

**IMPACT OF SALINITY AND TEMPERATURE ON WORMHOLE  
GENERATION AND MECHANICAL PROPERTIES DUE TO CO<sub>2</sub>  
SEQUESTRATION**

**BY  
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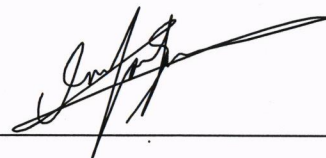
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2023

This Thesis is Dedicated to

My Father

***Shallah Bin Horran***

My Brother

***Homod Bin Horran***

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# TABLE OF CONTENTS

|                                                                                |      |
|--------------------------------------------------------------------------------|------|
| ACKNOWLEDGMENTS .....                                                          | V    |
| TABLE OF CONTENTS .....                                                        | VII  |
| LIST OF TABLES .....                                                           | IX   |
| LIST OF FIGURES .....                                                          | X    |
| LIST OF ABBREVIATIONS .....                                                    | XIII |
| ABSTRACT.....                                                                  | XIV  |
| ملخص الرسالة.....                                                              | XVI  |
| CHAPTER 1 INTRODUCTION .....                                                   | 1    |
| 1.1. CO <sub>2</sub> Sequestration.....                                        | 3    |
| 1.2. Carbonic Acid (H <sub>2</sub> CO <sub>3</sub> ) .....                     | 6    |
| CHAPTER 2 LITERATURE REVIEW .....                                              | 8    |
| 2.1. Acid impact on geomechanical and petrophysical properties .....           | 8    |
| 2.2. Temperature impact on acid reactivity .....                               | 10   |
| 2.3. Acid and wormhole generation .....                                        | 15   |
| 2.4. CO <sub>2</sub> impact on geomechanical and petrophysical properties..... | 24   |
| 2.5. Temperature impact on CO <sub>2</sub> solubility and reactivity.....      | 33   |
| 2.6. Salinity impact on CO <sub>2</sub> solubility and reactivity .....        | 38   |
| CHAPTER 3 PROBLEM STATEMENT AND RESEARCH OBJECTIVES .....                      | 42   |

|                                                                           |            |
|---------------------------------------------------------------------------|------------|
| <b>CHAPTER 4 RESEARCH METHODOLOGY AND EQUIPMENT .....</b>                 | <b>43</b>  |
| <b>4.1. Rock Measurements &amp; Selections.....</b>                       | <b>45</b>  |
| 4.1.1. Cores cutting.....                                                 | 45         |
| 4.1.2. Cores weight and Porosity measurements .....                       | 46         |
| 4.1.3. Hardness measurements .....                                        | 48         |
| 4.1.4. Acoustic measurements .....                                        | 50         |
| 4.1.5. Medical CT-Scan.....                                               | 51         |
| 4.1.6. Cores samples clustering .....                                     | 52         |
| <b>4.2. Carbonic Acid Injection.....</b>                                  | <b>53</b>  |
| <b>4.3. Rock Measurements &amp; Analyzation .....</b>                     | <b>57</b>  |
| <b>CHAPTER 5 RESULTS AND DISCUSSION.....</b>                              | <b>58</b>  |
| <b>5.1. Salinity Impact.....</b>                                          | <b>59</b>  |
| 5.1.1. Impact of Salinity on Porosity .....                               | 63         |
| 5.1.2. Impact of Salinity on Young's Modulus and Poisson's Ratio .....    | 68         |
| 5.1.3. Impact of Salinity on the Rock Hardness .....                      | 72         |
| <b>5.2. Temperature Impact .....</b>                                      | <b>74</b>  |
| 5.2.1. Impact of Temperature on Porosity .....                            | 77         |
| 5.2.2. Impact of Temperature on Young's Modulus and Poisson's Ratio ..... | 82         |
| 5.2.3. Impact of Temperature on the Rock Hardness .....                   | 87         |
| <b>CHAPTER 6 CONCLUSION .....</b>                                         | <b>89</b>  |
| <b>6.1. Salinity.....</b>                                                 | <b>89</b>  |
| <b>6.2. Temperature .....</b>                                             | <b>91</b>  |
| <b>REFERENCES.....</b>                                                    | <b>93</b>  |
| <b>VITAE.....</b>                                                         | <b>103</b> |

## LIST OF TABLES

|                                                                                          |    |
|------------------------------------------------------------------------------------------|----|
| Table 1: Mechanical properties after the carbon dioxide injection Zhang et al., (2016).. | 29 |
| Table 2: Core samples dimensions, weight, volumes, and porosity .....                    | 47 |
| Table 3: Low, mid, and high values of the tested parameters (Temperature, & Salinity)    | 52 |
| Table 4: The chemical composition of the synthetic formation brine .....                 | 56 |
| Table 5: The weight of the brine chemical composition.....                               | 56 |
| Table 6: Different experiments conditions (Salinities and Temperatures) .....            | 59 |
| Table 7: Generated wormholes time & PVBT for different salinities .....                  | 61 |
| Table 8: Change in porosity after the wormholes generation .....                         | 63 |
| Table 9: Wormholes volume for different salinity values .....                            | 65 |
| Table 10: Generated wormholes time & PVBT for different salinities .....                 | 75 |
| Table 11: Change in porosity after the wormholes generation .....                        | 77 |
| Table 12: Wormholes volume for different salinity values .....                           | 79 |

