

**THE EFFECTS OF ORGANIC ACID ON WATER-GAS
CAPILLARY PRESSURE: IMPLICATIONS FOR
UNDERGROUND GAS STORAGE**

BY

RASHAD AHADLI

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DEANSHIP OF GRADUATE STUDIES

This thesis, written by **Rashad Ahadli** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN PETROLEUM ENGINEERING**.



Dr. Dhafer Al-Shehri
Department Chairman



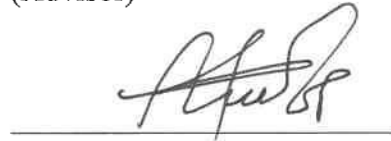
Prof. Suliman Salem Al-Homidan
Dean of Graduate Studies

19.05.2024

Date



Dr. Shirish Patil
(Advisor)



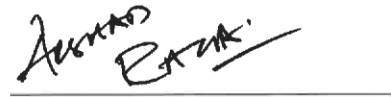
Dr. Ahmed Al-Yaseri
(Co-Advisor)



Dr. Dhafer Al-Shehri
(Member)



Dr. Mustafa Al-Ramadan
(Member)



Dr. Arshad Raza
(Member)

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To my family and friends who supported me on this journey.

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LIST OF ABBREVIATIONS

CCUS	:	Carbon Capture, Utilization and Storage
CCS	:	Carbon Capture and Storage
IFT	:	Interfacial Tension
TOC	:	Total Organic Content
NMR	:	Nuclear Magnetic Resonance
CPMG	:	Carr–Purcell–Meiboom–Gill

ABSTRACT

Full Name : Rashad Ahadli
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Fossil fuels are the backbone of world energy resources. The process of oil recovery is known to give rise to substantial emissions of carbon dioxide, which, in turn, exerts significant adverse impacts on the environment. Hence, there is an urgent need to promptly mitigate the detrimental effects of this greenhouse gas through the implementation of diverse and effective strategies. To address this problem, emphasis should be placed on renewable energy sources, developing smart energy networks and CO₂ capture and storage. Among these approaches, the capture and long-term sequestration of CO₂ emerges as a particularly promising method, with the potential to significantly reduce atmospheric CO₂ levels in the forthcoming years. While a considerable amount of knowledge has been generated through the study of wettability effect on carbon dioxide capillary trapping research that specifically investigates the effect of capillary pressure on the trapping and snap-off is relatively scarce. However, it is well-established that there exist certain sources of uncertainty associated with contact angle measurements, including factors like surface roughness and the influence of cleaning procedure.

Hence, we conducted an examination to assess the influence of organic acid on wettability by means of capillary pressure measurements, alongside of contact angles, and subsequently compared the results to discern disparities. For our investigation, we selected limestone and sandstone, recognized as optimal geological substrates for carbon dioxide storage. These rock samples were subjected to aging processes involving varying concentrations of organic acid, following which capillary pressure and contact angle measurements were obtained both prior to and post-aging. The experimental findings indicate that wettability can be modified a capillary pressure substantially reduced by even low concentrations of organic acid, with similar effects observed at higher concentrations.

Furthermore, it is noteworthy that organic acid exerts a more pronounced influence on contact angle compared to its impact on capillary pressure. The insights garnered from this research are expected to contribute to the enhanced implementation of Carbon Capture and Geological Storage (CCUS) projects on a broader scale, thereby aiding in the mitigation of project-related uncertainties. Moreover, investigation was conducted into the impact of cleaning procedures involving methanol and toluene on sample wettability. It was observed that post-cleaning, there was a notable shift towards increased water wettability.

ملخص الرسالة

الاسم الكامل:

رشاد العادلي

عنوان الرسالة:

تأثيرات الأحماض العضوية على الضغط الشعري للماء والغاز. الآثار المترتبة على تخزين الغاز تحت الأرض.
هندسة البترول

التخصص:

تاريخ الدرجة العلمية: مايو 2024

يعد الوقود الأحفوري العمود الفقري لموارد الطاقة العالمية. ومن المعروف أن عملية استخلاص النفط تؤدي إلى انبعاث كميات كبيرة من ثاني أكسيد الكربون، والذي بدوره يؤدي إلى آثار سلبية كبيرة على البيئة. ومن ثم، هناك حاجة ملحة للتخفيف الفوري من الآثار الضارة لهذا الغاز الدفيئة من خلال تنفيذ استراتيجيات متنوعة وفعالة. ولمعالجة هذه المشكلة، ينبغي التركيز على مصادر الطاقة المتجددة، وتطوير شبكات الطاقة الذكية، واحتجاز ثاني أكسيد الكربون وتخزينه. ومن بين هذه الأساليب، يبرز احتجاز ثاني أكسيد الكربون وعزله على المدى الطويل كوسيلة واحدة بشكل خاص، مع إمكانية خفض مستويات ثاني أكسيد الكربون في الغلاف الجوي بشكل كبير في السنوات المقبلة. في حين تم توليد قدر كبير من المعرفة من خلال دراسة تأثير قابلية التبلل على محاصرة الشعيرات الدموية لثاني أكسيد الكربون، إلا أن الأبحاث التي تبحث على وجه التحديد في تأثير الضغط الشعري على الملاءمة والقطع نادرة نسبيًا. ومع ذلك، فمن الثابت أن هناك مصادر معينة من عدم اليقين المرتبطة بقياسات زاوية الاتصال، بما في ذلك عوامل مثل خشونة السطح وتأثير إجراء التنظيف.

ومن ثم، أجرينا فحصًا لتقييم تأثير الحمض العضوي على قابلية التبلل عن طريق قياسات الضغط الشعري، جنبًا إلى جنب مع زوايا التلامس، ثم قمنا بعد ذلك بمقارنة النتائج لتمييز التباينات. في بحثنا، اخترنا الحجر الجيري والحجر الرملي، المعروفين بأنهما ركانز جيولوجية مثالية لتخزين ثاني أكسيد الكربون. تعرضت هذه العينات الصخرية لعمليات التعتيق التي تنطوي على تركيزات مختلفة من الأحماض العضوية، وبعد ذلك تم الحصول على قياسات الضغط الشعري وزاوية التلامس قبل وبعد التعتيق. تشير النتائج التجريبية إلى أنه يمكن تعديل قابلية التبلل من خلال تقليل الضغط الشعري بشكل كبير حتى عن طريق التركيزات المنخفضة من الحمض العضوي، مع ملاحظة تأثيرات مماثلة عند التركيزات الأعلى. علاوة على ذلك، تجدر الإشارة إلى أن الحمض العضوي يمارس تأثيرًا أكثر وضوحًا على زاوية التلامس مقارنة بتأثيره على الضغط الشعري. ومن المتوقع أن تساهم الأفكار التي تم الحصول عليها من هذا البحث على نطاق أوسع، مما يساعد في تخفيف (CGS) في تعزيز تنفيذ مشاريع احتجاز الكربون وتخزينه الجيولوجي الشكوك المتعلقة بالمشروع. علاوة على ذلك، تم إجراء بحث حول تأثير إجراءات التنظيف التي تتضمن الميثانول والتولوين على قابلية بلل العينة. وقد لوحظ أنه بعد التنظيف، كان هناك تحول ملحوظ نحو زيادة قابلية بلل الماء مع زيادة الضغط الشعري.

CHAPTER 1

INTRODUCTION

1.1 CCUS

Carbon Capture and Storage, is a technology that aims to reduce carbon dioxide emissions from industrial processes and power generation by facilities and store them in underground geological formations or other long-term storage solution. [\[1\]](#)

The fundamental concept underlying CCS (Carbon Capture and Storage) revolves around the prevention of CO₂ release into the atmosphere, a contributor to climate change. Instead, it involves capturing CO₂ as its source and securely storing it. CCS plays a pivotal role in mitigating greenhouse gas emissions, enabling the continued use of fossil fuels while minimizing their environmental impact. Furthermore, it's worth noting that deforestation can also trigger CO₂ emissions. In addition to its positive impact on climate change, CCS can serve as a means to reduce other airborne pollutants like sulfur dioxide, nitrogen oxides, and particulate matter, which can exert significant effects on both humans and the environment.

The CCS process typically involves three main steps: capture, transport, and storage. The capture step involves separation CO₂ from other gases produced during industrial processes or power generation. The transport step involves moving the captured CO₂ to a storage site using pipelines, ships, or other methods. The storage step involves injecting the CO₂ into geological formations such as depleted oil and gas reservoirs, saline formations, or other suitable storage sites.

Overall, CCS is an important tool for lessening climate change and ensuring a sustainable future for the planet. While there are still challenges associated with its implementation, such as cost and public acceptance, the potential benefits of CCS make it a critical tool in our efforts to reduce greenhouse gas emission and address climate change.

Types of CO₂ storage:

Carbon dioxide storage is divided into 2 types:

- 1) Natural
- 2) Artificial

An example of natural CO₂ storage can be terrestrial sequestration. However, the artificial type includes storage in geologic formations.

1) Terrestrial sequestration

This type of storage refers to the procedure of capturing CO₂ from the air and storing it in terrestrial ecosystem, such as forests, grasslands, and wetlands. This can be achieved through various natural and human-induced processes, such as photosynthesis, reforestation, and enhanced land management practices. [2]

2) Ocean sequestration

This is a type of CCS technique that aims to remove carbon dioxide from the atmosphere and store it in the ocean. This can be achieved through a variety of methods, such as enhancing ocean processes that absorb and store carbon, or by directly injecting CO₂ into the ocean. Different approaches to ocean sequestration: ocean fertilization, direct injection, and ocean alkalinity enhancement. [3]

3) Geological sequestration

[4] Geological sequestration is a widely employed process whereby carbon dioxide emissions originating from power plants or industrial sources are captured and subsequently transported to geologically suitable formations. These formations typically comprise deep saline aquifers, depleted oil and gas reservoirs, and unmineable coal seam, which serve as the primary repositories for CO₂ storage. Upon injection into these geological formations, the carbon dioxide undergoes retention through a combination of physical and chemical mechanisms. It is worth noting that various locations, including saline aquifer formations, depleted oil and gas reservoirs, and deep unmineable coal beds, can serve as viable sites for implementing geological sequestration. Additionally, it is feasible to execute CO₂ sequestration during enhanced oil recovery processes, further enhancing the potential for carbon dioxide mitigation and storage.

a) Saline aquifer formations:

Saline aquifers are a promising solution for carbon capture and storage, with the potential to store CO₂ through geological, geochemical, and hydrodynamic trapping mechanisms. Carbon dioxide storage capacity and injectivity depend upon several factors, including aquifer volume, porosity, permeability, and rock fracture characteristics. Suitable storage sites must be selected based on geological stability, strong confining seals, and sufficient dimensions, depth. Engineering considerations such as the type of wells, injection rates, and carbon dioxide purity also play a role in successful gas storage. What's more, brine injection can benefit storage during gas injection. [5]

b) Depleted oil and gas reservoirs:

The storage of carbon dioxide in depleted oil and gas reservoirs emerges as a highly feasible and practical solution for mitigating atmospheric CO₂ emission, with successful implementation witnessed across numerous global locations. [6] It is commonly known that the caprock's ability to seal, which effectively kept the original hydrocarbons contained within the reservoirs for a long period of time, is strong enough to stop the CO₂ from leaking into higher layers. [7]

One of the biggest advantages of depleted or almost depleted oil and gas reservoirs to store throughout exploration and production period, reservoir has been thoroughly examined. Moreover, during the process of extracting oil, all equipment and pipelines have been constructed which contributes to easier implementation of sequestration. Although depleted oil and gas reservoirs offer many benefits, such as their potential for use, there is a major disadvantage related to their storage capacity. This is significantly reduced because it is necessary to maintain pressure below the fracture point, which can result in damage to the caprock and significant leakage.

c) Deep unmineable coal beds: [8]

Coal seams give a huge chance to store large amounts of carbon dioxide at lower cost. Because coal is capable of absorbing significant amounts of carbon dioxide in a highly concentrated form. Also, coal is often found near power plants that emit a lot of CO₂s. Injecting carbon dioxide into coal seams helps extract more methane commercially. [9]

Types of trapping

- a) Structural trapping
- b) Capillary and residual trapping
- c) Dissolution trapping
- d) Mineral trapping

Trapping mechanisms

Carbon dioxide can be stored in three different states, namely compressed gas, liquid, and supercritical state, to facilitate effective and efficient storage. Depending on the strategy to store CO₂, it can be mineral trapping, structural trapping, solubility (dissolution) trapping and residual (or capillary) trapping. [10]

Hydrodynamic trapping (structural and stratigraphical trapping)

This phenomenon is referred to as “hydrodynamic” trapping, and it occurs as a result of specific attributes and circumstances within depleted hydrocarbon reservoirs, causing a significant decrease in flow velocity, which, in turn, leads to a gradual hydrodynamic process [11]. Within this trapping mechanism, either the vertical or lateral sides of the CO₂ plume are constrained by sealing formations. The upper boundary is formed by a cap rock with notable low permeability. Due to its lower density compared to the formation fluid, the CO₂ migrates upwards until it encounters the impermeable cap rock. The potential

storage capacity of CO₂ is determined by assessing the pore volume and structural characteristics of sedimentary basins.

