THE EFFECT OF WASTE COOKING OIL ON THE WETTABILTY OF WALLACE SANDSTONE

By

Zakir Ullah

Submitted in partial fulfillment of the requirements
for the degree of Master of Engineering

Major: Petroleum Engineering

at

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DALHOUSSIE UNIVERSITY
PETROLEUM ENGINEERING

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Dedicated to my family
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ABSTRACT

Geological sequestration of Carbon dioxide (CO$_2$) is considered as one of the most promising methods for the reduction of anthropogenic emissions of carbon dioxide (CO$_2$) into the atmosphere. Deep saline aquifers are considered to be the best storage sites for geological sequestration of CO$_2$ because of their huge storage capacity and widespread availability around the world. CO$_2$ injection into the saline aquifers will induce different coupled physical and chemical processes including multiphase flow, solute transport and chemical reaction of CO$_2$ with different reservoir fluids and minerals. The displacement of formation brine by supercritical CO$_2$ (SCCO$_2$) is considered to be an unstable immiscible displacement process due to unfavourable viscosity ratio and density contrast between CO$_2$ and the resident brine, resulting hydrodynamic instabilities including viscous fingering and gravity override. To reduce viscous fingering and improve the stability of the displacement process, the increase in viscosity of CO$_2$ by the use of soluble organics (animal fats, waste cooking oil) has been suggested.

The purpose of this study is to examine the effects of waste cooking oil on the wettability of the formation. In this project, spontaneous imbibition characteristics and how waste cooking oil-brine-rock interactions affects wettability are studied. A comparative study was performed for waste cooking oil and crude oil using four Wallace sandstone core samples. Spontaneous imbibition and Amott wettability test were conducted under laboratory conditions for Wallace sandstone core samples. The results obtained show that the interaction of both types of oil with Wallace sandstone core samples have changed their wettability from water wet to near neutral wet.
LIST OF ABBREVIATIONS AND SYMBOLS USED

API American Petroleum Institute
BRP Benchtop Relative Permeameter
BV Bulk Volume [cm$^3$]
CCS Carbon Capture and Storage
GHG Greenhouse Gases
Gt Giga Tonne
H Height [ft]
IFT Interfacial Tension [dynes/cm]
k Permeability [mD]
k$_r$ Relative permeability [Dimensionless]
k$_e$ Effective permeability [mD]
L Length [cm]
M Mobility ratio [Dimensionless]
P$_c$ Capillary pressure [psi]
P$_{nw}$ Pressure of the non-wetting phase [psi]
P$_w$ Pressure of the wetting phase [psi]
PV Pore volume [cm$^3$]
r Capillary-tube radius [ft]
SCCO$_2$ Supercritical Carbon Dioxide
W$_w$ Wet weight [g]
W$_d$ Dry weight [g]
q Flow rate [cm$^3$/sec]
SI Spontaneous Imbibition
S$_g$, S$_o$, S$_w$ Gas, oil and water saturation respectively [fraction]
WI Wettability index
µ Viscosity [cP]
ρ Density of brine [g/cm$^3$]
Ø Porosity [%]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{ws}$</td>
<td>Water-Soild IFT</td>
<td>dynes/cm</td>
</tr>
<tr>
<td>$\sigma_{ow}$</td>
<td>Oil-Water IFT</td>
<td>dynes/cm</td>
</tr>
<tr>
<td>$\theta_c$</td>
<td>Contact angle</td>
<td>Degrees</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Mobility</td>
<td>mD/cP</td>
</tr>
</tbody>
</table>
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Chapter 1 Introduction

1.1 Background

The global average temperature of the earth is maintained by greenhouse effect (Hartai, 2012). The concentration of greenhouse gases in the atmosphere has increased causing global warming. Carbon dioxide (CO\textsubscript{2}) is one of the most important greenhouse gases. The current concentration of CO\textsubscript{2} in the atmosphere is 390.5 ppm which has increased from the concentration before the Industrial Revolution (cdiac, 2012). Carbon Capture and Storage (CCS) is one of the technologies that can reduce the amount of CO\textsubscript{2} released into the atmosphere from the use of fossil fuel in power plants and other industries. CCS involves the collection or capture of CO\textsubscript{2} produced from power plants and other industries, transportation of the captured CO\textsubscript{2} to a suitable storage site and then pumping it deep underground into the rocks for permanent storage away from the atmosphere. These underground formations may be deep saline aquifers, depleted oil and gas reservoirs, unmineable coal seams, and deep ocean sediments (IPCC, 2005). Among these underground formations, deep saline aquifers are considered to be the best storage sites due to the fact that they are readily available and ubiquitous worldwide, providing an estimated potential storage volume of 10,000 Gt (Stauffer et al., 2011).

CO\textsubscript{2} sequestration in deep saline aquifers involves injection of SCCO\textsubscript{2} into these formations displacing in-situ fluids (brine) from the pore spaces of rocks. The displacement process is directly affected by the physical and chemical properties of both the injected SCCO\textsubscript{2} and displaced formation fluids (e.g. viscosity, interfacial tension, density, solubility), hydrodynamic
forces such as capillary pressure endured during the process, and physical and chemical properties of the porous matrix (e.g. pore size or permeability distribution, wettability of the solid surface) (Zhang et al, 2011). Due to lower density and viscosity of CO₂ as compared to that of water, the CO₂ produces hydrodynamic instabilities, causing viscous fingering and gravity override (Garcia and Pruess, 2003). To reduce viscous fingering and improve the stability of the displacement process, it has been suggested to increase the viscosity of CO₂ by the use of soluble organics (waste cooking oil, animal fats) (Amadu and Pegg, 2013).

In the petroleum industry, viscosification of CO₂ is achieved by the use different chemicals such as trialkytin fluorides and aluminum disoap, but these chemicals are very expensive which makes the cost of the project very high (Enick and Olsen, 2012). In geological sequestration of CO₂, where no valuable product is obtained, the use of such chemicals will increase the operating cost of the project. Therefore there is a need for a cheaper alternative that will dissolve in supercritical CO₂ and will increase its dynamic viscosity. One such possible cheap source for increasing the viscosity of CO₂ is fats, which are available in abundance (Stoytcheva, 2011). Organic compounds such as fats dissolve in SCCO₂ and increase its viscosity.

Wettability of reservoir rock and minerals is an important factor in controlling the mobility, residual trapping and caprock breakthrough pressure (leakage) of the injected CO₂. Wettability of reservoir rocks strongly influences CO₂ flow and distribution, and quantities of residual trapping. (Kim et al, 2012). Knowledge of the wettability of reservoir rock and its effects on petrophysical properties and CO₂ sequestration are important factors that are considered in CO₂ sequestration.
Displacement characteristics of gas-oil-brine-rock systems have been thoroughly investigated in petroleum sector and there is a lot of data available for CO$_2$-oil-brine-rock systems as a result of its use for enhanced oil recovery. There is also literature work which describes CO$_2$ and reservoir rocks interaction (Kim et al., 2012; Wang et al., 2012; Rosenbauer et al., 2005). However there is no data available for waste cooking oil-brine-rock interaction and this research, together with its primary objectives, serves to bridge this gap in knowledge and data availability of such systems.

1.2 Objectives

The main purpose of this study is to investigate the effect of waste cooking on the wettability. This will be investigated by performing a comparative study for waste cooking oil and crude oil. Wallace sandstone core samples will be subjected to spontaneous imbibition and Amott test. The changes in wettability will be observed from oil/brine/rock interaction.
Chapter 2 Literature Review

The literature review consists of two sections. The first section describes the global warming effect, geological sequestration of CO₂, waste cooking oil and the viscosity of SCCO₂ having waste cooking oil. The second part focuses on flow through porous media, the forces that influences flow in porous media, instable displacement, wettability and different mechanisms that may cause alteration in wettability.

2.1 The Global Warming Effect

The Earth’s atmosphere contains a number of different gases, including greenhouse gases (GHG). According to the Intergovernmental Panel on Climate Change (IPCC, 2001) "Greenhouse are those gaseous constituents of the atmosphere, both natural and anthropogenic, that absorb and emit radiation at specific wavelengths within the spectrum of infrared radiation emitted by the Earth's surface, the atmosphere and clouds. This property causes the greenhouse effect. Water vapour (H₂O), carbon dioxide (CO₂), nitrous oxide (N₂O), methane (CH₄) and ozone (O₃) are the primary greenhouse gases in the Earth's atmosphere."

The global average temperature of the Earth is maintained by sunlight received, reflected and heat energy trapped and reradiated back to the earth by the atmosphere. The gases which absorb and reradiate the emissions are GHG and this process is called the greenhouse effect. The earth is progressively becoming warmer by this process (Hartai, 2012). According to the U.S. Environmental Protection Agency, global warming is defined as “The average increase in the temperature of the atmosphere near the Earth’s surface and in the troposphere, which can
contribute to changes in global climate patterns. Global warming can occur from a variety of causes, both natural and human induced. In common usage, “global warming” often refers to the warming that can occur as a result of increased emissions of greenhouse gases from human activities.” Due to anthropogenic carbon dioxide (CO$_2$) emissions, the atmospheric concentrations of CO$_2$ have risen from 280 ppm to more than 392 ppm. This increase in concentration of CO$_2$ is affecting the Earth’s atmosphere energy balance, enhancing the greenhouse effect and thereby causing a warming influence at the Earth’s atmosphere (Bachu, 2003).

Currently more than 40% of CO$_2$ emissions are produced from power generation by electric power plants worldwide. About 90% of the total primary energy sources in the world are fossil fuel (Espinoza, 2011). The emission of CO$_2$ is closely related to the use of fossil fuel. The IPCC (2005) have suggested different options for the reduction of CO$_2$ emission into the atmosphere. Among them one potential method is the storage of CO$_2$ in underground geological formations.

2.2 Geological Sequestration of CO$_2$

According to Bachu (2003), geological sequestration of CO$_2$ is “the removal of CO$_2$ directly from anthropogenic sources (capture) and its disposal in geological media either permanently (sequestration) or for significant time periods (storage)”.

Geological sequestration is considered to have the greatest CO$_2$ storage potential significant enough to result in noticeable reduction of atmospheric CO$_2$.