## LIST OF FIGURES

|                                                                                                      |    |
|------------------------------------------------------------------------------------------------------|----|
| Figure 1: Average atmospheric CO <sub>2</sub> concentration (ppm). (Friedlingstein et al., 2021).... | 2  |
| Figure 2: Formation used for CO <sub>2</sub> sequestration (Zhang et al., 2019).....                 | 3  |
| Figure 3: Carbon dioxide phase diagram (Bachu 2000). ....                                            | 4  |
| Figure 4: Change in Young's modulus before & after an acid job (Mustafa et al., 2021) .              | 9  |
| Figure 5: Heat of reaction for limestone and dolomit (Lee and Roberts 1980).....                     | 10 |
| Figure 6: Heat of reaction impact on the penetration distances (Lee and Roberts 1980).               | 11 |
| Figure 7: The change in viscosity front with time (Kalia and Gerard 2009).....                       | 12 |
| Figure 8: Creation to two different wormholes (Kalia and Gerard 2009) .....                          | 12 |
| Figure 9: Injection rate impact on dissolution structures (Fredd and Fogler, 1999).....              | 16 |
| Figure 10: PVBT as a function of injection rate (velocity) (Fredd and Fogler, 1999) .....            | 17 |
| Figure 11: Efficiency curves as a function of permeability (Etten et al., 2015).....                 | 19 |
| Figure 12: PVBT as a function of permeability (Etten et al., 2015).....                              | 20 |
| Figure 13: Reduction in Young's modulus and Poisson's ratio (AlAmeri et al., 2016)...                | 26 |
| Figure 14: Sequestration time impact Young's modulus (AlAmeri et al., 2016).....                     | 26 |
| Figure 15: Pressure difference vs. pore volume to breakthrough (Zhang et al., 2016) ....             | 28 |
| Figure 16: CO <sub>2</sub> solubility as a function of temperature (Portier et al, 2005).....        | 33 |
| Figure 17: The change in viscosity as a function of temperature (Kumar et al., 2020)....             | 36 |
| Figure 18: Research Methodology.....                                                                 | 43 |
| Figure 19: Core cutting machine (Mecatome ST310) .....                                               | 45 |
| Figure 20: Helium Porosimeter for porosity measurements .....                                        | 46 |
| Figure 21: Cores weight measurements .....                                                           | 47 |

|                                                                                              |    |
|----------------------------------------------------------------------------------------------|----|
| Figure 22: Hardness measurements using a non-destructive AutoScan scanner .....              | 48 |
| Figure 23: Measurements for core hardness .....                                              | 49 |
| Figure 24: Acoustic measurements machine .....                                               | 50 |
| Figure 25: Medical CT scanning scanner .....                                                 | 51 |
| Figure 26: Carbonic acid coreflooding system .....                                           | 53 |
| Figure 27: The core holder attached to the live brine accumulator inside the oven. ....      | 54 |
| Figure 28: Back pressure regulator .....                                                     | 55 |
| Figure 29: Data logger and acquisition system.....                                           | 55 |
| Figure 30: Cores pressure difference Vs. Pore volume .....                                   | 60 |
| Figure 31: Cores samples inlet and outlet of wormholes for different salinities .....        | 62 |
| Figure 32: The linear relationship between the change porosity and salinity.....             | 64 |
| Figure 33: Injected live brine after breakthrough & change in porosity relationship.....     | 65 |
| Figure 34: Relationship between the wormhole volume and the change in porosity .....         | 66 |
| Figure 35: Relationship of wormhole volume & original porosity at different salinities.      | 66 |
| Figure 36: Medical CT scan of the wormholes at different salinities.....                     | 67 |
| Figure 37: The reduction in dynamic Young's modulus for (40,000 ppm) case.....               | 68 |
| Figure 38: The reduction in dynamic Young's modulus for (120,000 ppm) case.....              | 69 |
| Figure 39: The reduction in dynamic Young's modulus for (200,000 ppm) case.....              | 69 |
| Figure 40: Increase in Poisson's ratio for different salinity values. ....                   | 70 |
| Figure 41: Reduction in Young's modulus for different live brine salinity .....              | 71 |
| Figure 42: Rock hardness before and after live brine injection for different salinities .... | 72 |
| Figure 43: Reduction in core inlet hardness for different salinities.....                    | 73 |
| Figure 44: Cores pressure difference Vs. Pore volume .....                                   | 74 |

|                                                                                             |    |
|---------------------------------------------------------------------------------------------|----|
| Figure 45: Cores inlet and outlet of wormholes generation for different salinities .....    | 76 |
| Figure 46: The relationship between the change porosity and temperature .....               | 78 |
| Figure 47: Injected live brine after breakthrough and change in porosity relationship. .... | 79 |
| Figure 48: Relationship between the wormhole volume and the change in porosity .....        | 80 |
| Figure 49: Wormhole volume & original porosity relation at different temperatures.....      | 80 |
| Figure 50: Medical CT scan of the wormholes at different temperatures .....                 | 81 |
| Figure 51: The reduction in dynamic Young's modulus for (35°C) case.....                    | 82 |
| Figure 52: The reduction in dynamic Young's modulus for (60°C) case.....                    | 83 |
| Figure 53: The reduction in dynamic Young's modulus for (85°C) case.....                    | 83 |
| Figure 54: Increase in Poisson's ratio for different temperature values. ....               | 84 |
| Figure 55: Reduction in Young's modulus for different temperature .....                     | 86 |
| Figure 56: Rock hardness before & after live brine injection for different temperature ..   | 87 |
| Figure 57: Reduction in core inlet hardness for different temperature .....                 | 88 |

## LIST OF ABBREVIATIONS

|                       |   |                             |
|-----------------------|---|-----------------------------|
| <b>CO<sub>2</sub></b> | : | Carbon Dioxide Gas          |
| <b>V<sub>p</sub></b>  | : | Compressional velocity      |
| <b>v</b>              | : | Poisson ratio               |
| <b>PVBT</b>           | : | Pore Volume to Breakthrough |
| <b>V<sub>s</sub></b>  | : | Shear-wave velocity         |
| <b>E</b>              | : | Young's modulus             |

|

## **ABSTRACT**

Full Name : Abdullah Shallah K. AlHussaini AlDhafeeri  
Thesis Title : Impact of Salinity and Temperature on Wormhole Generation and Mechanical Properties Due to CO<sub>2</sub> Sequestration  
Major Field : Petroleum Engineering  
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Deep saline aquifers are good candidates for carbon dioxide (CO<sub>2</sub>) sequestration because of their huge reserves, wide distribution, cost effectiveness and relatively high security. The reaction between CO<sub>2</sub> gas and the aquifer saline water creates carbonic acid (live brine) that reacts with the formation rock to generate wormholes. As a result, the rock mechanical properties will be altered. The goal of this study is to understand the impact of salinity and temperature on creating wormholes due to live brine injection and the change in the mechanical and petrophysical properties of the rocks.

