Microfluidic and micro-core methods for enhanced oil recovery and carbon storage applications

by

Phong Nguyen

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Abstract

Injection of CO$_2$ into the subsurface, for both storage and oil recovery, is an emerging strategy to mitigate atmospheric CO$_2$ emissions and associated climate change. In this thesis microfluidic and micro-core methods were developed to inform combined CO$_2$-storage and oil recovery operations and determine relevant fluid properties.

Pore scale studies of nanoparticle stabilized CO$_2$-in-water foam and its application in oil recovery to show significant improvement in oil recovery rate with different oils from around the world (light, medium, and heavy). The CO$_2$ nanoparticle-stabilized CO$_2$ foams generate a three-fold increase in oil recovery (an additional 15% of initial oil in place) as compared to an otherwise similar CO$_2$ gas flood. Nanoparticle-stabilized CO$_2$ foam flooding also results in significantly smaller oil-in-water emulsion sizes. All three oils show substantial additional oil recovery and a positive reservoir homogenization effect.

A supporting microfluidic approach is developed to quantify the minimum miscibility pressure (MMP) – a critical parameter for combined CO$_2$ storage and enhanced oil recovery. The method leverages the inherent fluorescence of crude oils, is faster than conventional
technologies, and provides quantitative, operator-independent measurements. In terms of speed, a pressure scan for a single minimum miscibility pressure measurement required less than 30 min, in stark contrast to days or weeks with existing rising bubble and slimtube methods.

In practice, subsurface geology also interacts with injected CO₂. Commonly carbonate dissolution results in pore structure, porosity, and permeability changes. These changes are measured by x-ray microtomography (micro-CT), liquid permeability measurements, and chemical analysis. Chemical composition of the produced liquid analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES) shows concentrations of magnesium and calcium. This work leverages established advantages of microfluidics in the new context of core-sample analysis, providing a simple core sealing method, small sample size, small volumes of injection fluids, fast characterization times, and pore scale resolution.

Lastly, a microfluidic approach is developed to analyze the complex, multiphase fluid interactions in CO₂ enhanced oil recovery at relevant reservoir temperature and pressure. Fluorescence imaging is applied to visualize and measure the effect of CO₂ pressure on contact angles changes at the pore scale.
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1 Thesis Overview

1.1 Research motivation

Global CO₂ emission has continued to increase from rising fossil fuel consumptions worldwide. The projected fossil fuel consumption for next 50 year will continue to increase. The CO₂ emission rate is 32 Giga tonnes in 2011 and projected to be doubled by 2050.¹,² CO₂ enhanced oil recovery (EOR) and sequestrations are currently the most technically feasible methods to reduce the CO₂ emission on large scale. Saline aquifers and oil reservoirs have storage capacity of 25,000 Giga tonnes of CO₂.³,⁴

CO₂ EOR often has low recovery rates due to viscous fingering and gravity override as a result of low viscosity and density of CO₂ compared to oil. CO₂ foam is used to increase the apparent viscosity of gas injection and improve the sweep efficiency of the CO₂ injection process which results in higher recovery efficiency.

Nanoparticle stabilized foam has much higher stability than surfactant foam. Stabilizing CO₂ foams using nanoparticles is a classical approach, termed a Pickering emulsion.⁵–¹⁰ Nanoparticle stabilized CO₂ foams have recently shown potential for application to enhanced oil recovery applications.¹¹–¹³ These studies have shown nanoparticles foams are significantly more stable than surfactant foam due to the high adsorption energy of the nanoparticles at the gas-liquid interface. The second approach is the used of miscible CO₂ displacement where CO₂ is injected at pressure above minimum miscibility pressure (MMP) pressure.

Reservoir scale processes are affected by pore scale transport. In which microfluidic is great method for studying oil recovery at pore scale. Microfluidic method is very capable of studying pore scale mechanisms of oil recovery including oil recovery studies using micromodels and fluid properties in micro-channels.

Micro-core method was developed to study CO₂-brine-rock interactions at pore scale and changes in rock porosity and permeability.
1.2 Thesis organization

The application of microfluidic and micro-core method was used to study oil recovery using CO₂, foam and CO₂ injections measuring CO₂ and oil MMP. The thesis is organized into chapters with Chapter 1 presents a thesis motivation and overview, Chapter 2 is a review of backgrounds for research topics studied, Chapters 3-5 are based on published journal papers of the various microscale methods developed in this work, Chapter 6 work in progress, Chapter 7 conclusions. The brief highlights of these chapters are listed below:

Chapter 2 provides the introduction for the thesis which include the backgrounds on EOR, energy consumptions, CO₂ emissions and the need for CO₂ EOR and sequestrations. It explains the role of microfluidic technology in oil and gas applications. It also provides the needs for using nanoparticles foams to improve oil recovery.

Chapter 3 presents the assessment of nanoparticle foam using microfluidic method to improve oil recovery for three different type of crude oil ranging from light, medium, to heavy. This paper was published in Energy & Fuels.

Chapter 4 presents the development of a high pressure microfluidic system to measure CO₂ and oil MMP. This represents a much faster method than conventional RBA MMP measurements. This work was published in Analytical Chemistry.

Chapter 5 presents the development of a micro-core method to study rock structure changes at pore scale due to CO₂ injection in saline aquifers. This work was published in Journal of Fluids Engineering.

Chapter 6 is work in progress of using multiphase fluorescence imaging to study effect of CO₂ pressures on contact angle at pore scale.

Chapter 7 provides the conclusion and future work.
2 Introduction

2.1 Enhanced oil recovery (EOR)

Canada is the world leader in CO₂ EOR, with a long history of injection of CO₂ into the Weyburn field in Saskatchewan, this is the largest CO₂ project in the world with the production of 200 million barrels of oil produced and (2.4 MMt per year of CO₂ injected, total of 13 MMt to date), this is equivalent to sequestering the emissions from 500,000 cars per year, followed by the (higher profile) Sliepner project in the North Sea that has been in operation since 1996 (~ 1 MMt tons of CO₂ per year). Historically, the CO₂ was sourced and purchased from coal gasification plants in North Dakota. In many fields CO₂ is so useful that a common refrain among EOR oil representatives is “we agree there is a CO₂ problem, we can’t get enough of it”.¹⁴

From an environmental perspective CO₂-EOR has mixed appeal, particularly, since it is ultimately a hydrocarbon recovery mechanism. This superficial view, however, is not entirely accurate or fair, because: (i) CO₂ EOR is the only currently economic use for large quantities of CO₂ that would otherwise be vented (i.e. EOR is the only buyer), (ii) the reservoirs take up a great deal of CO₂ that is effectively stored (e.g. 1 ton of CO₂ injected for every 2.5 barrels of oil recovered). (iii) CO₂ that does come back to surface with produced oil is separated, and as a commodity, readily re-used by the oil industry (re-injected) (iv) CO₂ EOR projects are financing large CO₂ capture efforts and corresponding networks of high pressure CO₂ pipelines which would not be affordable otherwise. These pipelines could be employed later for any number of CO₂ downstream uses.

Oil recovery consists of primary, secondary and tertiary recovery or enhanced oil recovery (EOR). Primary recovery is using the reservoirs original pressures to recover ~ 10% of original oil in place (OOIP), follows by secondary recovery with water flooding which recovers another ~ 30%. The remaining oil can be recovered by EOR methods such as gas injection with CO₂, chemical flood, steam flood, surfactant flood (schematic of these methods).¹⁵ The challenges of CO₂ EOR is viscous fingering and gravity override can be reduced with the use of nanoparticle stabilized CO₂ in water foam as shown in Figure 2-1.
In this work, both CO$_2$ EOR and CO$_2$ sequestration are investigated.

**Figure 2-1 CO$_2$ EOR recovery gas fingering mobility challenge and nanoparticle foam mobility control method**
2.2 Nanoparticle stabilized CO\textsubscript{2} in water foam for mobility control in enhanced oil recovery

A review of surfactant stabilized foam and nanoparticle stabilized foam including foam generation mechanisms and foam stability mechanisms are provided in this section. Surfactant foams are generated by mixing aqueous surfactant solutions with gas phase or by injecting a surfactant or nanoparticle solution through a porous media at high flow rate. Nanoparticle foam can be generated in a similar way with high shear forces required. Nanoparticles stabilized foam and emulsions have been studied extensively. Originally, in 1907 Pickering, studied particles stabilized emulsions, hence Pickering emulsions.\textsuperscript{5} The remarkable stability of Pickering foam and emulsions have motivated many studies and research for applications in food and pharmaceutical by Binks,\textsuperscript{6,9,10,16–19} and others for fundamental foam stabilization method.\textsuperscript{8,20–25} Recently nanoparticles stabilized foam and emulsions have been used for EOR applications as its stability is much higher than surfactant foam.\textsuperscript{11,12,23,25–31}

\begin{itemize}
  \item[a)] Silica nanoparticle coating
  \begin{center}
  \includegraphics[width=\textwidth]{silica_nano_coating.png}
  \end{center}

  \item[b)] Nanoparticle stabilized foam
  \begin{center}
  \includegraphics[width=\textwidth]{nano_stabilized foam.png}
  \end{center}
\end{itemize}
Figure 2-2 a) Silica nanoparticle coating with dichlorodimethylsilane (DCDMS) b) Nanoparticle stabilized CO₂ in water foam structures.

It has been found that the contact angles of nanoparticles at the water and gas interface is critical for determining the foam stability and the contact angles depend on the nanoparticle coating.⁷,⁹,¹⁶ Coating particle with a hydrophobic chemical compound such as dichlorodimethylsilane (DCDMS) change its surface properties from hydrophilic to hydrophobic as shown in Figure 2-2. The intermediate surface coating coverage with remaining SiOH between 32% to 62% produces the best foam results with denser foam characteristics for higher surface coverage.¹⁰–¹²,¹⁸,¹⁹,²⁶–²⁸,³ⁱ–³³ The high adsorption energy of particles to the CO₂-water interfaces makes the process irreversible and hence the particle stabilized bubbles structures.¹¹,¹²,²⁶,³⁴–³⁶ Foam textures with different coating coverage are shown in Figure 2-3.
Figure 2-3 Nanoparticle coating surface coverage effects on foam generation and nanoparticle surface adsorption energy. a) foam formation as a function of surface coating with the first two vials with SiOH ≤ 20% produced no foam and stay in powder form, the intermediate surface coating (32% ≤ SiOH ≤ 62%) produced foam, for SiOH ≥ 66% particles remained in dispersed solution phase and does not form foam; b) water in air power made with silica nanoparticles with 20% SiOH surface particles; thick foam made from nanoparticles with 32% SiOH particles. Reproduced with permission from Nature,\textsuperscript{18} copyright 2006.
Foam EOR as mobility control method of gas injection to increase oil recovery rate has been extensively studied at both lab scale and pilot tests. Mobility control is required in gas injection to increase sweep efficiency, as low sweep efficiency leads to early breakthrough and low recovery rates.

Foam flooding is an effective EOR method to control the mobility of the injected gas in porous media. Foam flows through porous media as bubble trains of gas in liquid phases which provide higher resistance to flow than the gas phase viscosity. The mobility reduction strongly depends on foam texture. The apparent viscosity of foam and mobility reduction factor are given below:

\[ \mu_{\text{app}} = \frac{kA\Delta P}{QL} \]  

Where \( k \) is permeability of the core in Darcy, \( A \) is cross sectional area of the core in cm\(^2\), \( Q \) is flow rate in cm\(^3\)/s, \( L \) is core length in cm, \( \Delta P \) is pressure drop across the core in atm. \(^{12}\)

Core mobility reduction factor (MRF) is the ratio of the apparent viscosity of the foam at a given total flow rate to the apparent viscosity of the baseline case at the same total flow rate:

\[ \text{MRF} = \frac{\mu_{\text{app, foam}}}{\mu_{\text{app, baseline}}} \]  

2.3 Carbon Sequestration

2.3.1 CO\(_2\) storage mechanisms and global capacity

Carbon sequestration involves injecting CO\(_2\) into geological formations including saline aquifers, oil reservoirs and coal bed methane. The total amount of CO\(_2\) stored in these formations is very large with a capacity for 25,000 gigatonnes of storage (Figure 2-4). \(^{14,52–54}\)

Geological storage of CO\(_2\) consists of injecting supercritical CO\(_2\) into carbonate or sandstone formations in oil and gas reservoirs or saline aquifers. The storage reservoir must have the following characteristics: capacity to accept the intended volume of CO\(_2\), injectivity to take in
the CO₂ at the intended injection rates, confinement to prevent leakage of the buoyant and mobile CO₂ to shallow subsurface or surface. Four mechanisms of CO₂ trapping in reservoirs have been identified as structural and hydrodynamic trapping as shown in Figure 2-5: buoyancy trapping within the anticline, fold, fault block, and below the cap rock; residual trapping: residual CO₂ saturation in the pore space which makes the CO₂ immobile because of interfacial tension between CO₂ and formation water; dissolution trapping: CO₂ migrates through the reservoir beneath the seal and eventually dissolves in formation brine; iv) mineral trapping: dissolved CO₂ reacts with reservoir rocks to form new minerals. Structural and residual trapping mechanisms are dominant at the early phase of CO₂ migration in the reservoir and solubility and mineral trapping are more dominant at the later phase.