Solubility trapping

Solubility trapping primarily involves the dissolution of CO₂ in brine. Initially, the interface between CO₂ and brine initiates interactions, and molecular diffusion prompts the dissolution of CO₂ into the brine solution. This dissolution process results in an augmentation of the brine's density. Consequently, the denser brine situated at the uppermost portion is compelled to descend, thus enhancing the dissolution process. CO₂ has the capacity to elevate brine's density by approximately 1%. As greater quantities of CO₂ dissolve into the brine, it hinders the upward movement of gas, subsequently bolstering the overall storage capacity. This intricate mechanism is commonly referred to as "dissolution-diffusion convection" (DDC). Notable, a low solubility of CO₂ in brine poses a considerable risk of diminishing the efficacy of solubility mechanisms. [12]

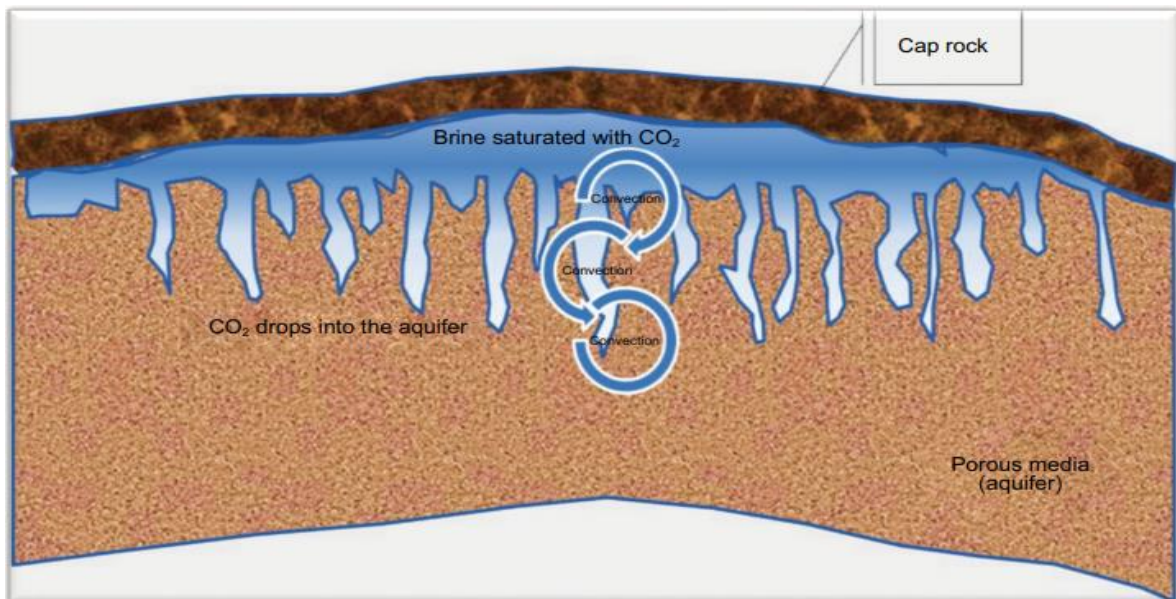


Figure 1: Illustration of solubility entrapment through convective mixing.[44]

Over time, as brine saturated with CO₂ gradually descends to the lower portion of the reservoir, it undergoes an increase in density compared to the other fluids within the formation. This evolving density differential enhances the effectiveness of CO₂ entrapment, rendering it a more dependable mechanism for carbon dioxide trapping. (Figure 1)

Mineral trapping

Mineral trapping is predicated on the chemical precipitation of carbon dioxide in conjunction with minerals and organic matter present within the rock formation. Over time, following the injection of CO₂, this has instigated interactions with the geological formation, a phenomenon that can yield either positive or negative outcomes. On the positive side, the formation serves as a reservoir, capturing CO₂ in a dissolved state. Conversely, the drawback lies in the potential for CO₂ to escape from the formation. The influence encompassing the reaction between CO₂ and the geological formation primarily comprise the structural characteristics, mineral composition, and hydrogeological attributes. Additionally, temperature pressure, and pH levels represent the fundamental components dictating the pace of these reactions. Thus, it becomes imperative to meticulously assess and comprehend the ramifications of these factors in order to attain optimal CO₂ trapping efficiency. Furthermore, the conversion of CO₂ into carbonate minerals holds substantial importance, as it can extend the duration of sequestration, ensuring a more protracted period of carbon storage. [13]

Residual trapping

Residual trapping predominantly hinges on the effects of capillary pressure. Initially, carbon dioxide is injected into the place where there is brine. Subsequent to the cessation of injection, CO₂ ascends due to disparities in density. This migration transpires as brine displaces CO₂, leading to the entrapment of a substantial volume of gas. This phenomenon is particularly pronounced when the rock exhibits water-wet characteristics. The optimal depth range for residual or capillary trapping typically falls within the bracket of 750 to 1000 meters.

Based on earlier experimentation, it has been ascertained that Berea formations at this depth interval can accommodate gas saturations ranging from 24% to 28%. The degree of trapped gas saturation is contingent upon a multitude of variables, including residual gas saturation, irreducible water saturation, wettability, critical gas saturation, as well as the permeability characteristics, both vertically and horizontally. Furthermore, factors such as heterogeneity and injection rates also exert notable influence on this phenomenon. [14]

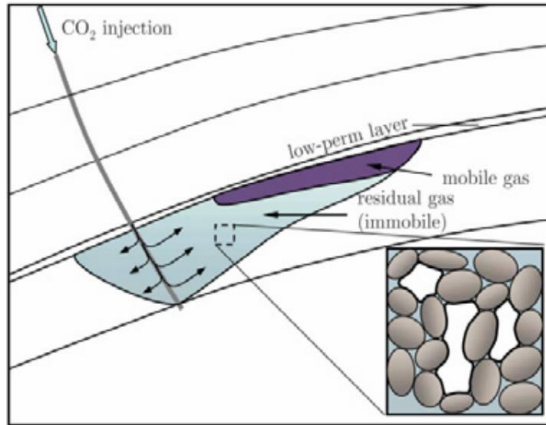


Figure 2: Residual trapping scheme.

Capillary trapping plays a pivotal role in the context of carbon dioxide (CO_2) storage and primarily manifests through two distinctive mechanisms: snap-off trapping and capillary pinning. This phenomenon is particularly pronounced in heterogeneous reservoirs, where its occurrence is contingent on several key factors, including intrinsic permeability, irreducible water saturation, the maximum saturation threshold for carbon dioxide, and the presence of a capillary entry pressure barrier. To elaborate further, snap-off trapping is a process that comes into play when the rocks exhibit a water-wet characteristic and is initially saturated with gas at irreducible water saturation. Subsequently, when brine is injected, CO_2 bubbles become entrapped due to the indicate interplay of capillary forces. [15].

1.2 Some factors that influence carbon dioxide storage.

According to the [16], the method used to introduce the CO₂ phase into the rock determines the kind and degree of residual CO₂ trapping. By introducing water into a core

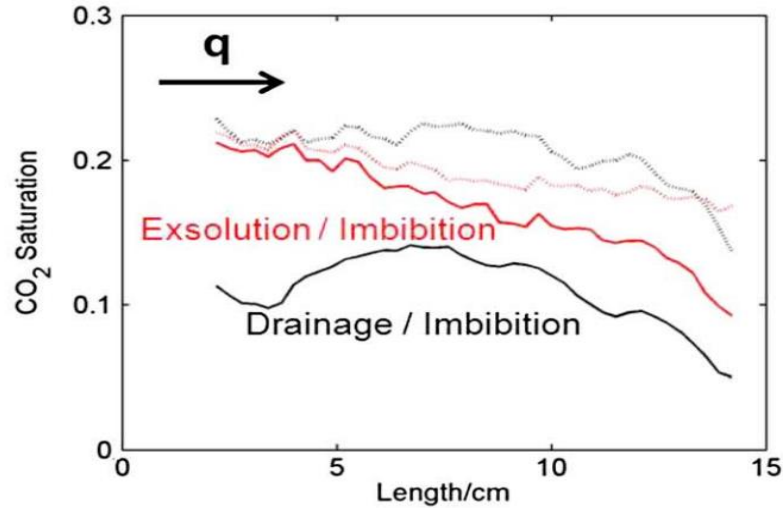


Figure 3: Porosity distribution of the cross-section carbon dioxide saturation profiles.

that contains either exsolved CO₂ or CO₂ injected by drainage, they investigated the diversification in the quantity of CO₂ trapped in Berea Sandstone. In this experiment they use x-ray tomography to define the areal distribution of carbon dioxide before and after imbibition. The information presented in **Figure 3** illustrates the carbon dioxide saturation profiles for two scenarios: drainage and exsolution, where residual gas saturations were equilibrated at a carbonated water injection of 15mL/min. The core under investigation exhibits an average porosity of 0.20 and alternately varying levels of porosity regions produce high-angle bedding planes over the length of the core. The high-angle bedding planes in the core show the significance of small-scale capillary heterogeneity on distribution of the phase that is nonwetting and have a major influence on the carbon dioxide saturation distribution during drainage. Regions with high porosity have carbon dioxide saturations that are noticeably greater than those with low porosity. However, compared to drainage, CO₂ exsolution is less impacted by capillary heterogeneity, resulting in a more equal distribution. In both scenarios, the average CO₂ saturations of whole core is comparable.

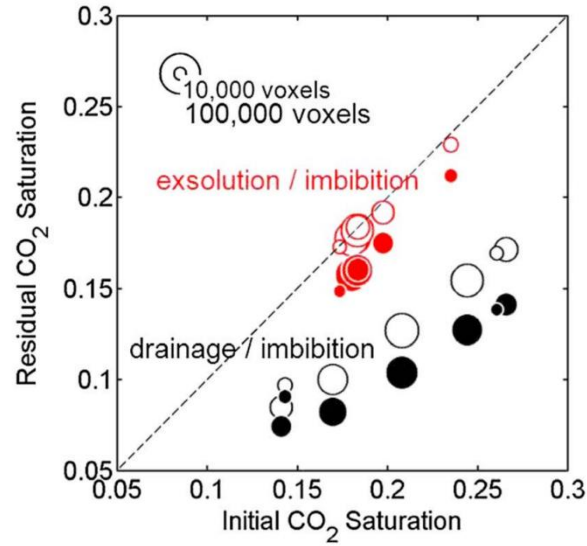


Figure 4: Dependence of residual carbon dioxide saturation on initial CO₂ saturation in drainage-imbibition and exsolution-imbibition.

In all four scenarios, the amount of residual carbon dioxide rises steadily as the initial saturation increases. But, with exsolved gas, capillary trapping is substantially more extensive.

In 2011, [17] carried out the study to investigate the influence of the porous media. The researcher implemented laboratory tests to obtain data on the maximum amount of non-wetting phase saturation and the permeability of wetting phase at the residual condition in 3 types of limestone cores and 4 types of sandstone cores. The main focus of this research was the residual condition created by low capillary number waterflooding.

The study concluded that the behavior of both absolute permeability and permeability at residual state can be explained by Darcy's law. As porosity increased, the residual saturation decreased proportionally. Moreover, data revealed that while increasing pore coordination number was undesirable, increasing pore body-throat aspect ratio was advantageous for improving residual saturation. It's also important to note that the pore networks used in the study did not account for microporosity related to intraparticle or intra-aggregate pores. Therefore, the results only apply to the larger pores and throats in the rocks. In simple terms, porous media heterogeneity in limestones and sandstones does not affect the relationship between residual saturation and porosity. This means that the

number of small pores within the rock does not impact the amount of liquid that remains after drainage. However, according to the [18] and [19], this case is different from previous studies that found a correlation between the amount of small pores and the maximum residual in sandstones.

Wettability is the phenomenon that explains the capability of a fluid to spread across or cling to a solid surface, also it holds significant importance in dictating fluid behavior within permeable media, particularly rock formations. In water-wet systems, the rock surface tends to be readily wetted by water, whereas non-wetting fluid, such as oil, tend to form separate droplets within the pores. This phenomenon confines non-wetting fluids and can significantly influence storage capacities and recovery methods, particularly in the context of Improved Oil Recovery and Carbon Capture and Storage (CCS) applications.

Capillary trapping, a phenomenon central to the retention of minuscule has bubbles within the intricate pore network of rock formation, is an area of critical investigation. Oil reservoirs, known to exhibit either oil-wet or mixed-wet characteristics, inherently elicit a mutual aversion between water or brine, precipitating a consequential reduction in residual saturation levels. A comprehensive exploration of this intricate has been undertaken with a notable study conducted by [20]. illuminating the phenomenon.

The findings from this study unveil a substantial distinction in the residual saturation of carbon dioxide within oil-wet pore spaces, amounting to approximately half of the saturation observed in water-wet environments. Specifically, the results indicate Values of 8.7% and 14.9% for oil-wet and water-wet, respectively. This significant variance underscores the heightened efficiency of deep saline aquifers in comparison to depleted oil and gas reservoirs as repositories for CO₂. This efficiency arises from the inherent alignment of pore space wettability with the characteristics of the fluids that previously resided within the reservoir.

To explore how the salinity and pressure effects the wettability, three distinct types of rock samples-specifically feldspar, calcite, mica and quartz were employed by [21] in conjunction with carious salt concentration. The findings unveiled that pressure exerted a

minimal impact on contact angle, with only marginal variations observed. Conversely, as the amount of NaCl climbed, the contact angle displayed a noteworthy decrease.

Remarkably, mica exhibited a more pronounced sensitivity to changes in salinity compared to the other rock samples. This heightened responsiveness can be attributed to the surplus of negative surface charge present on the mica particles.

CHAPTER 2

LITERATURE REVIEW

Evaluating the influence of CO₂ wettability on cap-rock formations holds paramount significance. This factor serves as a fundamental determinant governing the dispersion and migration of CO₂ within the CCS formation. Additionally, it exerts a pivotal influence on various facets, including flow characteristics, containment reliability, and the overall quantity of CO₂ successfully trapped within the reservoir.

Therefore, [22] carried out experiment to learn the impact of varying percentages of organic acid on the change of cap rock wettability. This investigation focused on wettability alteration, primarily through the analysis of contact angle changes. The findings underscored that even minimal concentrations of organic acid can exert a discernible influence on the wettability of cap-rock. Furthermore, their observations indicated that as the percentage of organic acid went up, both the receding and advancing contact angles exhibited notable increments. It's noteworthy that the advancing contact angle is particularly relevant to the phenomenon of residual trapping. In summary, it is deduced that the trapping potential within CO₂ storage formations (mica), particularly deep saline aquifers, might be less substantial than previously anticipated, owing to the presence of organic acid.

Capillary trapping involves trapping small gas bubbles within the rock's pore media. As we know, oil reservoirs are either oil-wet or mixed-wet which triggers repulsion of water or brine that in turn, leads to a drop in residual saturation. There are several experiments that have been conducted to learn this effect in detail. One of the implemented studies is [20]. The derived conclusion suggests that the residual saturation of carbon dioxide within oil-wet pore spaces is approximately half of that observed in water-wet environments. Specifically, the outcomes reveal values of 8.7% and 14.9% for oil-wet and water-wet rocks, respectively. This implies that deep saline aquifer may exhibit greater efficiency in storing carbon dioxide compared to depleted oil and gas reservoirs, primarily because the wettability of the pore space closely aligns with the characteristics of the fluids

previously present in the reservoir. It is worth noting that the heterogeneity of the pore space significantly influences the residual trapping capacity.

Regarding the organic acid effect on the wettability alteration, [22] conducted a study as well. In this research, sandstone was employed as the primary material. Before subjecting the core sample to aging processes, it was immersed in a 2wt% NaCl brine solution for a duration of 30 minutes, ensuring the maintenance of a pH level of 4. They aimed at understanding alterations in wettability induced by organic acid (stearic acid). Additionally, they delved into the relationship between the concentration of organic acid, contact angle, and their implications for residual trapping capacity. Their findings revealed that even minimal concentrations of organic acid can produce a significant increase in the contact angle (from 40° to 57°), signifying a shift in the hydrophilic properties of quartz. This reduction in the surface's affinity for water potentially translates to a decrease in the capacity for residual trapping as CO₂ plumes migrate within the storage formation.

[23] undertook a comprehensive investigation to examine the impact of salinity, pH, and fatty acids on wettability. Their analysis yielded several significant conclusions. Firstly, they observed a decrease in interfacial tension as salinity level increased, highlighting the inverse relationship between salinity and IFT. Furthermore, the study incorporated the use of stearic acid, characterized as long-chain fatty acid, along with naphthenic acid.

The results indicated that stearic acid induced a strong shift toward oil-wet wettability. In contrast, the influence of naphthenic acid on wettability was notably milder than compared to stearic acid. Additionally, the study revealed that SO₄ caused a shift toward water-wetness, while Mg was found to induce a shift towards slight oil-wet wettability when pH level exceeded 7.

[24] investigated the impacts of equilibrium contact angle and interfacial tension between solid and liquid or solid and gas on the carbon dioxide storage capacity and how contact angle and interfacial tensions are affected by the temperature and pressure and organic acid with different concentrations. However, because it is difficult to define the parameters experimentally, they are frequently computed using advancing and receding contact angles. In this experiment mica has been chosen as a solid phase, because we need to investigate caprock and gas interaction which is crucial for structural trapping.