Limestone core samples (1.5 inches x 3 inches) with a permeability of 1 – 4 mD and 15-17% porosity values were selected to perform the study. Coreflooding experiments were performed, after which the samples were scanned to observe the wormhole generation and the change in the pore structure. Carbon dioxide was mixed at 2,000 psi with a ratio of 30% CO<sub>2</sub> to 70% brine to formulate a live brine. The live brine was injected into the rock samples at different temperatures (35 °C, 60 °C, 85 °C). Also, CO<sub>2</sub> was mixed in the brine with different salts concentrations (40,000 ppm, 120,000 ppm, 200,000 ppm), which were then injected into the rock samples to test the impact of salinity. The mechanical and

petrophysical properties of the core samples before and after wormhole generation were measured and studied.

The injection of the live brine generated wormholes in all rock samples. Due to the wormhole's generation, the rock samples' porosity and permeability increased significantly. The time to generate the wormholes has a positive relationship with the salinity and temperature values. For instance, it took around 5.5 hours of live brine injection at 1 cc/min to create a wormhole at 35 °C, while it took more than 10 hours at 85 °C. Similarly, it took only 3 hours to generate a wormhole in the low salinity samples while double the time for the high salinity ones. The rock's mechanical properties, including the rock hardness, Young's modulus, and Poisson ratio, were measured before and after the live brine injection. Overall, the study demonstrated that the injection of live brine creates a wormhole, which weakens the rock strength and increases the porosity and permeability.

This research's novelty stems from its application to CO<sub>2</sub> sequestration by investigating the salinity and temperature of saline aquifers. These two parameters are significant and distinguish a potential aquifer. This is the first study to understand the impact of salinity and temperature on wormhole generation and the mechanical rock properties due to CO<sub>2</sub> sequestration.

## ملخص الرسالة

الاسم الكامل : عبدالله صلاح خليف الحسيني الظفيري  
عنوان الرسالة : تأثير درجات الملوحة والحرارة على توليد الثقوب والخواص الميكانيكية الناتجة عن تخزين غاز ثاني أكسيد الكربون في باطن الأرض  
التخصص : هندسة البترول  
تاريخ الدرجة العلمية : مايو 2023

تعتبر المياه المالحة العميقة في باطن الأرض خيار جيداً لتخزين غاز ثاني أكسيد الكربون لوفرة احتياطياتها وانتشارها الواسع و جودتها المادية و لارتفاع نسبة الأمان بها. ينتج عن التفاعل الكيميائي بين الماء المالح و غاز ثاني أكسيد الكربون، الأسيد الكربوني و الذي يتفاعل مع صخور طبقات الأرض ليحدث ثقباً فيها. نتيجة لذلك تتغير الخواص الميكانيكية للصخور. الهدف من هذه الدراسة هي فهم تأثير درجة الملوحة و درجة الحرارة على أحداث الثقوب الصخرية و التغيرات في الخواص الميكانيكية و البتروفيزيائية للصخور نتيجة حقنها بالأسيد الكربوني.

لعمل الدراسة، تم اختيار عينات من صخور اللام ستون بطول 3 انش و قطر 1.5 انش ذات انسيابية تتراوح بين 1 و 4 ملل دارسي و مسامية تتراوح بين 15% و 17%. تمت عملية الغمر و من ثم تمت عملية مسح للعينات لملاحظة تكون الثقوب الصخرية و التغير في تكوين مسام الصخور. لانتاج الأسيد الكربوني، تم خلط 70% من المحلول الملحي مع 30% غاز ثاني أكسيد الكربون تحت ضغط 2000 رطل للانش المربع. تم حقن الاسيد الكربوني في درجات حرارة 35 و 60 و 85 سيليزية. ايضاً، تم انتاج الاسيد الكربوني بدرجات ملوحة 40,000 و 120,000 و 200,000 جزء بالمليون و غمر العينات الصخرية لمعرفة تأثير الملوحة. تم قياس الخواص الميكانيكية و البتروفيزيائية قبل و بعد غمر العينات بالاكسيد الكربوني بواسطة.

نتج عن جميع عمليات الغمر أحداث ثقب في العينات. نتيجة لذلك ارتفعت المسامية و الانسيابية بشكل ملحوظ في جميع العينات. توجد علاقة طردية بين الوقت اللازم لأحداث الثقوب و درجات الملوحة و الحرارة. على سبيل المثال، و بمعدل ضخ 1 ملل بالدقيقة، استغرق الاسيد الكربوني 5.5 ساعة لأحداث الثقب في درجة حرارة 35 درجة سيليزية بينما استغرق 10 ساعات لأحداث ثقب في درجة حرارة 85 سيليزية. على جانب مشابه، استغرق الاسيد الكربوني

3 ساعات لاحداث الثقب في درجة الملوحة القليلة بينما استغرق ضعف الوقت في درجة الملوحة الاعلى. تم قياس الخواص الميكانيكية للصخور قبل و بعد عمليات حقن الاسيد الكربوني و تشمل الصلابة و معامل يونغ و نسبة بواسون. بشكل عام, أوضحت الدراسة قدرت الأسيد الكربوني على احداث الثقوب في الصخر و اللذي يزيد المسامية و الانسيابية في الصخور و يقلل صلابتها.

تتبع حادثة البحث في التطبيقات لعمليات تخزين غاز ثاني أكسيد الكربون في المياه الجوفية العميقة المالحة و تأثيرات درجات الملوحة و الحرارة. تعتبر درجات الملوحة و درجات الحرارة عوامل مهمة للتفريق بين مكامن المياه الجوفية المحتملة لعملية تخزين الغاز. تعد هذه الدراسة هي الأولى لفهم تأثير درجات الملوحة و الحرارة على احداث الثقوب الصخرية و على الخواص الميكانيكية للصخور نتيجة لعمليات تخزين غاز ثاني أكسيد الكربون.



# **CHAPTER 1**

## **INTRODUCTION**

Carbon dioxide (CO<sub>2</sub>) is one of the greenhouse gases. It absorbs heat that radiates from the surface of the Earth's and then releases the heat in all directions which includes releasing it back to the surface of the Earth. This is essential for life because without this phenomenon the temperature of the earth can not be maintained above the freezing temperature.

However, the increase in CO<sub>2</sub> emission will increase its concentration which will make it trap more of the heat in the atmosphere than what we really need. This is the main cause of global warming. One more reason that CO<sub>2</sub> emission is causing the increase in global temperature, is that hotter air will hold more water vapor. Water vapor by itself is a greenhouse gas which means that the CO<sub>2</sub> emission will have double effect on global warming.

