indicating that the brine solution could lower the possibility of clogging when the pore structure and fine concentration of both kaolinite and illite were the same. This finding is
consistent with the fabric behavior of platy-shaped fine particles. In comparison with particles in DW, those in brine formed more compact clusters and migrated easily through the pore throat.

**Effect of pore fluids on the clogging of fine particles with high electrical sensitivity.** Figure 7.9 shows the images of bentonite with DW and 2 M brine (o = 60 μm, P = 10 ± 1 kPa) at different fine concentrations. The clogging of bentonite easily occurred in 2 M brine even at a very low concentration (0.1%). In addition, the number of clogged pore throats per unit area was high in 2 M brine (Figure 7.9 (b)). However, clogging at the pore throat was not observed in DW at the same particle concentration (0.1%). Moreover, when the concentration of bentonite was increased to a high level (5%), clogging only occurred at one pore throat per unit area (Figure 7.9 (a)).

![Figure 7.9 Snapshots of bentonite with DW and 2 M brine injection into micromodel (o = 60 μm, P = 10 ± 1 kPa) at the critical clogging concentrations. (a) The clogging happens at 0.1% bentonite concentration in DW. Only one clogging pore throat per unit area was observed at high bentonite concentrations (5%) in DW, (b) the clogging happens at immense low bentonite concentrations (0.1%) in 2M brine.](attachment:image)
In the case of the highly electrically sensitive bentonite, the repulsive electrical interaction among particles is strong in DW; thus, bentonite particles would not be able to pack, settle, and grow into clusters (Jang et al., 2017). The DDL thickness of bentonite is bigger in DW compared with brine. Furthermore, bentonite particles are unable to get close enough to form clusters. Therefore, these relatively independent bentonite particles can easily migrate in the porous media. In other words, the possibility of pore throat clogging would be low for bentonite in DW. On the other hand, when an ionic solution (2 M brine) is added, it could shrink the DDL thickness among particles and enlarge the bentonite cluster size. Therefore, these large bentonite clusters can easily cause pore throat clogging. Figure 7.10 shows the boundary between clogging and non-clogging for bentonite according to fine/pore throat size ratio and fine particle concentration, which was different between fines in brine and DW. The clogging of bentonite easily occurred in 2 M brine solution even at a very low concentration and low fine/pore throat size ratio. On the contrary, DW resulted in a thick DDL; thus, bentonite did not pack and grow as clusters, which lowered the possibility of clogging in the porous media.

![Figure 7.10 Boundaries between clogging and non-clogging for high electrical sensitivity fines (bentonite) with fine/pore throat size ratio and fine particle concentration in different pore fluids (DW and 2 M brine) (Dots represent the experimental data, lower left part in the figure represents non-clogging area while higher right part in the figure represents clogging area).](image-url)
Effect of pore fluids on the clogging of fine particles with intermediate to low electrical sensitivity. Certain characteristics of fine clogging behavior were affected by changes in the pore fluid chemistry, whereas some characteristics were not affected. Figure 7.11 shows that the critical clogging concentration (0.1%) was the same for diatoms and CaCO₃ in both brine and DW. Regardless of the pore fluid, fines such as diatoms and CaCO₃ clogged the pore throat at a similar concentration. For example, the clogging of diatoms can occur at a low concentration (0.1%), and the differences between the effect of DW and brine on fine clogging were not distinct (Figure 7.11 (a)). Furthermore, the CaCO₃ critical clogging concentration (1%) at the pore throat was same in DW and brine (Figure 7.11 (b)).

Figure 7.11 Snapshots of DW and 2 M brine injection into the micromodel (o = 60 μm, P = 10 ± 1 kPa) for intermedia to low electrical sensitive fine particles at their critical fine clogging concentrations. (a) The diatoms clogging happens at 0.1% concentration for both DW and 2 M brine, (b) the CaCO₃ clogging happens at 1% concentration for both DW and 2 M brine.