The geological storage of CO$_2$ is a complex process and the important factors that should be considered include preferential flow, sweep efficiency, leakage rates, CO$_2$ dissolution kinetics, mineral trapping kinetics, microbial interactions with CO$_2$, and the influence of stress changes on cap rock and formation integrity (Shukla et al., 2010).
2.2.1 Options for Geological Storage of CO₂

There are several options available for the geological storage of CO₂.

**Depleted Oil and Gas Reservoirs**

Depleted oil and gas reservoirs are suitable candidates for geological storage of CO₂. After the depletion of oil and gas reservoirs, CO₂ may be stored in the available pore space previously occupied by hydrocarbons. The injection of CO₂ can also be used for the recovery of additional oil that was left behind during primary production, known as enhanced oil recovery (Dooley et al., 2006). The existing wells in these reservoirs provide immediate access to these reservoirs and also a large amount of data is available about the characteristics of these reservoirs which will be helpful in understanding the dynamics of CO₂ storage.

**Unmineable Coal Seams**

CO₂ can be stored in deep unmineable seams adsorption. Methane is found on the surface of coal. When CO₂ is injected, due to higher chemical preference for CO₂ than methane, the coal releases the previously adsorbed methane and adsorbs CO₂. Methane can then be recovered by enhanced coal bed methane (ECBM) technology. The theoretical global capacity for unmineable coal seam is 140 GtCO₂ (Dooley et al., 2006).

**Deep Saline Formations**

Deep saline formations offer encouraging storage opportunities because of their occurrence in sedimentary basins throughout the world. In many parts of the world, injection of waste fluids into deep saline formation is a common practice (Dooley et al., 2006). The minimum theoretical global capacity of CO₂ storage in deep saline aquifers is estimated to be 1000 GtCO₂ (IPCC, 2005).
2.2.2 CO₂ Trapping Mechanisms

The trapping of CO₂ in deep geological formation is based on physical as well as chemical processes. Structural and stratigraphic trapping by cap rocks, hydrodynamic trapping by slow aquifer currents and capillary trapping by interfacial forces are types of physical trapping mechanisms. While dissolution of CO₂ in water, mineralization, CO₂ adsorption on coal and rich organic shale, and CO₂ hydrate formation are included in chemical trapping (Espinoza et al, 2011).

Stratigraphic and Structural Trapping

This is the most dominant mechanism for trapping CO₂. This phase in the trapping process refers to the trapping of CO₂ beneath a seal and requires the presence of structural and stratigraphic trap of the same type as those that results in the accumulation of hydrocarbons. Structural trapping is considered to be an unreliable method because CO₂ remains mobile and the existence of pre-existing well or the activation of a fault may cause leakage of CO₂ to the shallow formations (MacMinn and Juanes, 2009).

Hydrodynamic Trapping

In hydrodynamic tapping, CO₂ is trapped as a gas or supercritical fluid under a low permeability cap rock. This method is considered to be a fast trapping mechanism. The density of CO₂ is less than that of formation water therefore it will naturally rise to the top of reservoir. To prevent its escape, low permeability cap rock is needed. Therefore, characterization of a caprock is important requirement (Sengul, 2006).
**Capillary Trapping**

Capillary trapping of CO₂ occurs during water flooding when the gas saturation is decreasing and water saturation increases as water invades the pore space. During CO₂ injection into the geological formation, the gas saturation increases in a drainage like process. Due to buoyancy forces the gas phase migrates upward to the top of the aquifer as it moves away from the injection well. Once the injection stops, the CO₂ continues to migrate upward. At the leading edge of the plume, gas continues to displace water in a drainage process (increasing gas saturations) while at the trailing edge water displaces gas in an imbibition process (increasing water saturations). The presence of an imbibition saturation path leads to snap-off and subsequently causes trapping of the gas phase. As the plume migrates upward a trail of residual immobile CO₂ is left behind (Juanes et al., 2006). This method is also known as residual trapping.

**Solubility Trapping**

CO₂ dissolves in other fluids in its gaseous and supercritical state. The injected CO₂ dissolves in formation brine. This dissolving of CO₂ in formation brine increases the density of the CO₂. The CO₂ saturated brine is denser than the surrounding formation fluids. Therefore it migrates deeper into the formation and slowly dilutes through contact with unsaturated brine at depth.

**Mineral Trapping**

Mineral trapping is also an important mechanism but it takes a very long time as compared to other trapping mechanisms. In this process, CO₂ dissolves in formation brine forming carbonic acid (H₂CO₃). This weak acid reacts with the minerals in the surrounding rock, forming carbonate minerals which are then stored as a chemical compound.
2.3 CO₂ Sequestration Mechanism

2.3.1 Phase Behaviour of CO₂

CO₂ gas is colourless, odourless and is denser than air. The critical point at which CO₂ becomes a supercritical fluid is 31.1 °C and 7.38 MPa. In the supercritical state, large gradients in properties such as density, viscosity and solvent strength can occur at conditions near the phase boundary. CO₂ is preferably injected in saline aquifers in the supercritical state. The density of CO₂ at supercritical state is higher than CO₂ gaseous state. The density of CO₂ at supercritical condition ranges from 150 kg/m³ to over 800 kg/m³. The density of CO₂ stored in underground formations depends on the pressure and temperature. Assuming hydrostatic pressure and a geothermal gradient of 25°C/km from 15°C at the surface, the density of CO₂ increases rapidly at approximately 800m depth, when CO₂ reaches a supercritical state as shown in figure 2.1. Cubes shown in the figure 2.1 represents the relative volume occupied by the CO₂ and down to 800m, this volume can be seen to dramatically decrease with depth. At depths below 1.5 km, the density and specific volume become nearly constant (IPCC, 2005). The solubility of CO₂ in water increases with increasing pressure and decreases with increasing temperature. In a typical sequestration reservoir, the temperature and pressure are generally higher than the super critical values of CO₂ but the hydro- mechanical conditions in the reservoir may change in some cases resulting a change in the phase and behaviour of injected CO₂ (Shukla et al., 2010).
2.3.2 CO₂ Flow in Reservoir Formation Rocks

CO₂ injection into saline aquifers for storage can be classified as an immiscible displacement process. During CO₂ sequestration, the injection of CO₂ into saline aquifers will induce different physical and chemical processes. The displacement of the resident brine by less dense and less viscous CO₂ is a complex process and is affected by viscous, capillary and buoyancy forces. The flow is subjected to hydrodynamic instabilities including viscous fingering and gravity override. According to Garcia (2003), the injection of CO₂ into saline aquifers also increases the pore pressure as there is no production of fluids which may balance the system pressure. As a result, the pore pressure increases which may alter the effective stress state causing variations in porosity and permeability. A large change in the stress field can cause leakage of CO₂ through the fractured rocks. Another important process that is considered in CO₂ sequestration is the effect of injected CO₂ on formation fluids and minerals. CO₂ dissolves in formation brine

Figure 2.1 Variation of CO₂ Density with depth (IPCC, 2005)
forming carbonic acid which may react with different rocks. CO₂ can also react with certain minerals directly forming precipitates of carbonates which decreases porosity and can also reduce permeability.

### 2.4 Waste Cooking Oil

Waste cooking oil and animal fats are available in huge quantities around the world. The management and disposal of such oils and fats is a great problem and requires the use of proper disposal method to avoid possible contamination of the water and land resources. Due to concerns over sustainability, environmental issues and raw material costs, the use of waste cooking oil is very attractive to industries. The use of all waste oils as domestic animal feed has been banned by the European Union because of the harmful compounds that are formed during frying process (Lam et al., 2010).

Cooking oil is glycerol ester of fatty acids. Cooking oil comprises of fat molecules, which are composed of triesters. When an acid and alcohol reacts it releases water and forms an organic compound known as ester. A triester is an organic compound that is formed as a result of chemical reaction of a molecule that contains three hydroxyl groups (−OH) called glycerol and three fatty acid molecules, each composed of long hydrocarbon chains (R) and a carboxylic acid group (−COOH). The terms “oils” is used for fats that are liquid at room temperature while “fats” that are solid at room temperature are known as fats (Nolte, 2011). Triglycerides are the main components of fats and oil (95%), while the minor components are mono and diglycerides, free fatty acids, phosphatides, sterols, fat soluble vitamins, tocopherols, pigment, waxes, and fatty alcohols. Based on the source of oil, the free fatty content varies from oil to oil (AOCS, 2006). Triglycerides molecules are composed of carbon and hydrogen atoms with only six
oxygen atoms per molecule which means that fats and oil are highly reduced (un-oxidized). In this way they are similar to the hydrocarbons in petroleum (Shakhashiri, 2008).

Waste cooking oil is the product of used cooking oil. Most of the cooking oil is used for deep-frying processes. During frying, oil is heated under atmospheric condition at temperature of (160-190 °C) for long period of time again and again. Due to continuous use of same oil for frying, various physical and chemical changes occur in the oil. Some physical changes that are commonly observed in vegetable oil after frying are increase in viscosity, increase in specific heat, change in surface tension and change in colour. In addition, the oil is also subjected to three types of reactions during frying, mainly thermolytic, oxidative and hydrolytic. These three reactions cause the formation of many undesirable and harmful compounds if the oil is used repeatedly (Lam et al., 2010). The table below summarizes the main group of alteration compounds that are formed during frying process in the presence of air and moisture from oil and fats at high temperature of around 180° C.

**Table 2.1 Main groups of compounds formed during frying (Dobarganes, 2009)**

<table>
<thead>
<tr>
<th>ALTERATION</th>
<th>CAUSATIVE AGENT</th>
<th>NEW COMPOUNDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
<td>Moisture</td>
<td>Fatty acids</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diacylglycerols</td>
</tr>
<tr>
<td>Oxidation</td>
<td>Air</td>
<td>Oxidized monomeric triacylglycerols</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oxidized dimeric and oligomeric triacylglycerols</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Volatile compounds (aldehydes, ketones, alcohols,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>hydrocarbons, etc.)</td>
</tr>
<tr>
<td>Thermal alteration</td>
<td>Temperature</td>
<td>Cyclic monomeric triacylglycerols</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Isomeric monomeric triacylglycerols</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nonpolar dimeric and oligomeric triacylglycerols</td>
</tr>
</tbody>
</table>
Hydrolysis takes place due to the presence of moisture in the food. The process involves the breaking of ester bonds, releasing free fatty acids, diacylglycerols and non-volatile compounds with molecular weight significantly lower than that of the parent triacylglycerols. Additionally, oxidation and thermal alteration occurs in the unsaturated fatty acids due to the presence of air and exposure to high temperature forming triacylglycerols with at least one of the three fatty acyl chains altered. The new compounds that are formed have higher polarity than the polarity possessed by the initial triglycerides (Ruiz-Méndez et al., 2008).