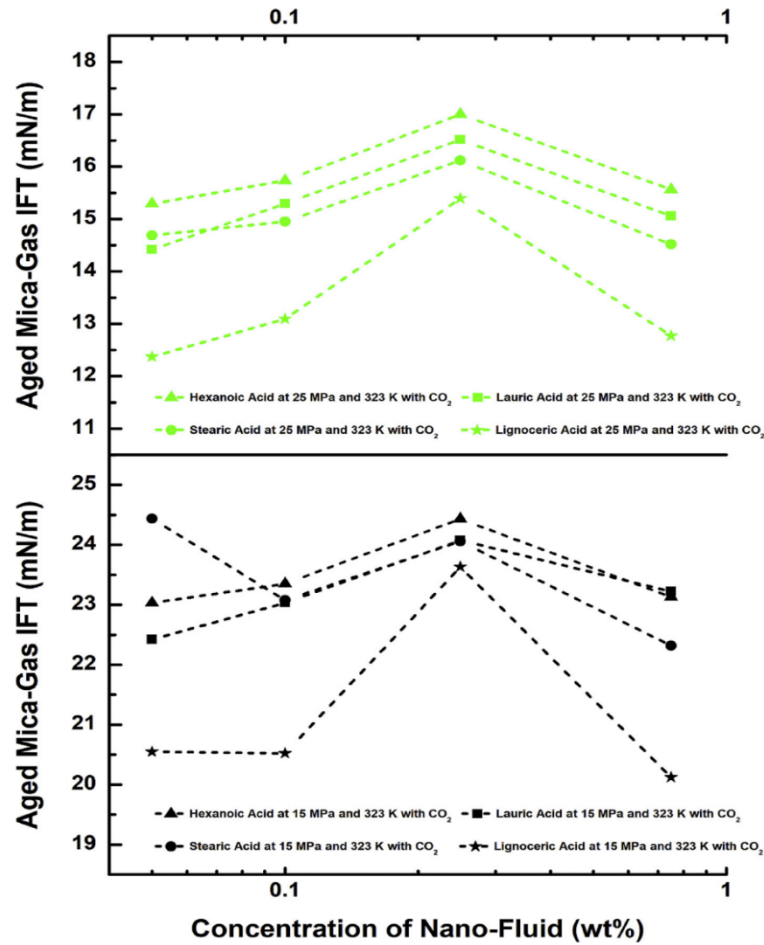


Figure 5: Impact of alumina nanofluid percentage and pressure on CO₂ and mica interfacial tension.

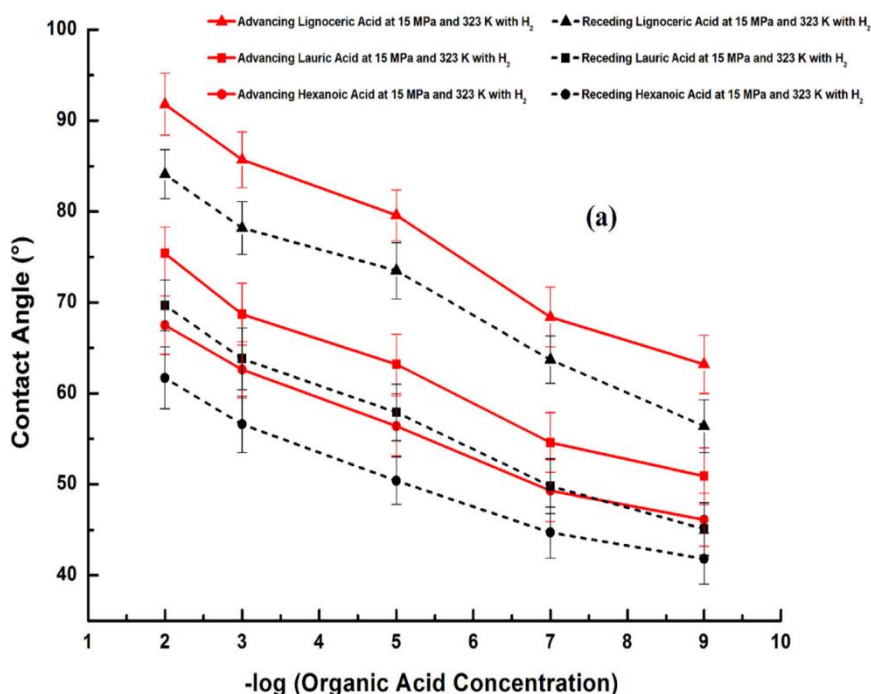
From the conducted experiment they concluded that the equilibrium contact angle value rises when the amount of organic acid increases, however while temperature increases

contact angle decreases. Thus, they discovered that higher pressure and the presence of organic acids are inconvenient for carbon dioxide storage. We can conclude that reservoirs that have higher temperature are better places for storage.

The study conducted by [25] also confirmed that the wettability can be altered by the organic acids considerably.

[26] undertook a comprehensive exploration into how the organic acid effects wettability characteristics of carbonate formations. This examination was carried out through measurements of contact angles. Their results revealed a significant increase in contact angles after the aging process, exceeding 90 degrees. According to Young-Laplace equation, it is understood that when the contact angle is more than 90 degrees, the capillary pressure (P_c) is calculated as zero, which is an unrealistic scenario. Consequently, the outcomes of this study underscore the persistent disparities observed in experimental outcomes.

As per [26] perspective, it is evident that the wettability of rocks is not solely altered by the concentration of organic acid. Additionally, the size of the organic acid chain is a phenomenon that can exert an impact on the degree of wettability alteration (contact angle). **(Figure 6)**



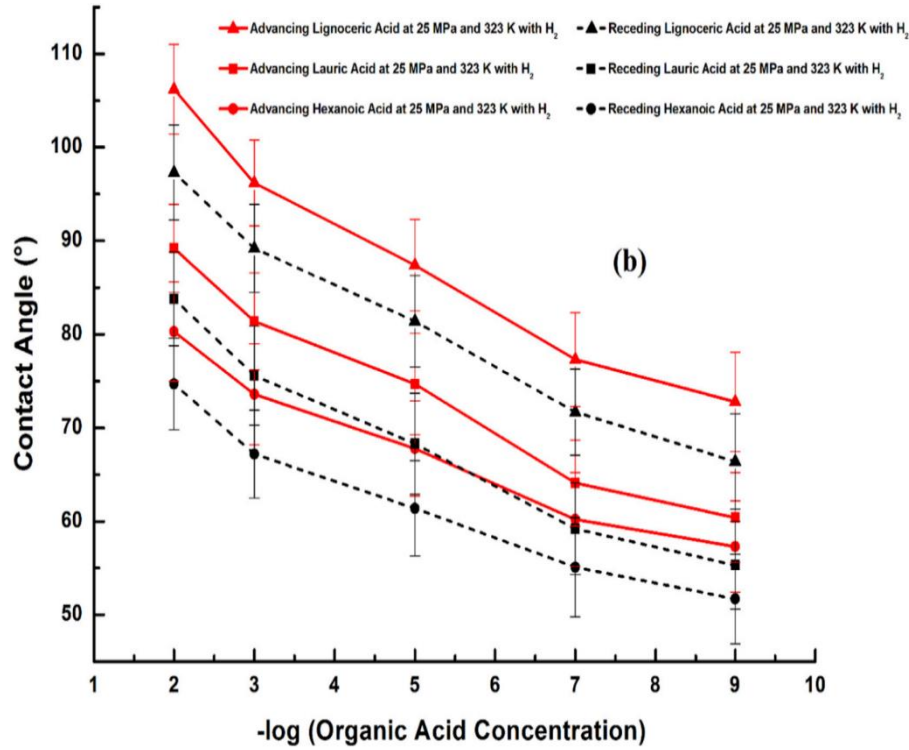


Figure 6: The contact angle as a function of carbon number of organic acid

Wettability stands out as the primary determinant influencing the carbon dioxide (CO_2) retention capacity. An in-depth exploration into this phenomenon was undertaken by Yaseri in one of their studies. The objective was to discern the distinctions in CO_2 immobilization between water-wet and mixed-wet rock formations. As discerned from the graph depicted below (**Figure 6**), a conspicuous trend emerges with increasing oil-wettability of the rock (using crude oil with organic precipitant heptane), there is a notable decrease in residual saturation. Furthermore, within the same wetting phase, it is evident that nitrogen exhibits a higher propensity for retention compared to carbon dioxide.

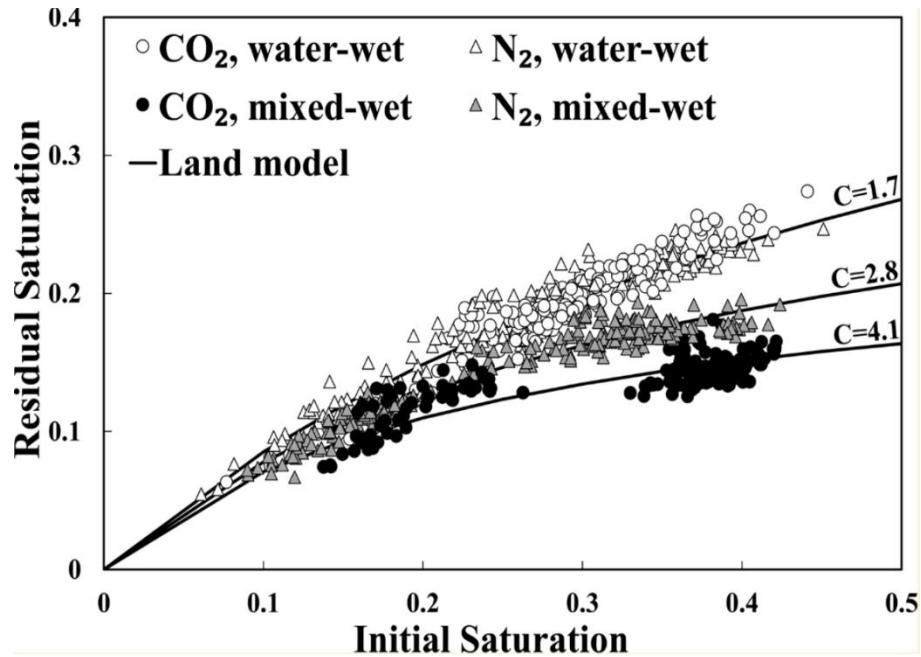


Figure 7: The residual saturation changes of carbon dioxide and nitrogen depending on the initial saturation in different wetting phases.

[27] performed experiment to discover the effect of wettability and shape of the grain on the s-CO₂ trapping capacity. In this experiment he utilized columns wrapped up with glass bead that is water wet which represents the reservoir precisely. By employing synthetic media rather than reservoir rock, they managed to isolate the features that they were interested in, without the natural diversity of physicochemical properties, particularly wettability. The authors took columns packed in beads with different parameters: glass beads(water-wet), angular glass grains(water-wet) and Teflon (CO₂-wet) beads which had very close porosity. This experiment has 3 main steps: saturate with brine, supercritical CO₂ flooding and finally brine reinjection. Initially, after brine saturation, CO₂ flood was implemented and resulted in almost the same percentages (24%,22% and 25%). After CO₂ flood, the clusters were not connected, which means the CO₂ flow was not continuous, and there was some backflow of brine because of gravity settling. Thus, it caused 24% of CO₂

initial saturation. After implementation of last step (brine reinjection), 39% of CO₂ was pushed out and trapped saturation became 61%: (overall 15%)

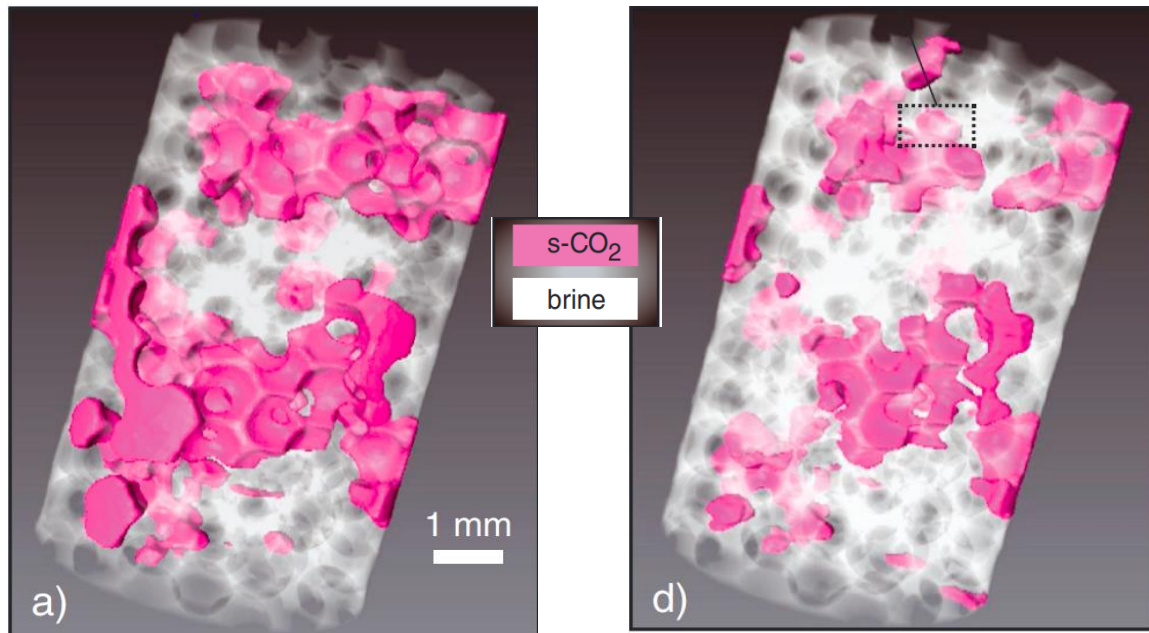


Figure 8: a) CO₂ saturation before brine reinjection and d) CO₂ trapping distribution after brine reinjection (snap-off)

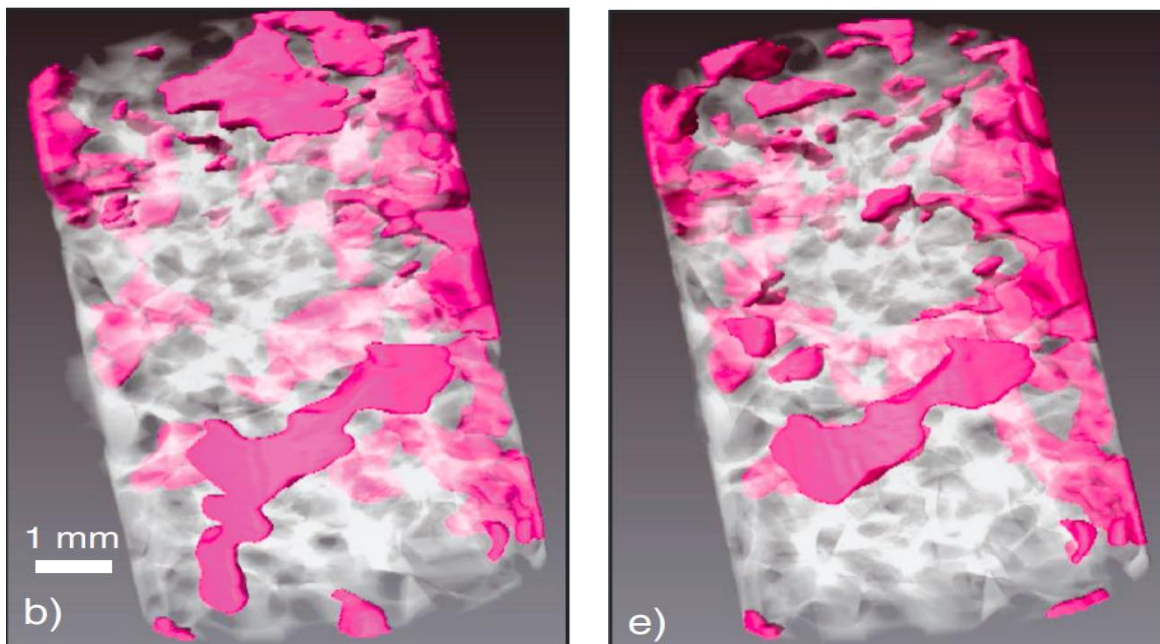


Figure 9: b) CO₂ distribution before the brine flood and e) after brine flood (trapping)