Mica, CaCO₃, and diatoms are considered to have an intermediate to low electrical sensitivity, which indicates that clogging ability may be similar between the fines in DW and brine.

Although an increased salt concentration (2 M brine) has more ions, individual particles tend not
to form a larger cluster due to their low electrical sensitivity. In other words, the clogging ability of these fines would be more dependent on individual particle sizes. When the average particle size is larger (i.e., mica and diatoms) (Table 7.1), clogging would be easier, and the critical clogging concentration would be lower (0.1%). Accordingly, the critical clogging concentration of diatoms and mica was lower (0.1%) than that of CaCO$_3$ (1%) (Figure 7.11). This result is consistent with the smaller particle size of CaCO$_3$ compared with that of mica and diatoms. Figure 7.12 shows the boundary between clogging and non-clogging for intermediate to low electrical sensitivity fines (i.e., mica, CaCO$_3$, and diatoms) according to fine/pore throat size ratio and fine particle concentration in DW and 2 M brine.

Figure 7.12 Boundaries between clogging and non-clogging for intermediate to low electrical sensitivity fines with fine/pore throat size ratio and fine particle concentration in different pore fluids (DW and 2 M brine) (Dots represent the experimental data, lower left part in the figure represents non-clogging area while higher right part in the figure represents clogging area). (a) Data of mica, (b) data of CaCO$_3$, (c) data of diatoms.
There was no noticeable difference in the clogging boundary between fines in DW and 2 M brine due to their relatively low electrical sensitivity. Potential differences in the critical clogging concentration among these fine particles may be attributed to the average particle size. A larger $D_{50}$ (i.e., mica and diatoms) with a lower fine concentration (0.1%) can still result in a higher possibility of clogging regardless of the pore fluid type.

**Effect of non-polar pore fluid on fine particle clogging.** To fully understand the effect of pore-fluid chemistry on fine clogging, the non-polar pore fluid kerosene was evaluated in this study. Kaolinite was used as an example to explain the effect of non-polar pore fluids on fine clogging in porous media. Figure 7.13 shows a comparison of kaolinite migration and clogging behavior in DW, 2 M brine, and kerosene. The supplementary tubing system was added to elucidate the fabric of fines in a non-polar pore fluid (kerosene) (Figure 7.13 (f)).

In a non-polar fluid (kerosene), ions prefer to precipitate on the particle surface, and surface charges are unbalanced (Sposito, 1989; Santamarina et al., 2001). Surface charges can contribute to the formation of clusters (Figure 7.13 (f)) (Sridharan and Prakash, 2000; Jang and Santamarina, 2015, 2017). While in DW and brine, the fines did not easily form a flocculated fabric with the unbalanced charges on the particle surface; moreover, settlement time in DW and brine was slow compared with that in kerosene ((Figure 7.13 (d), (e)). This phenomenon could directly affect the behavior of fine migration and clogging. On the other hand, the higher viscosity of kerosene compared with DW and brine could impede the movement of fines in the porous media (Figure 7.13 (c)). In addition, the gravitational difference between kerosene and fines was distinct; thus, most fines would prefer to settle and resist movement with kerosene unless the flow velocity reaches a certain value. Therefore, the fine particles (i.e., kaolinite) in kerosene had the lowest critical clogging concentration (0.2%) (Figure 7.13 (c)) compared with
those in DW (0.5%) and brine (2%). As mentioned previously, the fabric of platy fine particles (i.e., kaolinite) was different in DW and brine. Brine can cause these platy fines to flocculate and form face-to-face fabrics, leading to smaller voids among particles. Therefore, kaolinite had a higher critical clogging concentration in brine (2%) compared with DW (0.5%) (Figure 7.13 (a, b)).