Particularly with the recent Boundary Dam project in Saskatchewan, Canada has become a leader in carbon sequestration development. This project sequesters 1 million tonnes of CO₂ per year (equivalent to emissions from ~ 200,000 cars) from a ~ 4,000 MW coal power station. In general the challenges with CO₂ sequestration in saline aquifers are multifold including high costs, lack of pipeline infrastructure. The CO₂ EOR will provide the economic benefits for building the CO₂ economy.
Figure 2-4 a) CO$_2$ storage in geological formations b) Global capacity for CO$_2$ storage, blue bars represent minimum estimate and red bars represent maximum estimate. Reproduced with permission from Annual Review of Environment and Resources, copyright 2014.
2.3.2 CO₂ chemistry at reservoir conditions

CO₂ reaches critical temperature and pressure at 31.1°C and 7.38 MPa respectively. CO₂ reaches supercritical state at temperatures and pressures above the critical point. In supercritical state, CO₂ behaves still like a gas by filling all the available volume, but has a liquid-like density that ranges from 200 to 900 kg/m³. The higher the density of CO₂ the more efficiently the pore space can be used to store CO₂. Higher density also decreases the upward movement of CO₂ due to lower buoyancy forces. In general, a depth of about 800m is necessary for achieving supercritical CO₂ state. Figure 2-5(b) shows the variation of CO₂ density changes with temperature and pressure.
density with pressures at various temperatures with increasing density with higher pressures, and lower density with higher temperatures. The solubility of CO₂ in water and brine increases with pressure and temperature and decreases with brine salinity.⁵⁵ In general, CO₂ solubility increases from 1% at 1MPa to ~7% at 30 MPa for a reservoir temperature of 50 °C.

2.4 Microfluidic and micromodel methods to study EOR and carbon sequestration

The application of microfluidic technology to oil and gas research is gaining traction in many areas of oil gas recovery and fluid properties analysis. The applicability of microfluidics to study reservoir processes are illustrated in Figure 2-7. Some recent publications include CO₂ and toluene diffusivity in bitumen measurements,⁵⁶,⁵⁷ phase diagram measurements of gas liquid systems,⁵⁸ CO₂ and oil minimum miscibility pressure measurements.⁵⁹ Microfluidics have been used extensively in other fields of research including chemistry for chemical synthesis in micro-reactor,⁴⁵,⁶⁰–⁶⁹ biology and medicine for disease screening and cell studies.⁷⁰,⁷¹

Micromodels have been a long-established method in geological sciences and reservoir engineering,⁷² that are finding renewed interest and applications with microfluidic technology and modern high-resolution microscopy imaging methods. Recent advances in chip fabrication techniques including silicon/glass chips, glass/glass chips, and improved imaging methods including high resolution microscopy, fluorescence imaging, confocal imaging methods, and nanoparticle tracking PIV allow for advanced studies of EOR technique at pore scale level.²⁹,⁷³,⁷⁴

Micromodels are 2D pore network representation of the reservoir rock structures etched onto a substrate of glass, silicon, and polymer with the top surface sealed with a blank substrate. Methods of making the pore network photomask pattern include round posts, Delaunay triangles, and SEM images from actual rock core samples.²⁹,⁷³,⁷⁵–⁸¹ Illustrations of micromodel development techniques are summarized in Figure 2-6.
Figure 2-6 a) Glass chip with round post patterns.\textsuperscript{29} b) rock on chip made form rock imaging with FIB-SEM. Reproduced with permission from Royal Society of Chemistry,\textsuperscript{82} copyright 2011. c) Micromodel development using SEM image pattern from sandstone. Reproduced with permission from Springer,\textsuperscript{78} copyright 2012.
Figure 2-7 Application of microfluidic methods to study pore scale transport in oil reservoirs and fluid properties analysis. Reproduced with permission from Royal Society of Chemistry,\textsuperscript{83} copyright 2014.

Micromodels used in EOR and carbon sequestrations include reservoir on chips studies of oil displacement by non-wetting fluids,\textsuperscript{81} visualization of salt precipitation dynamics during \( \text{CO}_2 \) injection.\textsuperscript{84}
Like all methods, micromodels have advantages and disadvantages. The most important advantages are (i) real-time dynamics, pore-scale resolution, fluorescence capability, data gathered in the two-dimensional format is straightforward to image, analyze, and plot. The key disadvantages are not 3D, not the real material/geology, small scale compare to large reservoir scale. A notable exception to the material/geology point is a recent study in our group, chip-off-the-old-rock whereby the dissolution of carbonate limestone was observed using a calcite microfluidic chip.85

2.5 Micro core method to study EOR

An alternative to micromodel testing is core-based testing. ‘Micro’ cores are considered to be core studies. Due to the opacity of rock, Micro Computed Tomograph (Micro-CT) must be employed to resolve the fluid motion within the rock.86–94 Figure 2-8 shows the Micro-CT core holder method developed in this work and other groups. Micro-CT have been widely used in other field of research including materials engineering and fuel cells to medical diagnostics.95–99 Typically lab scale core flood studies use reservoir rock cores (diameters in 10 cm and lengths ~ 1 m long) and core plugs (diameter ~ few centimeters and length ~ 10 cm).46,100–103

Most core studies only monitor injection parameters and oil recovery without direct visualization. Visualization of core studies have been performed using medical Computed Tomography Scan (CT scan) where course scale oil recovery fluid visualization can be observed with resolution in the range of millimeters.87,104–107 By using smaller core in this study, Micro-CT was able to provide pore scale resolution of rock carbonate core samples. In this thesis, micro-core methods are applied in Chapter 5 to better understand the carbon sequestration process in carbonates. Notably, the micro-core method enables the study of changes in the carbonate core structures (pore sizes, flow routes) due to CO2 injection not possible with microfluidic or micromodel methods.

Like all methods, micro-core visualization has advantages and disadvantages. The most important advantages are that (i) the real material is used (not a silicon or glass chip) and (ii) the full three-dimensional nature of the real sample is represented (unlike two-dimensional micromodels). The disadvantages are requiring more complex imaging technique using Micro-
CT scanning, which has lower temporal resolution and spatial resolution than optical microscopes, size of the core limits the degree of heterogeneity that can be include ultimately reservoirs are heterogeneous over length scales much larger than cores.)
Figure 2-8 a) High pressure, high temperature micro-core holder developed in this work\textsuperscript{108} with Swagelok connection ports for confining pressure injection and fluids injections b) High P and T Micro-CT core holder for in-situ measurement of fluid rock interactions. Reproduced with permission from American Geophysical Union,\textsuperscript{91} copyright 2011.

2.6 Summary

This chapter provides an overview of the topics covered in this thesis with the main theme on the development and application of microfluidic and micro-core methods to study pore scale processes in enhanced oil recovery and carbon sequestration. High temperature, high pressure, and chemical resistant microfluidic chips such glass or silicon are very suitable for oil recovery method evaluation with the injection of different chemicals including water flooding, gas flooding, steam flooding, and other chemical flooding. Besides micromodel of pore network pattern chips, microchannels type chips which have been commonly used in other fields of research are also gaining more acceptance in oil and gas applications. In addition to chip based methods, core based method allows for investigation of pore structure changes in conjunction with Micro-CT. Nanoparticle foam based on Pickering emulsion can stabilize foams and improve sweep efficiency of gas injection.
3 Pore-scale Assessment of Nanoparticle Stabilized CO₂ Foam for Enhanced Oil Recovery

In this thesis, we evaluate nanoparticle-stabilized CO₂ foam stability and effectiveness in enhanced oil recovery at the pore scale and the micromodel scale. The nanoparticle stabilized CO₂ gas-in-brine foams maintain excellent stability within micro-confined media, and continue to be stable after 10 days as compared to less than one day for surfactant foam. The CO₂ nanoparticle-stabilized CO₂ foams are shown to generate a three-fold increase in oil recovery (an additional 15% of initial oil in place) as compared to an otherwise similar CO₂ gas flood. Fluorescence imaging is applied to quantify emulsion size distribution (down to 1µm) in both CO₂ and nanoparticle-stabilized CO₂ foam flood cases. Nanoparticle-stabilized CO₂ foam flooding results in significantly smaller oil-in-water emulsion sizes with an average size of 1.7 µm (~ 80 % smaller than a CO₂ gas flood), with negligible impact on water-in-oil emulsions. The effectiveness of nanoparticle-stabilized CO₂ foam is compared for representative light, medium and heavy oils. All three oils show substantial additional oil recovery and a potentially valuable reservoir-homogenization effect. Collectively, these results highlight the pore-scale dynamics, effectiveness and potential for nanoparticle stabilized foams in enhanced oil recovery.


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3.1 Introduction

Carbon dioxide flooding is a common method of Enhanced Oil Recovery (EOR). The carbon dioxide phase can be either miscible or immiscible with the oil phase, depending on reservoir depth and type of oil. Miscible CO₂ flooding is preferred and generally possible for light oil (API > 30), with viscosity less than 10 cP, and at reservoir depths deeper than 3000 ft. The depth must be sufficient such that the reservoir pressure surpasses the Minimum Miscibility Pressure (MMP) for the CO₂ and oil in question. There has been additional
interest in using CO₂ for heavier oil recovery where miscible operation is not possible (e.g. a shallow thin pay zone heavy oil reservoirs that are not economical for thermal operations). The primary mechanisms in immiscible CO₂ injection process in heavy oil are viscosity reduction and oil swelling. A challenge in this approach is the extreme viscosity contrast between heavy oil and the CO₂ (e.g. 200:1 light oil, 4000:1 medium heavy oil, 20,000:1 heavy oil) which causes viscous fingering of the CO₂ within the oil, poor conformance, and poor sweep efficiency. Sweep efficiency can be improved by viscosity reduction of the oil phase or viscosity enhancement of the CO₂ phase. Approaches to increase the viscosity (or effective viscosity) of the CO₂ phase include addition of polymer thickeners, and foaming the CO₂. Polymer thickeners are often prohibitively expensive, however, and current surfactant foams suffer from coalescence and destabilization when in contact with oil.

Stabilizing CO₂ foams using nanoparticles is a classical approach, termed a Pickering emulsion. Nanoparticle stabilized CO₂ foams have recently shown potential for application to enhanced oil recovery applications. These studies have shown nanoparticles foams are significantly more stable than surfactant foam due to the high adsorption energy of the nanoparticles at the gas-liquid interface. Furthermore, Worthen et. al. demonstrated nanoparticle foams stabilized with methyl-coated silica nanoparticles to be significantly more stable than those with Polyethylene Glycol (PEG) coated silica nanoparticles. In addition to stabilization benefits, the strong attraction between nanoparticles and the gas-liquid interface is thought to minimize nanoparticle loss to the rock surface, and solid silica nanoparticles are expected to endure the high temperature reservoir conditions better than surfactants.

The current methods applied to assessing CO₂ foams for EOR include bulk foam stability analysis and the generation of foam in a core and analysis in a downstream visualization cell. The simplest approach for initial screening of surfactants is to produce foam in a vial and monitor the total foam height over time. Selected surfactants can then be applied to a core test where foam is generated by co-injecting surfactants and CO₂ into a porous core sample to create the foam, and transferred to a downstream visualization cell where foam stability is again measured as changes in height over time. These methods report characteristics of bulk foams which can be very different from those of micro-confined foam. Recently, a microscope
cell made up of two plates spaced at 25 µm, was employed to better visualize CO₂ foam upon exiting a core sample. These recent studies have demonstrated the potential of coated nanoparticle CO₂ foams, and their characterization at the core scale and stability in one-dimension of micro-confinements.