The CO₂ saturation of column with glass beads (22%) resulted in predominantly at the column's margins, and an extremely tiny number of isolated clusters inside the column and the brine flood caused 87% s-CO₂ residual trapping. (Overall, 20%)

However, residual CO₂ in Teflon was very different than other because it was CO₂-wet. Although it had 25% of CO₂ initial saturation, after brine reinjection only 7% of that CO₂ could be trapped. (Overall, 2%):

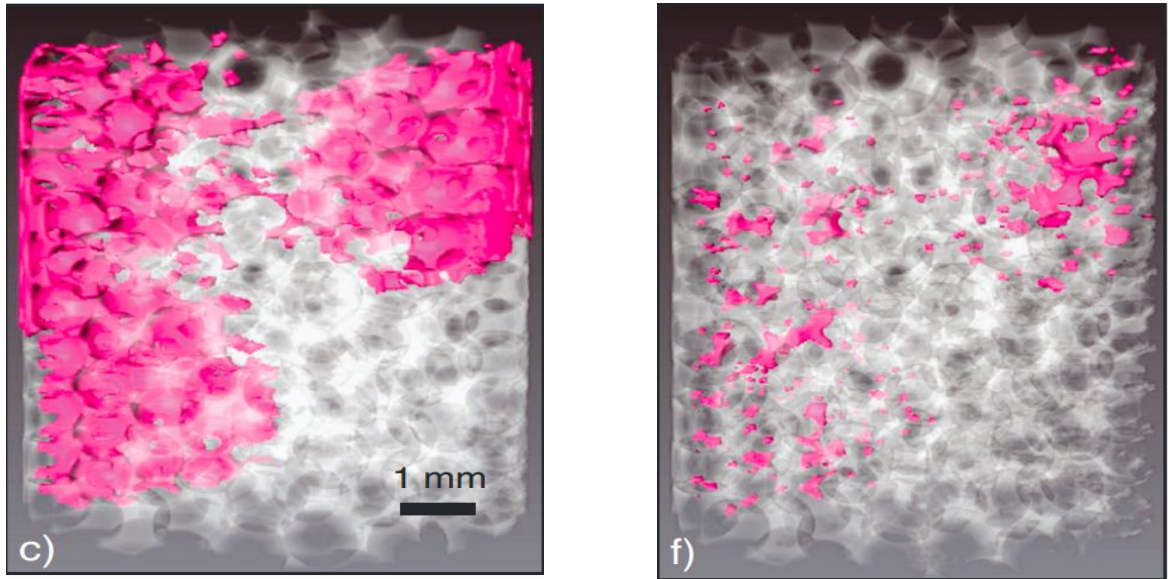


Figure 10: c) CO₂ distribution before the brine flood and f) after brine flood (trapping)

[28] elucidated the concept of snap-off by providing both illustration (**Figure 10**) and a mathematical **formula 1**. The underlying principle of Roof snap-off criterion postulates

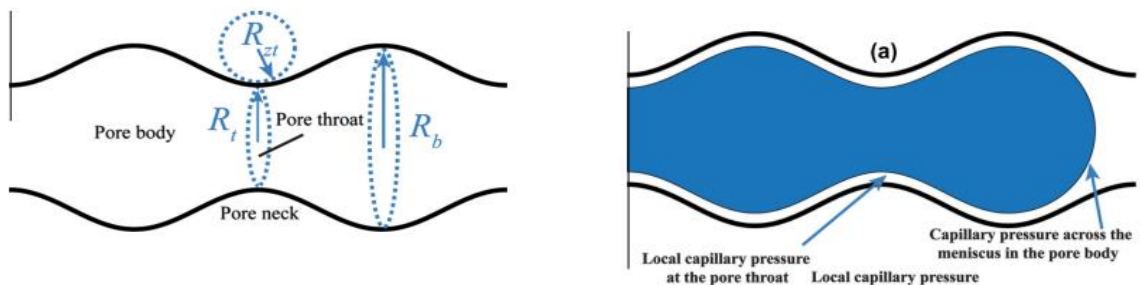


Figure 11: Illustration of the geometric properties and pressure of core sample

that when the local capillary pressure at the pore throat exceeds the capillary pressure at the meniscus in the adjacent pore body, it results the destabilization of the nonwetting fluid, causing it to detach at the pore throat.

Snap off possibility also can be shown with following formula:

$$\frac{2}{R_b} < \frac{1}{R_t} + \frac{1}{R_{zt}} \quad (1)$$

The author states that there is a common assumption that residual trapping in mixed-wet systems is not as effective as in water-wet systems. To test this assumption, the author and their team conducted a study [29] where they compared the efficiency of residual trapping in mixed-wet and water-wet carbonates systems on a single rock sample. The study involves conducting tests before and after the rock was exposed to crude oil in order to alter its wettability. Even though there are not exact number results, the researcher observed obvious difference between the residual changes of water-wet and mixed-wet carbonate rock sample which confirms one more time that wettability is crucial for CO₂ residual trapping.

[30] investigated how the wettability impacts the residual saturation. The alteration of wettability was achieved through the application of both organic acid and crude oil. Their analysis led to the determination that organic acid exerts a more pronounced impact on wettability alteration compared to crude oil. Moreover, the transition from a water-wetting to a mixed-wetting resulted in a substantial reduction in residual saturation (**Figure 12**).

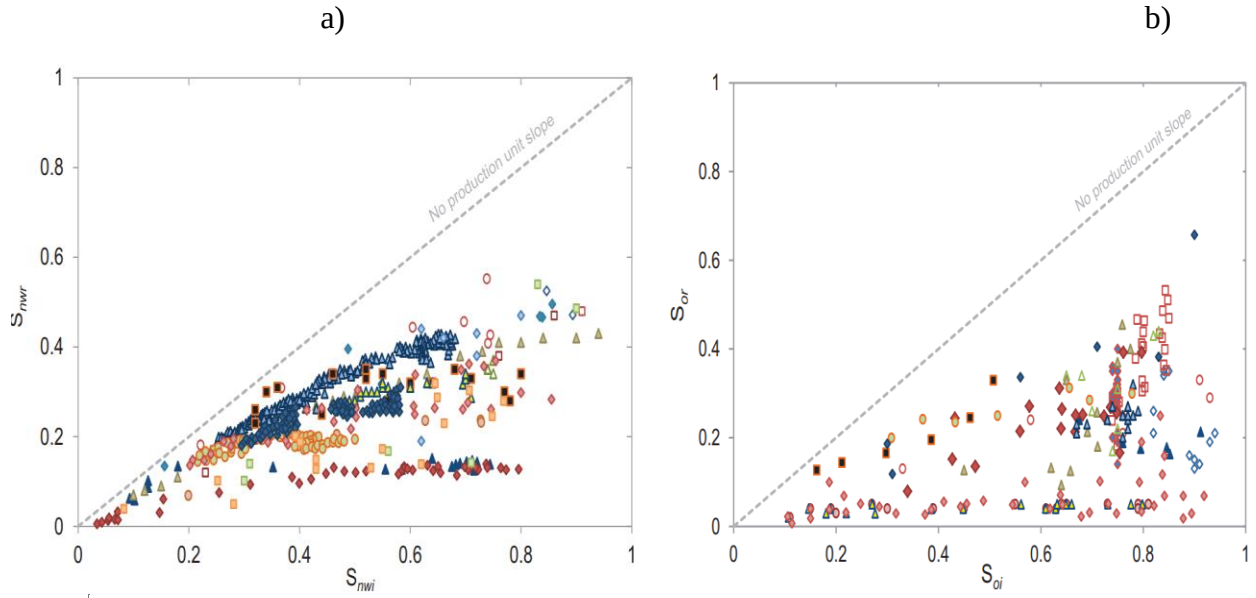
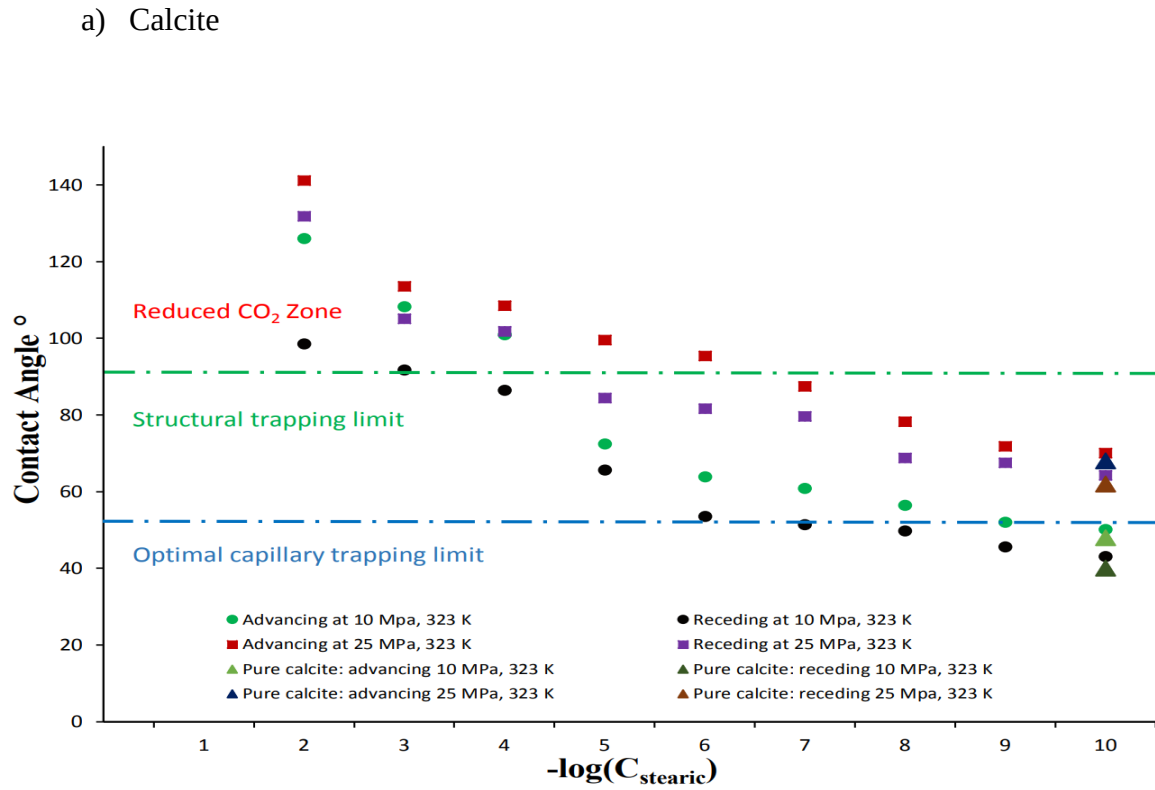


Figure 12: The dependence of residual saturation on initial saturation before (a) and after aging(b)



b) Quartz

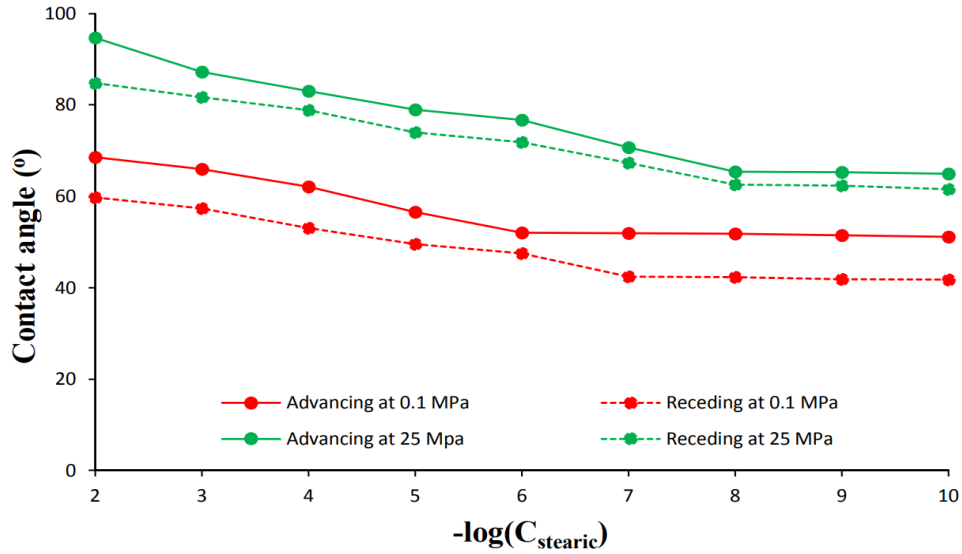


Figure 13: The effect of the stearic acid concentration on the advancing and receding contact angle of calcite and quartz

In this experiment[31] , from the result graph we can obviously see that as the amount of organic acid grows the contact angle is rising in both calcite and quartz.

They also investigated how the pressure impact the contact angle for each concentration of stearic acid. The findings indicate that the more pressure is applied the more contact angle is obtained.

Stearic acid concentration (molarity)	CO ₂ /calcite/brine contact angle (10 MPa and 323 K)		CO ₂ /calcite/brine contact angle (25 MPa and 323 K)	
	θ_a	θ_r	θ_a	θ_r
10^{-2}	126.0 ⁿ⁼³	98.6 ⁿ⁼³	141.2 ⁿ⁼³	131.8 ⁿ⁼³
10^{-3}	108.2 ⁿ⁼³	91.8 ⁿ⁼³	113.5 ⁿ⁼³	105.1 ⁿ⁼³
10^{-4}	100.9 ⁿ⁼³	86.5 ⁿ⁼³	108.5 ⁿ⁼³	101.8 ⁿ⁼³
10^{-5}	72.4 ⁿ⁼³	65.7 ⁿ⁼³	99.6 ⁿ⁼³	84.4 ⁿ⁼³
10^{-6}	63.9 ⁿ⁼³	53.5 ⁿ⁼³	95.4 ⁿ⁼³	81.7 ⁿ⁼³
10^{-7}	60.9 ⁿ⁼³	51.4 ⁿ⁼³	87.5 ⁿ⁼³	79.6 ⁿ⁼³
10^{-8}	56.4 ⁿ⁼³	49.7 ⁿ⁼³	78.2 ⁿ⁼³	68.8 ⁿ⁼³
10^{-9}	52.0 ⁿ⁼³	45.6 ⁿ⁼³	71.8 ⁿ⁼³	67.5 ⁿ⁼³

Table 1: The effect of the stearic acid concentration on the advancing and receding contact angle at different pressure and the same pressure

As previously highlighted, the contact angle is subject to the influence of various factors beyond organic acid and wettability alterations. An investigation conducted by [32]. delved into the impact of different surface roughness levels (ranging from 56 to 1300 nm) on quartz, specifically examining their effects on both receding and advancing contact angles at different pressures. The results of the study (**Figure 15**) unveiled a discernible trend: as the surface roughness increased, the advancing contact angle exhibited a notable reduction.