Figure 7.13 Snapshots of three different fluids with kaolinite injection into the micromodel (o = 100 μm) and capillary tubing (ID=1/16 in) at same flow condition (flow rate=50 μl/min, pressure P = 10 ± 1 kPa), which illustrates the comparison of kaolinite migration and clogging behaviors within DW, 2 M brine, and kerosene. (a) The pore throat clogging occurs at 0.5% kaolinite concentration in DW, (b) the pore throat clogging occurs at 2% kaolinite concentration in brine, (c) the pore throat clogging occurs at 0.2% kaolinite concentration in kerosene, (d) side view of tubing test for DW with kaolinite, (e) side view of tubing test for brine with kaolinite, (f) side view of tubing test for kerosene with kaolinite clusters.

7.3.2 Effect of multiphase fluids and meniscus on fine migration and clogging

Effect of gas invasion on fine clogging. Figure 7.14 shows the injection of gas (CO₂) into the fluid-saturated microfluidic pore models with kaolinite.
Figure 7.14 Snapshots of gas phase (CO$_2$) before and after injecting into three pore fluids with fines (kaolinite) saturated micromodel ($\sigma = 60 \, \mu m$, $P = 10 \pm 1 \, kPa$). (a) CO$_2$ injected into fines (kaolinite, 0.2%) with brine saturated micromodel, the local concentration of fines (kaolinite) and residual brine saturation in pores are enhanced after CO$_2$ injection and more clogging pore throats are observed, (b) CO$_2$ injected into DW with fines (kaolinite, 0.2%) saturated micromodel, the local concentration of fines (kaolinite) in pores is enhanced and pore plugging occurs, (c) CO$_2$ injected into kerosene with fines (kaolinite, 0.1%) saturated microfluidic pore model. The high viscosity pore fluid kerosene presents the low mobility for fines (the fine clogging behavior is barely to be observed due to fine’s high gravity in kerosene).
In water- and brine-saturated micromodels (Figure 7.14 (a), (b)), the local concentration of fines (kaolinite) in pores was enhanced after CO$_2$ injection due to the further clogging of pore throats by fine particles. In addition, the clogged pore throats reduced CO$_2$ permeability, which caused more fines to accumulate at the pore throats. Mechanical bridging and interfacial forces could strongly influence particle mobility as a result of the formation of permanent bridges and reduction in the permeability of the porous media. Fine particles were localized at the interface between two fluids and followed the interface contour until reaching regions with either a low local velocity or clogged pores. The differences in the effect of gas (CO$_2$) flushing between the brine- and DW-saturated porous media were compared and expressed as the change in residual fluid saturation. For example, the brine-saturated porous media with fines (i.e., kaolinite) had a lower residual fluid (brine) saturation after CO$_2$ flushing (Figure 7.14 (a)). In contrast, the DW-saturated porous media had a higher residual fluid saturation after CO$_2$ injection (Figure 7.14 (b)). In the kerosene-saturated porous media (Figure 7.14 (c)), the high-viscosity pore fluid (kerosene) disrupted the movement of fines in the porous media. Furthermore, kerosene is not sufficiently mobile to carry the fines; thus, the critical clogging concentration of fines in kerosene was low (0.1%) compared with those in high-mobility fluids such as DW and brine. Consequently, the local fine concentration in kerosene after CO$_2$ flushing was not increased (Figure 7.14 (c)).

Figure 7.15 shows the video snapshots of fine particle migration, bridging, and clogging in a multiphase flow. Figure 7.15 (a) shows the injection of DW with 0.1% of fine particles (diatoms) into the microfluidic pore model ($o = 100$ μm, flow rate = 50 μl/min). Subsequently, CO$_2$ was injected into the DW-saturated micromodel (Figure 7.15 (b)). The local concentration of fine particles in pores was increased when CO$_2$ was injected, and more fines were accumulated at the
clogged pore throats due to the agitated fine particles in the pores (Figures 7.15 (c)). The fine particles remained at the DW-CO$_2$ interface and migrated along the DW-CO$_2$ interface contour, which increased the local concentration of fine particles in the pores (Figures 7.15 (c), 7.15 (d), and 7.15 (e)). At the same time, the pore throats were clogged as the concentration of fine particles continued to increase (Figures 7.15 (c), 7.15 (d), 7.15 (e), and 7.15 (f)). Under the given experimental conditions (0.1% diatoms, o = 100 μm, flow rate = 50 μl/min, P = 10 ± 1 kPa), fine particle migration could locally change the pore geometry such as by enhancing the clogging area and increasing the number of clogged pore throats in a multiphase flow. Therefore, the findings of this study can clarify the mechanism of fine particle migration along the liquid-gas interface, the meniscus force on the fines, and the bridging and clogging caused by an increased fine particle concentration.