2.5 Solubility of Waste Cooking Oil in SCCO$_2$

CO$_2$ is the most widely used fluid in supercritical fluid extraction (SFE) technology. SCCO$_2$ is nontoxic, shows greater affinity to volatile (lipophilic) compounds, easily and completely removable from any extract at low critical temperature and pressure (Mićić et al, 2011). The solubility of fats in SCCO$_2$ is evident from food and pharmaceutical industry. The use of SCCO$_2$ for the production of high grade leather products also shows the solubility of animal fats in SCCO$_2$ (Marsal et al., 2000). The solubility of fats in SCCO$_2$ can be seen from Table 2.2
Table 2.2 Extractability as a function of CO₂ Density (Marsal et al., 2000)

<table>
<thead>
<tr>
<th>CO₂ Density (g/ml)</th>
<th>Extracted fat&lt;sup&gt;a&lt;/sup&gt; (mg)</th>
<th>Residual fat&lt;sup&gt;b&lt;/sup&gt; (mg)</th>
<th>Total fat (mg)</th>
<th>Degreasing Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55 (104 bar)</td>
<td>2.5</td>
<td>40.4</td>
<td>42.9</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>45.2</td>
<td>46.6</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>37.4</td>
<td>38.9</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>36.6</td>
<td>40.6</td>
<td>9.8</td>
</tr>
<tr>
<td>0.70 (133 bar)</td>
<td>6.1</td>
<td>41.1</td>
<td>47.2</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>36.5</td>
<td>41.7</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>13.7</td>
<td>31.5</td>
<td>45.2</td>
<td>30.3</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>30.7</td>
<td>37.2</td>
<td>17.5</td>
</tr>
<tr>
<td>0.85 (240 bar)</td>
<td>24.5</td>
<td>18.3</td>
<td>42.8</td>
<td>57.2</td>
</tr>
<tr>
<td></td>
<td>22.4</td>
<td>21.7</td>
<td>44.1</td>
<td>50.8</td>
</tr>
<tr>
<td></td>
<td>23.6</td>
<td>19.4</td>
<td>43.0</td>
<td>54.9</td>
</tr>
<tr>
<td></td>
<td>23.8</td>
<td>21.4</td>
<td>45.2</td>
<td>52.6</td>
</tr>
</tbody>
</table>

<sup>a</sup> Fat extracted by SCCO<sub>2</sub>

<sup>b</sup> Fat determined by extraction with methylene chloride after the degreasing process

### 2.6 Viscosity of SCCO<sub>2</sub> Containing Fats

SCCO<sub>2</sub> behave like a liquid due to high density and at the same time behave like a gas due to its viscosity that is in the range of gases. To get an idea about the viscosity of SCCO<sub>2</sub> containing fats, the previous published work is reviewed. Yener et al. (1998) measured the viscosities of SCCO<sub>2</sub> containing different levels of methyl oleate and oleic acid. Both the systems were evaluated at different pressures and temperatures. The evaluation indicated the linear increase of relative viscosity with concentration. The SCCO<sub>2</sub> viscosity increased by 15-20% at maximum ethyl oleate concentration (4-5 wt. %) and 6-12 % at the maximum oleic acid concentration (2-3 wt. %). Table 2.3 shows the estimated viscosity of SCCO<sub>2</sub> saturated with solute at various temperatures.
Table 2.3 Estimated viscosity of SCCO$_2$ saturated with a solute at various temperatures and pressures (Tuan et al., 1999).

<table>
<thead>
<tr>
<th>Solute</th>
<th>Pres. (MPa)</th>
<th>Temp. (K)</th>
<th>CO$_2$ Density (Kg/m$^3$)</th>
<th>CO$_2$ Viscosity (E +07 Pa.s)</th>
<th>Solute mass fraction at saturation (E+02)</th>
<th>Increase in viscosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO</td>
<td>10.6</td>
<td>313.15</td>
<td>666.0</td>
<td>513.2</td>
<td>6.07</td>
<td>25.8</td>
</tr>
<tr>
<td></td>
<td>11.5</td>
<td>313.15</td>
<td>704.8</td>
<td>566.7</td>
<td>8.88</td>
<td>35.3</td>
</tr>
<tr>
<td></td>
<td>13.7</td>
<td>323.15</td>
<td>665.4</td>
<td>512.6</td>
<td>6.24</td>
<td>24.7</td>
</tr>
<tr>
<td></td>
<td>15.5</td>
<td>333.15</td>
<td>624.5</td>
<td>487.3</td>
<td>4.39</td>
<td>14.8</td>
</tr>
<tr>
<td>OA</td>
<td>20.5</td>
<td>313.15</td>
<td>846.5</td>
<td>778.8</td>
<td>1.90</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>313.15</td>
<td>911.8</td>
<td>930.2</td>
<td>3.68</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>333.15</td>
<td>831.3</td>
<td>773.7</td>
<td>3.83</td>
<td>14.2</td>
</tr>
<tr>
<td>AMF</td>
<td>25.0</td>
<td>313.15</td>
<td>881.5</td>
<td>850.5</td>
<td>2.32</td>
<td>12.0</td>
</tr>
</tbody>
</table>

MO: Metheyl Oleate
OA: Oleic Acid
AMF: Anhydrous Milk Fat
Chapter 3 Flow through Porous Media

3.1 Porosity

Porosity is defined as the ratio of pore volume (or void space) in a reservoir rock to the total volume (bulk volume) and is expressed as a percentage. The pore volume basically refers to the summation or combined volume of all the pore spaces in a given reservoir rock. It is denoted by \( \phi \) and is mathematically expressed by the following relationship (Dandekar, 2006)

\[
\phi = \frac{\text{pore volume}}{\text{total or bulk Volume}}
\]  

(3.1)

According to Ahmad (2000), after the deposition of sediments and the formation of rocks during past geological times, some void spaces that developed became isolated from the other void spaces due to excessive cementation. As a result, some of the pores become interconnected while some of the pore spaces are completely isolated, leading to two different types of porosity, absolute and effective. Absolute porosity is the ratio of the total pore volume in the rock to the bulk volume while effective porosity is the ratio of interconnected pore volume to the bulk volume.

The initial (pre-diagenesis) porosity depends on various factors such as grain size, grain packing, particle shape, and the distribution of grain sizes. Porosity is also controlled by different secondary processes that result in compaction and dilatation. These can be categorised into mechanical process (stress compaction, plastic deformation, brittle deformation, fracture evolution etc.) and geochemical processes (dissolution, reprecipitation, volume reductions concomitant upon mineralogical changes etc.) (Glover, 1998). The porosities of petroleum
reservoir rocks typically range from 5 to 40%, with a range of 10 to 20% being more common (Dandekar, 2006).

3.2 Permeability

Permeability is defined as is the measure of the capacity and ability of the medium to transmit fluids. Permeability is one of the most important fluid flow parameters of porous media providing information about the fluid flow rate in the reservoir rock. It is denoted by k.

In 1856 a French hydraulic engineer Henry Darcy presented a law known as Darcy’s law. This law defines permeability in terms of measureable quantities. Mathematically Darcy’s law can be expressed as (Cosse, 1993)

\[ q = \frac{k \Delta P}{\mu \frac{A}{L}} \]

Where

- \( q \) = flow rate \([m^3/s]\)
- \( \Delta P \) = Difference between inlet and outlet pressure \([Pa]\)
- \( k \) = Permeability coefficient \([m^2]\)
- \( \mu \) = Viscosity \([Pa.s]\)
- \( L \) = Core length \([m]\)
- \( A \) = Cross sectional area to flow \([m^2]\)

In the SI International system, \( k \) is expressed in square meters \((m^2)\). The practical unit of permeability is Darcy \((D)\) but it is a large unit therefore milli-Darcy \((mD)\) is commonly used in the industry. The permeability of a medium will be one Darcy, if a fluid having a viscosity of one centiPoise is flowing through a cross sectional area of one square centimeter at a flow rate of one cubic centimeter per second and a pressure gradient of one atmosphere per centimeter of length.
1 \text{mD} = 0.987 \times 10^{-15} \text{ m}^2

Therefore for non SI units permeability can be expressed as

\[ k = \frac{q \mu L}{A \Delta P} \times 2.449593767 \]  \hspace{1cm} (3.3)

Where

\( q = \text{flow rate [cm}^3/\text{min]} \)

\( \Delta P = \text{Difference between inlet and outlet pressure [Psi]} \)

\( k = \text{Permeability coefficient [mD]} \)

\( \mu = \text{Viscosity [cP]} \)

\( L = \text{Core length [cm]} \)

\( A = \text{Cross sectional area to flow [cm}^2] \)

The range of permeability found is very wide. The table 3.1 shows the classification of permeability.

**Table 3.1 Classification of rock permeability (Zhangxin, 1962)**

<table>
<thead>
<tr>
<th>Classification</th>
<th>Permeability range (mD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poor to Fair</td>
<td>1 – 15</td>
</tr>
<tr>
<td>Moderate</td>
<td>15 – 20</td>
</tr>
<tr>
<td>Good</td>
<td>52 – 250</td>
</tr>
<tr>
<td>Very good</td>
<td>250 – 1000</td>
</tr>
<tr>
<td>Excellent</td>
<td>Over 1000</td>
</tr>
</tbody>
</table>
Permeability is generally classified into three types according to the number of fluids that are present in the reservoir.

**Absolute Permeability**

It is the measure of the ability or capability to pass or transfer fluids through a rock, performed when a single fluid, or phase, exists in the rock.

**Effective Permeability**

If more than one fluid is present in the reservoir together at some partial saturation, we then measure effective permeability. Effective permeability is the ability of one fluid to flow in the presence of more than one fluid that is present.