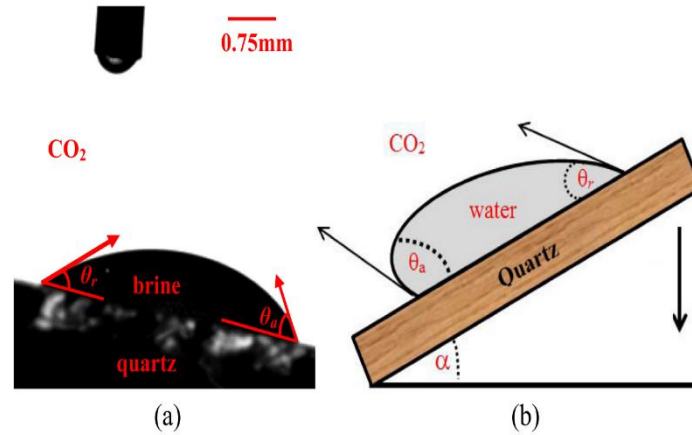


Figure 14: Image captured under optical microscopy, depicting a water droplet resting upon the surface of quartz in CO₂-rich environment.

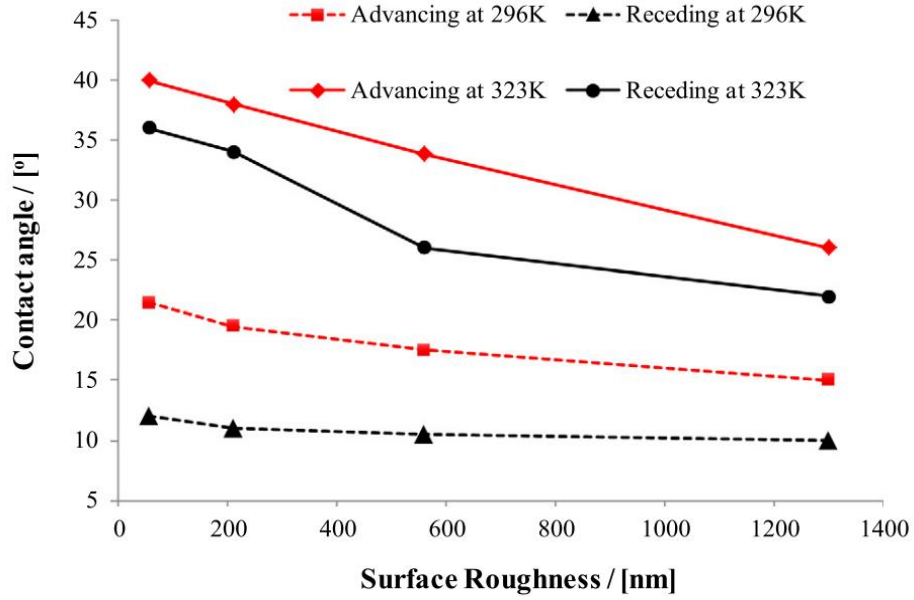


Figure 15: The influence of surface roughness and temperature on the contact angles at 323 and 296K pressure

The study conducted by [33] also shows the effect of surface roughness on wettability. In this research endeavor, the assessment of wettability was conducted through the measurement of contact angles in deionized water (DI). Three distinct rock samples were utilized, each characterized by differing surface roughness values of 7.5, 30 and 140 nanometers. The investigation also delved into the influence of fluid equilibrium on the augmented diffusion coefficient of CO₂ in water. It was determined that an escalation in surface roughness results in a reduction of the contact angle. Moreover, it was concluded

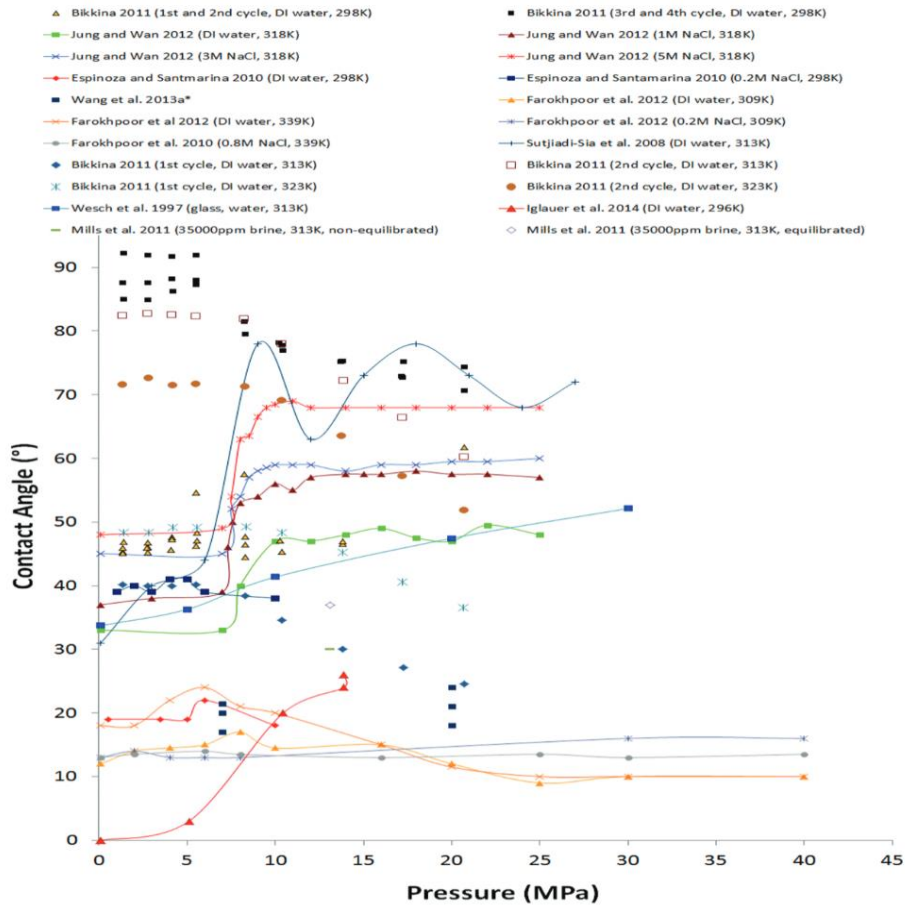


Figure 16: The effect of the surface roughness on the contact angle

that low pressure, elevated temperature, and reduced salinity play pivotal roles in promoting a water-wet surface.

[33] can be shown as another example which proves that surface roughness can be the reason why contact angle is not only affected by pressure, temperature and the presence of organic acid.

In addition to considering surface roughness, it is important to acknowledge the potential impact of surface contamination on the contact angle [34], [35]. Nevertheless, the prevailing trend in existing scholarly works reveals that a significant portion of researchers evaluating the influence of organic acids on contact angles tend to neglect the issue of contamination [36] [37][38]. Consequently, , [39]’s research endeavors to delve comprehensively into the relationship between contamination and its effect on contact angles. They combined a handful of results of contact angle as a function of a pressure and observed very high scattered data (**Figure 17**). However, in studies of obtained data no authors gave a decent explanation to this uncertainty. Hence, they concluded that the contamination is the main reason for distinct contact angles which means it is not only because of pressure.

Figure 17: The impact of contamination on the contact angle.

[40] conducted a research study with the primary objective of examining how silane influences the wettability of sandstone (quartz) and carbonate (calcite). This investigation involved assessing changes in wettability by centrifuge tests, contact angle measurements and capillary pressure measurements. Furthermore, core flooding experiments were

conducted to analyze alterations in water relative permeability. Prior to these experiments, sandstone was cleaned with HCl and carbonate with NaOH, but only samples used in contact angle measurements (in order to mimic in-situ conditions for centrifuge testing). The study employed a saline solution with varying concentrations (0.5%, 1%, and 2%), different temperatures, and treatment durations.

They also determined that, following the treatment, capillary pressure decreased, providing evidence that not only the surface properties of the samples but also the internal pore structure became more inclined toward oil-wet characteristics. The capillary pressure results were derived using a formula and parameters acquired from the centrifuge tests conducted in the core flooding experiment. This experiment reaffirmed the influence of saline on wettability. Post-treatment, it became evident that gas could more effectively displace water, indicating a reduced water-wet nature of the surface.

In summary, their findings suggest that even with extremely low concentrations of saline, it is feasible to enhance the reservoir's hydrophobicity, as proved by a significant growth in the contact angle, enhanced brine displacement during centrifugation, and a reduction in capillary pressure.

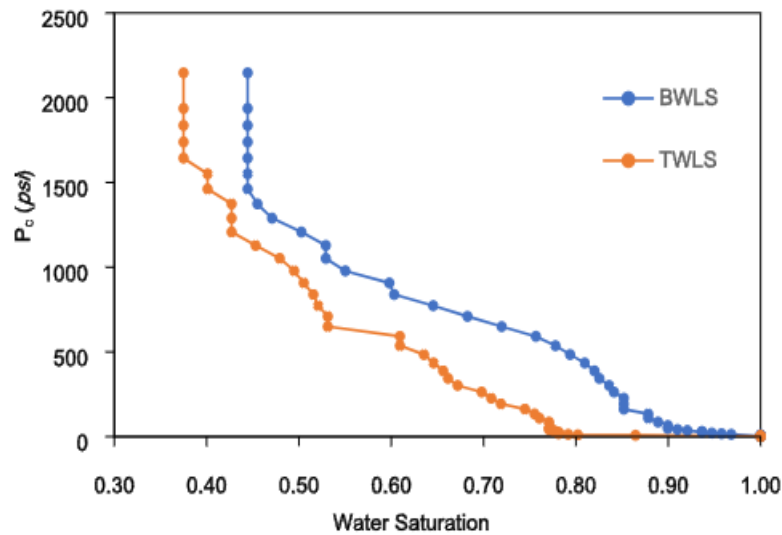


Figure 18: Capillary pressure curve obtained from centrifuge.

[41] conducted a study into how changes in wettability for both quartz and carbonates impact capillary pressure, relative permeability, and irreducible saturation in air-brine (prior to aging) and air-oil (post aging) systems. In this research, the capillary pressure was

quantified using the porous plate method, recognized for its high precision. Notably, there was no assessment of wettability for the samples before or after aging. To alter wettability, Glycerophthalic paint dissolved in acetone was applied.

The findings of this investigation showed that after the treatment, the core samples became more hydrophobic, resulting in a decrease in wetting phase irreducible saturation (brine before aging, oil after aging) in the capillary pressure measurements. It was observed that the relative permeabilities of the wetting phase in an air-oil system were more compared to the relative permeabilities of the wetting phase in an air-water system, whereas relative permeabilities of their non-wetting phases were contrary.

CHAPTER 3

METHODOLOGY & EXPERIMENTAL PROCEDURES

3.1 Overview of procedures

1) Measuring some of the petrophysical properties of Indiana Limestone (Carbonate) and sandstone (Berea):

- Porosity (Porosimeter)
- Permeability (AutoScan) + Core Flooding and Nitrogen Gas Permeameter.

2) Contact angle and Capillary pressure measurement (Drop Shape Analyzer, Multi sample capillary pressure cell and Centrifuge)

3) Aging the core sample with different concentrations of organic acid (0.5, 2, 5, 10 wt. %). (Plastic Vacuum desiccator)

4) Contact angle and Capillary pressure measurement

5) TOC measurement (Elementar Soli TOC)

6) NMR measurements (Geospec2 Rock Core Analyzer)

7) Investigate the effect of cleaning on Capillary Pressure

8) The effect of mixture of crude oil and organic acid on Capillary Pressure

8) The effect of mixture of crude oil and organic acid on Capillary Pressure

3.2 Experimental Procedure:

3.2.1 Rock Samples

Indiana Limestone and Sandstone are the sort of rock that was chosen for this research. At the beginning, long core samples were cut by a Mecatome ST310 cutting device (**Figure 18**) into small one with the dimensions of around 3 inches in length and 1.5 inches in diameter. In this experiment we used overall 9 Berea and 7 Carbonate samples.



Figure 19: Mecatome ST310

3.2.2 Porosity measurements

Initially, we conducted porosity measurements on all specimens employing a Helium Porosimeter, as depicted in (**Figure 18**). We subjected the samples to a pressure of 190 psi using Helium gas to ascertain their effective porosity. For all samples the average porosity value was around 19-20%.

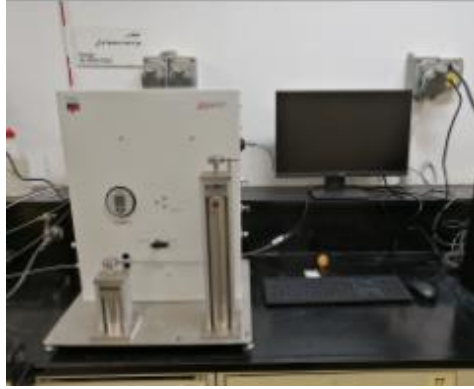


Figure 20: Helium Porosimeter

3.2.3 Permeability measurements

Subsequently, Auto-Scan (**Figure 19**) was used to measure the permeability of the core samples. 12 points were taken (6 points from top and bottom) and scanned and found the average of the values of all points which gives the absolute permeability result. The



Figure 21: Auto-Scan

permeability of Berea was between 150-250 mD and Carbonate was around 50-150 mD. Apart from the AutoScan, in order to doublecheck we also measured the permeability with Nitrogen gas permeameter and results were almost identical.

Next, we saturated all the cores with sea water brine with AutoSaturator (**Figure 23**) under 3000psi pressure for 24 hours.

3.2.4 Saturation

Procedure to saturate samples:

1) Brine preparation:

Name of the salts	Amount (g/L)
NaHCO_3	0.165
Na_2SO_4	6.345
NaCl	41.162
MgCl_2	8.266
CaCl_2	1.8

Table 2: The chemical composition of the sea water brine

All salt was added to the DI water and stirred for 24 hours at room temperature.

2) Putting samples in the core holder and vacuuming for 1.5 hours with Fume Hood Vacuum (**Figure 21**).

3) Filling the pumps and core holder with brine

4) Applying 3000psi pressure by the pumps

5) Waiting for 24 hours to saturate 100%.



Figure 22: Fume Hood Vacuum



Figure 23: Auto-Saturator

After saturation, in order to make sure that core samples are 100% saturated, we measured brine density and wet weights of samples (we already had had the dry weight) and used following formulas:

$$\text{Volume of brine inside pores} = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Brine density}} \quad (2)$$

$$\text{Saturation} = \frac{\text{Volume of brine inside pores}}{\text{Pore Volume}} \quad (3)$$

3.2.5 Contact Angle Measurement



Figure 24: Drop Shape Analyzer.

3.2.6 Capillary Pressure measurement

Multi sample capillary pressure cell (Vinci Technologies) connected to the desaturator (**Figure 22**) was used to construct capillary pressure curve (Pressure (PSI) vs Saturation (Fraction)). First, the porous plate inside the chamber was saturated with the DI water in Desiccator for a day. Then, samples were loaded, and pressure was applied by the Nitrogen gas. Pressure was increased gradually every day starting from the 20psi. Each day the chamber was depressurized, samples were unloaded, and wet weight was measured. Formula 2 and 3 were used to calculate saturation corresponding to each pressure. This was repeated until we observed the stabilization in brine saturation.