![Figure 7.15 Video snapshots of endmember fine particles (0.1% diatom) migration in multiphase (DW/CO$_2$) flow system (o = 100 μm, P = 10 ± 1 kPa). (a) and (b) The completion of fine particles migration in single-phase flow, (c) and (d) CO$_2$ injecting in DW with fines saturated micromodel enhances the pore clogging area, (e) and (f) the local fine particles concentration increases in pores and more residual water surrounds clogged pore throat. Yellow area represents injected CO$_2$. Red circle indicates the clogging pore throat.](image)

**Effect of fluid meniscus on the gas/liquid interface.** To better understating the effects of kerosene with fine particles and gas interface behavior on fine clogging, a tubing system was used in this
study. The meniscus of kerosene and CO\(_2\) was observed from the side view of the tube. Figure 7.16 shows the kerosene flow with 0.5% kaolinite in a 1/16 inch (ID) tube when CO\(_2\) was injected at two different flow rates: 200 μl/min (Figure 7.16 (a)) and 500 μl/min (Figure 7.16 (b)). The kerosene/CO\(_2\) meniscus led to the accumulation and movement of fines (Figure 7.16). In addition, the tubing system demonstrated the effect of pore-fluid (kerosene) chemistry on fine particles, which showed a great gravitational difference between kerosene and fines; thus, the fines would prefer to settle instead of migrating with kerosene (Figure 7.16). In kerosene, the resulting surface charges can contribute to the formation of clusters and cause the fine particles to be bigger, easier to settle, and clog the pore throat. Furthermore, the rate of injection plays a crucial role in the accumulation of fines at the interface. A higher flow rate could result in a higher mobility for fines (Figure 7.16 (b)) so that more fines can accumulate at the interface.

![Figure 7.16](image)

**Figure 7.16** Fines (0.5% kaolinite) with kerosene flow in tubing (ID=1/16 in) while injecting with CO\(_2\) at two different flow rates (P = 10 ± 1 kPa). (a) The CO\(_2\) injection rate is 200 μl/min, (b) the CO\(_2\) injection rate is 500 μl/min.

**Effect of pore-fluid chemistry and fine/pore throat size ratio on fine clogging.** Figure 7.17 shows the distribution maps of critical clogging concentration in both water and brine for different endmember fine particles at various fine/pore throat size ratios.
Figure 7.17 Various endmember fine particles critical clogging concentration distribution maps at different fine/pore throat ratio. (a) Critical fine clogging concentration distribution map at different fine/pore throat ratio for DW flow and CO$_2$ invasion, (b) critical fine clogging concentration distribution map at different fine/pore throat ratio for brine flow and CO$_2$ invasion.

For bentonite and silica, fine clogging was easier in the brine solution (Figure 7.17 (b)) compared with DW (Figure 7.17 (a)). On the other hand, fine clogging was easier in DW for kaolinite and illite because of the unique platy particle fabric. Mica, diatoms, and CaCO$_3$ did not show marked differences in migration and clogging in DW or brine. With a higher LL$_{DW/brine}$ number (bentonite and kaolinite), which represents a greater fluid sensitivity difference between DW and brine, the maps of bentonite and kaolinite showed the largest difference in the fine critical clogging concentration between DW and brine (Figure 7.17). Moreover, the maps indicated a lower critical clogging concentration for all endmember fines under multiphase flow conditions. A comparison of the fine clogging behaviors between a single-phase flow and multiphase flow (Figure 7.17) revealed that gas invasion reduced the critical clogging
concentration for all endmember fines. This finding indicated gas (CO\(_2\)) invasion could increase the fine clogging potential regardless of the fine species.