**Relative Permeability**

Relative permeability is the ratio of the effective permeability of a given phase to the absolute permeability. Relative permeability is used when multi-phases are present and flowing through the porous medium.

\[ k_r = \frac{k_e}{k} \]  

(3.4)

Where

- \( k_r \) = Relative permeability
- \( k_e \) = Effective permeability [mD]
- \( k \) = Absolute permeability [mD]

**3.3 Surface and interfacial tension**
Surface and interfacial tension (IFT) are measure of the forces that act on the interface when two immiscible fluids are in contact. The term surface tension is usually used for the tension of a liquid which is in contact with its vapor or with air. IFT refers to the energy between two liquids or a liquid and a surface. When two immiscible fluids (gas-liquid or liquid-liquid) are in contact, there exists a well-defined interface which is only a few molecular diameters in thickness. The molecules attract each other within the fluid, away from the interface and the walls of the container. At the surface between two immiscible fluids there are no similar molecules beyond the interface and therefore there is an inward directed force that attempts to minimize the surface by pulling it into the shape of a sphere. This surface activity creates a film-like layer of molecules that are in tension, which is the function of the specific free energy of the interface. The IFT has the unit of force per unit length (N/m). It is also expressed as dynes/cm (Tiab, 2011).

3.4 Capillary Pressure

Capillary pressure can be defined as the pressure difference across a curved interface between two immiscible fluids in contact as shown in figure 3.1. When two immiscible fluids are in contact, a discontinuity in pressure exists between the two fluids that depend upon the curvature of the interface separating the fluids. This pressure difference is known as capillary pressure and is denoted by $P_c$. In petroleum reservoir, capillary pressure is the result of combined effects of the surface and interfacial tensions of the rock and fluids, the pore size and geometry and IFT of the rock and fluids. The displacement of one fluid by another in a porous medium is either aided or opposed by the surface forces of capillary pressure. The pressure of the non-wetting phase must be greater than the pressure in the wetting phase in order to maintain a porous media partially saturated with non-wetting fluid in the presence of wetting fluid (Ahmed, 2000).
Figure 3.1 Use of capillary tube to measure capillary pressure (Melberg, 2010)

Mathematically, capillary pressure can therefore be expressed as (Melberg, 2010),

\[ P_c = \frac{2\sigma \cos \theta_c}{r} \] (3.5)

Where,

- \( P_c \) = Capillary pressure
- \( \sigma \) = IFT between non wetting and wetting phase [ ]
- \( \theta_c \) = Contact angle measure through the wetting phase [Degrees]
- \( r \) = Radius of cylindrical pore channel

3.5 Saturation

The fraction or percent of the pore volume occupied by a particular fluid (oil, gas or water) is known as saturation (Ahmed, 2000). Mathematically it can be expressed as,
fluid saturation = \frac{\text{total volume of the fluid in the pore}}{\text{PV}}

For different reservoir fluids, the expression can be applied as,

\[ S_g = \frac{\text{Volume of gas}}{\text{PV}}, \quad S_o = \frac{\text{Volume of oil}}{\text{PV}}, \quad S_w = \frac{\text{Volume of water}}{\text{PV}} \]

Where,

\( \text{PV} = \text{pore volume [cm}^3\text{]} \)

\( S_g = \text{gas saturation [fraction]} \)

\( S_o = \text{oil saturation [fraction]} \)

\( S_w = \text{water saturation [fraction]} \)

The sum of the saturation of the various fluid phases is 100%, therefore

\[ S_g + S_o + S_w = 1.0 \quad (3.6) \]

3.6 Gravity Forces

The gravity force is caused by the difference in density between two or more fluids. The fluid which has the lowest density will have the tendency to flow upward in the presence of more dense fluid. The gravity forces are important when the density difference between two fluids is very high, i.e. density difference between oil and gas, or water and gas (Olsen, 2007).

3.7 Viscous Forces

Viscous force arises due to the viscosity of the fluid. The magnitude of the pressure drop that occurs as a result of flow of a fluid through the medium reflects viscous forces in a porous media (Green, 1998).
3.8 Wettability

Wettability can be defined as the tendency of a fluid to adhere to or spread on a solid surface in the presence of other immiscible fluids (Anderson, 1986a). Wettability is a very important characteristic of the rock/fluid system. The origin of wettability is not fully understood however it is admitted that wettability is established as result of the adsorption of polar compounds or deposition of organic materials on the rock surface. Wettability is influenced by different variables that include temperature, contact time, roughness, crystal structure, composition, surface pre-treatment, interfacial segregation, adsorption, and reactions (Donnez, 2007).

The wettability is quantified by the contact angle ($\theta_c$). The contact angle depends on the oil-soil IFT, water-soil IFT and oil-water IFT, as described by Young’s equation,

$$
\sigma_{os} = \sigma_{ws} + \sigma_{ow} \cos \theta_c
$$

(3.7)

Where $\sigma_{os}$ is oil-soil IFT, $\sigma_{ws}$ is water-soil IFT and $\sigma_{ow}$ is oil-water IFT as shown in figure 3.2.

![Figure 3.2 Wettability of oil, water and rock system (Jim, 1992)](image-url)
The contact angle has become a commonly used measure of wettability. $\theta_c$ is always measured through the liquid to the solid surface. For solid with a tendency for water, if the contact angle is less than 90 then the surface is referred to as water wet. Similarly if the surface has the tendency for oil and the contact angle is greater than 90, the surface will be oil-wet. The term strongly oil-wet and strongly water-wet has been used for wetting angles near the extreme points as shown in the table 3.2.

Table 3.2 Wettability preference expressed by contact angle (Zolotukhin, 2000)

<table>
<thead>
<tr>
<th>Wetting angle (degrees)</th>
<th>Wettability preference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-30</td>
<td>Strongly water-wet</td>
</tr>
<tr>
<td>30-90</td>
<td>Preferentially water-wet</td>
</tr>
<tr>
<td>90</td>
<td>Neutral wettability</td>
</tr>
<tr>
<td>90-150</td>
<td>Preferentially oil-wet</td>
</tr>
<tr>
<td>150-180</td>
<td>Strongly oil-wet</td>
</tr>
</tbody>
</table>

Laboratory studies show that wettability of ranges from pure water wet (through neutral wet) to oil wet can occur within a porous medium. The rocks which have greater affinity for water called water wet while those rocks which show greater affinity for oil are known to be oil wet. Fractional wettability also known as heterogeneous or spotted wettability refers to the wettability condition where the oil is assumed to alter some part of the rock surface to strongly oil-wet while the remaining parts of the rock remain water-wet. Fractional wettability is different from intermediate wettability. In intermediate wettability all portions of the rock have a constant contact angle around 90°, equivalent to an equal affinity to imbibe oil and/or water (Al Sayari, 2009). Mixed wettability is special type of fractional wettability where water wet and oil wet
areas are interconnected (Salathiel, 1973). The rocks having mixed wettability contain continuous water- and oil-wet paths respectively and they are able to imbibe and take up water and oil spontaneously (Anderson, 1986b).

3.8.1 Wettability Measurement

Different methods have been proposed for the measurement of wettability of a system. Anderson (1986b) has divided these methods into quantitative and qualitative methods. The quantitative methods include contact angles, imbibition and forced displacement (Amott), and USBM wettability method. While qualitative methods are imbibition rates, microscope examination, flotation, glass slide method, relative permeability curves, permeability/saturation relationships, capillary pressure curves, capillarimetric method, displacement capillary pressure, reservoir logs, nuclear magnetic resonance, and dye adsorption. Although no single accepted method exists, three quantitative methods for determining wettability are generally accepted and most widely used.

1. Contact-angle measurement
2. The Amott method (imbibition and force displacement)
3. The USBM Method.

Contact Angle Measurement

This method is considered to be the best measurement method when pure fluids and artificial cores are used because there is no possibility of surfactants or other compounds altering the wettability. This method is also used to determine whether a crude oil can alter wettability and to examine the effects of temperature, pressure, and brine chemistry on wettability. Many methods
of contact-angle measurement are used but the methods that are generally used in petroleum industry are the static sessile drop method and dynamic sessile drop method. The contact angle measures the wettability of a specific surface (Anderson, 1986b).

The Amott Method

The Amott method is commonly used for measuring the wettability of cores. This method is based on spontaneous and forced imbibition of fluids (Tripathi and Mohanty, 2007). This method is based on the fact that the wetting fluid will imbibe spontaneously into the core, displacing the non-wetting fluid. The influence of other factors, such as relative permeability, viscosity, and the initial saturation of the rock is reduced by using the ratio of fluid displaced by spontaneous imbibition to forced imbibition (Anderson, 1986b).

The Amott method consists of the following four steps.

1. The core sample is saturated with oil by placing it in oil for a certain period of time that depends on the duration of the experiment. When the core sample is saturated with oil, it is removed and placed in an imbibition cell surrounded by water as shown in step 1 of figure 3.3. The water is allowed to imbibe into the core sample which displaces oil out of the sample until equilibrium is reached. The volume of water imbibed is measured.

2. The core sample is then removed and the remaining oil in the sample is forced down to residual saturation by displacement with water in a sealed core holder using centrifuge or pump as shown in step 2 of figure 3.3. The volume of oil recovered is measured.

3. The core now saturated with water at residual oil saturation is again placed in an imbibition cell surrounded by oil. Oil is allowed to imbibe into the core sample
displacing water out of the sample. The volume of water displaced is recorded after the equilibrium is achieved.

4. Finally the core is removed from the imbibition cell and the remaining water is removed by forced displacement. The volume of water displaced is recorded as shown in step 4 of figure 3.3.

![Figure 3.3 Amott test techniques (Glover, 1998)](image)

The wettability index is calculated by the following equation (Torsæter and Abtahi, 2000),

\[
WI = \frac{v_{o1}}{v_{o1} + v_{o2}} - \frac{v_{w1}}{v_{w1} + v_{w2}} = r_w - r_o
\]  

(3.8)

Where

\(v_{o1}\) = volume of oil produced during water imbibition

\(v_{o2}\) = volume of oil produced during water flooding
\[ V_{w1} = \text{volume of water produced during oil imbibition} \]
\[ V_{w2} = \text{volume of water produced during oil flooding} \]
\[ r_w = \text{displacement with water ratio} \]
\[ r_o = \text{displacement with oil ratio} \]

The wettability index will be a number between -1.0 and 1.0 where

WI = 1.0 completely water wetting
WI = 0.0 neutral
WI = -1.0 completely oil wetting.