Micromodels providing two-dimensional micro-confinements have long been applied to study pore-scale EOR processes, the most relevant examples include CO₂ gas injection at high pressure (600 psi) and supercritical CO₂ injection, gas CO₂ surfactant foam injection, and air surfactant foam injection at low pressure. In general, low pressure foam micromodel tests show the effect of foam as a physical structure within the porous media. To additionally include representative chemical interactions with the oil phase requires all phases to be at reservoir pressure. Other recent examples of related micromodel and microfluidic approaches include: CO₂ diffusion in oil and brine, an oil reservoir-on-a-chip, phase diagrams of gas-liquid systems, coalescence kinetics of water in oil emulsions, determination of asphaltene content in crude oil, carboxylic acid content in heavy oil, and recently a method for steam-on-a-chip quantify the effect of alkaline additives in bitumen recovery via steam assisted gravity drainage (SAGD). In addition, Ma et.al. used a micromodel model to investigate the sweep efficiency of surfactant CO₂ foam in heterogeneous network without oil at ambient conditions. Sun et.al. studied the influence of supplementing a surfactant N₂ foam with nanoparticles showing a significant improvement in stability and temperature tolerance. Collectively these studies demonstrate the relevance and potential for microfluidic/micromodel-based investigations of CO₂ foams for subsurface applications.

In this thesis, we employ a micromodel approach to quantify nanoparticle CO₂ foam stability and EOR efficiency. Foam stability within the pore space is evaluated for the cases of surfactant foam and nanoparticle-stabilized foam using gas CO₂ phase. With oil-loaded micromodels, the sweep efficiency for a direct CO₂ flood is compared to that of a nanoparticle-CO₂ flood (both following a standard water flood). The nanoparticle-stabilized CO₂ foam strategy is then applied to oil recovery tests with light, medium and heavy oil. Pore-scale imaging of the flooding process reveals the mechanisms of gas fingering versus foam sweep efficiency that contribute to the overall residual oil distribution and oil recovery results.
addition to pore-scale imaging, fluorescence imaging is applied to quantify emulsion size distribution (down to 1µm) in both CO2 and nanoparticle-CO2 cases.

3.2 Experimental Section

3.2.1 Experimental Setup

The experimental setup is shown in Figure 3-1. The central part of this setup is the micromodel chip fabricated from glass. The micromodel consists of microfluidic channels and a pore network of circular posts with sizes representative of reservoir sandstone grains of 200 µm and 280 µm and depth of 70 µm. These posts are arranged to create pores (~120 µm to 200 µm in diameter) and pore throats (~70 µm diameter). The total chip dimension is 50 mm × 100 mm with a microfluidic network region of 13 mm × 60 mm. The chip was fabricated from borosilicate glass using lithography technique in which a chrome masked substrate was wet etched by HF to generate the microfluidic network. Then, the etched glass substrate was bonded to a blank cover glass plate by bringing them into contact, and heating to 350 °C for two hours, and then 650 °C for 4 hours. The oven was at atmospheric pressure, and no external pressure was applied to bond the assembly (i.e. gravity only).74 The inverted microscope (Olympus, Model CKX41) was used to image the changes in foam size over time.

An inverted fluorescent microscope (Leica, Model DMI-3000) was used for imaging emulsion and oil/foam partition in the network. A digital camera (Nikon, Model D60) equipped with (Micro Nikkor 105 mm) lens was used for imaging the flooding processes and then the captured images were processed using ImageJ software to assess the oil recovery. Research grade carbon dioxide (99.9% purity, Praxair) is supplied from the high pressure tank fitted with regulator and the flow rate is controlled by the micro-valve flow meter (Upchurch, Model P470). For water flooding, brine was injected with a syringe pump (Harvard Apparatus, Model 704500). Nanoparticle foam was formed externally by shearing the nanoparticle solution through a micro-needle (Gauge 30). This was performed in a glass tube filled with continuous flowing CO2 gas at 20 psi to ensure the water phase was saturated with CO2 and minimize the effect of gas dissolution from the foam phase into the liquid phase. The tube has two openings, one for CO2 injection and one for the syringe needle that provides the high shear via in-out cycling. Once the vial is full, the foam is then injected to the chip with a syringe pump (Harvard Apparatus, Model 704500).
3.2.2 Materials and Procedure

Several commercially available coated silica nanoparticles were employed in initial testing. Bare silica with 7 nm diameter was obtained from Sigma Aldrich. Methyl coated silica nanoparticle (12 nm) was obtained from Wacker Chemie with two different coatings of 50% (HDK H20) and 75% (HDK H18) dichlorodimethyl silane coverage. The silane surface coverage calculation is based on the percentage of conversion of silanol group (Si-OH) to methyl silyl group (Si-CH₃) as per manufacturer’s specification. These particles were employed directly as purchased, without further surface modification. The surface properties of such particles have been characterized extensively elsewhere.\textsuperscript{8,18} Nanoparticle solutions were prepared by initially dispersing the nanoparticles in ethanol and sonicating for 1 hour followed by centrifugation to remove the ethanol.\textsuperscript{11} The collected nanoparticles were then re-dispersed by sonication for 2 hours in de-ionized (DI) water to make a 1% w/v solution.
Figure 3-1 Experimental setup for nanoparticle stabilized CO₂ foam injection (and pure CO₂ injection) into the micromodel. After initial water injection (water flood), CO₂ foam (or pure CO₂) is injected into the microfluidic network as shown.

The micromodel surfaces were borosilicate glass (Schott Borofloat 33) throughout, as fabricated, and were natively water-wet (contact angle ~ 30°). The cleaning procedure ensured a similar water-wet surface condition at the start of each experimental run. Before each test, the chip is cleaned with toluene to remove all residual oil, followed by purging with IPA, then DI water to remove all traces of toluene and IPA. Once clean, the chip was vacuum injected with brine solution of 1% w/v NaCl to simulate connate water. Oil was injected into the brine filled chip to achieve a reservoir-relevant velocity of 1 m/day (11.6 µm/s) in the pores. Three different crude oils were employed: light oil (37 API), medium oil (24 API), and heavy oil (14 API). The oil recovery experiment began with water flooding where the brine was injected at reservoir pore velocity to displace the oil. For pure CO₂ enhanced oil recovery, CO₂ gas was injected following the water flood. For nanoparticle stabilized CO₂ foam enhanced oil recovery, nanoparticle stabilized CO₂ in water foam was injected following the water flood. The evolution of each flooding process was imaged with the camera every 30 seconds. Pore-scale measurements of foam and emulsion sizes were imaged via the inverted fluorescence microscope. All experiments were performed at ~ 22 °C.

3.3 Results and Discussion

3.3.1 Effect of Nanoparticle Coating

Nanoparticle surface properties are critical to foam function, and generally a balance between hydrophilic behavior and hydrophobic behavior is desired (that is, nanoparticles sufficiently hydrophilic to disperse in water, and sufficiently hydrophobic to accumulate at the interfaces). Here, three coating conditions for silica nanoparticles were tested: uncoated (0%); 50% methylsilyl; and 75% methylsilyl. The uncoated nanoparticles did not form CO₂ foams while both the 50% and 75% particles formed very stable foams. The 75% methylsilyl particles, however, aggregated significantly in water, and the 50% methylsilyl particles were employed for all subsequent tests.
3.3.2 Foam Stability Analysis

The stability of nanoparticle stabilized CO$_2$ in brine foam and surfactant stabilized CO$_2$ in brine foam were measured in the micromodel chip. Bulk foam tests served as a reference, and all results are plotted in Figure 3-2. The chip was filled with foam and imaged under the microscope over 20 hours to monitor the changes in bubble size and bubble density. Bubble density is calculated using image analysis software (Image J). It is based on the total bubble count in the imaged regions of the chip divided by the total area of the imaged regions in units of (bubbles/mm$^2$). The average total number of bubbles used in each calculation is $\sim 500$.

Foam coalescence was measured as the increase in average bubble size and decrease in bubble density and plotted in Figure 3-2c, and d. For SDS surfactant foam the bubble diameter increases from 83 µm to 198 µm during the course of the experiment and the corresponding foam density decreases from 31 bubbles per mm$^2$ to 9 bubbles per mm$^2$. These changes show that SDS foam has low stability due to coalescence. Similarly rapid changes were observed for bulk SDS foam in the vial tests conducted here and elsewhere.$^8$ In contrast to surfactant foam, nanoparticle foam was much more stable. The bubble diameter and foam density remain almost unchanged at 72 µm and an average of 29 bubbles per mm$^2$ respectively over the duration of the experiment (20+ hours). The bulk foam test in the vial was extended over 10 days, and showed negligible change over this period. The excellent stability of these foams, measured here agree with bulk measurements reported previously,$^8,11$ and motivate the application of nanoparticle-stabilized foams in the subsurface. On-chip foam analyses presented here (i) provide a quantitative measurement of bubble size and coalescence dynamics that cannot be observed or quantified in bulk foam testing methods, and (ii) indicate that the excellent stability characteristics of nanoparticle-stabilized foams are maintained in micro-confined media.
Figure 3-2 Foam stability analysis a) SDS surfactant foam b) nanoparticle-stabilized CO₂ foam c) foam coalescence measurement as function of changes in bubble diameter d) foam quality measurement as a function of bubble density (bubbles per mm²). Scale bars: 400 µm.
3.3.3 Enhanced Oil Recovery with CO$_2$ vs. Nanoparticle-Stabilized CO$_2$ Foam.

Figure 3 shows the oil recovery results obtained with CO$_2$ injection are compared to nanoparticle-stabilized CO$_2$ foam injection with medium heavy oil (24 API). The dynamics of oil production were observed at the chip-scale with a field of view ~ 100 mm, at the pore-scale with field of view ~ 2 mm, and the micro-scale ~ 100 µm. Oil recovery is calculated from images taken at chip scale as shown in Figure 3-3. The images were processed in ImageJ to analyze the residual oil saturation based on the clear light intensity difference between foam/gas filled pores and oil filled pores. The cumulative oil recovery as a percentage of initial oil in place (IOIP) is calculated for both the water flooding and the subsequent CO$_2$ or CO$_2$-foam flooding. Water flooding results viscous fingering patterns due to the low viscosity of water compared to oil which result in a recovery of ~ 41% of IOIP. The end of the water flood is indicated in Figure 3-3c by the dashed line. As with reservoir processes, the recovery rate is high until water breakthrough, after which additional water injection flows mostly through the water filled pores resulting in low recovery between 1 and 2 pore-volumes (PV) in Figure 3-3c. For the case in Figure 3-3a, pure CO$_2$ was injected following the water flood, giving an additional 5% recovery (IOIP). This low recovery from CO$_2$ injection is due to transport of gas through the preferential path developed from the water flood, bypassing most of the oil-filled areas, as shown in Figure 3-3a. For the case in Figure 3-3b, nanoparticle-stabilized CO$_2$ foam injection significantly improved the oil recovery following the water flood. In contrast to CO$_2$ gas flooding, nanoparticle-stabilized CO$_2$ foam flooding open up new paths through the micromodel and comprehensively sweep through the micromodel (Figure 3-3b). Notably, the preferential path formed during the water flood is not visible after the foam flood – a ‘homogenization’ of the reservoir. The high sweep efficiency results in a large increase in oil recovery with an additional of 15% IOIP after water flooding, representing a three-fold improvement over the otherwise similar CO$_2$ gas flooding case.
Figure 3-3. Comparison of oil recovery following a water flood with CO$_2$ vs. nanoparticle-stabilized CO$_2$ foams. Images of initial oil in place (IOIP), following the water flood, and the CO$_2$ (a) or nanoparticle-stabilized CO$_2$ foam (b) floods. Cumulative oil recovery as percentage of IOIP for both cases (c), with enlarged plot of the recovery following water flood (d).

**Pore-scale and Micro-scale Assessments of Foam Dynamics.** Pore-scale images of the CO$_2$ flooding and foam flooding reveal the mechanisms of high foam sweeping efficiency as shown in Figure 3-4. Areal sweep efficiency in micromodel is defined as the ratio of the area
contacted by the displacement fluid over the total area of the oil filled area. The viscous fingering pattern of CO$_2$ gas flooding is observed at the pore scale as continuous gas phase channels extended through many pores in the flow direction (left to right) with a narrow spread in the transverse direction. The connected, sinuous nature of the oil phase is illustrated by the fluorescence image in Figure 3-4a, employing the natural fluorescence of the oil phase (excited at 450-500 nm and collected at 510-560 nm). In contrast, the nanoparticle-stabilized CO$_2$ foam flood was observed to spread stable nanoparticle-stabilized CO$_2$ foam bubbles during the entire flooding process. A representative example obtained with bright field microscopy is shown in Figure 3-4b. The foam is well-distributed throughout the network, trapping and transporting interstitial oil.
Figure 3-4. Pore-scale images of CO$_2$ gas flooding and nanoparticle-stabilized CO$_2$ foam flooding. (a) CO$_2$ gas flooding resulting in a long sinuous oil phase (imaged through native oil fluorescence) and connected gas channels (black) fingering through the network; (b) Nanoparticle-stabilized CO$_2$ foam bubbles visible through bright field microscopy, trapping and transporting interstitial oil. Scale bars: 250µm.