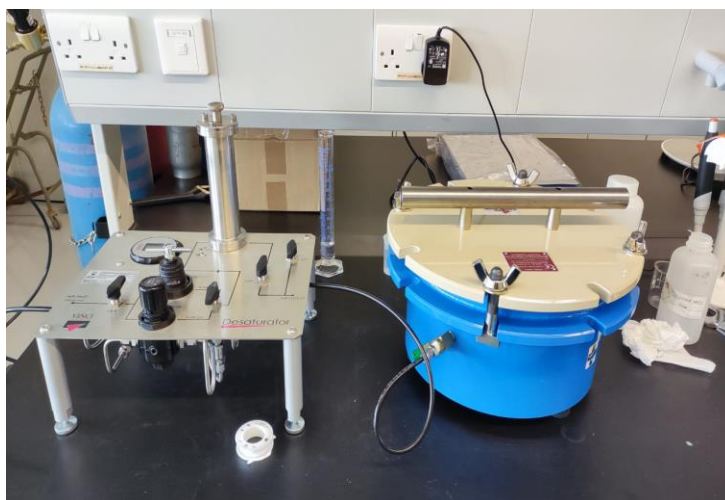


Figure 25: Multi-sample capillary pressure cell and Desaturator.

After Capillary Pressure the samples were put in the oven at 100°C for a day to dry. Furthermore, to refine the accuracy of our measurements, we implemented centrifuge-based approach to gauge capillary pressure. Prior to the initiation of the experimental procedure, the samples underwent saturation with the same brine utilized in previous measurements conducted with a porous plate, after which they were carefully loaded into cups. This specialized equipment facilitated the displacement of the brine through the application of centrifugal forces. Operating at varying speeds ranging from 1000 to 8000 RPM, we meticulously observed the saturation stabilization process. To ensure uniform

pressure exertion across all three cups, attention was paid to matching the exact weight of each cup.



Figure 26: Centrifuge

3.2.7 Aging

Then, we implemented the aging process. The aging process starts with the vacuuming using Plastic Vacuum desiccator (**Figure 23**).

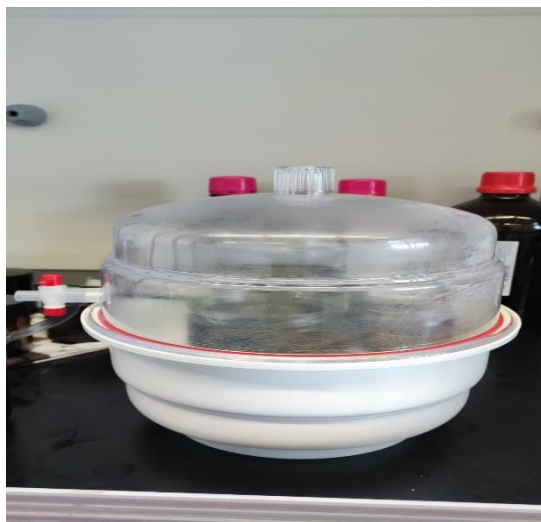


Figure 27: Plastic Vacuum desiccator

We immersed the core samples in the solution and put the container in the equipment. We waited until no bubbles came out which took approximately 4.5 hours. Then, we kept the samples inside the solution for 4 days at 80°C temperature for the reaction. After the aging process, they were dried at 50°C for a day. Next, we measured Capillary Pressure again to see the difference prior to aging and followed the same steps as mentioned before for saturation with brine.

3.2.8 NMR measurements

The H1 NMR T2 relaxation time measurements were performed using Geospec2 Rock Core Analyzer from Oxford instruments, and it is operating at Larmor frequency of 2 MHz (equivalent to 0.05 Tesla). The T2 relaxation time data conventionally acquired using Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence to detect the transverse relaxation decay (Carr & Purcell, 1954; Meiboom & Gill, 1958). The CPMG pulse sequence starts with a 90° radio frequency pulse followed by a train 180° pulses. The 180° radio frequency pulses are separated by a time called echo time in which the relaxation data are acquired. The amplitude of the received NMR signal at time t, which is the amplitude of the transverse magnetization M(t) is given by:

$$\frac{M(t)}{M_0} = \exp\left(-\frac{t}{T_2}\right) \quad (4)$$

where M0 is the total initial magnetization at time t=0. The NMR porosity (ϕ_{NMR}) is calculated based on the maximum signal received, M0, from the CPMG data in which the spins are fully excited. The NMR measurements were performed at the three different saturation states which are: full water saturation ($S_w = 1$), and after desaturation with pressure of 20, and 180 psi ($S_w@20\text{psi}$ and $S_w@180\text{psi}$), respectively. To cross-validate the fluid's saturation measured gravimetrically, the ϕ_{NMR} at $S_w = 1$ value for each sample was used to calculate the NMR-derived water saturation after desaturation using the following equations:

$$S_{w@20psi} = \frac{\phi_{NMR}(S_{w@20psi})}{\phi_{NMR}(S_w=1)}$$

(5)

$$S_{w@180psi} = \frac{\phi_{NMR}(S_{w@180psi})}{\phi_{NMR}(S_w=1)}$$

(6)



Figure 28: NMR

3.2.9 TOC measurements

In addition, the Total Organic Carbon (TOC) analysis test was conducted by Elemental Soli TOC equipment to determine the adsorption of oleic acid (carbon) on the samples of limestone and sandstone. Prior to measuring the TOC, the rock sample was ground into a powder and then aged under the same conditions as the reference samples. In this aging procedure, a 300-milligram portion of the powdered sample was allowed to mature for 4 days in a 7.5-milliliter solution at 80oC temperature. Following the aging process, we conducted a filtration step and subsequently subjected the resulting powder to 50oC drying period lasting one day. After the drying process, we proceeded to measure Total Organic Carbon (TOC) content.

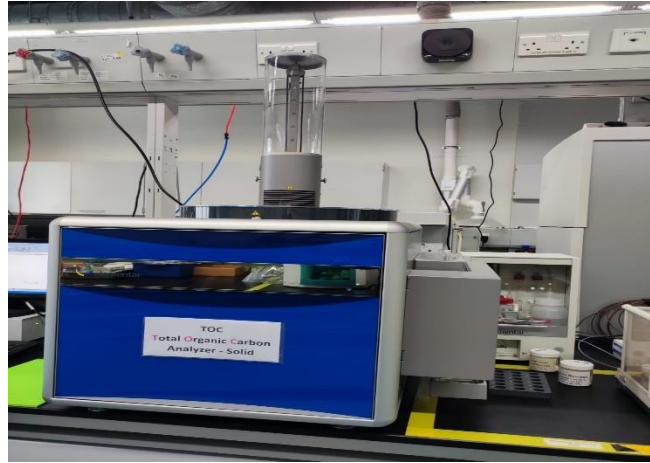


Figure 29: TOC

CHAPTER 4:

RESULTS AND DISCUSSION

It is essential to investigate the impact of wettability on capillary pressure for sandstone and limestone formations, as this may share similarities with the principles governing gas storage, such as the storage of H_2 and CO_2 (Sakthivel et al., 2024, Al-Yaseri et al., 2023), which considers the dynamics of gas distribution (Abdulelah et al., 2021, Jha et al., 2021). Baseline conditions were established through the determination of capillary pressure curves during gas drainage process (i.e., N_2 gas displacing sea water brine). The subsequent section offers an advanced examination of the impact of organic acid on the wettability and capillary pressure of sandstone and limestone core samples as the concentration of organic acid increases. It is important to mention that the petrophysical properties of selected samples were examined both before and after wettability modification. Table 3 clearly shows that the change in porosity and dry weight are insignificant.

Sample ID	Length [mm]	Width [mm]	Dry weight [mg]	Porosity [%]	Oleic acid concentration Wt. %	Dry weight After aging [mg]	Porosity after aging [%]
Sandstone-1	49.84	37.9	120.04	20.13%	0.5	119.93	19.69%
Sandstone-2	51.33	37.83	124.29	18.99%	2	125.31	18.35%
Sandstone-3	47.01	37.89	114.07	19.18%	5	114.66	18.74%
Sandstone-4	49.44	37.81	120.58	18.39%	10	121.88	17.98%
Carbonate-1	58.98	37.54	141.28	19.09%	0.5	141.81	18.87%
Carbonate-2	37.57	62.61	150.62	18.79%	2	151.60	18.59%
Carbonate-3	60.01	37.85	150.07	16.90%	5	150.79	16.65%
Carbonate-4	37.53	63.5	152.56	18.82%	10	154.21	18.35%

Table 3: Porosity change after treatment.

We investigated the effect of organic acids on rock wettability by measuring capillary pressure curves before and after wettability modification, as shown in Figure 30. The gas, as expected, was able to displace more water from the rock at lower capillary pressure values, indicating that the rock became less water-wet or oil-wet (Hachem et al., 2022, Lord et al., 1997).

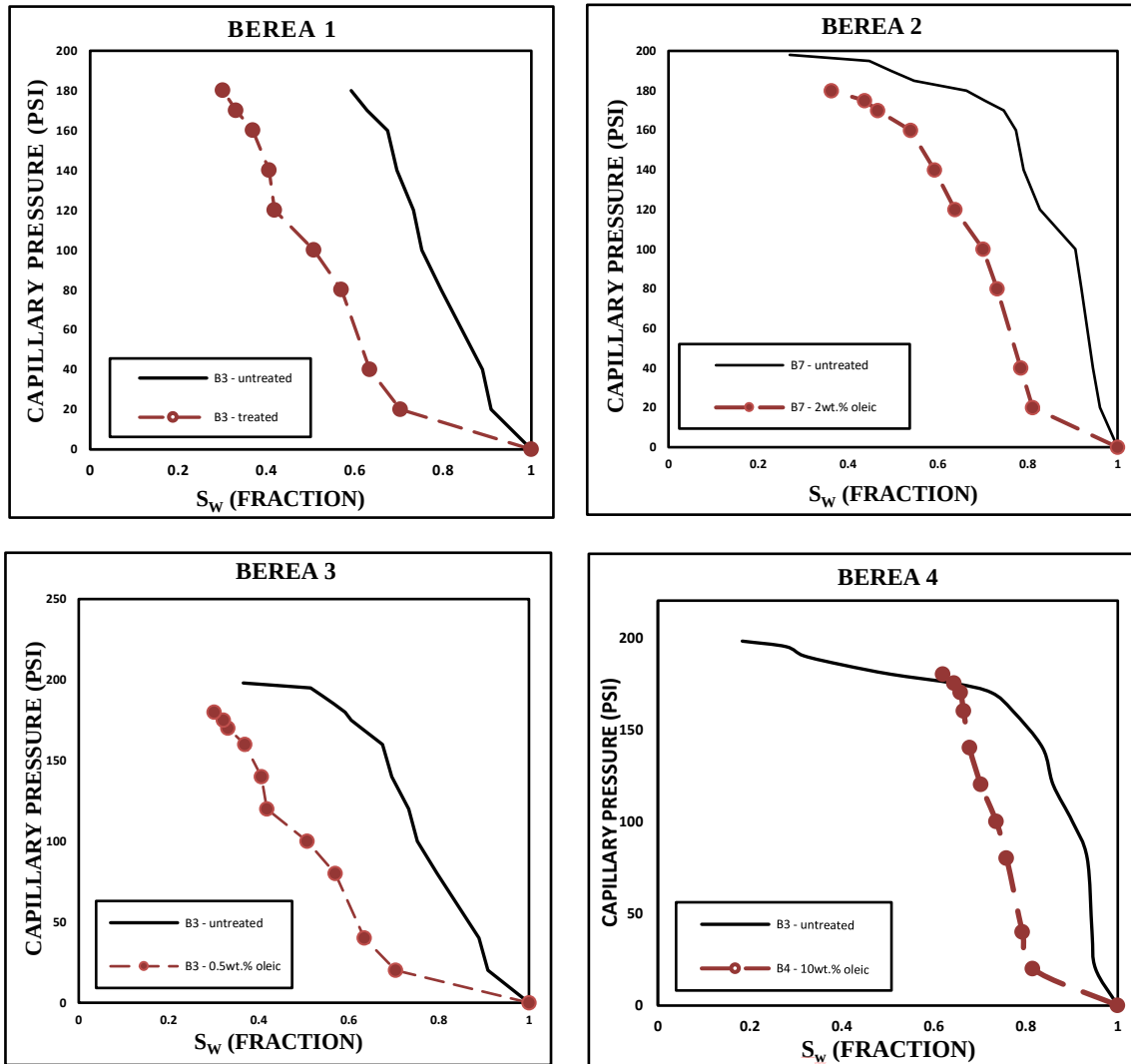


Figure 30: Sandstone rocks before and after wettability alteration

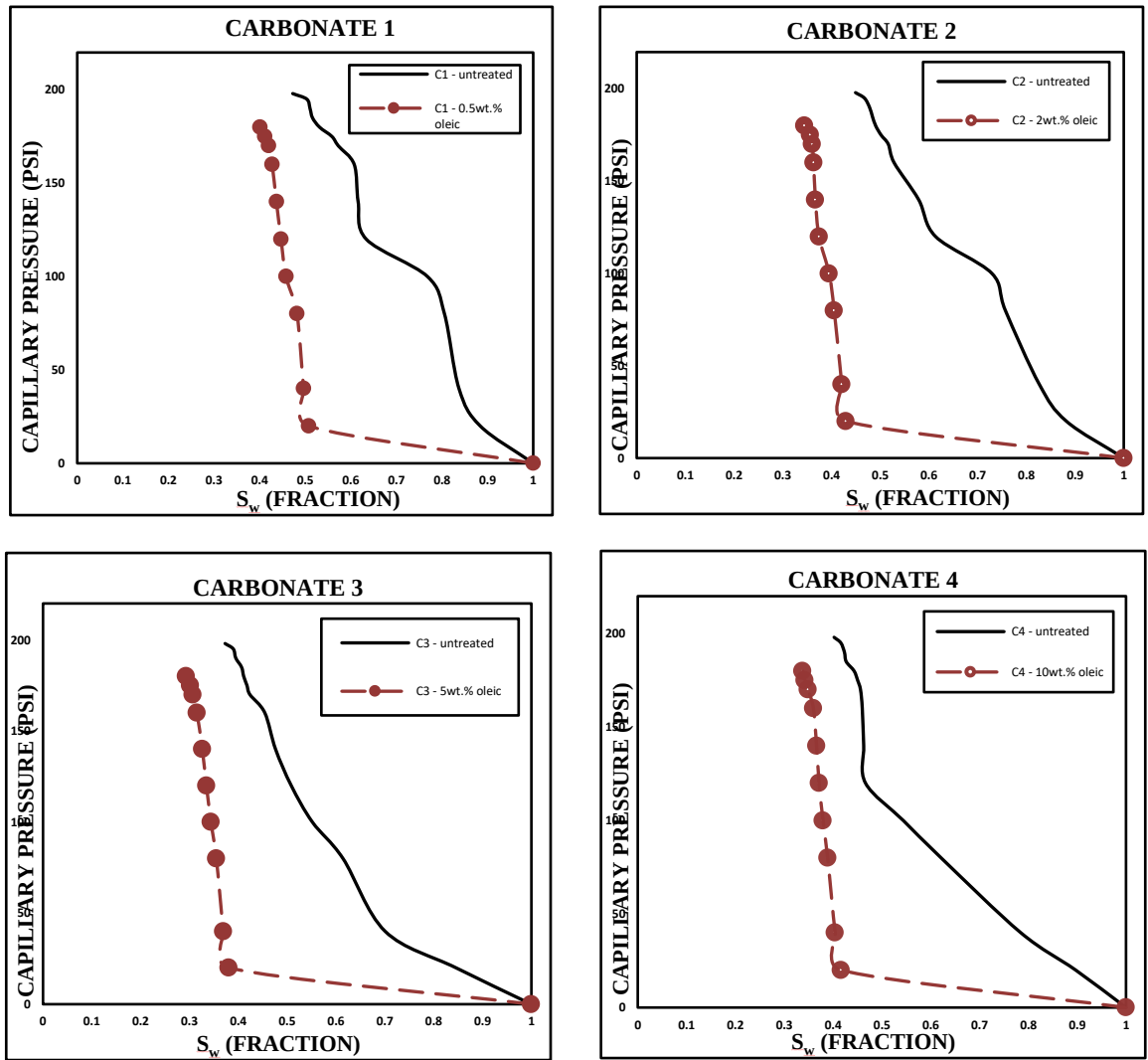


Figure 31: Carbonate rocks before and after wettability alteration

The impact of organic acid on the wettability of the rock is documented by quantifying the difference in capillary pressure. The application of oleic acid resulted in a notable transformation in the rock sample's characteristics became evident, with a discernible increase in its hydrophobic nature, as graphically illustrated (Figure 30). This alteration in hydrophobicity had a significant impact on the rate of brine discharge, which accelerated notable compared to the untreated samples. This observation is consistent with the empirical findings and theoretical foundations laid out in the provided reference. (Mwangi et al., 2018). Furthermore, carbonate rock was shown to be more affected by wettability alteration than sandstone, Table 4. This is due to the fact that the interaction between calcite

(carbonate) and organic acids are significantly more robust than those involving silica (sandstone). This is associated with the continuous distribution of Ca^{2+} ions on the calcite surface, which maximizes the potential for interaction with carboxylate groups present in oleic acid. Consequently, this heightened affinity results in a greater adsorption of organic acid molecules onto calcite surfaces. (Mihajlović et al., 2013).