Also, the increase in CO<sub>2</sub> emission will have an impact on the ocean chemistry. When carbon dioxide dissolves in the water, carbonic acid will be formed which will lower the pH value of the water. lowering the pH value of the ocean water is called ocean acidification. This will impact a lot of the marine organisms, especially the ones that use calcium carbonate to build their shells and skeletons. These organisms will face a problem when the pH value decreases. First, their skeletons and shells will be dissolving more often.

Second, with the lower pH value, water chemistry will change in a way that there will be less carbonate ions which are needed to make the skeletons and shells ([Fabry et al., 2008](#)).

In each year, humans activities are responsible of increasing the emission of carbon dioxide ( $\text{CO}_2$ ) into the atmosphere in a bigger rate than what the nature can eliminate ([Friedlingstein et al., 2021](#)). Figure 1 shows the rapid increase in  $\text{CO}_2$  concentration (ppm) between 1960 and 2021. This requires reducing  $\text{CO}_2$  concentration in the atmosphere using different technologies and approaches. Reducing  $\text{CO}_2$  concentration in the atmosphere can be achieved by using the energy more efficiently, the usage of renewable energy, or by  $\text{CO}_2$  sequestration.  $\text{CO}_2$  sequestration includes capturing and storing carbon dioxide emissions from industrial and energy related sources to prevent the release of  $\text{CO}_2$  into the atmosphere.

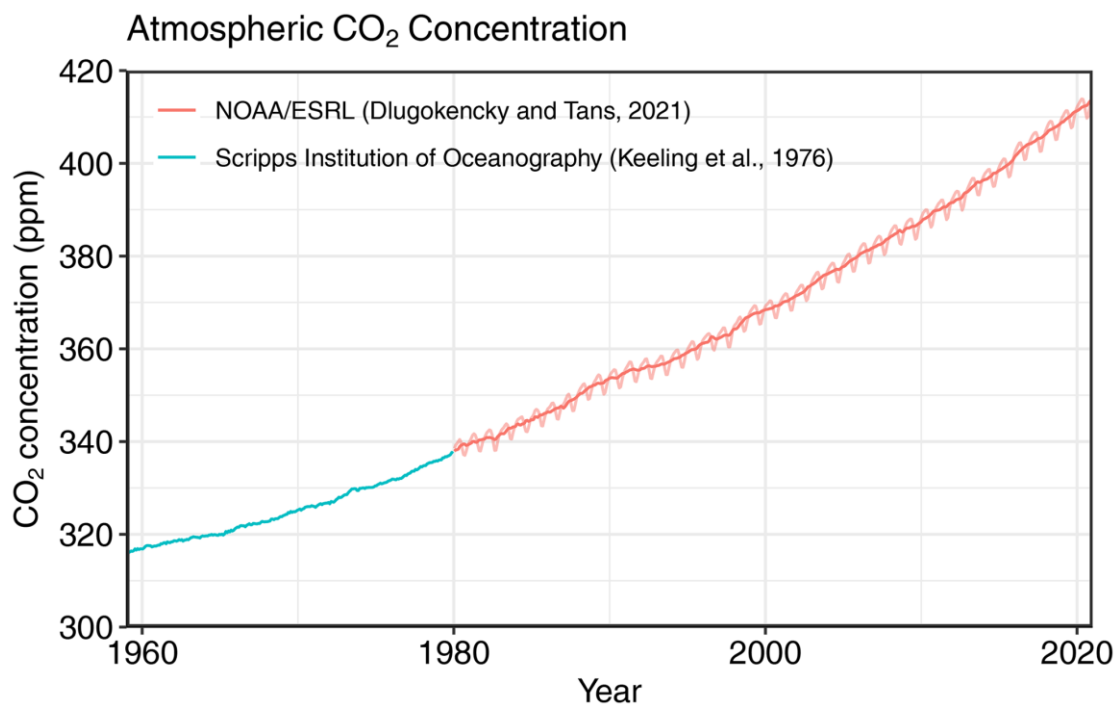


Figure 1: Average atmospheric  $\text{CO}_2$  concentration (ppm). ([Friedlingstein et al., 2021](#))

## 1.1. CO<sub>2</sub> Sequestration

The first step of the CO<sub>2</sub> sequestration is separating and concentrating CO<sub>2</sub> from the industrial and energy related sources. After that, transfer the compressed CO<sub>2</sub> to the injection site through pipelines. The second step of the CO<sub>2</sub> sequestration process is to inject the dense CO<sub>2</sub> into the ground. The first operation where an acid gas was injected in the ground started in 1989 in the outskirts of Edmonton, Alberta, Canada.

There are different formations where CO<sub>2</sub> can be injected in, such as oil reservoirs, natural gas reservoirs, unminable coalbeds, shale gas reservoirs, and saline aquifers ([Zhang et al., 2019](#); [Bachu, 2000](#); [Olabi et al., 2022](#)). Figure 2 shows the different formations where CO<sub>2</sub> can be injected. By comparing these injection formations options, saline aquifers are the most desirable option due to its huge reserve, wide distribution, cost-effectiveness, and relatively high security.

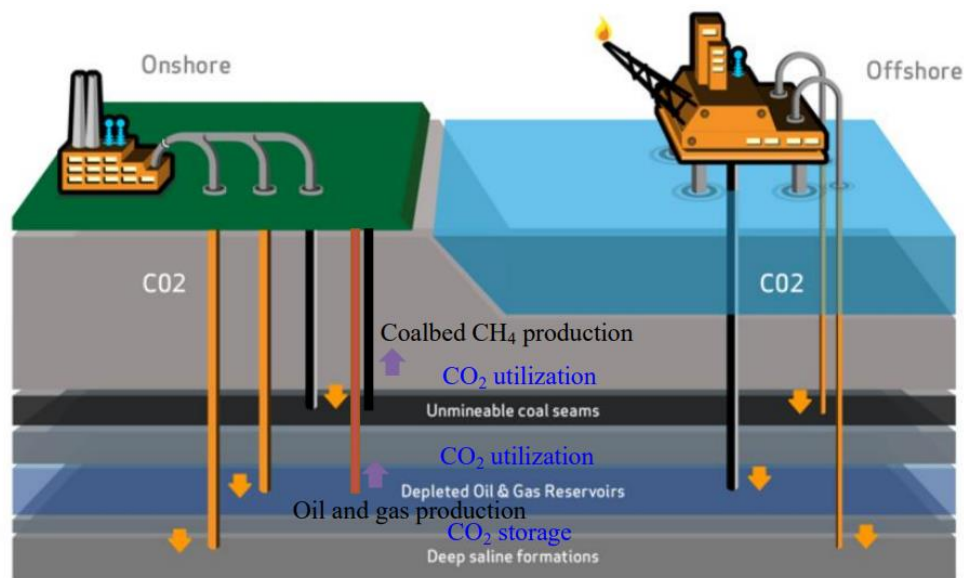


Figure 2: Formation used for CO<sub>2</sub> sequestration ([Zhang et al., 2019](#))