Fluorescence imaging at the micro-scale enables quantification of the oil-in-water and water-in-oil emulsion size distributions, as shown in Figure 3-5. Images of both types of emulsions are shown for both the CO$_2$ flood case and the nanoparticle-stabilized CO$_2$ foam case, in Figure 3-5a. Oil-in-water emulsions from the CO$_2$ flooding case range from 1 µm to 40 µm, with an average size of 7.8 µm. Nanoparticle foam flooding results in significantly smaller oil-in-water emulsion sizes ranging from 1µm to 6 µm, with an average size of 1.7 µm (~ 80 % smaller). Likewise, the oil-in-water emulsion density in the nanoparticle foam flooding case (2067 emulsions per mm$^2$) is much higher than CO$_2$ gas flooding case (459 emulsions per mm$^2$). This effect is attributed here to the interfacially-active nanoparticles being active at the oil-water interface with high adsorption energy. That is, the same physics that aids in the formation and stabilization of CO$_2$-in-water foams/emulsions, aids in formation and stabilization of oil-in-water emulsions. The latter is an unreported mechanism that likely contributes to increased oil recovery observed with nanoparticle-stabilized CO$_2$ floods. As with other enhanced oil recovery methods, smaller oil-in-water emulsion sizes improve recovery rates$^{74}$ (though, admittedly, complicating surface-separation operations). Notably, a reduction in emulsion size is not observed for water-in-oil emulsions in the CO$_2$ foam case. Water-in-oil emulsions for CO$_2$ and foam flooding show similar distribution and average size of 2.5 µm in CO$_2$ flooding and 3.4 µm in foam flooding. These results also point to the specific emulsion formation dynamics of the nanoparticles (50%-coated silica), preferring to stabilize emulsions of non-polar fluids within water (and not vice versa). A lack of an effect on water-in-oil emulsions is also likely a positive for operators, particularly in the context of downstream water/oil separation processes.
Figure 3-5. Micrometer-scale quantification of emulsion sizes using the native fluorescence of the oil phase. a) Images of oil-in-water and water-in-oil emulsions produced by a CO₂ flood and a nanoparticle-stabilized CO₂ foam flood (bright phase is the oil). b) Size distribution of oil-in-water emulsions (n = 3840). c) Size distribution of water-in-oil emulsions (n = 4080). Scale bars: 50 µm.
Effect of Oil Viscosity on Foam-based Enhanced Oil Recovery. As oil viscosity increases from light oil to heavy oil, the efficiency of water flooding decreases dramatically due to viscous fingering. Figure 3-6 shows the results of nanoparticle-stabilized CO₂ foam floods (following water floods) for typical light, medium and heavy oils (37, 24, and 14 API, respectively). As expected, the water flooding is most effective in light oil recovery with a recovery of ~ 55%. In contrast, water flooding in medium and heavy oils provided 41% and 12% IOIP, respectively. Very pronounced water fingering is observed in the heavy oil case, in Figure 3-6c. With injection of nanoparticle-stabilized CO₂ foam, all three oils show substantial additional oil recovery (11% IOIP for light oil, 15% IOIP for medium heavy oil, and 8% IOIP for heavy oil). The absolute recovery resulting from CO₂ foam injection is maximum for the medium oil case. Specifically, the foam was particularly effective in the middle-viscosity case where the water flood left significant oil in place (unlike the light oil case), and yet the viscosity of the oil was not prohibitively high (unlike the heavy oil case). It is noteworthy that in all cases that the foam injection had a homogenization effect on the reservoir. That is, the foam smoothed the distribution of oil throughout the pore space considerably, improving the reservoir characteristics significantly over that resulting from the water flood. In summary these results indicate significantly improved oil recovery, particularly for medium oil, and a reservoir- homogenization (continuous oil is partially displaced by foam) effect for all oils.
Figure 3-6. Nanoparticle CO₂ foam oil recovery using oil with different viscosity a) light oil, 37 API b) medium heavy oil, 24 API c) heavy oil, 14 API. Each figure shows the initial saturation, then the water injection and subsequent foam injection d) cumulative oil recovery as percentage of initial oil in place (IOIP).

### 3.4 Conclusions

Nanoparticle CO₂ foam stability and EOR efficiency were evaluated here using a micromodel approach. Foam stability tests within the micromodel provided a quantitative measurement of bubble size and coalescence dynamics that cannot be observed or quantified in bulk foam testing methods. The nanoparticle-stabilized CO₂ foams maintained excellent stability within micro-confined media, and continued to be stable after 10 days as compared to less than one day for surfactant foam. A nanoparticle-stabilized CO₂ foam flood was performed following a water-flood in an initially oil-filled micromodel. As compared to an otherwise similar case
with CO\textsubscript{2} gas, the nanoparticle-stabilized CO\textsubscript{2} foam showed a three-fold increase in oil recovery (an additional 15\% of IOIP) comprehensively sweeping the reservoir. With other factors controlled, the higher sweep efficiency obtained with CO\textsubscript{2} nanoparticle foams is predominantly attributed to the role of the physical pore-scale bubble structures which are rendered very stable by the presence of nanoparticles. Secondary effects, such as nanoparticle-influenced wetting characteristics may also play a role. Fluorescence imaging was applied to quantify emulsion size distribution (down to 1\textmu m) in both CO\textsubscript{2} and nanoparticle-stabilized CO\textsubscript{2} foam flood cases. Nanoparticle-stabilized CO\textsubscript{2} foam flooding resulted in significantly smaller oil-in-water emulsion sizes with an average size of 1.7 \textmu m (~ 80 \% smaller than a CO\textsubscript{2} gas flood), and negligible impact on water-in-oil emulsions. Lastly the nanoparticle-stabilized CO\textsubscript{2} foam strategy was applied to oil recovery tests (post water-flood) with light, medium and heavy oil. All three oils show substantial additional oil recovery (11\% IOIP for light oil, 15\% IOIP for medium heavy oil, and 8\% IOIP for heavy oil). These results indicate significantly improved oil recovery, particularly for medium oil, and a potentially valuable reservoir-homogenization effect for all oils tested.
4 Fast fluorescence-based microfluidic method for measuring minimum miscibility pressure of CO₂ in crude oils

Carbon capture, storage and utilization has emerged as an essential technology for near-term CO₂ emission control. The largest CO₂ projects globally combine storage and oil recovery. The efficiency of this process relies critically on the miscibility of CO₂ in crude oils at reservoir conditions. We present a microfluidic approach to quantify the minimum miscibility pressure (MMP) that leverages the inherent fluorescence of crude oils, is faster than conventional technologies, and provides quantitative, operator-independent measurements of CO₂ and oil MMP. To validate the approach, synthetic oil mixtures of known composition (pentane, hexadecane) are tested and MMP values are compared to reported values. Results differ by less than 0.5 MPa on average, in contrast to comparison between conventional methods with variations on the order of 1-2 MPa. In terms of speed, a pressure scan for a single MMP measurement required less than 30 min (with potential to be less than 10 min), in stark contrast to days or weeks with existing approaches. The method is applied to determine the MMP for Pennsylvania, West Texas, and Saudi crudes. Importantly, our fluorescence-based approach enables rapid, automated, operator-independent measurement of MMP as needed to inform the world’s largest CO₂ projects.


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4.1 Introduction

Global energy consumption has led to an increase in CO₂ emissions with climate implications. Carbon capture, utilization, and storage technologies target the reduction of CO₂ emissions and sustainable global economic development. Recent research has focused on developing effective methods of carbon capture, CO₂ conversion to fuels, sequestration in underground saline aquifers and combined storage/utilization of CO₂ in enhanced oil recovery
Currently, CO2 EOR is the most economically and technically feasible approach (Figure 4-1a). The majority of current CO2 EOR projects are in North America (~120 projects). The total world storage potential in enhanced oil recovery reservoirs is estimated to be 370 gigatonnes and recoverable oil with this technology is 1.3 trillion barrels.

A key parameter in CO2 EOR is the minimum miscibility pressure (MMP) of the injected CO2 and oil. The lowest pressure at which a gas can develop miscibility through a multiple contact process with oil at a given reservoir temperature - as commonly described on the ternary phase diagram of CO2 and oil (Figure 4-1b) - is defined as MMP. At pressures below MMP, the main driving force of mass transfer at the interface between CO2 and oil is diffusion, which is mitigated by interfacial tension (Figure 4-1c). At MMP, the interfacial tension between CO2 and oil vanishes as CO2 vaporizes the light components of the oil to create an enriched mixture which further becomes enriched with heavier oil components, eventually becoming fully miscible with the oil (Figure 4-1d). Injecting CO2 at or above MMP increases both the uptake of CO2 in the reservoir and oil production as interfacial force barriers are eliminated and the oil is displaced as a single phase liquid. Current methods used to measure the MMP of gas and oil include the rising bubble apparatus (RBA), slim-tube test, and vanishing interfacial tension method. The RBA method is illustrated in Figure 4-1e. These current methods suffer from long measurement times (days, weeks) and/or measurement subjectivity (operator-dependent). Motivated by the cost of current experimental approaches, simulation-based methods for MMP determination have been developed. Simulations can be comparatively inexpensive and fast. The full composition of the test oil is required, however, and simulation results can have significant error. In general, simulations are best paired or fit with select experimental data.

Recently, there have been a number of new applications of microfluidics to CO2 storage and oil recovery applications. In addition to the traditional benefits of microfluidic systems (speed, small volumes, rapid diffusive transport, multiplexing), subsurface CO2, oil and gas applications benefit from (i) high temperature and pressure tolerance of silicon/glass, and (ii) a match between microfluidic channels and microporous media typical of reservoirs. While no microfluidic method for MMP measurement has been developed to date, both bubble generation and droplet based micro-reactors
are relevant to this approach. These microfluidic platforms have been extensively applied in lab-on-chip technology, chemical synthesis, and phase behaviour studies.

Herein, we report a rapid, user-independent method for measuring CO₂-in-oil MMP at reservoir-relevant temperatures and pressures. The mixing of continuously-generated CO₂ bubbles within a microchannel embedded in silicon are observed quantitatively, leveraging the inherent fluorescence of crude oil sample (Figure 4-1f). To validate and benchmark the method, a set of synthetic oil mixtures with known compositions of pentane and hexadecane are tested with results compared to those from the RBA method. The dependence of MMP on temperature and density (API gravity) is also demonstrated. To demonstrate wide applicability, the method is applied to measure the MMP of relevant crude oils: Pennsylvania, West Texas, and Saudi crudes.
Figure 4-1(a) Schematic of CO₂ storage and enhanced oil recovery, CO₂ EOR. (b) Schematic of ternary diagram of CO₂ and model synthetic crude oil components (pentane and hexadecane). Schematics illustrating molecular behavior at the oil/CO₂ interface are presented at pressures (c) below MMP and (d) at MMP. The conventional rising bubble apparatus (RBA)
method (e) is compared to the microfluidic MMP method (f), each inset with corresponding bubble behaviors at pressures below and at MMP

4.2 Experimental method

The microfluidic chip was fabricated through deep reactive ion etching of silicon, and subsequent anodic bonding to glass. Hybrid silicon-glass chips can withstand a high range of pressures and temperatures ($P \leq 40$ MPa, $T \leq 200$ °C), sufficient for all practical CO$_2$ EOR applications. The chip design consists of a T-junction with a main channel width of 250 µm and a CO$_2$ nozzle width of 50 µm. Both the CO$_2$ and oil channels have resistors upstream of the T-junction to dampen pressure fluctuations, and all channels have a depth of 100 µm. The chip was installed on a stainless steel manifold with high pressure compression fittings (Swagelok) to provide high pressure connections to the fluid lines as shown in Appendix 1: Figure S1. High pressure pumps (Teledyne Incommode 260D) were used to pump CO$_2$ into the chip and to set the reference pressure on the backpressure regulator (Equilibar Model EB1ULF1-SS316). A third high pressure pump (Eldex, Optos Series 1SMP) was used to flow oil into the chip, and the backpressure regulator was used to set the system pressure. A 60W tape heater was attached to the back of the chip to provide a set temperature on the chip. The heating tape was controlled by a temperature controller (Omega Model CNi3222) within ±1°C. A fluorescent microscope (Leica DMLM) was used to image the bubble formation and CO$_2$/oil phases in the chip with a 10X objective and a Semrock BrightLine filter cube (Ex 375-400, Em LP405). The images were captured with a high speed camera (Model PCO 1200s) at a frame rate of 100 frame per second. The recorded images were processed in ImageJ to perform image calibration and intensity analysis. Image calibration for background removal was performed using dark and bright image based on an shading correction method given by Wilkinson et al.$^{167}$ Materials used in this work are presented in Appendix 1: Table S1.