	Before treatment	After treatment		Before treatment	After treatment	
Sample ID	Water saturation at 20 psi [%]	Water saturation at 20 psi [%]	Reduction in Sw [%] at 20 psi	Residual Water saturation at 200 psi [%]	Residual Water saturation at 200 psi [%]	Reduction In Sw [%] at 200 psi
Sandstone-1	90	70	22	59	30	49
Sandstone-2	96	81	15.6	66	36	45
Sandstone-3	95	75	21	50	32	36
Sandstone-4	98	81	17	64	62	3
			Ave: 19%			Ave :33%
Carbonate-1	88	50	43	53	40	24
Carbonate-2	88	42	52	49	34	30
Carbonate-3	84	38	54	41	29	29
Carbonate-4	89	41	54	44	33	25
			Ave: 50%			Ave: 27%

Table 4: Average reduction in water saturation at capillary of 20psi and 200psi

Table 4 shows that, after wettability alteration and when subjected to a 20 psi capillary pressure, there was a significant reduction in brine saturation (i.e., higher gas saturation), equal to an average reduction in saturation of 19% for the sandstone and 50% for the carbonate. Furthermore, at a capillary pressure of 200 psi, the reduction shifted to 33% and 27% for the sandstone and carbonate, respectively. However, this study also demonstrated

that increasing the organic acid concentration had no influence on capillary pressure curves. To delve into this phenomenon, we employed Total Organic Carbon (TOC) measurements, which provided a clear insight into the extent of adsorption. The TOC results (Figure 32) showed low carbon (oleic acid) adsorption in general regardless of oleic acid concentration, which is due to the fact that oleic acid exists in neutral form, while calcite and silica are naturally negatively charged (Li et al., 2016, Leroy et al., 2022). However, due to the nature of interactions between calcite and organic acid in compared to silica, limestone shows slightly higher adsorption levels than sandstone (Mihajlović et al., 2013). It is important to be aware that increasing the adsorption of organic acid on the rock surface is responsible for increasing hydrophobicity (Lord et al., 1997).

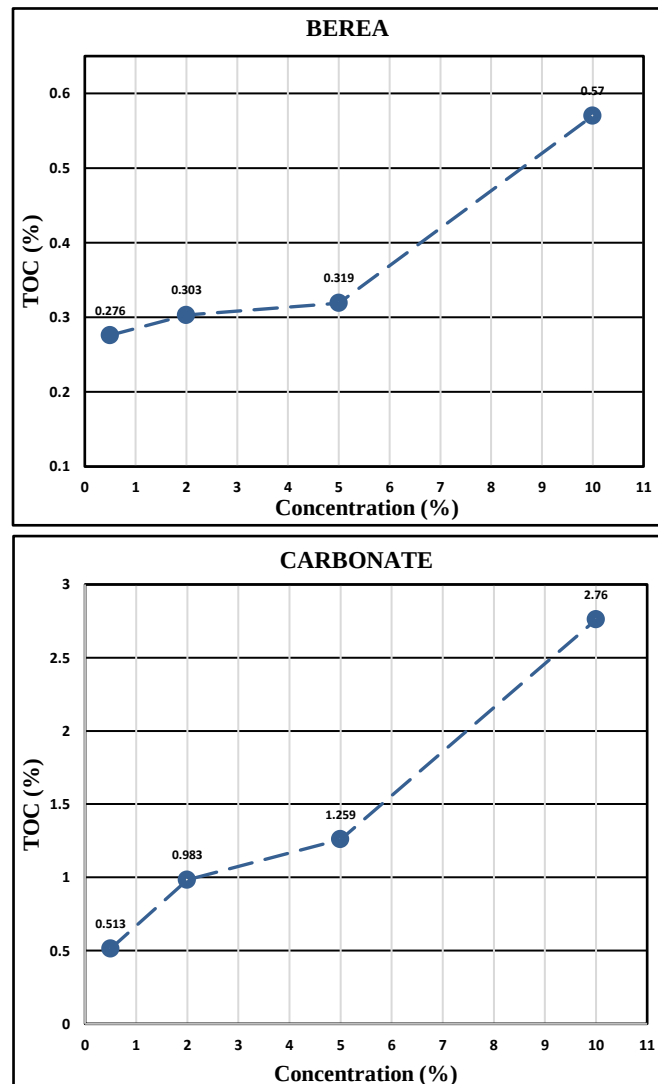


Figure 32: TOC

Moreover, analyzing the capillary curves reveals a notable trend: post-treatment, it requires only 20 psi to expel approximately 50% of the brine in carbonate and 20% in sandstone. However, beyond this point, it becomes considerably more challenging to displace the remaining water. To elucidate this behavior, we conducted Nuclear Magnetic Resonance (NMR) tests. These tests were conducted on fully saturated rock cores ($S_w = 1$), and after subjecting them to 20 and 200 psi pressure, respectively.

The T_2 relaxation time distribution for Berea Sandstone samples at $S_w = 1$ (Figure 5 a to d) demonstrate that it has a homogenous dominant pore size along a smaller peak at lower T_2 components (< 10 ms) representing the clay bound water. Following the application of 20 psi pressure, the T_2 dominant peak shifted to the left, and the large T_2 components (> 200 ms) are no longer exist. This indicates that the water in the large dominant pores have been partially displaced. It is worth mentioning that the area under the T_2 relaxation time distribution represent the NMR porosity. It can be seen that after applying 20 psi in (Figure 33 B and C) the amplitude has increased, however, the overall area under the curve is less than when the samples were fully saturated with water ($S_w = 1$). After applying 200 psi, a significant reduction in the amplitude of T_2 relaxation time distribution was observed with a T_2 peak value centering around 10 ms. This confirms that most of the brine was displaced from the large pores, and the vast majority of the NMR signal is detected from the clay bound water.

The carbonate samples are mainly characterized by two distinct peaks representing two pore sizes (macro- and micro pore sizes) as the T_2 relaxation time distribution illustrates in (Figure 33 a to d). The large T_2 components (> 200 ms) represent the macro pores which contributes more to the overall porosity while the T_2 that are less than 200 ms represents the micropores system. It can be clearly observed that a capillary pressure of 20 psi was fairly enough to displace all the brine that exist in the macropores as observed from the capillary pressure measurements. This behavior agrees with the results in table 3 in which the water saturation for the carbonate samples were reduced to 50% at most. The brine in the micropores was partially displaced after applying a capillary pressure of 200 psi. However, it seems that 200 psi is not enough to push out all the brine due to the small pore radius of the micropores system.

As evident from the capillary curves, the drainage effect in sandstone appears to be relatively less pronounced than in carbonate. Specifically, at 20 psi, a substantial portion of the brine is displaced from pores with dimensions ranging from approximately 7 μm to 10 μm in limestone, whereas in sandstone, this phenomenon occurs across a broader size spectrum, spanning from roughly 2 μm to 10 μm .

However, upon subjecting the samples to 200 psi of pressure, a noteworthy observation emerges: a minimal volume of water is expelled from the smaller pores (1 to 2 μm) in carbonates, a phenomenon consistent with the capillary curves. In contrast, in sandstones, where approximately half of the discharged water is attributed to the expulsion from larger pores at 20psi, it becomes evident that the remaining half is discharged from smaller pores (1 to 7 μm) following the application of 200 psi.

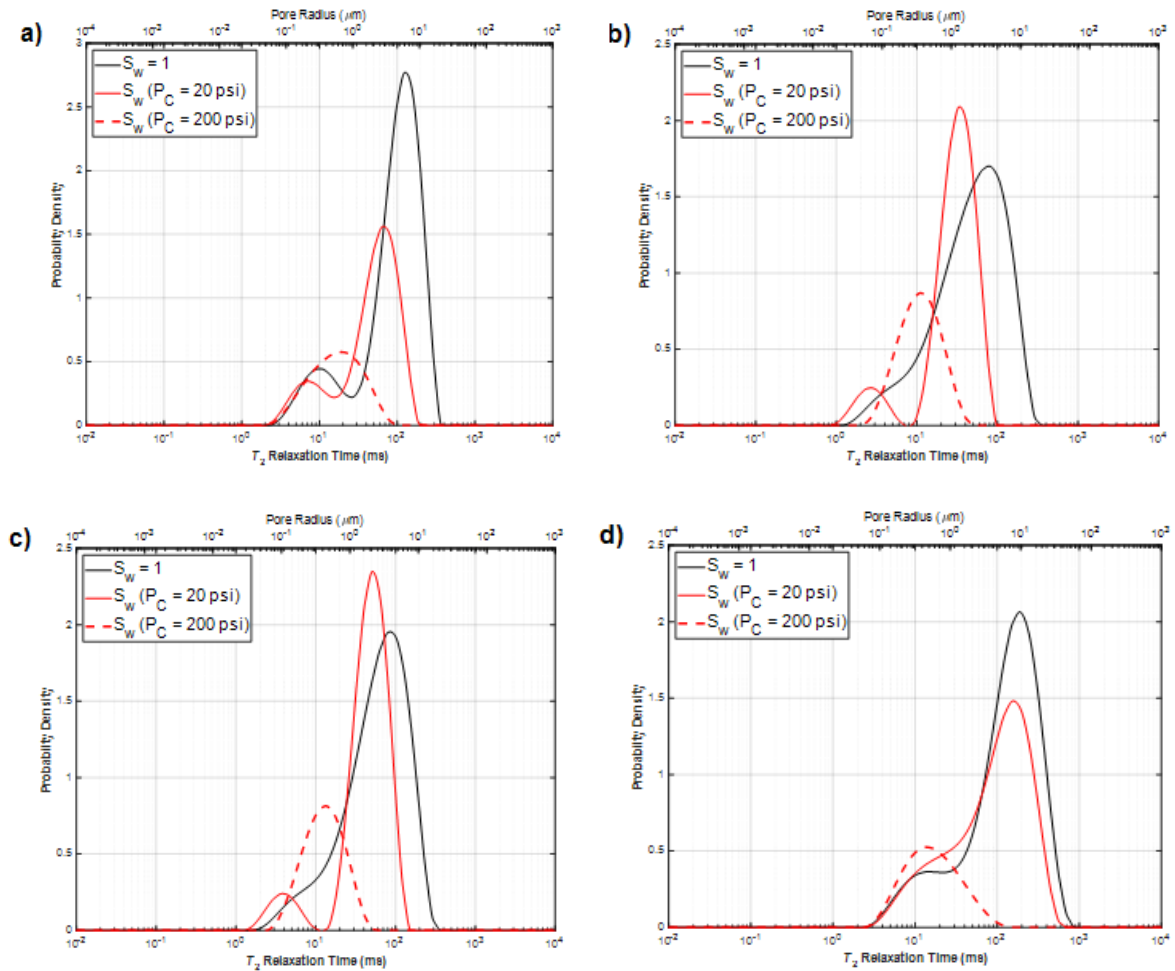


Figure 33: NMR T_2 distributions and pore radius of sandstone at 100% saturation and after applying pressures of 20 psi and 200 psi