Under the reservoir conditions (temperatures greater than 31.1 °C, pressures greater than 7.38 MPa), the injected CO<sub>2</sub> gas is at the state of supercritical as shown in Figure 3. Some of the injected CO<sub>2</sub> will dissolve in brine and the rest will form a plume at the top of the saline aquifer.

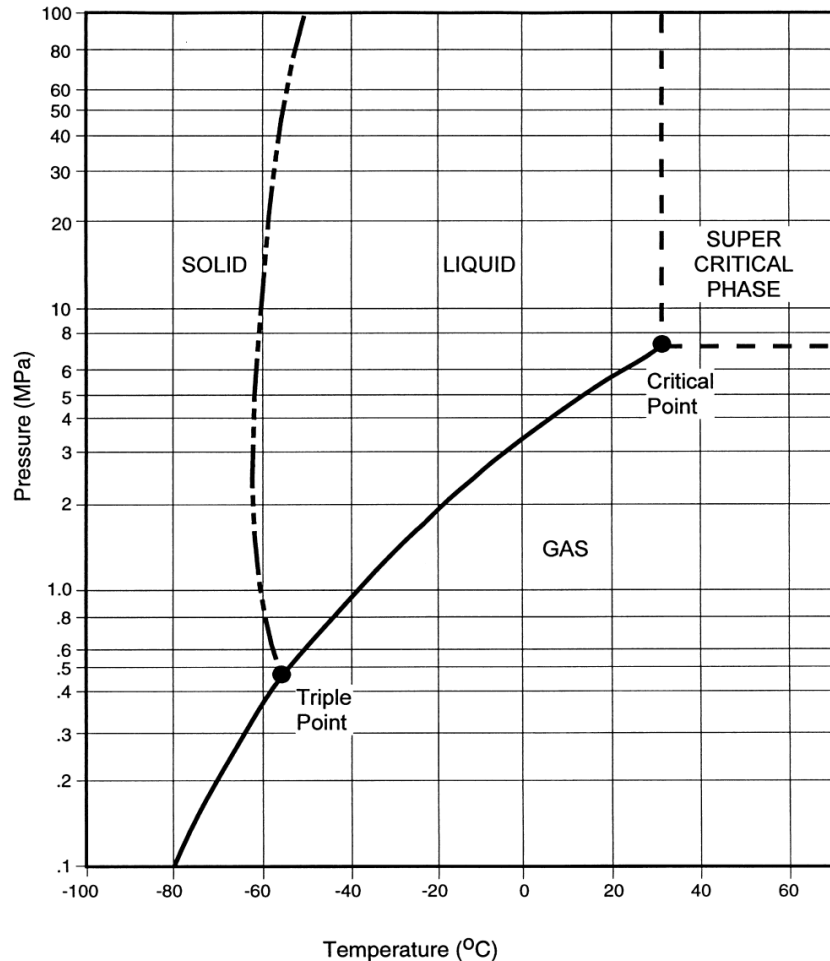


Figure 3: Carbon dioxide phase diagram (Bachu 2000).

Some of the injected CO<sub>2</sub> will dissolve in the formation salty water through diffusion, convection, and/or dispersion (solubility trapping). The solubility trapping rate will depend mainly on the amount of carbon dioxide that contacts the formation water surface (P.N.K. De Silva et al., 2011).

The dissolved gas in water will form carbonic acid ( $\text{H}_2\text{CO}_3$ ). Carbonic acid can change the mechanical properties of the reservoir rock. The change in Coulomb failure stress of the reservoir formation rock and caprock caused by the perturbation can lead to strength reduction and failure of the caprock ([Wei et al., 2015](#)).

There are parameters that needed to be studied before a carbon dioxide sequestration operation. Among these parameters are the salinity of the aquifer water and the temperature. The solubility of  $\text{CO}_2$  in water is the measurement of the maximum amount of a substance ( $\text{CO}_2$ ) that can dissolve in a given quantity of solvent (water) at given temperature.

The water salinity of an aquifer water affects the amount of  $\text{CO}_2$  that can dissolve in water. Water with higher concentration of salt will tend to allow less  $\text{CO}_2$  to dissolve in the water. That's mean that there is an inverse relationship between salinity and solubility of in  $\text{CO}_2$  water ([Portier et al, 2005](#)).

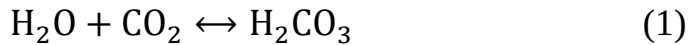
Temperature has an impact on the solubility of the carbon dioxide in water. It is a parameter that should be studied when considering  $\text{CO}_2$  sequestration. The change in carbon dioxide solubility is because the dissociation constant,  $K$  is temperature dependent ([P.N.K. De Silva et al., 2011](#)). Also, the temperature has an impact on the efficiency curve. So, any change in the temperature will shift the efficiency curve either up or down ([McDuff et al., 2010](#)).

The mixer of the dissolved carbon dioxide in a saline aquifer is carbonic acid ( $\text{H}_2\text{CO}_3$ ). Studying the impact of carbonic acid on the mechanical properties of the formation is essential prior to the start of any  $\text{CO}_2$  sequestration project.