For each data set, the main channel was filled with oil to the pressure set by the backpressure regulator. Subsequently, CO$_2$ was injected into the oil channel from the smaller T-junction side channel (Figure 4-1f). The pressure was then incrementally increased, and the fluid mixing properties at the T-junction and downstream were monitored via fluorescence microscopy. In the case of synthetic oil tests, fluorescent dye (Dye-Lite, Tracerline) was added to the oil
mixture at a concentration of 50 ppm to enable fluorescent imaging. In the case of crude oils, no dye was added as the inherent fluorescence was used. Between experiments, the chip was cleaned with successive flushing of toluene and acetone. In this work, we performed a vaporizing gas drive by introducing pure CO$_2$ into fresh oil. Although not the focus here, our microfluidic technique could in principle be expanded to measure the MMP of alternate gases, such as enriched CO$_2$ mixtures which are used in condensing gas drives.

4.3 Results and discussion

Figure 4-2a shows the changes in bubble shape with pressures below, at, and above MMP, as observed in the microfluidic chip. Below MMP, the interfacial tension between the CO$_2$ and oil is high, which allowed the bubbles to retain their shape with sharp channel-blocking interfaces as shown for the case of $P = 5.9$ MPa. In this regime, the mass transfer between the CO$_2$ phase to the oil phase is through diffusion across the interface. As a result, the CO$_2$ bubbles shrink as they flow downstream, as is familiar in gas-liquid droplet reactors. As the pressure was increased to MMP ($P = 6.1$ MPa), the interfacial tension decreased and the injected CO$_2$ bubbles deformed readily in response to flow-induced stresses. Specifically, round nose shaped bubbles were formed with trailing boundaries that were rapidly eroded as they mixed with the continuous oil phase, unimpeded by interfacial tension. Likewise, the bubble shape shown ($P = 6.1$ MPa) is reminiscent of miscible band broadening in Poiseuille flow, and also characteristic of the shape observed in RBA at MMP.$^{136}$ Above MMP ($P = 6.2$ MPa), mixing is rapid, and the two phases are largely indistinguishable at the downstream location shown in Figure 4-2a. At the injector distinct phases are observed at pressures moderately above MMP, and progressively less so as interfacial tension vanishes with increasing pressure.

The microfluidic method was validated by comparing measured MMP values to those measured with the RBA method.$^{136}$ These validation tests were conducted with various synthetic oil mixtures (hexadecane/pentane, 63 to 79 API) at different temperatures (25 °C to 60 °C). As shown in Figure 4-2b, MMP measurements demonstrated strong agreement with reported RBA measurements, with an average difference of 0.5 MPa. This degree of agreement is significant in the context of comparisons among MMP methods: previously reported MMP measurements using RBA and slim tube methods differ on average by 0.86 MPa,$^{130,136,137}$ and
MMP measurements with vanishing interfacial tension and slim tube methods differ by 2.2 MPa.\textsuperscript{168} Figure 4-2c plots the temperature dependence for MMP measurements for synthetic oils of different density. The linear fit for 68 API has a slope of 0.168 MPa/°C which compares well to the 0.188 MPa/°C as measured by the RBA method for this synthetic oil mixture.\textsuperscript{137} The method was applied to other synthetic oil mixtures (63 API, 71 API, and 79 API), each providing a distinct MMP, increasing with temperature.
Figure 4-2 (a) Demonstration of high-contrast fluorescence imaging of CO₂ bubbles flowing through synthetic oil at pressures below, at, and above MMP. (b) Cross plot comparing microfluidic MMP measurements to literature MMP values from the RBA method. The 45° dashed line represents the ideal perfect correlation case. (c) Demonstration of the linear dependence of MMP on temperature for various synthetic oil mixtures (63 API, 68 API, 71 API, and 79 API). MMP increases with oil density from light to heavy oil.

The method was applied to measure MMP of crude oils from large EOR candidate reservoirs worldwide. The MMP measured for Pennsylvania crude (8.34 ± 0.07 MPa) and West Texas crude (10.0 ± 0.3 MPa) at 40 °C compare well to literature data of 7.3 MPa (estimated based on Cronquist correlation) and 9.7 MPa (measured with slim tube) respectively (Table 4-1). Figure 3 illustrates how the fluidic mixing behavior varies between the three different crude oils. This variation can be attributed mainly to differences in crude oil compositions. Despite the natural variability in these oils, all three exhibit recognizable shifts in flow condition signaling MMP.

<table>
<thead>
<tr>
<th>Oil type</th>
<th>Density (°API)</th>
<th>Temperature (°C)</th>
<th>Microfluidic MMP (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pennsylvania</td>
<td>48.8</td>
<td>25</td>
<td>5.52 ± 0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>8.34 ± 0.07</td>
</tr>
<tr>
<td>West Texas</td>
<td>38.9</td>
<td>25</td>
<td>7.4 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>10.0 ± 0.3</td>
</tr>
<tr>
<td>Saudi Berri</td>
<td>37.0</td>
<td>25</td>
<td>8.3 ± 0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>10.7 ± 0.3</td>
</tr>
</tbody>
</table>

Table 4-1 Crude oil MMP measurements.
Figure 4-3 Microfluidic fluorescent visualization of West Texas and Pennsylvania crude oil at MMP, at 25°C and 40°C, as indicated. Each crude exhibiting a characteristic mixing pattern due to differences in oil compositions.

In contrast to all existing methods, a fluorescence-based microfluidic approach presents the opportunity for direct, user-independent, measurement of MMP. To demonstrate, fluorescence image sequences (1.45 s) were analysed using ImageJ software, each corresponding to a given inlet pressure in the range of MMP. The average intensity over a 35 µm x 185 µm detection region within the channel was sampled in each frame and plotted over time (Figure 4-4a,b). At sub-MMP values, oil and CO₂ plugs traversed the detection region in sequence, which generated a strong periodic oscillation between intensity plateaus. At higher pressures (6.07 MPa) fluid plugs quickly interweaved and mixed. On occasion, shrunken CO₂ plugs traversed the detection region, which caused a detectable dip in fluorescence signal. Figure 4-4c shows how this intensity changed over time at various pressure settings, each normalized to unity. As the MMP region was approached, sharp changes in fluorescence became infrequent and eventually ceased to occur. At a pressure above MMP, the intensity signal fully stabilized. To quantify MMP directly from this data, the intensity profiles were differentiated with respect to
time as shown in Appendix 1: Figure S3. The variance of each of these data sets was calculated for each video segment, and plotted in log format in Figure 4-4d. The data points were fit to the Boltzian sigmoidal equation:

\[
y = \frac{A_1 - A_2}{1 + e^{-\frac{x-x_0}{dx}}} + A_2
\]

Fit parameters: \(A_1 = 1.44 \pm 0.2, \ A_2 = -1.9 \pm 0.2, \ x_0 = 6.14 \pm 0.02\) and \(dx = 0.05 \pm 0.02\). A MMP value of 6.14 MPa was determined by the inflection point, that is, the minimum of the derivative of the sigmoidal curve. This measured value compares well to the 6.1 MPa MMP value obtained by direct visualization method.
Figure 4-4 Operator-independent fluorescence-based measurement of MMP: fluctuations in fluorescence intensity at pressures of (a) 4.83 MPa and (b) 6.07 MPa measured over time. Data points highlighted with red circles are shown with corresponding images. (c) Variation in average intensity within the detection region over time at different pressures. The variance of the derivative of these data sets is plotted in log format in (d). The derivative of this curve is plotted to highlight the point of greatest slope, which corresponds to MMP – in this case, 6.14 MPa.

4.4 CONCLUSION

In summary, we demonstrate a microfluidic method for measuring CO$_2$ and oil MMP which provides two distinct advantages over conventional methods: fast measurement speed and quantitative analysis. In terms of speed, MMP can be obtained within 30 min using our microfluidic technique, compared to days or weeks using traditional methods such as RBA, slim tube or vanishing interface methods. Further, in leveraging the inherent fluorescence of crude oils, we achieved heightened contrast between CO$_2$ and oil, and provided the means of quantitative, user-independent, MMP measurement. Microfluidic MMP measurements were validated with the established RBA method data, showing a strong agreement with expected values under CO$_2$ reservoir-relevant conditions. Collectively these results demonstrate the potential to inform and improve the largest current CO$_2$ operations worldwide.
5 Microfluidics Underground: A Micro-Core Method for Pore Scale Analysis of Supercritical CO$_2$ Reactive Transport in Saline Aquifers

Carbon sequestration in microporous geological formations is an emerging strategy for mitigating CO$_2$ emissions from fossil fuel consumption. Injection of CO$_2$ in carbonate reservoirs can change the porosity and permeability of the reservoir regions, along the CO$_2$ plume migration path, due to CO$_2$-brine-rock interactions. Carbon sequestration is effectively a microfluidic process over large scales, and can readily benefit from microfluidic tools and analysis methods. In this study, a micro-core method was developed to investigate the effect of CO$_2$ saturated brine and supercritical CO$_2$ injection, under reservoir temperature and pressure conditions of 8.4MPa and 40 °C, on the microstructure of limestone core samples. Specifically, carbonate dissolution results in pore structure, porosity, and permeability changes. These changes were measured by x-ray microtomography (micro-CT), liquid permeability measurements, and chemical analysis. Chemical composition of the produced liquid analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES) shows concentrations of magnesium and calcium in the produced liquid. Chemical analysis results are consistent with the micro-CT imaging and permeability measurements which all show high dissolution for CO$_2$ saturated brine injection and very minor dissolution under supercritical CO$_2$ injection. This work leverages established advantages of microfluidics in the new context of core-sample analysis, providing a simple core sealing method, small sample size, small volumes of injection fluids, fast characterization times, and pore scale resolution.


Link to publication online:

http://fluidsengineering.asmedigitalcollection.asme.org/article.aspx?articleid=1671766&result=1
5.1 Introduction

Microfluidics has been widely used in many areas of science and engineering to study biological, medical, and chemical applications.\textsuperscript{69,171} Recent applications of microfluidics to study fluid transport phenomena in oil reservoirs and saline aquifers has sparked a new interest in leveraging some attributes of microfluidics such as small sample size, fast reaction time, rapid transport, and real time micro scale visualization in the study of multiphase fluid interactions underground.\textsuperscript{81,172–174} Reservoirs are made up of porous media that consists of a network of channels and voids with length scales on the order of 0.1\(\mu\)m to 100 \(\mu\)m.\textsuperscript{175,176} These length scales match those of traditional microfluidics applications.