Figure 7.18 shows the difference in fine clogging behavior between a single-phase flow and multiphase flow. When only the single-fluid phase was present, fines migrated with the flowing fluid (water/brine/oil) unless there was bridging or blocking in the pore (Figure 7.18 (a)). However, with the second non-wetting fluid phase (gas), the clogging potential can be enhanced (Figure 7.18 (b)). This may be attributed to (1) the accumulation of fine particles along the gas-liquid interface, (2) the increase in local fine concentration in pores, and (3) the accumulation and movement of fines due to the gas/liquid meniscus in porous media.

Figure 7.18 Behavior of fine particles migration and clogging in porous media for both single and two fluids system. (a) Single-fluid phase presents, fines migrate with the flowing fluid (water/brine/oil) unless bridging or blocking at pore, (b) Gas invading in the wetting phase (water/brine/oil), fines are constrained to move along the gas-liquid interface. Meniscus gathering fines and pushing the fines ahead until bridging and clogging happen in pores. The residual water/brine/oil increases due to fines clogging compared to fluids flow without fines.

7.4 Conclusions

To evaluate the changes in fine migration and clogging behavior in porous media, 2D micromodel and tubing experiments were conducted with various pure fines, pore fluids, and pore throat sizes. Additionally, tests were run with and without an invading gas phase (CO\(_2\)) to determine the significance of a moving meniscus in fine mobility and clogging. The endmember
fine particles selected for this study included silica silt, mica, CaCO₃, diatoms, kaolinite, illite, and bentonite (primarily made of montmorillonite). The pore fluids included DW, sodium chloride (NaCl) brine (2 M), and kerosene. The 2D microfluidic pore models, used as porous media analogs, were fabricated with various pore throat widths. The results of this study revealed that in addition to the expected dependence of clogging on the particle-to-pore throat size ratio, pore-fluid chemistry is also a significant factor because the interaction between a particular type of fine and the pore fluid can affect its capacity to form clusters and effectively increase its particle “size” relative to the pore throat width. Clogging can easily occur at a higher particle-to-pore throat size ratio and a higher particle concentration. Therefore, pore-fluid chemistry could directly affect the fine’s capacity to grow as a cluster. Fine clogging was easier for a larger cluster of fines in the brine solution, such as bentonite and silica, and it was relatively difficult for a smaller cluster of fines in the brine solution, such as kaolinite and illite. There was no distinct difference in the fine cluster size of mica, diatoms, and CaCO₃ between DW and brine; thus, their clogging potential was similar. The pore fluid kerosene resulted in the fastest settlement time for all endmember fine particles due to the flocculated fabric resulting from the unbalanced charges on the particle surface.

The presence of a moving gas/liquid meniscus increased the clogging potential regardless of the fine type as the advancing meniscus led to the accumulation and concentration of the fines. When gas (CO₂) was injected into fluid-saturated sediments including a small fine fraction, we found that (1) fine particles accumulated along the DW/brine-gas interface, (2) the fine concentration in pores was increased, (3) bridging or clogging occurred in the pore throat, and (4) the gas/liquid meniscus exerted a force on fines and moved the fines, leading to bridging and blocking at the pore.
In summary, the findings of this study demonstrated the need to identify both the type and concentration of fines prior to evaluating whether the clogging potential of a system will increase or decrease following pore fluid exchange and gas invasion.

7.5 References


CHAPTER 8. CONCLUSIONS

This dissertation focuses on uncovering and understanding physical and geomechanical parameters influencing fluids flow behavior in porous media with various related engineering applications, via designed and developed experimental methods to probe the characterization and effect factors of fluids flow behavior changes in porous media. The main findings and their important engineering implications are summarized as below groups.