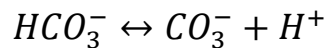
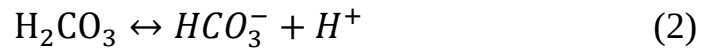
## 1.2. Carbonic Acid (H<sub>2</sub>CO<sub>3</sub>)

Carbonic acid is a compound of the elements carbon, hydrogen, and oxygen which exists only as a solution. Even that carbonic acid is considered a weak acid with a pH value of around 4.18, it still can alter the mechanical properties of a reservoir rock. The carbonic acid interaction with rocks will cause the degradation of the rock's strength and elastic property ([Denney 2013](#)). Also, when exposed to the air, carbonic acid will form carbonate and bicarbonate salts.

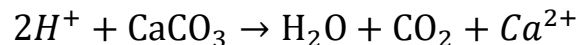
Carbonic acid will result from the dissolution and hydrolysis of carbon dioxide in water as shown in equation (1).



After that, the carbonic acid will quickly be decomposed into  $\text{HCO}_3^-$  and  $\text{H}^+$  as show in equation (2).



When the limestone (CaCO<sub>3</sub>) reacts with the hydrogen ions ( $\text{H}^+$ ), water, carbon dioxide and calcium cation will be produced as shown below.



Also, carbonic acid can dissolve limestone. By dissolving limestone, calcium bicarbonate will be created (Ca(H<sub>2</sub>CO<sub>3</sub>)<sub>2</sub>). This process is responsible for many of the limestone characteristics, such as stalactites and stalagmites.

The physical characteristics of the carbonic acid are as follow:

- The molecular mass of carbonic acid is 62.024 grams per mole.
- It has a density of 1.668 grammes per cubic centimetre when in its standard state of composition.
- The pKa value 6.35 is of the chemical molecule  $\text{H}_2\text{CO}_3$ .
- The bicarbonate is the conjugate base that corresponds to carbonic acid in the equation.
- This chemical is most seen in solution form. Although it has been stated that NASA scientists have created solid  $\text{H}_2\text{CO}_3$  samples, it is unclear whether this is true or not.

In addition to the physical characteristics, one of the chemical characteristics of carbonic acid is that in the presence of water, it undergoes partial dissociation, resulting in the formation of  $\text{H}^+$  and  $\text{HCO}_3^-$  (bicarbonate) ions.

During  $\text{CO}_2$  sequestration, some of the carbon dioxide does not dissolve in the water and will be in the gas phase or wet gas. As a result, the carbon dioxide will be in contact with the cap rock which might impact the integrity cap rock.

|

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1. Acid impact on geomechanical and petrophysical properties

[Hao et al., \(2020\)](#) studied the impact of acidizing on the mechanical properties of limestone and limy dolomite rocks. Acid was injected to the core samples of both rock types for a certain rate until break through. Under the same acidified conditions, it was found that limestone rock is more susceptible to acid dissolution than limy dolomite rock. Also, the reaction rate between the acid and the rocks was increasing with the increase in the acid concentration.

Limestone was found more reactive than the limy dolomite. Based on the experiments, it was found that the limestone rock reaction rate constant  $K$  is much greater than the limy dolomite rock reaction rate constant  $K$  under acidified conditions. This means that the acid rock reaction rate increases with the reaction rate constant. Also, for both rock types, it was found that the increase in temperature has a positive impact on the reaction between the acid and the rocks.

By comparing the mechanical properties before and after the acidizing of both rock types, the compression strength, and elastic modulus were reduced. Also, the mechanical properties of the relatively low cementation strength rocks could be highly or lowly weakened. On the other hand, the limestone rocks mechanical properties that have

relatively high cementation strength is more than the relatively high cementation strength limy dolomite rocks.

[Mustafa et al., \(2021\)](#) studied the acid impact on the deterioration of the mechanical properties of three type of rocks (limestone, chalk, and dolomite). For each type of the rocks, acid was injected at different rates in order to establish the efficiency curves. Also, they constructed a finite element model to estimate the deformation in each of the rock types. After the acid job, they found a reduction in the surface hardness of the rocks, and Young's modulus. Example of one of the rock types change in Young's modulus that is derived from the acoustic velocities is shown in Figure 4

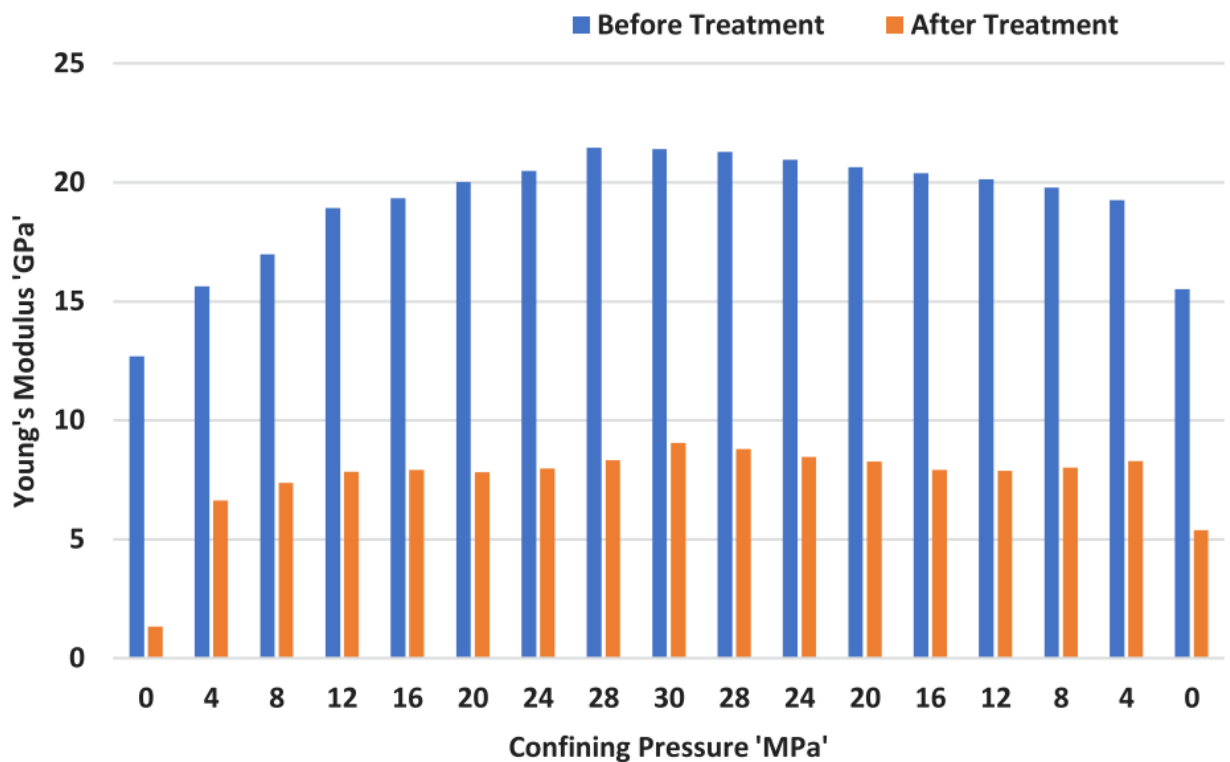


Figure 4: Change in Young's modulus before & after an acid job ([Mustafa et al., 2021](#))