Carbon sequestration in geological formations is one potential solution for mitigating carbon dioxide emissions from fossil fuel consumption.\textsuperscript{177} Deep saline aquifers can sequester carbon dioxide by four main mechanisms: structural and hydrodynamic trapping in which CO\(_2\) moves upward towards the cap rock since it is lighter than brine, residual trapping of CO\(_2\) in the pore spaces of the reservoir rock formation, solubility trapping through the dissolution of CO\(_2\) in formation water, and mineral trapping where dissolved CO\(_2\) reacts with mineral cations to form stable carbonate minerals.\textsuperscript{178} Deep saline aquifers have capacity for large scale storage of CO\(_2\) on the order of 1000 of Gigatons. Injecting CO\(_2\) in saline aquifers causes the pH to decrease due to the formation of carbonic acid which leads to carbonate mineral dissolution in limestone or dolomite formations. The chemical reactions governing carbonate dissolution are presented in Eqn. (4) - Eqn. (6).\textsuperscript{55,179–181} The microstructure porosity and permeability of the porous media change as the result of this dissolution. Understanding local mass transfer between CO\(_2\)-brine-rock interactions is critical for designing, assessing and monitoring CO\(_2\) sequestration processes.

\[
\begin{align*}
\text{CO}_2(\text{g}) + \text{H}_2\text{O} &\leftrightarrow \text{H}_2\text{CO}_3(\text{aq}) \quad (4) \\
\text{H}_2\text{CO}_3(\text{aq}) &\leftrightarrow \text{HCO}_3^- + \text{H}^+ \quad (5) \\
\text{CaCO}_3 + \text{H}^+ &\rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \quad (6)
\end{align*}
\]
Most previous studies of calcite dissolution were performed at low pressure up to 55 atm and using cores with dimensions in the range of 0.1 m diameter and 0.3 m-1 m in length. The spatial resolution for x-ray imaging for these core sizes is larger than the pore sizes of reservoir rocks, and thus pore-scale dynamics are obscured. Izgec et al.182 and Perrin et al.183 use core plugs of a few centimeters in diameter to study bulk saturation and porosity of the core plugs in CO2 injection processes. A few studies visualized the CO2-fluid-rock interactions in the core sample at the pore scale level under supercritical CO2 conditions. Luquot et al.184 and Gouze et al.185 characterized porosity and permeability changes due to CO2 injection at pore scale level using x-ray micro-CT. Iglauer et al.186 calculated residual CO2 saturation, CO2 cluster size and distributions at reservoir conditions in sandstone core samples using micro-CT. All of these works employed X-ray and associated microscopic image analysis methods to calculate porosity and permeability in dry cores and in the case of core flooding experiments, to measure the saturations of injected and displaced fluids. These previous studies measured the macroscopic properties of CO2 brine rock interactions and bulk core saturations using core plugs, with the exception of Luquot et al. who demonstrated the potential for using smaller core sizes for pore scale analysis of supercritical CO2 transport and reactivity in porous media. The core size used in that study, however, was still too large to image the whole core with pore scale resolution and their experiments employed a standard core experimental setup.

In this study, a micro-core method is used to analyze reactive transport during supercritical CO2 transport through brine-saturated limestone. This method allows for high resolution imaging of the pore scale changes due to injection of supercritical CO2 using X-ray microtomography and SEM, and employs a microfluidic experimental setup which is simpler than traditional core flooding methods. The pore structure changes due to dissolution of calcium carbonate are imaged and the related porosity changes are obtained from image processing. This micro-core method takes advantage of microfluidics fabrication in core sealing and supporting infrastructure. The result is a faster analysis method, readily applicable to microfluidics laboratories, that provides high resolution imaging compared to conventional core flooding and is a suitable technique for studying the porosity and permeability changes under supercritical CO2 conditions. In addition to pore scale imaging of carbonate dissolution, chemical analysis of the produced liquid was also performed over the core flooding period to monitor the concentrations of calcium and magnesium ions in the produced liquids. This thesis
presents a proof of concept of the micro-core method that can be used to characterize pore scale changes in carbonate core samples due to CO₂ injection.

5.2 Experimental Setup

The experimental setup is shown in Figure 5-1. The system uses a microfluidic chip style holder and connections which simplify the apparatus as compared to conventional core-study methods. Carbonate core samples, Indiana Limestone obtained from Kocurek Industries were used in this study. The micro-cores were 6.35mm in diameter and 10mm long with an average pore volume of 57 µL. Prior to each experiment, the cores were cleaned by injecting ~ 100 pore volumes of deionized water through the core. The cores were then dried in the vacuum oven at 110 °C for 10 hours to remove any trapped water, and subsequently imaged by micro-CT to measure initial pore structures. The cores were wrapped in polyvinylidene fluoride (PVDF) heat shrink tube and the formed tube ends were sealed with epoxy and attached to 1/16 stainless steel tubing. Small scale tubing provides easy connection to inlet and outlet instruments using high pressure fittings from Upchurch Ltd. In addition, the small size of the micro-core holder makes it simple to fit both the core holder and the CO₂/brine reservoir in the water bath for very precise temperature control. The smaller setup reaches equilibrium conditions quickly, reduced fluid volumes, and reduced characterization times. Brine with concentration of 1.81 M NaCl similar to the Alberta Redwater Leduc formation was initially injected into the core by vacuum injection to displace all air in the pore space. The brine-saturated core was then placed in the stainless steel micro-core holder which was then connected to the high pressure CO₂ system as shown in Figure 5-1. Stainless steel micro-core holder was used to withstand the high confining pressure required for supercritical CO₂ injection through the core. Confining pressure was provided by the high pressure hydraulic hand pump. The confining pressure was kept at 2 MPa above the injection pressure to ensure there was no flow along the core surface between the core and the heat shrink tubing. The pressure drop across the core was measured by a pressure differential transducer (Honeywell model TJE ultra precision) with accuracy of 0.1% full scale. The experimental temperature was kept constant by using a heating water bath (Fischer Scientific, Isotemp 2340) to within ± 0.1 °C.
5.3 Experimental Procedure

5.3.1 Experimental conditions

The experimental conditions listed in Table 5-1 were selected to simulate different regions of the CO₂ plume migration path in the reservoir. Close to the injection well the CO₂ saturation is high due to CO₂ displacing brine and free phase CO₂ saturation decreases as it dissolves into brine at the front interface of the plume.¹⁸⁷ To simulate the near well condition, pure supercritical CO₂ was injected through the core at 8.4 MPa and 40 °C, displacing the brine solution. To simulate the conditions further from the injector well, at the CO₂ front, CO₂ saturated brine was injected into the core at 8.4 MPa and 40 °C. Prior to injection, supercritical CO₂ and brine equilibrium was achieved by pressurizing the brine vessel with supercritical CO₂ for at least 2 hours.
Figure 5-1 Schematic of the experimental setup for the micro-core flooding experiments with pure CO$_2$ and CO$_2$ saturated brine. The system uses a microfluidic chip style holder and connections which simplify the apparatus as compared to conventional core-study methods. The parts inside the dotted line were kept at constant temperature of 40 °C in a water bath. An image of the micro-core is shown inset.
Table 5-1. Experimental conditions for CO₂ core flooding experiments to simulate different regions of the CO₂ plume in saline aquifer

<table>
<thead>
<tr>
<th>Test condition</th>
<th>Case 1</th>
<th>Case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection fluid</td>
<td>CO₂</td>
<td>Pure CO₂</td>
</tr>
<tr>
<td>Temperature</td>
<td>40 °C</td>
<td>40 °C</td>
</tr>
<tr>
<td>Injection pressure</td>
<td>8.4 MPa</td>
<td>8.4 MPa</td>
</tr>
<tr>
<td>Brine concentration</td>
<td>1.81 M NaCl</td>
<td>1.81 M NaCl</td>
</tr>
<tr>
<td>Confining pressure</td>
<td>10.4 MPa</td>
<td>10.4MPa</td>
</tr>
</tbody>
</table>

5.3.2 Core flooding with pure CO₂ and CO₂ saturated brine

Supercritical CO₂ was generated by compressing liquid CO₂ at 5.4 MPa with the high pressure screw pump to 8.4 MPa. The liquid CO₂ was then transferred to the brine reservoir vessel submerged in the water bath at 40 °C to reach supercritical state. The brine was saturated with CO₂ before core flooding. The temperature and pressure conditions were chosen to simulate the Alberta Redwater Leduc limestone reservoir conditions. Supercritical CO₂ saturated brine was then injected through the core at a flow rate of 80µL/min. This flow rate was chosen based on typical reservoir pore velocity in the range of a few feet per day [24]. The flow rate was controlled by a micro control needle valve (HiP Model 15-11AF1-V). The injection duration was 3 hours (253 pore volumes) for each case. Produced liquid samples were collected every 10 minutes for chemical analysis. At the end of the core flooding period, the cores were taken out of the micro-core holder and placed in the vacuum oven to remove all CO₂ and water in preparation for post injection permeability measurements.

5.3.3 Permeability measurements

The core permeability was measured before and after core flooding for each case. Permeability was measured using deionized water injection. Deionized water was used to prevent the possibility of salt blockage of the pores upon drying of the core sample (prior to imaging). Water was injected at constant flow rates and pressure drops across the core sample were measured with the pressure differential transducer. Permeability was then calculated based on Darcy’s law:
\[ Q = \frac{kA}{\mu L} \Delta P \]  

(7)

Where \( Q \) is flow rate in cm\(^3\)/s, \( \Delta P \) is pressure drop across the core in atm, \( k \) is permeability in Darcy, and \( \mu \) is viscosity in cP, \( A \) is cross-section area of the core in cm\(^2\), \( L \) is core length in cm.

### 5.3.4 Scanning electron microscope, x-ray micro-CT, and image analysis

X-ray micro-CT images of the samples were taken before and after each core flooding experiment to characterize the original pore structure and the pore structure after each core flooding experiment. The x-ray micro-CT scanner used in this work was SkyScan 1172. The micro-CT images were scanned with a setting of a voltage of 100k V, a current of 100\( \mu \)A, and a resolution of 4.9 \( \mu \)m per pixel. An aluminum filter was used to reduce the beam hardening effects on the images since limestone has large variation in attenuation coefficient between grains and pores. The raw micro-CT projection images were first reconstructed into cross-section images using the NRecon Software (Skyscan Ltd.). This software uses the Feldkamp algorithm to reconstruct the images, and also has a number of built in functions to enhance the reconstructed image such as beam hardening correction, ring artifacts reduction, and image smoothing. The reconstructed cross-section images were analyzed in CTAn (Skyscan Ltd.), and the Otsu algorithm (internal feature of CTAn) was used to threshold the gray images to binary images. Figure 5-3(c) shows the conversion of a gray image to a binary image and the corresponding histogram of the pixel intensities. The binary image conversion was performed on the selected region of interest, which is the diameter of the micro-core, for each image cross-section. The average porosity of the entire image stack was then calculated for each micro-core. In addition to micro-CT imaging, scanning electron microscope (SEM) equipped with energy dispersive spectrometry (EDS) was used to characterize the initial pore and grain matrix as well as its material composition. The SEM used in this experiment was JEOL JSM6610-Lv model with maximum resolution of 3.0 nm, and EDS was Oxford Aztec model.

### 5.3.5 Atomic emission spectroscopy analysis of produced liquid

Produced liquid was collected and analyzed for concentrations of dissolved Ca\(^{2+}\) and Mg\(^{2+}\) ions with Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). The instrument
model used (PerkinElmer Optima 7300) was capable of detecting Ca\textsuperscript{2+} and Mg\textsuperscript{2+} ion concentration as low as 20 parts per billion (ppb).

5.4 Results and Analysis

5.4.1 Initial characterization of limestone core samples

The pore structures of a thin piece (3mm x 6.35mm in diameter) cut from the same micro-core stock were examined with SEM as shown in Figure 5-2. The intergranular pore size (Fig. 5-2(a)) is on the order of a few hundred microns, whereas the intragranular pores (Fig. 5-2(b)) are on the order of a few microns. The limestone samples used in this study have larger pore sizes than the typical carbonates. In addition, carbonates typically have a pore size distribution down to the nanoscale as well. While the net effect of chemistry acting on these pores may be apparent at the scales imaged here, pore dynamics below 5 µm are not resolvable with the imaging methods applied herein. Energy dispersive spectrometer analysis showed that the limestone samples were 99% calcium carbonate and ~1% magnesium carbonate.
Figure 5-2 SEM images of Indiana limestone core samples used in this study: (a) intergranular pores (b) intragranular pores of the dotted red line region in part (a). For both cases, the black areas are pores and grey areas are grains. Scale bars indicate 500 µm in (a) and 10 µm in (b).

5.4.2 Pore structure and porosity changes due to carbonate dissolution

The micro-cores were imaged using Micro-CT, sealed, placed in the chip holder, and vacuum-injected with brine solution (experimental details in the Section 2). Two types of core flooding experiments were performed, scCO2-saturated brine and pure scCO2 injection. Micro-CT images of the core taken before and after each flooding test are presented in Figure 5-3 and Figure 5-4 for the scCO2 and CO2-saturated brine flood cases, respectively. A marker was placed along the length of the core to landmark the approximate location of recognizable grains and pores used to match the before and after images. As shown in Fig. 5-3, core flooding with CO2 saturated brine solution caused major calcite dissolution. This is indicated by the increase of the black regions in the after-flooding images compared to the before images. The dissolution is due to the reaction between the carbonic acid in the brine phase and calcium carbonate grains.