8.1 Fluids Wetting Properties Influence on Fluids Flow Behavior in Porous Media

The wetting properties of porous media control the distribution of the immiscible fluids. Modifying the wettability of fluid is an efficient method for improving flooding performance in the reservoir. A series of modified fluids (i.e., polymer and biopolymer) flooding tests indicate that increasing the injection fluid velocity, viscosity, contact angle, as well as decreasing fluids interfacial tension (or surface tension) resulting in raising of viscous number (Nm) and capillary number (Nc) can improve the sweep efficiency in porous media. In addition, within the function of effective stress of capillary pressure, estimation of capillary pressure can be achieved with measured interfacial tension and contact angle of fluids at different effective stress levels. The higher capillary pressure can be expected within a reduction in contact angle, an increase in surface tension, a higher density mineral, a rise in the effective stress of sediments, a higher specific surface of mineral, and a higher compressive index material, as well as a lower sediments void ratio. Besides, five different bio-chemical modified fluids (biopolymer solutions) and their wetting properties, including contact angle, surface tension, interfacial tension, and viscosity that influence on capillary pressure, fluids flow, and invaded fluid-oil displacement ratio have been explored. And the engineering behavior and characteristic of these biopolymer solutions have been well recognized in this research. The great ability and effect for improving
soil remediation and enhanced oil recovery by these modified fluids (biopolymers solution) have been approved.

8.2 Pressure and Temperature Effects on Multiphase Flow Behavior in Porous Media

The reservoir physical properties such as temperature, pressure, and pore fluid salinity can directly affect the fluids wetting properties and consequence of fluids flow behavior in porous media. This research intensively chooses the supercritical CO₂ to replace brine resulting in predicting CO₂ displacement efficiency in deep saline aquifers to study the influences for fluids flow behavior in porous media. The high pressure and temperature supercritical CO₂-brine displacement tests combined with the pore network modeling shows the supercritical CO₂-brine displacement ratio increases with the increased CO₂ injection rate. However, a higher reservoir salinity decreases the overall displacement ratio because of altered contact properties and displacement patterns. And the supercritical CO₂-brine displacement ratio increases with the capillary number (Nc). Moreover, the pore network modeling for CO₂-brine displacement study predicts that the capillarity at entry period is relatively lower as a result of both increased contact angle and decreased interfacial tension in high-pressure condition. Besides, the relative permeability of supercritical CO₂ during imbibition is lower than that during drainage, primarily due to the trapping of supercritical CO₂, particularly at narrower pore throats where the snap-off of the non-wetting phase and the shut-off by the wetting phase occur.

8.3 Pore Fluid Related Geomechanical Properties Effects for Fine-Grained Sediments

Regarding fluids flow in porous media, fine-grained materials exist within coarse sediments, as well as forming interbeds between coarse grains layers are significant for reservoir performance with pore fluids flow. Fine-grained sediments play a crucial role while responding with different pore fluids. The responses of fine sediments to pore fluid chemistry are investigated in this
research to provide a particular information on how geomechanical properties of fine materials change in different pore fluids. The findings can be implicated when nature sediments are disturbed by human activities such as pore fluid replacement, depressurization of formation, groundwater production, and gas production. A set of experimental tests is conducted to evaluate the electrical sensitivity, compressibility, and hydraulic conductivity of fine sediments dependence on pore fluid chemistry. The results of these tests show either segregated sedimentation or uniform sedimentation occurs among different pore fluids due to various fabrics of fine particles. It means that the invading pore-fluid replacement changes pore-fluid chemistry thereby alters the fabric of fine sediments. Therefore, the geomechanical properties of fine sediments such as compressibility and hydraulic conductivity can be changed. The specific findings include: (1) a decrease in effective stress can be observed for high electrical sensitivity sediments during the water freshen due to diffusive double layer thickness raising and pore fluid pressure increasing; (2) when water freshen happens in low electrical sensitivity fines, the compressibility of sediments in brine can change toward to a lower compressibility in deionized water so that the raising of effective stress can be observed; (3) the fine sediments contain gravimetrically controlled large particles mixed with electrically controlled small particles can be more compressible in brine than in fresh water; (4) low sensitivity fine materials can maintain fabric and keep similar hydraulic conductivity in fresh water compared within brine, but the overall compressibility would decrease in brine; (5) the relatively high electrical sensitivity sediments can be rearranged in to higher void ratio condition with fresh water that is more susceptible to recompression and reduce the hydraulic conductivity; (6) the non-polar fluid kerosene rarely expresses influences on hydraulic conductivity for non-clay fine materials but indicates the significantly enhanced hydraulic conductivity for clay fine materials.
8.4 Fines Migration/Clogging Mechanism and Influences for Fluids Flow in Porous Media