The **USBM Method**

This method was developed by Donaldson et al. (1969) and is called U.S. Bureau of Mines method. The USBM method is similar to the Amott’s method but considers the required work for forced displacement. The USBM test compares the work necessary for one fluid to displace the other. This method gives an average wettability value of the core. This method is used in industry to compare various core plugs (Glover et al., 1998).

A major advantage of the USBM wettability test over the Amott test is its sensitivity near neutral wettability. The USBM test cannot determine whether a system has fractional or mixed wettability, while the Amott test is sometimes sensitive. In some fractional or mixed wet system both water and oil will imbibe freely. The Amott method will have positive displacement by water and displacement by oil ratios, indicating that the system is non-uniformly wetted (Anderson, 1986b).
3.8.2 Spontaneous Imbibition

The process by which a wetting phase displaces a non-wetting phase from a porous medium as a result of capillary forces is called spontaneous imbibition. Imbibition is an immiscible displacement process whereby a non-wetting fluid within a porous medium is spontaneously expelled by wetting fluid that surrounds the medium. Wetting fluid is drawn into the medium by capillary suction. This phenomenon is caused by the differential attraction forces between the pore walls and fluids. The rate of imbibition is primarily dependent on the rock permeability, pore structure, wettability and the interfacial tension between the resident phase and the imbibing phase (Anderson, 1986b).

The Amott and USBM wettability indices are based on spontaneous imbibition. The main difference between the Amott test and the spontaneous imbibition is that the Amott test depends mainly on the saturation at which imbibition capillary pressure falls to zero while spontaneous imbibition rates depend on the magnitude of the imbibition capillary pressure. Measurements of imbibition rates are of special value as a sensitive measure of wetting in the range where WI is or close to unity. In an imbibition test core sample is submerged saturated with oil is submerged in brine underneath a graduated cylinder and the rate and amount of oil displaced by brine imbibition are measured. The core is strongly water wet if large volumes of brine are rapidly imbibed, while lower rates and smaller volumes indicate a more weakly water-wet core. The core either neutrally wet or oil wet if no water is imbibed. Non water wet cores are then driven to residual oil saturation and submerged in oil. The imbibition apparatus is inverted and the rate and volume of oil displaced by water is recorded in the graduated cylinder below the core. The core is oil wet if it imbibes oil. The strength of oil wetness is indicated by the rate and volume of oil imbibition. The core is neutrally wet in that case when neither oil nor water is imbibed. The
cores which have fractional or mixed wettability will imbibe both water and oil (Anderson, 1986b). The imbibition rates measurement also provides information on dynamic interfacial tension and wetting phenomenon that may be useful in the reservoir but are not reflected by Amott or USBM wettability test (Morrow, 1990).

3.9 Instability Phenomenon

The flow of different fluids is influenced by several forces acting in the porous medium. It is not possible to ignore the vertical components of the velocities if the reservoir is thick. The analyses of these forces show that interfaces and fronts are generally distorted (encroachment). The term “tongue” refers to the encroachment that occurs on the scale of the front while on smaller scale (meter or decameter) it is known as “fingering”. These encroachments are governed by conditions of stability and instability. If a small change in the initial conditions of the movement (initial coordinates, initial speed) causes a variation in the movement that remains small over time, of the same order as the initial disturbance then it is called a stable movement otherwise in opposite case it will be unstable displacement. Studies show that these instabilities depend on the mobility ratio (Cosse, 1993).

3.9.1 Mobility

Mobility is the relative measure of how easily a fluid moves through a porous media. It is defined as the ratio of effective phase permeability to phase viscosity.

\[ \lambda = \frac{k}{\mu} \] (3.9)

Where

\( \lambda \) = Mobility [mD/cP]
\[ k = \text{Effective Permeability [mD]} \]
\[ \mu = \text{Viscosity [cP]} \]

### 3.9.2 Mobility Ratio

Mobility ratio is defined as the mobility of the displacing fluid “\( \lambda_D \)” behind the front divided by the mobility of the displaced fluid “\( \lambda_d \)” ahead of the front, thus

\[ M = \frac{\lambda_D}{\lambda_d} \quad (3.10) \]

Mobility control can be achieved by injection of chemicals to change displacing fluid viscosity or to preferentially reduce specific fluid relative permeability through injection of foams, or even through injection of chemicals to modify wettability (Sheng, 2011). A mobility ratio of approximately 1, or less, is considered favorable, which indicates that the injected fluid cannot travel faster than the displaced fluid while above 1 is called unfavourable (Cosse, 1993).

### 3.9.3 Fingering

The term fingering is used to describe the bypassing of a resident fluid by a displacing agent in a homogenous, non-uniform medium. The bypassed region is known as finger as shown in figure 3.4. The definition of fingering encompasses the instabilities that are caused by viscous forces (viscous fingers) and gravity forces (gravity fingers) but does not include bypassing due to permeability heterogeneities (Lake, 1988). Viscous fingering generally refers to the instability that occurs in the displacement of fluids in porous media. The mechanism of instability in most cases is due to the variations in viscosity between phases. When a less dense and less viscous
fluid displaces a denser and more viscous fluid, in that case both the density and viscosity are responsible for unstable displacement. The analysis of displacement instabilities shows that lower mobility ratio results better displacement stability. If the mobility ratio is higher than 1, then instabilities (tongues, fingering) are more likely to appear (Cosse, 1993).

**Figure 3.4** Viscous fingering process (Cosse, 1993) Fluid 1 displaces fluid 2 due to high pressure in fluid 1. Due to low viscosity of fluid 1, it moves faster than fluid 2 as a result fluid 1 tends to penetrate and form fingers through fluid 2.

### 3.10 Crude Oil/Brine/Rock Interaction

The wetting characteristics of pore surfaces within reservoir rock play an important role in immiscible displacement and fluid distribution. It has been recognized that most of the clean rock forming mineral surfaces are strongly water wet and interaction with different components that are present in crude oil can alter their wettability (Anderson. 1986a).

The interaction of crude oil/brine/rock is a complex process and it is difficult to explain the interaction mechanisms from core tests because of the coupled effects of wetting and pore
morphology. Crude oil consists of different components that can adsorb on solid surfaces. It is not possible to isolate the effect of different components or mechanisms for real crude oil. Therefore by characterizing acidic and basic oils and oils of varying solvent quality it is possible to see wetting alteration mechanism that dominates for one or another of the possible interaction mechanism. The four main types of crude oil/brine/rock interactions that are identified by Buckley (1998) are discussed here.

**Surface Precipitation**

Surface precipitation is based and dependent on crude oil solvent properties with respect to asphaltenes. The tendency of wetting alteration is increased if the oil is not a good solvent for its asphaltenes. It has been recognized by experimental studies that as the oil become a poor solvent for its asphaltenes, the tendency of asphaltene adsorption on the rock surface increases and causes less water wet conditions (Buckley, 1998).

**Acid/Base Interactions**

Acid/base interaction is the result of surface charge at oil/water and solid/water interfaces. Both the solid and oil surfaces are charged in the presence of water. The polar functional groups of oil and mineral behave as acids and bases. The phenomenon of surface charge affects the interaction between crude oils, brine and solid surfaces in two major ways. First for a given oil or solid surface, the surface charge depends on the degree of acid base dissociation reactions which in turn depends on pH at the surface. In case where both oil/water and solid/water interfaces have similar charge, the resulting repulsive force will stabilize the leading water film. Strongly water wet conditions are achieved if the water film is stable. If the water film is not stable it will collapse. At this phase, crude oil components at the oil/brine interface can adsorb on the solid surface. Weakly water wet condition (WI =0.5) is the result of low pH which favor positive
charge of basic functional groups while strongly water wet condition (WI=1) is maintained by higher pH (Buckley, 2005).

**Ion Binding Interaction**

When divalent and multivalent ions are present in the aqueous phase then ion-binding interaction occurs. The divalent and multivalent ion can bind at both oil and solid/water interfaces and/or bridge between them. Acid/base interaction is important but it cannot be isolated from complex contributions of the ion binding mechanism. Oil which has higher acid number and low base number can alter the wettability by ion-binding interaction (Buckley, 2005).

**Polar Interaction**

Polar interaction occurs between oil and solid surface in the absence of water. Adsorption of asphaltene directly from oil onto the mineral surface has often been reported. The adsorption of high molecular weight material on dry mica surfaces have been shown by immersion of dry mica surfaces in crude oil. The important variables that affect adsorption onto the clay mineral surface in the absence of water include the type of clay, nitrogen content of the oil, and the solvent in which the polar compounds are dissolved. In core studies, polar interaction is not considered important due to the presence of water (Buckley, 1998).
Chapter 4 Experimental Work

This section describes the details of the material used in this experiment, i.e., rocks, brine and oil and the experimental methods that were performed in this experiment. The purpose of this experiment was to investigate the effects of waste cooking oil and crude oil on wettability of Wallace sandstone core samples. Spontaneous imbibition and Amott test were performed to measure the wettability of Wallace sandstone core samples.

4.1 Rock materials

In this experiment, the cores used were Wallace Sandstone obtained from Wallace Quarry (Nova Scotia, Canada). The mineral analysis of the Wallace Sandstone performed by Dalhousie University’s Mineral Engineering Center Halifax, Nova Scotia, on February 19th, 2001 is presented in the table 4.1.