For the CO2 saturated brine injection case (Fig. 5-3), the carbonate dissolution results in a porosity increase from 18.1% to 26.8%. Although the pore connectivity was not explicitly quantified here through image analysis, a notable increase in pore connectivity is apparent from the images. The sagittal plane (horizontal along the axis of the core) in Fig. 5-3 shows the pore width increases to 674 µm and the longest connected path of 3.98 mm (these dimensions were measured based on the image resolution of 4.9 microns per pixel). In stark contrast, pure CO2 core flooding results in much less calcite dissolution as shown in. The calcite dissolution in this case was caused only by the dissolution of injected CO2 into the initial water saturation present in the pore spaces. The amount of this acidified water is comparatively small and results in very little carbonate dissolution. This effect can be clearly seen in Fig. 5-4 where the before and after images are almost identical. Image analysis shows that the porosity increase was minor, from 17.5% to 19.5%.
Figure 5-3 Pore structure changes due to CO₂-saturated brine injection for 3 hours: a) before CO₂ injection; b) after CO₂ injection; c) Binary image conversion from gray image and histogram. Coronal plane is the horizontal plane, sagittal plane is the vertical plane, and transaxial plane is the axial plane. The image resolution is 4.9 µm per pixel. Black areas are
pores and grey areas are grains. The degree of dissolution is significant, with a porosity increase from 18.1% to 26.8% and an observable increase in pore connectivity.

Figure 5-4 Pore structure changes due to pure CO$_2$ injection through the core for 3 hours: a) before CO$_2$ injection; b) after CO$_2$ injection. Coronal plane is the horizontal plane, sagittal plane is the vertical plane, and transaxial plane is the axial plane. The image resolution is 4.9 µm per pixel. Black areas are pores and grey areas are grain. In comparison with CO$_2$-saturated brine flooding (Fig. 5-3), very little dissolution occurs in this case. Porosity increase is minor, from 17.5% – 19.5%.
5.4.3 Permeability change due to carbonate dissolution

For each core sample, permeability was calculated using Darcy’s law in Eqn. 4 with the slope of the linear fit through the measured flow rate versus pressure drop relationship. Figure 5-5(a) shows the plot of flow rate versus pressure drop for the CO₂ saturated brine injection case. The permeability increases from 5.3 mD before core flooding to 2480 mD after core flooding. This large permeability increase is in agreement with the observations in micro-CT images (Fig. 5-3) showing a major pore size increase and extensive pore connectivity increase. Large increase in permeability is in keeping with previous core studies on CO₂-brine-limestone interaction. Specifically, this high permeability is similar to that measured by Grigg et al.106 ~2000 mD, based on the inlet 17 cm of a 56 cm long core with a diameter of 5 cm (Indiana limestone). For the pure CO₂ case, the plot of flow rate versus pressure drop is shown in Figure 5-5(b). The permeability increase is much less in this case due to very minor porosity increase and low pore connectivity enhancement as observed in the micro-CT images. The permeability increases from 4.1 mD to 10.5 mD.
Figure 5-5 Pressure drop across the core at each flow rate for permeability calculations before and after core flooding for 3 hours at reservoir conditions of 8.4 MPa and 40 °C. (a) CO₂-saturated brine core flooding. The linear fit of the flow rate versus pressure drop correlation $R^2$ value is 0.999 for before and 0.996 for after core flooding. (b) ScCO₂ core flooding. The linear fit of the flow rate versus pressure drop correlation $R^2$ value is 0.993 for before and 0.966 for after core flooding.

5.5 Calcium and magnesium ion concentrations in produced solution

The produced liquid samples were collected every 10 minutes during the core flooding experiments, and analyzed by the ICP-AES instrument to measure the calcium and magnesium ion concentrations. The results are plotted in Fig. 5-6. For CO₂ saturated brine case, the average calcium ion concentration produced in the first 20 minutes is 1423 mg/L. This concentration increases to 1811 mg/L then gradually decreases over time to about 600 mg/L.
The high dissolution rate in the first hour of core flooding can be related to the large initial reactive surface roughness area of the carbonate grains. The graduate decrease as the test proceeds is attributed to several changes including the smoothing and net reduction of reactive surface area, as well as changes in local chemistry, reaction rates, and concentration gradients throughout the core. This result is in keeping with previous study where they also reported a decrease in calcium concentration produced with CO2-saturated brine (approximately 60% after 1 hour of core flooding).

The magnesium ion concentration production also shows a similar trend to that of the calcium ions. The initial magnesium concentration produced is about 13.5 mg/L and it gradually decreases to ~6.5 mg/L. The magnesium ion produced is about two orders of magnitude less than calcium ion which is in agreement with the material composition of these limestone core samples as analyzed by EDS in Section 3.1. Pure CO2 core flooding results in much less calcium and magnesium production. The initial Ca2+ ion concentration produced is about 24 mg/L and it decreases to 3.8 mg/L after 30 minutes. The concentrations of calcium and magnesium ions produced give insight into the CO2-brine-rock interaction with respect to the rate of carbonate dissolution which should be accounted for in the reservoir simulation models of CO2 injection.
Figure 5-6 Chemical analysis of the produced liquid showing both the Ca$^{2+}$ and Mg$^{2+}$ ion concentrations over time. (a) Ca$^{2+}$ ion concentrations in the produced liquid measured with ICP-AES over the 3 hours core flooding experiments with CO$_2$-saturated brine and pure scCO$_2$. (b) Mg$^{2+}$ ion concentrations in the produced liquid measured with ICP-AES over the 3 hours core flooding experiments with CO$_2$-saturated brine and pure scCO$_2$. 
5.6 Conclusions

A micro-core method was developed to study the porosity and permeability changes in limestone due to supercritical CO$_2$ and CO$_2$-saturated brine core flooding at reservoir temperature and pressure conditions of 8.4MPa and 40 °C. Encasing a small scale core sample within a microfluidics-type infrastructure enabled excellent experimental control and rapid testing as compared to traditional core-study methods. Pore scale imaging of the carbonate dissolution in the case of CO$_2$-saturated brine injection reveals large pore size increase and extensive increase in pores connectivity, and a resulting increase in permeability. For the case of pure CO$_2$ injection, very minor changes in pore structures were observed which results in a small increase in permeability. The results from chemical analysis are also consistent with the pore scale visualization of carbonate dissolution and the permeability measurements. The concentration of the produced calcium and magnesium ions are much higher for the CO$_2$-saturated brine injection than the pure CO$_2$ injection. The carbonate dissolution rate is higher during the first hour and then reduces to an almost constant rate for the last 2 hours in the CO$_2$-saturated brine injection case. This thesis demonstrates the efficacy of the micro-core method for rapid pore scale characterization of CO$_2$-brine-rock interactions. This work leverages established advantages of microfluidics in the new context of core-sample analysis, specifically providing a simple core sealing method, small sample size, small volumes of injection fluids, fast characterization time, and pore scale visualization.
6 Multiphase fluorescence imaging of CO$_2$, brine, nanoparticles, and oil in microchannels

6.1 Introduction

Nanoparticles are used in the oil industry to reduce the interfacial tension between oil/water and CO$_2$/water, and modify the surface wettability of reservoir rocks. The contact angle, which depends on wettability and interfacial tension, is a critical measurement. Current methods used to measure contact angles are pendant drops and capillary tube methods. A pore scale measurement of this contact angles is important in EOR applications. In addition, the particles distribution at fluid/fluid interfaces and fluid/rock interfaces provide insight into the particle retention characteristics in reservoir media.

Wettability is a very important parameter in oil recovery mechanisms. Wettability modification of reservoir rock methods and interfacial tension changes using surfactants, low salinity water, microbial method, ionic liquids, and recently nanofluids. Microfluidics offers a great opportunity to investigate pore scale wettability modifications of reservoir fluids applicable for oil and gas recovery processes.

In this chapter, multiphase fluorescence imaging is used to visualize and measure the effect of CO$_2$ pressure on contact angles changes at the pore scale. Four types of experiments were carried out to investigate the interactions between various phases of oil/water/nanofluid/rock within a high pressure, high temperature microfluidic system. Multiphase fluorescence visualization of CO$_2$ enhanced oil recovery processes is performed with focus on improving fundamental understanding of CO$_2$, water, nanoparticle, and oil interactions. Specifically we examine the fluid interface contact angles, rock surface wettability modification, nanoparticle distribution and retention, and effects of nanoparticle coating on its interfacial characteristics in four different cases: i) CO$_2$ and oil, ii) CO$_2$ water and oil, iii) CO$_2$ nanoparticle and oil, iv) CO$_2$ surfactant and oil. Multiphase fluorescence visualization allows for the examination of the phase partitioning of CO$_2$, water, nanoparticle, and oil at pressures below MMP and above MMP. We also examine the swelling mechanism of oil due to CO$_2$ absorption in the oil phase.
6.2 Experimental setup

Four types of experiments were carried out to investigate the interactions between various phases of oil, water, nanofluid, rock. For each case, contact angle measurements in microchannels were performed at different injection pressures using the following combinations: CO₂ and oil, CO₂ and water, CO₂ and nanofluids, CO₂/nanofluid/oil. The experimental setup is shown in Appendix 1: Figure S1. The chip was fabricated from silicon and glass anodic bonding to produce high pressure bond. The chip was fabricated with etched channels using deep reactive ion etching (DRIE), with channel dimensions in the main channel of (100µm x 100µm) cross sectional area and channel dimension of the side channels are also (100µm x 100µm). The connections on the chip were made with a stainless steel manifold with Viton ring seals, enabling high pressures.

In each experiment, the chip is filled with oil then displaced by CO₂, brine, or nanofluid. Then the system is pressurized with CO₂. For each step of CO₂ pressurization a video image sequence is taken to record the contact angles, volumetric shape changes of the phases.

Multiphase imaging was obtained using a series of dyes and matching filter sets which have been selected based on excitation and emission wavelengths of fluorophores. The fluorophores used range from blue to red with match filter sets with wave lengths from 400 to 700 nm. The fluorophore used for water phase is cascade blue which excite and emit the blue region. Fluorescent nanoparticles have absorption and emission in the green region. The dye for oil phase is Nile Blue with absorption/emission in the red wavelength region.

6.3 Results and Discussions

Contact angle measurements in microchannels were performed for four cases: CO₂ and oil, CO₂ and water, CO₂ and nanofluids, CO₂/nanofluid/oil. The interaction of CO₂ and brine results in changes to the contact angle of the water phase from 108° to 151° as the pressure increases from 7 bars to 104 bars. There are three distinct regions of contact angle changes with pressure as shown in Figure 6-2. At pressure below 50 bar the contact angle increases slowly to ~120°, a sharp increase in contact angle is then observed (120° to 150°) at pressures
between 50 – 80 bar due to the phase change of CO₂ from gas to liquid phase which causes the interfacial tension changes of gas/liquid to liquid/liquid terms of the Young’s equation it can be inferred that that liquid/liquid interfacial tension is smaller than the gas/liquid interfacial tension which causes the increase in contact angles. Further increases in pressure beyond 80 bar, CO₂ is in the liquid phase and the change in contact angle is small since there are no phase change. It can also be inferred from the contact angles that the micro-channel surface become more hydrophobic as the pressure is increased.

Contact angle measurement for CO₂ and nanofluid of silica fluorescent nanoparticles also show three distinct regions of contact angles as pressure is increased. The low pressure region below 50 bar the contact angle of the water phase increase from 105° to 115°. At the phase change region pressure from 50 – 80 bar the contact angles increase sharply from 115° to 130°, after that in the liquid CO₂ region the contact angle increases slowly to 134°. The nanofluid contact angles are generally lower than the contact angles of water, indicating that nanofluid makes the microchannel more water wet; this is good for oil recovery.

Contact angle measurements are based on Young’s equation

\[ \cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \]  

(8)

Where the interfacial tension terms are:

\( \gamma_{sv} \) is the solid/vapour interfacial tension which is silicon/CO₂ interfacial tension.

\( \gamma_{sl} \) is the solid/liquid interfacial tension which is the silicon/brine or silicon/oil interfacial tension.