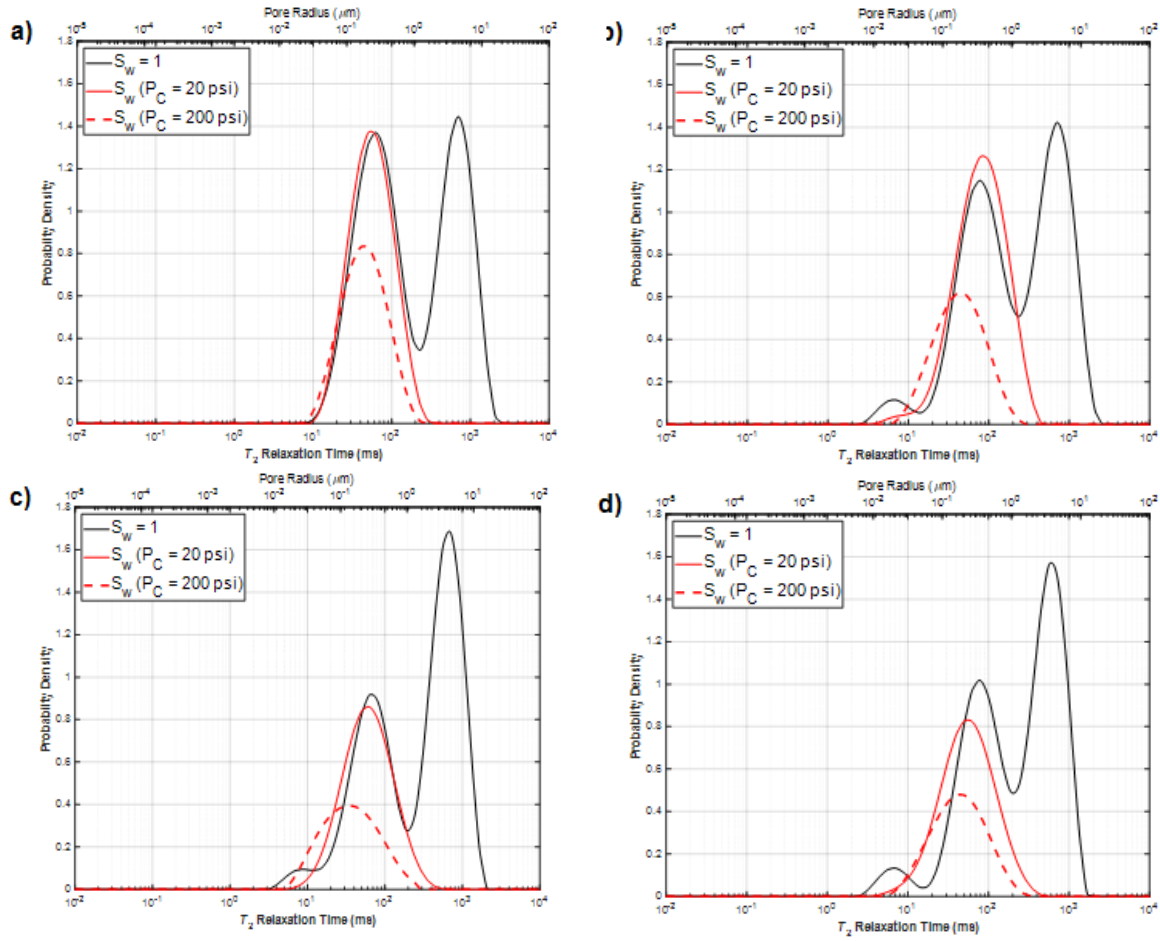
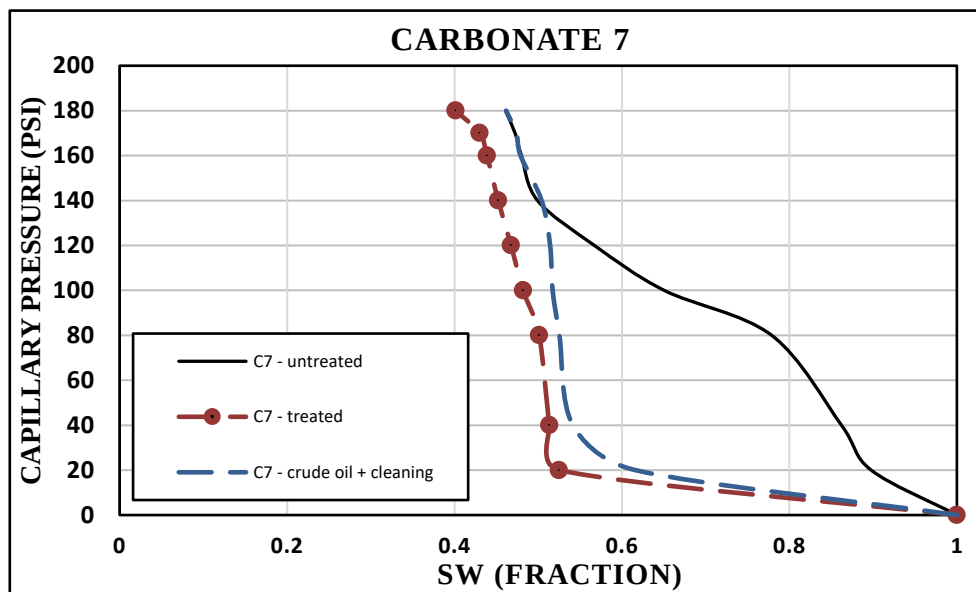
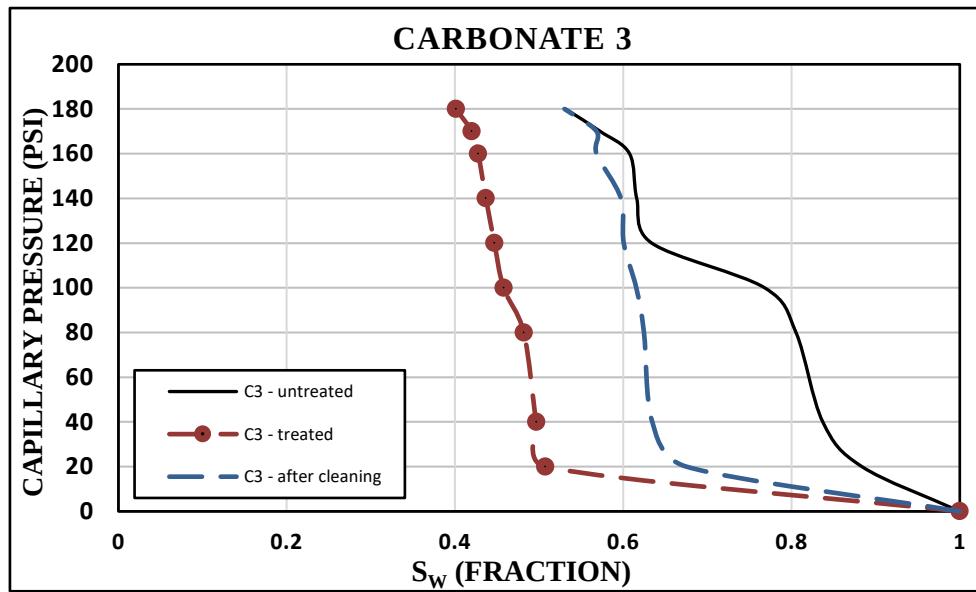


Figure 34: NMR T2 distributions and pore radius of limestone at 100% saturation and after applying pressures of 20 psi and 200 psi.

Furthermore, as part of the experiment protocol, two samples underwent a 73-day aging process at room temperature, immersed in a solution comprising crude oil dissolved in a 1% stearic acid and toluene mixture. It was imperative to immediately clean the samples post-aging to maintain consistent pore size, as any delay could alter the intended conditions. Subsequently, capillary pressure measurements were conducted after the cleaning process, yielding the following outcomes:

The obtained results diverge from the prevailing findings in the literature, particularly concerning the impact of cleaning methodologies on wettability. Traditionally, researchers employ cleaning agents such as methanol and toluene to eliminate contaminants prior to measuring contact angles, yet this procedure inadvertently alters wettability index. After cleaning it was noticed that the graph shifted in right direction which mean samples became more water-wet.



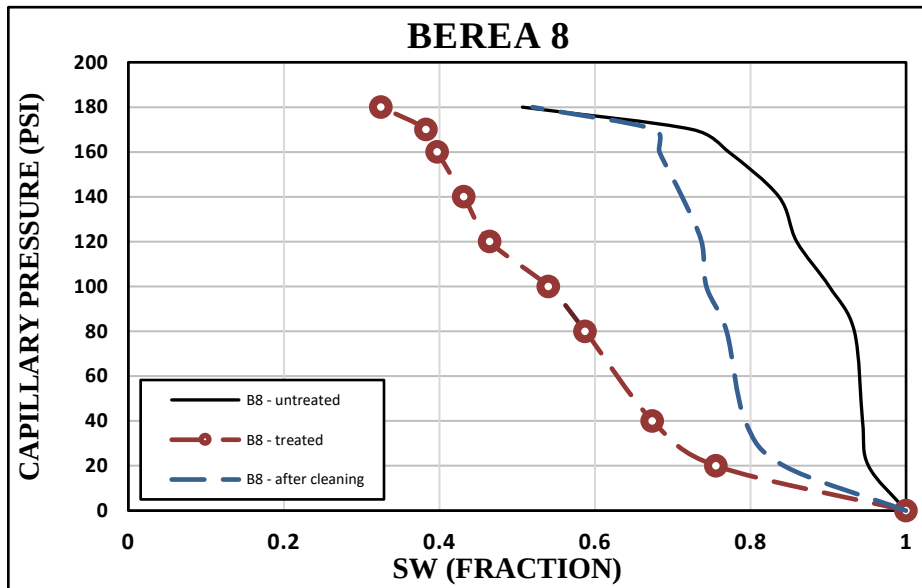
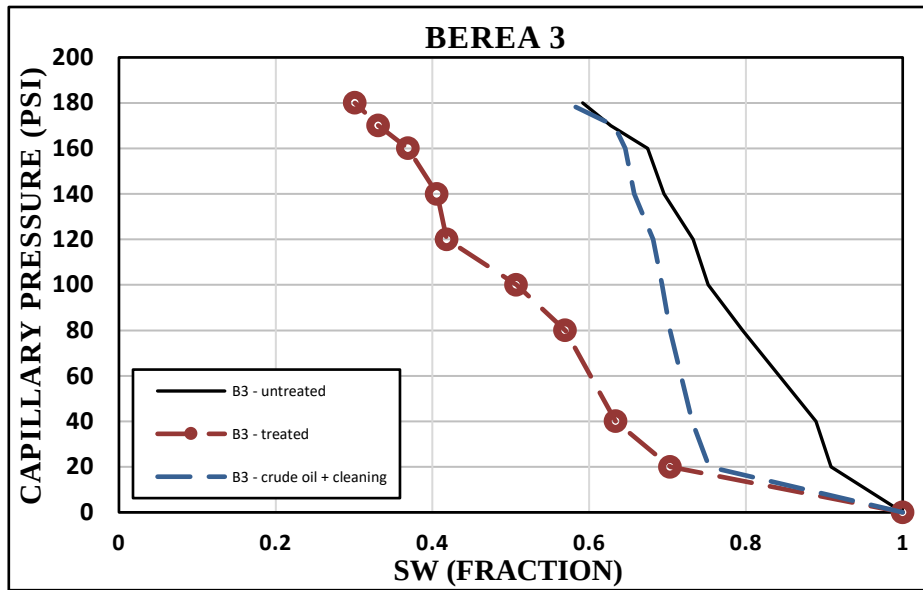
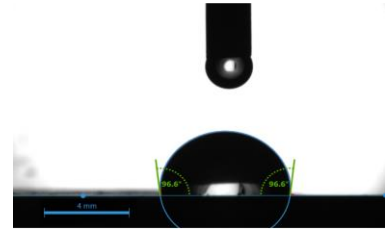


Figure 35: Cleaning effect of capillary pressure

Obtained results diverge from the prevailing findings in the literature, particularly concerning the impact of cleaning methodologies on wettability. Traditionally, researchers employ cleaning agents such as methanol and toluene to eliminate contaminants prior to measuring contact angles, yet this procedure inadvertently alters wettability index. After cleaning it was noticed that the graph shifted in right direction which mean samples became more water-wet.

Sample ID	Contact angle before treatment	Contact angle after treatment	Contact angle image after treatment at 0.5 wt.% Oleic acid
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Sandstone	0	96.6	
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Carbonate	0	95	
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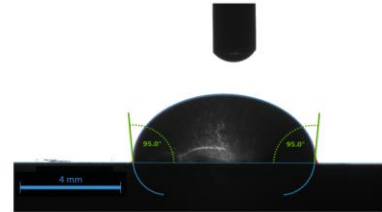


Figure 36: Capillary Pressure results before and after aging the sandstone and carbonate.

Furthermore, we measured capillary pressure by centrifuge before and after aging. We observed wettability change as the capillary pressure curve shifted to the left side. But the difference was not as much as we experienced in porous plate measurement results.

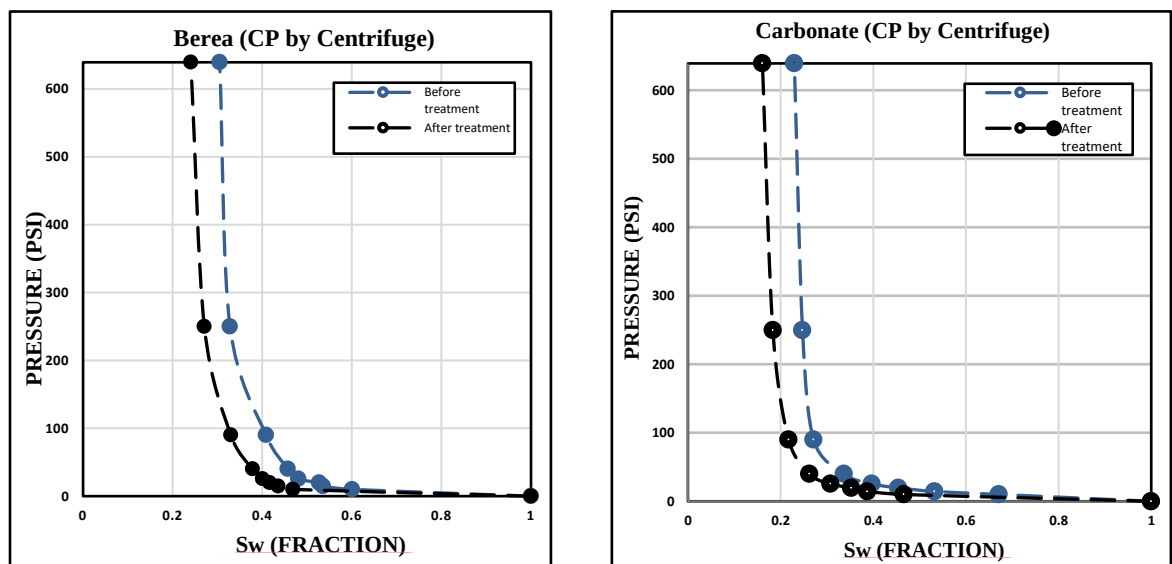


Figure 37: CP curves obtained from centrifuge

CHAPTER 5

CONCLUSION

The present work investigated the use of oleic acid to change the wettability of rock to simulate conditions of a subsurface depleted hydrocarbon reservoir, as well as its effect on capillary pressure curves as an application of storing CO₂/H₂ in the subsurface. This study demonstrated that 1) the effect of organic acid on capillary pressure is less pronounced than its effect on contact angle; 2) carbonate rock was affected more by oleic acid than sandstone rock; 3) low oleic acid concentration is sufficient to modify rock wettability; 4) low adsorption of oleic acid on the carbonate and sandstone surfaces at tested conditions; and 5) oleic acid has a relatively minor effect on smaller pores than large pores.

Concerning the NMR findings, it was observed that pore structure exhibits heterogeneity, with a significant portion of irreducible water persisting within micropores following the application of 200 pressure. Consequently, it can be inferred that the influence of oleic acid predominantly affect larger pores rather than smaller ones.

Additionally, contact angle measurements can lead engineers astray in another aspect. Although samples are typically cleaned to mitigate the influence of contamination on contact angle measurements, the use of methanol and toluene for cleaning can inadvertently modify the wettability, increasing water wetness and thereby altering the ultimate outcome.

In conclusion, these findings underscore the importance of accounting for contact angle when calculation capillary pressure for reservoir simulation in engineering application. When contact angle equals to or exceeds 90 degrees, conventional calculations yield a misleading result of zero capillary pressure, indicating gas migration during storage without residual trapping. However, as capillary pressure is inherently nonzero, such simulations may yield highly inaccurate results, compromising the precision of carbon storage capacity estimates.

CP shift due to the treatment can be observed in porous plate more clearly than centrifuge

This study also concludes that a trace of organic acid may enhance the gas (i.e., CO₂/H₂) storage capacity of sandstone reservoirs by up to 33% and carbonate reservoirs by up to 50%. As a result, we propose that storing gas in depleted hydrocarbon reserves may be more efficient.

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Vitae

Name : Rashad Ahadli

Nationality : Azerbaijan

Date of Birth :8/28/2000

Email : rashad.ahadli@gmail.com

Address : Azerbaijan, Baku, Suleyman Sani Akhundov 1b/70, 0116

Academic Background : - B.Sc. Petroleum Engineering (2021)
Azerbaijan State Oil and Industry University (Azerbaijan)

-M.Sc. Petroleum Engineering (2024)
King Fahd University of Petroleum & Minerals (KSA)