Four cores were drilled from the same block of Wallace sandstone in the Mining Engineering Lab at Dalhousie University on December 12, 2012 to ensure that they have the same composition. The edges of the cores were properly cut in order to get a cylindrical shape for accurate results as shown in figure 4.1. The important properties of the cores along with porosity and permeability are presented in table 4.2.
### Table 4.1 Mineral Analysis of Wallace Sandstone (Wallace Quarries Ltd, 2001)

<table>
<thead>
<tr>
<th>MINERAL</th>
<th>COMPOSITION (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon Dioxide (SiO$_2$)</td>
<td>82.00</td>
</tr>
<tr>
<td>Aluminium Oxide (Al$_2$O$_3$)</td>
<td>8.12</td>
</tr>
<tr>
<td>Ferric Oxide (Fe$_2$O$_3$)</td>
<td>3.19</td>
</tr>
<tr>
<td>Sodium Oxide (Na$_2$O)</td>
<td>1.67</td>
</tr>
<tr>
<td>Potassium Oxide (K$_2$O)</td>
<td>1.13</td>
</tr>
<tr>
<td>Magnesium Oxide (MgO)</td>
<td>0.72</td>
</tr>
<tr>
<td>Calcium Oxide (CaO)</td>
<td>0.81</td>
</tr>
<tr>
<td>Titanium Oxide (TiO)</td>
<td>0.29</td>
</tr>
<tr>
<td>Manganese Oxide (MnO)</td>
<td>0.10</td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>2.59</td>
</tr>
</tbody>
</table>

**Figure 4.1** Wallace sandstone cores used in this experiment
Table 4.2 Properties of core samples

<table>
<thead>
<tr>
<th>Core</th>
<th>L [cm]</th>
<th>D [cm]</th>
<th>V_b [cm^3]</th>
<th>W_d [g]</th>
<th>W_w [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS-1</td>
<td>7.16</td>
<td>3.78</td>
<td>80.30</td>
<td>187</td>
<td>199</td>
</tr>
<tr>
<td>WS-2</td>
<td>7.20</td>
<td>3.78</td>
<td>80.75</td>
<td>188</td>
<td>199</td>
</tr>
<tr>
<td>WS-3</td>
<td>7.14</td>
<td>3.78</td>
<td>80.08</td>
<td>185</td>
<td>197</td>
</tr>
<tr>
<td>WS-4</td>
<td>7.17</td>
<td>3.78</td>
<td>80.28</td>
<td>187</td>
<td>199</td>
</tr>
</tbody>
</table>

Where

L = Length of core

D = Diameter of core

V_b = Bulk volume of core

W_d = Weight of dry core

W_w = Weight of 100% saturated with brine core

4.2 Fluid System

4.2.1 Brine

The brine used in this experiment was prepared in laboratory based on the work of Martel et al. (2001). The brine was prepared by using distilled water, sodium chloride and calcium chloride. Details of the salts used are attached in Appendix B. The details of the brine composition are given below in the Table 4.3. The density of the brine was measured at room temperature (20° C) using hydrometer (cat. No. 2540, class H). The density was 1.044g/cm^3. The viscosity of the brine was measured using Ubbelohde viscometer (cat. no. 13614 H) and kinematic viscosity
bath. The viscosity was 1.13 cP at 20° C. The pH of brine was determined by Waterproof pH tester. The accuracy of the pH tester was 0.01 pH. The pH was found to be 7.5.

Table 4.3 Composition of the brine used in experiment

<table>
<thead>
<tr>
<th>Composition</th>
<th>Na</th>
<th>Ca</th>
<th>Cl</th>
<th>TDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/L</td>
<td>43450</td>
<td>12300</td>
<td>68050</td>
<td>92650</td>
</tr>
</tbody>
</table>

4.2.2 Waste Cooking Oil

Waste cooking oil used in experiment was collected from a local restaurant in Halifax, Nova Scotia Canada. Four liters of waste cooking oil was collected which was a representative sample of canola oil used for deep frying and was exposed to temperature between 170-180° C for seven days. The oil sample contained waste and dust particles which were removed by filtering it through a 20 micron filter paper. The viscosity of the oil was measured at 20° C using Ubbelohde viscometer (cat. no. 13614 H) and kinematic viscosity bath. The viscosity was 64.95cP while the density of the oil was measured with hydrometer (cat. no. 2534, Class L) at 20 °C and was 0.981g/cm³. The pH of waste cooking oil was determined by Waterproof pH tester. The accuracy of the pH tester was 0.01 pH.

4.2.3 Crude Oil

Reservoir crude oil ARAB 50 was used in this experiment. The viscosity of the oil at 16 °C was 42.57 cP while the density of the oil at 16°C was 0.8870 g/cm³. The pH of crude oil is 6. The properties of crude oil used in this experiment were based on the information provided by the supplier.
4.3 Experimental Procedures

4.3.1 Core Cleaning

The purpose of the core cleaning process is to achieve the original wettability state of the core. Based on Anderson’s (1986a) work, toluene and methanol were selected for core cleaning. The core samples were cleaned by injecting several pore volume of a 50/50 mixture of toluene/methanol in order to remove all components of oil and brine. The core samples were mounted one by one in the BRP 350. The BRP 350 was degassed and checked for leakages. Several pore volume of the mixture was injected into the core samples. The injection rate water was cm³/min. Finally the core samples were rinse by injection of distilled water. All the core samples were cleaned at laboratory temperature of 20 °C. Then the core samples were dried in the roller oven at 90 °C for 24 hours. The weight of the core samples were measured every time after cleaning to ensure complete dryness.

4.3.2 Core Saturation

To saturate core samples with brine, cooking oil and crude oil, vacuum oven was used. Cores were immersed in a beaker containing brine or oil and kept in the vacuum oven under vacuum of 0.147 psia for 72 hours at 20°C.

4.3.3 Determination of Porosity

Porosity was determined by gravimetric method. This method is based on the difference between dry and wet weight of the cores. The dry weight of the cores was observed. Then the cores were saturated with brine for 24 hours using vacuum chamber and again the weight of the saturated cores were observed by EC 4000 digital scale. Then by using the following equation porosity was calculated.
\[ \phi = \frac{PV}{BV} \times 100 \]  
(4.1)

Where

\[ PV = \frac{W_w - W_d}{\rho} \]  
(4.2)

\[ BV = L \times A \]  
(4.3)

Where,

PV = Pore volume of core [cm³]

BV = Bulk volume of core [cm³]

Ww = Wet weight, [g]

Wd = Dry weight, [g]

\( \rho \) = Density of brine, [g/cm³]

\( \phi \) = Porosity [%]

L = Core length [cm]

A = Cross sectional area of the core [cm²]

4.3.4 Determination of Absolute Permeability

The absolute permeability was measured using the Benchtop Relative Permeameter (BRP-350): The Benchtop Relative Permeameter BRP 350 is designed to perform tests in order to determine monophonic permeability and liquid/liquid relative permeability and optionally liquid/gas relative permeability. The test consists of direct measurement of permeability while injecting brine, oil and gas through the rock. This system includes a fluid delivery pump, two piston accumulators, a core-holder, a back pressure regulator, a confining pressure system, a pressure measurement system, a video tracker and a gas meter. Operation of the system is controlled
through a computer interface. The Applilab software included with the system is designed to allow for automated data acquisition and pump control. Some important features of the BRP 350 are given below while more details of the instrument are present in Appendix.

Table 4.4 Benchtop relative permeameter (BRP 350) features

<table>
<thead>
<tr>
<th>Working Confining Pressure</th>
<th>Up to 5000 psi (option 10000 psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working Pore Pressure</td>
<td>Up to 5000 psi (option 10000 psi)</td>
</tr>
<tr>
<td>Core Diameter</td>
<td>2.54 - 3.81 cm</td>
</tr>
<tr>
<td>Core Length</td>
<td>2.54 - 7.62 cm</td>
</tr>
<tr>
<td>Wetted Material</td>
<td>Stainless Steel 316 for chemical compatibility and corrosion resistance</td>
</tr>
<tr>
<td>(N_2)</td>
<td>2,000 Psi</td>
</tr>
<tr>
<td>Power</td>
<td>220 VAC, 50 Hz</td>
</tr>
</tbody>
</table>

The core samples were loaded into the Hassler Core Holder of the Benchtop Relative Permeameter equipment. Before starting the injection of brine into the core sample, the tubes connected to the Hassler Core Holder were drained to remove any trapped air in it. A confining pressure of 700 psi and a back pressure of 200 psi (\(N_2\)) were used in the set up as recommended by Vinci Technologies. The confining pressure was kept higher than the back pressure to ensure good sealing between the core and the rubber sleeve inside the core holder. The flooding was conducted at room temperature of 20 °C. The tubes were then connected and brine was injected at different flow rates across the sample. The initial flooding rate was 0.2 cm\(^3\)/min while the final flow rate was 4 cm\(^3\)/min.
Finally absolute permeability was calculated using the excel file “Permeability Template” provided with the Applilab software of the Benchtop Relative Permeameter. The “Permeability Template” works on the principal of Darcy’s law of flow through porous media and calculates the permeability using equation 3.3.

4.4 Spontaneous Imbibition and Amott wettability test

4.4.1 Spontaneous Imbibition Equipment
All spontaneous imbibition tests were performed in Amott’s cell. The Amott cell consists of a sealed glass cell for the core sample and a graduation tube to measure the volume of fluid expelled from the core. The imbibition Amott cell stands by itself while the drainage Amott cell is maintained using a stand as shown in figure 4.8. The experiments were carried out at laboratory conditions of 14.7 psi and 20° C.
4.4.2 Spontaneous imbibition of core samples

Core sample WS-1, WS-2 and WS-3 were saturated with cooking oil while core sample WS-4 was saturated with crude oil. WS-1 and WS-4 were saturated for 6 days (144 hours) while core samples WS-2 and WS-3 were saturated for 3 days (72 hours) before the start of the initial phase of imbibition. The saturated core were then placed vertically inside the Amott’s cell and surrounded by synthetic brine with all sides subjected to imbibition. The amount of oil recovered was measured at different time intervals and a graph of oil recovered against imbibition time was plotted. The total spontaneous imbibition time for the core WS-1 and WS-4 was 144 hours (6 days) while for the cores WS-2 and WS-3 it was 72 hours (3 days).
Figure 4.4 Oil recovery by spontaneous Imbibition

4.4.3 Water Flooding of Core samples after Spontaneous Imbibition

After spontaneous imbibition, the core samples were subjected to forced displacement by brine using the Benchtop Relative Permeameter (BRP 350). The flooding tank was filled with synthetic brine and a displacement pump was used to force the piston of the tank in order to pump brine through the pipeline. The core samples were loaded one by one and flooded with brine. The confining pressure of the system was 700-750 psi while the back pressure was between 190-200 psi and the temperature was 20° C. The injection flow rate was 3 cm³/min. Once the inlet pressure exceeded the outlet pressure, the water flooding was initiated and the core sample was subjected to counter current flow of brine. A mixture of brine and cooking oil was observed in the separator when the outlet pressure exceeded the back pressure. The separator was already filled with 20 cm³ of brine and cooking oil prior the experiment inorder to
distinguish between the brine and oil phases and record the rise in level of each fluid. The initial level of the interface was recorded. Vinci Acquisition (V2.3) software was used to monitor and record the rise in the level of oil in order to determine the volume of oil recovered after flooding. The software calculates the volume of oil and brine recovered using diameter of the separator. Each core sample was subjected to water flooding for 48 hours. The core samples were cleaned and dried at 90°C for 24 hours in oven. All the dried samples were weighed again and found to be the same weight as before the start of experiment. The core samples were then subjected to the second phase of experiment.