## 2.2. Temperature impact on acid reactivity

[Lee and Roberts \(1980\)](#) constructed a model that can estimate the heat generated from the acid reaction with a rock along the acid fracturing. This model predicts the temperature profile along the fracture. Also, the model should help predicting the acid penetration length. The model started with the mass balance equation for an acid flowing in the fracture. Then, and by Applying the boundary conditions, the authors solved for the heat flux. Finally, the partial differential equations were coupled together and solved using a lumping technique. The equation was solved for different variables for the cases of considering heat of reaction and neglecting heat of reaction for comparison as shown in Figure 5. In the curves below, we can see the raise of temperature is faster in limestone. This is an indication of the faster reaction between the acid and the limestone compare with dolomite.

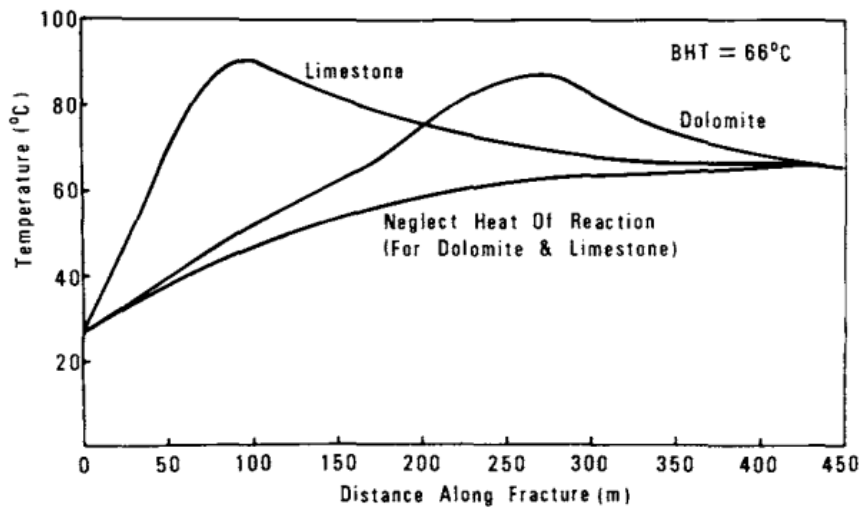


Figure 5: Heat of reaction for limestone and dolomite ([Lee and Roberts 1980](#))

The heat of reaction has an impact on the penetration distances. We can see in Figure 6 below the different penetration distances as a function of temperature. These curves are plotted for the change in distance when the heat of reaction is considered and when it is ignored for comparison.

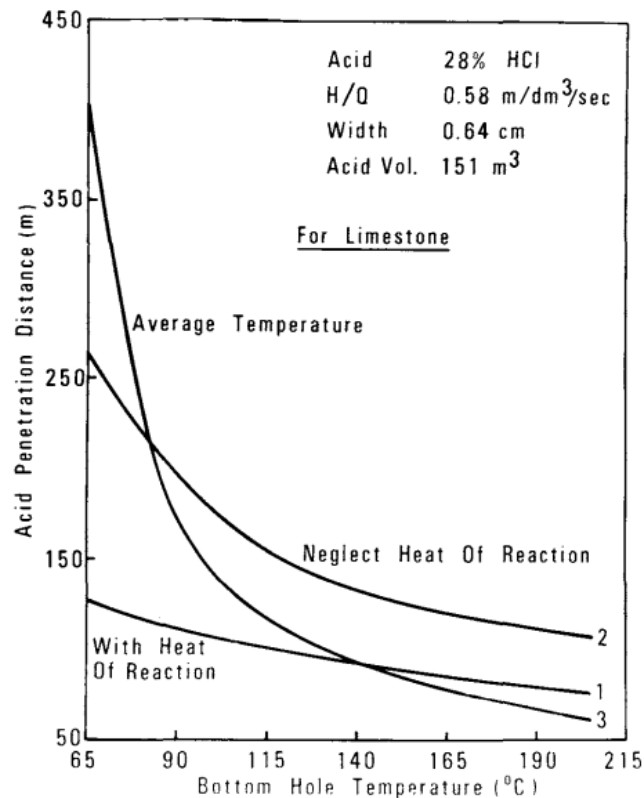


Figure 6: Heat of reaction impact on the penetration distances (Lee and Roberts 1980)

[Lempp et al., \(1994\)](#) have studied the impact of the change in temperature on rock mechanical properties and showed that the rock becomes more elastic with the increase in temperature.

[Kalia and Gerard \(2009\)](#) developed a model to investigate the change in temperature on wormholing. The formation permeability and the viscosity of the injected fluid will change during the injection process. The temperature of the injected fluid can change at the tip because of the heat generated from the reaction of the acid and the rock. As a result, the viscosity front will change with time as shown in Figure 7. This lowering in the viscosity and the change in permeability will result in two wormholes as shown in Figure 8. Also, we can see the creation of these wormholes can be seen from the evolution in porosity.