Fines migration in porous media can cause challenging problems of both scientific and industrial importance. Understanding the impact of fines existing in porous media can help to evaluate the performance of fluids flow behavior in porous media. This research has conducted the 2D micromodel experiments on a selection of pure fines, pore-fluids, and micromodel pore-throat sizes to evaluate fines migration/clogging mechanism and influences for fluids flow in porous media. Results indicate the behaviors of fine particles migration and clogging in porous media are affected by pore throat and fine particle size ratio, fine particle concentration, and flow rate. Clogging can be observed at lower pore throat and fine particle size ratios, higher fine particle concentrations, and relatively higher flow rates. Addition results from this research show the expected dependence of fine clogging on pore fluid chemistry. It presents pore fluid chemistry directly influences the capacity of fine particle to grow as the cluster. Fines clogging is easier occurs for the larger cluster of fines and relatively harder to happen for the smaller cluster of fine. Bentonite, silica, kaolinite, and illite express cluster size change in between deionized water and brine. But there is no intensive cluster size change for mica, diatom, and CaCO$_3$ between DW and brine. The non-polar pore fluid kerosene provides the highest ability and the fast settlement time to all tested fine particles. On the other hand, findings present that clogging in multiphase flow can be more expected and more readily occur than in single phase fluid flow. Also, the presence of a moving gas/liquid meniscus increases the clogging potential regardless of fine type. When gas is injected into initially fluid-saturated sediments including a small fraction of fines: (1) fine particles can accumulate along the water-gas interface; (2) the fine concentration in pores can be increased; (3) bridging or clogging in pore throat occurs at pore throat; (4) the gas/liquid meniscus gathers fines and pushes the fines ahead until bridging and
blocking happen at pore. In summary, results emphasize the need to identify both the type and concentration of fines prior to evaluating whether a system’s clogging potential will increase or decrease during pore fluids changes.
APPENDIX: PERMISSIONS

The permission of reprinting or reusing Chapter 3 in this dissertation has been requested through Sustainability. The details are as below

Dear Sustainability Editor,

This is Shuang Cao. I published a paper in Sustainability in 2016.

May I ask to obtain the written permission from Sustainability to use it in my Ph.D. dissertation? Could you please send me the written permission and/or proof of authorship? I need to attach the permission letter in my dissertation. Let me know if you require more information to offer this kind of permission. Thank you.

Please see the detailed information about published paper and my Ph.D. dissertation:

This paper will be reprinted in my Ph.D. dissertation and my dissertation will be viewable on the web.
Dissertation name: Microfluidic pore model study on physical and geomechanical factors influencing fluid flow behavior in porous media.

Best Regard,

Cindy Shuang Cao
Research Assistant
Department of Civil and Environmental Engineering
3277 Patrick F. Taylor Hall
Louisiana State University
Baton Rouge, LA, 70803

Dear Dr. Cao,

Thank you very much for your inquiry. You could use it in your Ph.D. dissertation, just need to cite the published paper as a reference in your Ph.D. dissertation. /Sustainability/ is an open access journal, the copyright belongs to the authors. You do not need to ask for our permission.

Have a nice day,

Best regards,
Leanne Fan
Senior Assistant Editor
The permission of reprinting or reusing Chapter 4 in this dissertation has been requested through Copyright Clearance Center’s Rights Link service. The details are as below.