The core samples were saturated with brine this time under vacuum. The core sample WS-1 and WS-4 was saturated for 6 days (144 hours) while WS-2 and WS-3 were saturated for 3 days (72 hours) under vacuum. After that the core samples were placed in Amott cell. For WS-1, WS-2 and WS-3 cooking oil was used as imbibing fluid while for WS-4 crude oil was used. The volume of brine displaced by oil imbibition is recorded after equilibrium is achieved. The core sample WS-1 and WS-4 was exposed to oil for 6 days (144 hours) while WS-2 and WS-3 cores were placed in oil for 3 days (72 hours).
The core samples were then removed from Amott cell and subjected to forced displacement by oil. Again BRP-350 was used. This time the flooding tank was filled with cooking oil for WS-1, WS-2 and WS-3 while for WS-4 crude oil was used as injecting fluid. The volume of brine recovered by oil flooding was calculated with the help of Vinci Acquisition (V2.3) software.
Chapter 5 Results and Discussions

The results of the experiment are presented and discussed in this section after the experiment has been completed successfully.

5.1 Core Sample Properties

The important petrophysical properties of the core samples determined during the experiment are summarized in Table 5.1.

Table 5.1 Summary of petrophysical properties of cores

<table>
<thead>
<tr>
<th>Core</th>
<th>PV [cm³]</th>
<th>Ø [%]</th>
<th>k [mD]</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS-1</td>
<td>11.94</td>
<td>14.3</td>
<td>1.84</td>
</tr>
<tr>
<td>WS-2</td>
<td>10.53</td>
<td>13.9</td>
<td>1.89</td>
</tr>
<tr>
<td>WS-3</td>
<td>11.49</td>
<td>14.3</td>
<td>1.82</td>
</tr>
<tr>
<td>WS-4</td>
<td>11.90</td>
<td>14.3</td>
<td>1.83</td>
</tr>
</tbody>
</table>

5.2 Spontaneous Imbibition Test Results

As described in section 4.3.6, four Wallace Sandstone cores were exposed to spontaneous imbibition by placing it in Amott cells to get indication of wettability of the cores. Core WS-1, WS-2, WS-3 and WS-4 were used in this experiment. Core sample WS-2 and WS-3 were exposed to spontaneous imbibition for 3 days while core samples WS-1 and WS-4 were exposed to spontaneous imbibition for 6 days. The purpose of this time difference was to know about the oil recovery with time. Figure 5.1 shows the spontaneous imbibition characteristics for all the
cores. The plot of oil recovery vs. time depicts the spontaneous imbibition rate for each core sample.

![Plot of oil recovery vs. time for different core samples](image)

**Figure 5.1** Spontaneous imbibition with brine results for all cores (100% oil saturation)

The plot of oil recovery vs. imbibition time for all the cores show that the oil recovery was high during the first 3 hours and after that it decreased and stopped almost after 10 hours. From Table 5.1, the PV of WS-1 is 11.94 cm$^3$, the oil recovery due to SI of brine is 0.22 cm$^3$ which is very low i.e. only 1.84% of the total oil in place. This shows that the core sample WS-1 is not water wet. The PV of WS-2 is 10.53 cm$^3$ and the oil recovery due to SI of brine is 0.24 cm$^3$ which is just 2.27% of the total oil in place, which means that the core sample WS-2 is also not water wet. Similarly, the PV of WS-3 is 11.49 cm$^3$ and the volume of oil recovered as a result of SI of brine is 0.19 cm$^3$. The oil recovery from WS-3 is 1.65%. The PV of WS-4 is 11.90 cm$^3$ and the oil recovery by SI is 0.20 cm$^3$. Therefore, the oil recovery for WS-4 is 1.68% of the original oil in place. It is clear that the oil recovery by SI of brine from every core is very low and is less than
2% of the original oil in place. It is also clear from this data that although the core saturation time and spontaneous imbibition time for WS-2 and WS-3 were different but still the overall oil recovery from each of them as compared to their pore volume is not high. Although the oil recovery from WS-2 is higher than other cores which are the result of higher permeability of WS-2 but still the oil recovery as compared to its pore volume is just 2.27% of the total oil in place which is still very low.

5.2 Results of Amott Wettability Test on all core

The Amott wettability measurement involves the amount of fluids spontaneously and forcibly imbibed by a rock sample. This method is used in petroleum industry for comparing wettability of various core samples.

After the SI of brine, the core samples were subjected to forced displacement by brine. Table 5.1 shows the oil recovered as a result of forced displacement by brine. In the next part of experiment, the core samples were cleaned dried and 100% saturated with brine. The brine saturated samples were exposed to SI by oil. As shown in Table 5.1, the core samples have not imbibed oil. The core samples were then subjected to forced displacement by oil. The brine recovered due to forced displacement of oil is shown in Table 5.1.
Table 5.2 Amott wettability index for core samples

<table>
<thead>
<tr>
<th>Core Sample</th>
<th>Displacement by brine (Oil Recovery) cm(^3)</th>
<th>Displacement by oil (Brine Recovery) cm(^3)</th>
<th>Amott Wettability Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spontaneous (V_{o1})</td>
<td>Forced (V_{o2})</td>
<td>Spontaneous (V_{w1})</td>
</tr>
<tr>
<td>WS-1</td>
<td>0.22</td>
<td>4.8</td>
<td>0</td>
</tr>
<tr>
<td>WS-2</td>
<td>0.24</td>
<td>4.4</td>
<td>0</td>
</tr>
<tr>
<td>WS-3</td>
<td>0.19</td>
<td>4.5</td>
<td>0</td>
</tr>
<tr>
<td>WS-4</td>
<td>0.20</td>
<td>4.3</td>
<td>0</td>
</tr>
</tbody>
</table>

5.3 General Discussion

Sedimentary rocks were formed by deposition of sediments in an aqueous environment. Most sandstone are therefore water wet by nature, but in contact with oil the wettability of rock surface may be altered to more oil-wet (Melberg, 2010). Fresh sandstone core samples are water wet unless they are in contact with crude oil. The Wallace sandstone core samples used in this experiment were fresh cores which were not previously exposed to any oil contact before this experiment.

The porosity measurement of the core sample shows that Wallace sandstone core samples have high porosity while the permeability measurement indicates it has poor permeability. The spontaneous imbibition data for the cores shows that the spontaneous imbibition rate was very slow and that the total brine imbibed by each core sample was very low as compared to the total
pore volume of the core sample. Also from the above table which shows the Amott wettability indices, it is clear that Wallace sandstone core samples have now near neutral wettability.

The oil recovered in the separator after waterflooding was also observed and there was no sign of precipitation or solid particles in it. Also the core samples were weighted every time after they were cleaned and dried. All the core samples were found of the same weight as they were at the beginning of the experiment. This shows that there was no dissolution.

Wettability alteration is a complex phenomenon. The wettability of reservoir rocks is affected by different factors including oil composition, rock mineralogy, connate water composition and pH, reservoir pressure and temperature (Zolotukhin, 2000). It is possible that more than one mechanism at a time contributes to oil/brine/rock interaction. Buckley (1998) performed different experiments in order to identify the different mechanisms which cause wettability alteration. These mechanisms by which wettability is altered are discussed in chapter 3 (section 3.10).

In this experimental work, we can see that the pH value of the waste cooking oil used was 5. It has been stated earlier in chapter 3 (section 3.10) that low pH promotes a positive charge of basic functional groups which causes weakly water wet conditions (Buckley, 1998). Therefore it may be one of the causes which have altered the wettability from strongly water wet to near neutral wet condition for cores saturated with waste cooking oil.

The crude oil contains asphaltenes and resins which have polar and polynuclear organic compounds. High polar compounds adsorb on the surfaces of the grains and alter the wettability from water wet to oil wet (Anderson, 1986a; Buckley, 1998).

It is also found that the pH of the brine used in this experiment is greater than 7.5, in this case the dissociation of hydrogen ions is repressed and the surface of Wallace sandstone acidic organic
compounds. The divalent ions Ca\(^{++}\) present in the brine adsorbs on the negative silica surface then permit the adsorption of acidic compounds on the silica rocks which may also be a cause for wettability alteration from water wet to near neutral wet condition (Tiab and Donaldson, 2011). It is difficult to explain the interaction mechanisms from core tests because of the coupled effects of wetting and pore morphology. However it is clear from this experiment that waste cooking oil and crude oil both have changed the wettability of the Wallace sandstone core samples from strongly water wet to near neutral wet conditions.
Chapter 6 Conclusions and Recommendations

Geological sequestration of CO$_2$ is one of the possible options for reducing large scale CO$_2$ emissions into the atmosphere. The sequestration mechanism is coupled with different physical and chemical processes. A thorough knowledge and understanding of the displacement process of CO$_2$ and brine is essential for successful execution of any project.

6.1 Conclusions

From this work, it can be concluded that core samples from Wallace quarry have high porosity in the range of 7-20% and poor permeability in the range of 1-15mD. Moreover, the experiments performed on the Wallace sandstone core samples using waste cooking oil and crude oil show that they have similar effect on the core samples. Both types of oils used have changed the original wettability of Wallace sandstone core samples from strongly water wet to near neutral wet conditions.