\( \gamma_{lv} \) is the liquid/vapour interfacial tension which is the brine/CO₂ or oil/CO₂ interfacial tension.
Figure 6-1 CO₂ and water phases in closed-end microfluidic channels at various pressures.
Figure 6-2 Contact angles changes with CO₂ pressure increases. CO₂/brine (blue) and CO₂/nanoparticles (green) were measured in this study using microfluidic channels, the red dotted line was measured using capillary tube from literature data.
Figure 6-3 CO₂ and nanofluid phases in closed-end microfluidic channels at various pressures.
Pore scale interaction of CO₂/brine/oil/rock were examined by observing the change in contact in contact angles and oil swelling as the pressure of CO₂ is increased from 5 bar to 100 bar. At low pressure the oil contact angle is ~ 70° indicating that the microchannel is oil wet initially. As the pressure is increased from 5 bar to 100 bar the oil contact angle gradually increases to 135°, indicating the microchannel is water wet at high pressure. The high pressure CO₂ changes the wettability of the silicon/glass microchannel surface due the acidification of the brine phase. The oil phase also swells significantly as the pressure is increased.

For the case of CO₂/nanofluid/oil/rock interactions, contact angles were measured by increasing pressure from 5 bar to 100 bar, the oil contact angles changes with CO₂ pressure (Figure 6-4). At low pressure contact angle was around 80° indicating an oil wet surface, as pressure is increased from 5 bar to 100 bar the oil contact angles gradually increases to ~140° indicating the channel surface has changed from oil wet to water wet at high pressure. The higher oil contact angle of nanofluid case shows that nanofluid makes the channel surface more water wet than the pure brine case. Making the pore surface more water wet can help increase oil recovery.

These two observations carbonate water injection would improve oil recovery with pore surface wettability modification. Nanofluids make the surfaces even more water wet.
As the pressure of CO₂ increases, the oil swells with high initial CO₂ absorption rate as can be seen from the rising oil volume as shown in Figure 6-5. At saturation pressure, further increase in CO₂ pressure results in small increases in oil volume. The oil volume stays almost constant until reaches close to MMP pressure then CO₂ starts to displace oil from the side channels. These processes have been observed using high pressure cell method to measured CO₂ and oil MMP based on the vaporization and extraction oil components from the tube volume.
Figure 6-5 Oil swelling due to CO₂ injection pressure increases, initial swelling rate is fast then it stabilize.

6.4 Conclusions

The work in this chapter shows that multiphase fluorescence imaging with microfluidic channels is very capable of assessing and measuring the effects of reservoir fluid interactions with pore wettability modifications and interfacial tensions changes through contact angle measurements. Increasing CO₂ pressure changes contact angles from oil wet to water wet. Nanofluid also changes the channel surface to become more water wet. Increasing water wettability is favorable for oil recovery processes.
7 Conclusions

This thesis describes the microfluidic and micro-core methods used to study CO₂ enhanced oil recovery and carbon storage with several projects summarized below:

7.1 Nanoparticle stabilized CO₂ foam EOR

Nanoparticle CO₂ foam stability and EOR efficiency were evaluated here using a micromodel approach. Foam stability tests within the micromodel provided a quantitative measurement of bubble size and coalescence dynamics that cannot be observed or quantified in bulk foam testing methods. The nanoparticle-stabilized CO₂ foams maintained excellent stability within micro-confined media, and continued to be stable after 10 days as compared to less than one day for surfactant foam. A nanoparticle-stabilized CO₂ foam flood was performed following a water-flood in an initially oil-filled micromodel. As compared to an otherwise similar case with CO₂ gas, the nanoparticle-stabilized CO₂ foam showed a three-fold increase in oil recovery (an additional 15% of IOIP) comprehensively sweeping the reservoir. With other factors controlled, the higher sweep efficiency obtained with CO₂ nanoparticle foams is predominantly attributed to the role of the physical pore-scale bubble structures which are rendered very stable by the presence of nanoparticles. Secondary effects, such as nanoparticle-influenced wetting characteristics may also play a role. Fluorescence imaging was applied to quantify emulsion size distribution (down to 1µm) in both CO₂ and nanoparticle-stabilized CO₂ foam flood cases. Nanoparticle-stabilized CO₂ foam flooding resulted in significantly smaller oil-in-water emulsion sizes with an average size of 1.7 µm (~ 80 % smaller than a CO₂ gas flood), and negligible impact on water-in-oil emulsions. Lastly the nanoparticle-stabilized CO₂ foam strategy was applied to oil recovery tests (post water-flood) with light, medium and heavy oil. All three oils show substantial additional oil recovery (11% IOIP for light oil, 15% IOIP for medium heavy oil, and 8% IOIP for heavy oil). These results indicate significantly improved oil recovery, particularly for medium oil, and a potentially valuable reservoir-homogenization effect for all oils tested.
7.2 Microfluidic method for measuring CO\textsubscript{2} and oil MMP

In summary, we demonstrate a microfluidic method for measuring CO\textsubscript{2} and oil MMP which provides two distinct advantages over conventional methods: fast measurement speed and quantitative analysis. In terms of speed, MMP can be obtained within 30 min using our microfluidic technique, compared to days or weeks using traditional methods such as RBA, slim tube or vanishing interface methods. Further, in leveraging the inherent fluorescence of crude oils, we achieved heightened contrast between CO\textsubscript{2} and oil, and provided the means of quantitative, user-independent, MMP measurement. Microfluidic MMP measurements were validated with the established RBA method data, showing a strong agreement with expected values under CO\textsubscript{2} reservoir-relevant conditions. Collectively these results demonstrate the potential to inform and improve the largest current CO\textsubscript{2} operations worldwide.

7.3 Micro-core method for examining porosity and permeability changes due to CO\textsubscript{2} injection in carbonate reservoir

A micro-core method was developed to study the porosity and permeability changes in limestone due to supercritical CO\textsubscript{2} and CO\textsubscript{2}-saturated brine core flooding at reservoir temperature and pressure conditions of 8.4MPa and 40 °C. Encasing a small scale core sample within a microfluidics-type infrastructure enabled excellent experimental control and rapid testing as compared to traditional core-study methods. Pore scale imaging of the carbonate dissolution in the case of CO\textsubscript{2}-saturated brine injection reveals large pore size increase and extensive increase in pores connectivity, and a resulting increase in permeability. For the case of pure CO\textsubscript{2} injection, very minor changes in pore structures were observed which results in a small increase in permeability. The results from chemical analysis are also consistent with the pore scale visualization of carbonate dissolution and the permeability measurements. The concentration of the produced calcium and magnesium ions are much higher for the CO\textsubscript{2}-saturated brine injection than the pure CO\textsubscript{2} injection. The carbonate dissolution rate is higher during the first hour and then reduces to an almost constant rate for the last 2 hours in the CO\textsubscript{2}-saturated brine injection case. This thesis demonstrates the efficacy of the micro-core method for rapid pore scale characterization of CO\textsubscript{2}-brine-rock interactions. This work leverages established advantages of microfluidics in the new context of core-sample analysis, specifically
providing a simple core sealing method, small sample size, small volumes of injection fluids, fast characterization time, and pore scale visualization.

### 7.4 Contact angle measurements and wettability modifications of pores due to reservoir fluids

Four cases of experiments were carried out to investigate the interactions between various phases of oil/water/nanofluid/rock interactions. For each case contact angle measurements in microchannels were performed at different injection pressures: CO$_2$ and oil, CO$_2$ and water, CO$_2$ and nanofluids, CO$_2$/nanofluid/oil. The interaction of CO$_2$ and brine results in changes of contact angle of the water phase from 108° to 151° as the pressure increases from 7 bars to 104 bars. There are three distinct regions of contact angle changes: at pressure below 50 bar the contact angle increases slowly to ~ 120°, a sharp increase in contact angles from 120° to 150° occurs at pressures between 50 – 80 bar due to the phase change of CO$_2$ from gas to liquid phase which causes the interfacial tension changes of gas/liquid to liquid/liquid terms of the Young’s equation it can be inferred that that liquid/liquid interfacial tension is smaller than the gas/liquid interfacial tension which causes the increase in contact angles. Further increases in pressure beyond 80 bar, CO$_2$ is in the liquid phase and the change in contact angle is small since there are no phase change. It can also be inferred from the contact angles that the microchannel surface become more hydrophobic as the pressure is increased.

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References


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Appendix 1: Chapter 4 Supporting Information

S1. MMP experimental setup

Figure S1. Schematic of the microfluidic MMP measurement experimental setup.

S2. Materials

Synthetic oil mixtures were prepared with various compositions of pentane and hexadecane (99.9% purity, Sigma Aldrich). Carbon dioxide was of 99% purity (Praxair). Synthetic oil mixtures and crude oils studied in this work are listed in Table S1. A ternary diagram (Figure S2) was prepared using CMG Winprop reservoir fluids simulation software showing multiple contact miscibility between CO₂ and synthetic oil.
Table S1. Synthetic oil and crude oil compositions and densities

<table>
<thead>
<tr>
<th>Oil</th>
<th>Density (API)</th>
</tr>
</thead>
<tbody>
<tr>
<td>67.5% pentane + 32.5% hexadecane</td>
<td>79</td>
</tr>
<tr>
<td>50% pentane + 50% hexadecane</td>
<td>72</td>
</tr>
<tr>
<td>43% pentane + 57% hexadecane</td>
<td>68</td>
</tr>
<tr>
<td>30% pentane + 70% hexadecane</td>
<td>63</td>
</tr>
<tr>
<td>Pennsylvania crude</td>
<td>48.8</td>
</tr>
<tr>
<td>Saudi crude</td>
<td>37</td>
</tr>
<tr>
<td>West Texas Intermediate crude</td>
<td>38.9</td>
</tr>
</tbody>
</table>

Figure S2. Ternary phase diagram of synthetic oil (pentane and hexadecane) multiple contact miscibility with CO₂.
S3. Fluorescence intensity analysis

Figure S3. Differentiated intensity plots at various pressures in a range spanning MMP.
Appendix 2: Silicon Chip Fabrication

Fabrication process layout:

- Silicon wafer
- Photoresist coating
- Exposed and developed
- DRIE etching
- Photoresist removal
- Anodic bonding to glass
Silicon chip fabrication materials and process procedures:

**Materials:**

- Silicon wafer
- Photoresist: S1818
- Primer: HMDS
- Developer: MF312

**Lithography**

1. Coat the wafer with HMDS cycle 90sec at 3000rpm with medium accel.
2. Coat the wafer with S1818 at 3000rpm for 90sec
3. Soft bake at 100C for 5 to 10 min
4. Expose on MA4 for 90sec
5. Develop in 1:1 MF312:1DI water for about 2min.

**DRIE Etching**

1. Use general Bosch process (~10 um/min)
2. Etch 252 cycles for 12 minutes (etch depth ~100um)
3. Or Fast etch process (~20 um/min)
4. Etch 5 min (50 cycles)
Anodic Bonding

1. Apply heat to 400 C

2. Apply force 100N

3. Apply voltage 600V

4. Set current limit 4 mA

5. Bond 10 minutes
Appendix: 3 Microbial enhanced oil recovery using sandstone rock pattern micromodel

Microbial enhanced oil recovery (MEOR) is a tertiary oil recovery process, where either indigenous reservoir microorganisms are stimulated or a specific, customized blend of microbes are injected deep into an oil well. Nutrients are pumped down as well, and generally consist of a low cost fermentable carbohydrate (e.g. molasses), along with phosphates and nitrates, the latter which act as electron donors during anaerobic cell growth. Over the course of several months, these micro-organisms liberate pore-confined oil through a variety of mechanisms, including interfacial tension (IFT) reduction and wettability alteration, bioclogging or selective plugging, biofilm formation, biogenic gas production, mineral biogenesis and acid production. MEOR has gained momentum of late, both in laboratory trials and in the field, particularly in the context of mature, high water cut reservoirs. Part of the draw of MEOR is that the technique is low-cost and simple to implement, requiring very few modifications to existing infrastructure.
The microfluidic pore network was modelled after the grain structure of a Berea sandstone core. First, a 9 x 9 array of images was taken of a core sample using a scanning electron microscope (SEM), covering an area just under 1 cm² (Fig. 1a). Images were converted to binary by manually thresholding individual images, and stitched together using ImageJ image processing software. After performing image processing detailed in supplementary material, a 5mm x 7.5mm section of the image was copied, and folded over itself 6 times to form the 5 mm wide, 45 mm long microchannel shown in Fig. 1b. Two inlet channels lead into the pore network, labelled “main” and “bypass”. A single outlet channel extrudes from the network, and passes through a resistive element before exiting the device. This configuration was designed to allow inlet fluids to be rapidly and easily replaced, without perturbing the pore network. 
Appendix: 4 High pressure chip manifold

Photo of the high pressure manifold assembly

CAD model of the high pressure manifold assembly