**ELSEVIER LICENSE TERMS AND CONDITIONS**

Jan 09, 2018

This Agreement between Shuang Cao (“You”) and Elsevier (“Elsevier”) consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

<table>
<thead>
<tr>
<th>License Number</th>
<th>4175071441128</th>
</tr>
</thead>
<tbody>
<tr>
<td>License date</td>
<td>Aug 23, 2017</td>
</tr>
<tr>
<td>Licensed Content Publisher</td>
<td>Elsevier</td>
</tr>
<tr>
<td>Licensed Content Publication</td>
<td>International Journal of Greenhouse Gas Control</td>
</tr>
<tr>
<td>Licensed Content Title</td>
<td>Supercritical CO2 and brine displacement in geological carbon sequestration: Micromodel and pore network simulation studies</td>
</tr>
<tr>
<td>Licensed Content Author</td>
<td>Shuang Cindy Cao, Sheng Dai, Jongwon Jung</td>
</tr>
<tr>
<td>Licensed Content Date</td>
<td>Jan 1, 2016</td>
</tr>
<tr>
<td>Licensed Content Volume</td>
<td>44</td>
</tr>
<tr>
<td>Licensed Content Issue</td>
<td>n/a</td>
</tr>
<tr>
<td>Licensed Content Pages</td>
<td>11</td>
</tr>
<tr>
<td>Start Page</td>
<td>104</td>
</tr>
<tr>
<td>End Page</td>
<td>114</td>
</tr>
<tr>
<td>Type of Use</td>
<td>reuse in a thesis/dissertation</td>
</tr>
<tr>
<td>Portion</td>
<td>full article</td>
</tr>
<tr>
<td>Format</td>
<td>electronic</td>
</tr>
<tr>
<td>Are you the author of this Elsevier article?</td>
<td>Yes</td>
</tr>
<tr>
<td>Will you be translating?</td>
<td>No</td>
</tr>
<tr>
<td>Title of your thesis/dissertation</td>
<td>MICROFLUIDIC PORE MODEL STUDY ON PHYSICAL AND GEOMECHANICAL FACTORS INFLUENCING FLUID FLOW BEHAVIOR IN POROUS MEDIA</td>
</tr>
<tr>
<td>Expected completion date</td>
<td>Dec 2017</td>
</tr>
<tr>
<td>Estimated size (number of pages)</td>
<td>200</td>
</tr>
<tr>
<td>Requestor Location</td>
<td>Shuang Cao</td>
</tr>
<tr>
<td></td>
<td>Dept. of Civil &amp; Environment Eng.</td>
</tr>
<tr>
<td></td>
<td>Louisiana State University</td>
</tr>
<tr>
<td></td>
<td>BATON ROUGE, LA 70803</td>
</tr>
<tr>
<td></td>
<td>United States</td>
</tr>
<tr>
<td></td>
<td>Attn: Shuang Cao</td>
</tr>
<tr>
<td>Publisher Tax ID</td>
<td>98-0397604</td>
</tr>
<tr>
<td>Total</td>
<td>0.00 USD</td>
</tr>
</tbody>
</table>
VITA

Shuang (Cindy) Cao was born in Lenghu, Qinghai, China on July 10, 1988. In September 2006, she enrolled in China University of Petroleum, in Beijing, China; in August 2009, she enrolled in University of Alaska Fairbanks, in Fairbanks, Alaska. In May 2011, she received her Bachelor of Science degree in Geological Engineering from both China University of Petroleum and University of Alaska Fairbanks. In the fall of 2011, she enrolled in the University of Mississippi, in Oxford, Mississippi, and received her Master of Science in Geological Engineering in December of 2013.

Shuang (Cindy) Cao joined the Department of Civil and Environmental Engineering (in the Ph.D. program of Civil Engineering) at Louisiana State University in August 2013 as a Graduate Research Assistant. Financially supported by the LSU Civil and Environmental Engineering Department. Ms. Cao expects to finish all study and work, and receive the degree of Doctor of Philosophy in Civil Engineering in spring 2018.