6.2 Recommendations

Wettability plays an important role in CO$_2$ sequestration. This experiment shows that waste cooking oil has changed the wettability of Wallace sandstone cores from strongly water wet to near neutral wet. Therefore, it is suggested that experiments should be perform by using a mixture of CO$_2$ and waste cooking oil to determine the effects on the wettability of reservoir rocks. It is also recommended that further study should be performed to know the effect of change in wettability of reservoir rocks on trapping of CO$_2$ in saline aquifers. Pressure and temperature also effects wettability of reservoir rocks. This experiment was performed at laboratory pressure and temperature while the pressure and temperature conditions in the reservoir are different from the laboratory pressure and temperature. Therefore it is suggested
that experiments should also be performed in future under reservoir pressure and temperature to verify the effect of waste cooking oil on spontaneous imbibition and wettability at reservoir conditions. It is also recommended that a comprehensive study should be performed about the cost and feasibility of using waste cooking oil as a CO$_2$ thickener in carbon dioxide sequestration projects.
REFERENCES


IPCC (2001). *IPCC Third Assessment Report - Climate Change 2001 (Intergovernmental Panel on Climate Change)*. IPCC.


InTech Publishing.


APPENDIX A: Spontaneous imbibition tests results

Table A-1 Spontaneous imbibition test data of WS-1 (100% oil saturation)

<table>
<thead>
<tr>
<th>Imbibition Time (min)</th>
<th>Oil Recovery (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>60</td>
<td>0.07</td>
</tr>
<tr>
<td>90</td>
<td>0.13</td>
</tr>
<tr>
<td>180</td>
<td>0.17</td>
</tr>
<tr>
<td>260</td>
<td>0.22</td>
</tr>
<tr>
<td>480</td>
<td>0.22</td>
</tr>
<tr>
<td>600</td>
<td>0.22</td>
</tr>
<tr>
<td>800</td>
<td>0.22</td>
</tr>
<tr>
<td>1540</td>
<td>0.22</td>
</tr>
<tr>
<td>2150</td>
<td>0.22</td>
</tr>
<tr>
<td>2860</td>
<td>0.22</td>
</tr>
<tr>
<td>3300</td>
<td>0.22</td>
</tr>
<tr>
<td>5020</td>
<td>0.22</td>
</tr>
<tr>
<td>5740</td>
<td>0.22</td>
</tr>
<tr>
<td>6280</td>
<td>0.22</td>
</tr>
<tr>
<td>7020</td>
<td>0.22</td>
</tr>
<tr>
<td>7720</td>
<td>0.22</td>
</tr>
<tr>
<td>8440</td>
<td>0.22</td>
</tr>
</tbody>
</table>
### Table A-2 Spontaneous imbibition test data of WS-2 (100% oil saturation)

<table>
<thead>
<tr>
<th>Imbibition Time (min)</th>
<th>Oil Recovery (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>60</td>
<td>0.05</td>
</tr>
<tr>
<td>90</td>
<td>0.15</td>
</tr>
<tr>
<td>180</td>
<td>0.18</td>
</tr>
<tr>
<td>260</td>
<td>0.24</td>
</tr>
<tr>
<td>480</td>
<td>0.24</td>
</tr>
<tr>
<td>600</td>
<td>0.24</td>
</tr>
<tr>
<td>800</td>
<td>0.24</td>
</tr>
<tr>
<td>1540</td>
<td>0.24</td>
</tr>
<tr>
<td>2150</td>
<td>0.24</td>
</tr>
<tr>
<td>2860</td>
<td>0.24</td>
</tr>
<tr>
<td>3300</td>
<td>0.24</td>
</tr>
<tr>
<td>4320</td>
<td>0.24</td>
</tr>
</tbody>
</table>
**Table A-3** Spontaneous imbibition test data of WS-3 (100% oil saturation)

<table>
<thead>
<tr>
<th>Imbibition Time (min)</th>
<th>Oil Recovery (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>60</td>
<td>0.03</td>
</tr>
<tr>
<td>90</td>
<td>0.15</td>
</tr>
<tr>
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<td>0.19</td>
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<tr>
<td>4320</td>
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</table>
Table A-4 Spontaneous imbibition test data of WS-4 (100% oil saturation)

<table>
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<tr>
<th>Imbibition Time (min)</th>
<th>Oil Recovery (ml)</th>
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<tbody>
<tr>
<td>0</td>
<td>0.00</td>
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<tr>
<td>60</td>
<td>0.07</td>
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<td>90</td>
<td>0.15</td>
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<tr>
<td>480</td>
<td>0.20</td>
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<tr>
<td>600</td>
<td>0.20</td>
</tr>
<tr>
<td>800</td>
<td>0.20</td>
</tr>
<tr>
<td>1540</td>
<td>0.20</td>
</tr>
<tr>
<td>2150</td>
<td>0.20</td>
</tr>
<tr>
<td>2860</td>
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</tr>
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<td>3300</td>
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<td>5020</td>
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<td>5740</td>
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<td>6280</td>
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<tr>
<td>7020</td>
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<td>7720</td>
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<tr>
<td>8440</td>
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<tr>
<td>9660</td>
<td>0.20</td>
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APPENDIX B: Details of Instruments and Chemical Used in this Experiment

Table B-1 Lists of instruments used in the experiment

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Manufacturer</th>
<th>Purpose</th>
<th>Model #</th>
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</thead>
<tbody>
<tr>
<td>Vernier Calliper</td>
<td>Fisher Scientific</td>
<td>Core Dimension Measurement</td>
<td>700-127</td>
</tr>
<tr>
<td>Thermometer</td>
<td>Fisher Scientific</td>
<td>Temperature Measurement</td>
<td>08285-90</td>
</tr>
<tr>
<td>Vacuum Oven</td>
<td>Cole Parmer</td>
<td>Core Saturation</td>
<td>281-A</td>
</tr>
<tr>
<td>Hydrometer</td>
<td>Thermo Fisher</td>
<td>Density Measurement</td>
<td>08285-90</td>
</tr>
<tr>
<td>Viscometer</td>
<td>Canon Instruments Company</td>
<td>Viscosity Measurement</td>
<td>3C-K926</td>
</tr>
<tr>
<td>Kinematic Viscosity Bath</td>
<td>Kohler Instruments Company Inc.</td>
<td>Constant Temperature Viscosity Measurement</td>
<td>K23702</td>
</tr>
<tr>
<td>Roller Oven</td>
<td>Fann Instruments Company Texas</td>
<td>Core Drying</td>
<td>704ES</td>
</tr>
<tr>
<td>Benchtop Relative Permeameter</td>
<td>Vinci Technologies France</td>
<td>Permeability Measurement, Core Flooding</td>
<td>BRP-350</td>
</tr>
<tr>
<td>Digital Scale</td>
<td>Denver Instruments</td>
<td>Weight</td>
<td>TP-12</td>
</tr>
<tr>
<td>Amott Imbibition Cell</td>
<td>Vinci Technologies France</td>
<td>Spontaneous Imbibition</td>
<td>custom</td>
</tr>
<tr>
<td>Filter Paper</td>
<td>Fisher Scientific</td>
<td>Filtration</td>
<td>09-801D</td>
</tr>
<tr>
<td>Waterproof pH Tester 30</td>
<td>EUTECH Instruments</td>
<td>pH value measurement</td>
<td>1350684</td>
</tr>
</tbody>
</table>
Table B-2 List of chemicals used in experiment

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
<th>Purity</th>
<th>CAS #</th>
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<tr>
<td>Methanol</td>
<td>Fisher Scientific</td>
<td>$\geq 99.8%$ A.C.S.</td>
<td>67-56-1</td>
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<tr>
<td>Toluene</td>
<td>Fisher Scientific</td>
<td>Lab Grade</td>
<td>108-88-3</td>
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<tr>
<td>NaCl</td>
<td>Fisher Scientific</td>
<td>100%</td>
<td>7647-14-5</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>Sigma Aldrich Company</td>
<td>$&gt;99%$</td>
<td>10043-52-4</td>
</tr>
</tbody>
</table>
APPENDIX C: Benchtop Relative Permeameter Part List (BRP-350)
## Benchtop Relative Permeameter Parts List (BRP-350)

<table>
<thead>
<tr>
<th>ITEM</th>
<th>DESCRIPTION</th>
<th>ITEM</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HV01 Process Valve</td>
<td>18</td>
<td>Confining Pressure Indicator</td>
</tr>
<tr>
<td>2</td>
<td>HV04 Vacuum Valve</td>
<td>19</td>
<td>HV05 +/- 500 psi Safety Valve</td>
</tr>
<tr>
<td>3</td>
<td>HV02 Oil Process Valve</td>
<td>20</td>
<td>Outlet Pressure Indicator</td>
</tr>
<tr>
<td>4</td>
<td>HV03 Brine Process Valve</td>
<td>21</td>
<td>Differential Pressure Indicator</td>
</tr>
<tr>
<td>5</td>
<td>HV11 Gas Process Valve</td>
<td>22</td>
<td>Inlet Pressure Indicator</td>
</tr>
<tr>
<td>6</td>
<td>Hassler Core-Holder</td>
<td>23</td>
<td>Brine Accumulator</td>
</tr>
<tr>
<td>7</td>
<td>HV06 Confining Pressure Valve</td>
<td>24</td>
<td>Oil Accumulator</td>
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<tr>
<td>8</td>
<td>Back Pressure Regulator</td>
<td>25</td>
<td>HV09 Gas Process Valve</td>
</tr>
<tr>
<td>9</td>
<td>Video Tracker Light</td>
<td>26</td>
<td>Gas Regulator 3-200 psi</td>
</tr>
<tr>
<td>10</td>
<td>Enerpac Hand Pump</td>
<td>27</td>
<td>Brine Accumulator Pressure Gauge</td>
</tr>
<tr>
<td>11</td>
<td>Video Tracker Burette</td>
<td>28</td>
<td>Oil Accumulator Pressure Gauge</td>
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<tr>
<td>12</td>
<td>HV07 Back Pressure Valve</td>
<td>29</td>
<td>Video Tracker Camera</td>
</tr>
<tr>
<td>13</td>
<td>HV08 Back Pressure Buffer Line</td>
<td>30</td>
<td>Back Pressure Buffer</td>
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<tr>
<td>14</td>
<td>Gas Volume Indicator</td>
<td>31</td>
<td>Differential Pressure Sensor</td>
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<tr>
<td>15</td>
<td>Gas Meter</td>
<td>32</td>
<td>Pressure Sensor</td>
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<tr>
<td>16</td>
<td>Main Frame</td>
<td>33</td>
<td>Gas Humidifier</td>
</tr>
<tr>
<td>17</td>
<td>Back Pressure Indicator</td>
<td>34</td>
<td>ON/OFF Switch and Fuse</td>
</tr>
</tbody>
</table>