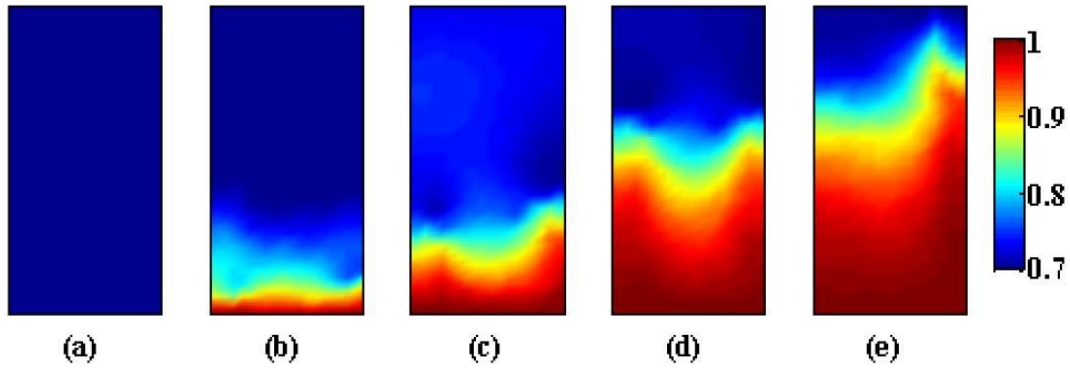


Figure 7: The change in viscosity front with time ([Kalia and Gerard 2009](#))

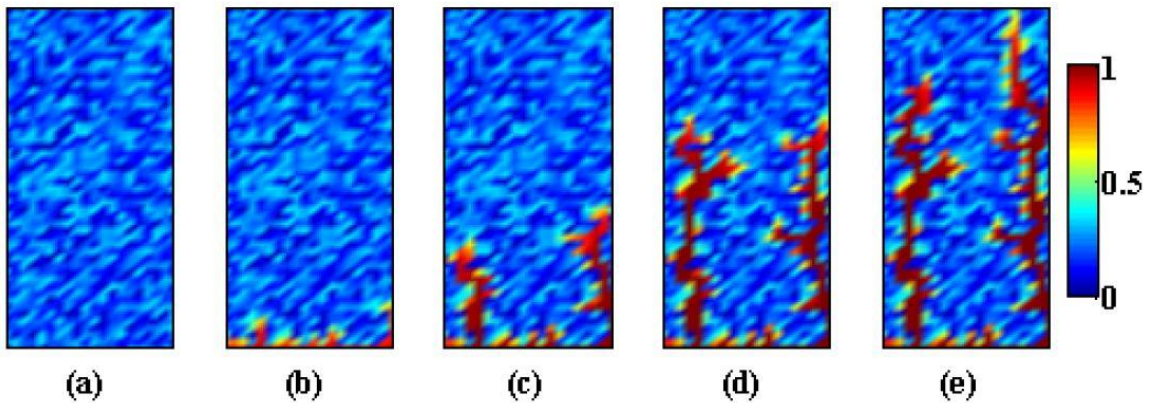


Figure 8: Creation to two different wormholes ([Kalia and Gerard 2009](#))

[Cheng et al., \(2016\)](#) injected HCl into limestone cores to study wormholes and because of the reaction between  $\text{CaCO}_3$  and HCl carbon dioxide was made. Carbon dioxide reduces the propagation of the wormhole when it is in the gaseous form. The negative impact of carbon dioxide on the wormhole propagation diminishes at low temperature (70 F) and disappears at higher temperature (150 F).

[Daeffler et al., \(2018\)](#) used a single-phase retarded acid for fracturing limestones because the fractures formed by HCl tend to have high near-wellbore conductivity but short etched half-lengths. Also, the organic acids and chelants have lower diffusion rates. As a result, they can travel more deeply into the formation before molecular motion transports the reactive component to the rock surface. However, the organic acids and chelants solubility of the reaction products (calcium acetate, calcium formate) is not as high as calcium chloride.

Two single-phase retarded acid formulations (SPRA1 and SPRA2) were used, and they were compared to the performance of the emulsified acid and the 15% HCl based on the basis of Pore Volume to Break Through (PVBT). The emulsified acid has the lower PVBT for all rates and the two single-phase retarded acids are close to the emulsified acid at high rates where the 15% HCl had the highest PVBT. At low rates, SPRA1 PVBT increases and becomes closer to the 15% HCl but the SPRA2 was similar to the emulsified acid. The PVBT was similar at the two different temperatures of 200 °F and 300 °F.

With the use of heat transfer model, ([Aljawad et al., 2021](#)) simulated the temperature impact of HCl acid job on limestone, dolomite, and mixed mineralogy. The study was on both linear and radial flow where the linear mimicked the treatment in core samples and the radial mimicked field treatment to understand if there is a relation between linear and radial acidizing job. To accomplish that, they studied the following parameters:

### **Heat of reaction impact**

The heat of reaction impact is resulted from the acid reaction with the carbonate minerals. For limestone, the heat of reaction had little impact on the acid efficiency curve. On the other hand, dolomite is more sensitive to the heat of reaction and as a result, the acid efficiency curve was shifted down due to the heat of reaction. Also, it required more PVBT for dolomite since the reaction is slower than the limestone reaction and the wormholes are thicker. The dolomite radial acid injection resulted in thicker and shorter wormholes.

### **Reservoir and injected fluid temperature impact**

For the limestone, the higher the temperature will result in reducing the wormhole size and as a result will reduce the efficiency of the acid job. Also, the temperature of the reservoir has no little impact on the acidizing efficiency compared to the injected acid temperature. For dolomite, as temperature increases, a wormhole becomes longer and thinner. As a result, the efficiency of the acid job increases as the acid temperature increases.

Also, the impact of having vugs in the dolomite was studied and found that the more vugs each rock has the larger the size of the wormhole. More vugs in a rock will result in less PVBT which is more efficient. Also, and like limestone, the temperature of the reservoir has no impact on the acidizing efficiency compared to the injected acid temperature.

### **Mixed limestone & dolomite**

The more the percentage of dolomite, the less is the efficiency of the acid job and this will make the wormholes thicker.

For a mineralogy that contains 50% dolomite and 50% calcite which are randomly mixed, the wormholes are still generated at low temperature. However, as the temperature increased, the wormholes became thinner, with more branches, and with a little increase in size.

### **2.3. Acid and wormhole generation**

[Fredd and Fogler, \(1999\)](#) describe in his paper some of the properties that impact the structures of the dissolution channels when the acid is being transported and reacted in the porous media such as the injection rate and fluid/mineral properties. These dissolution structures are face dissolution, conical wormholes, dominant wormholes, ramified wormholes, and uniform dissolution and can be seen in Figure 9. This change in the dissolution structure from the face up to the uniform dissolution happens as the velocity of the injected acid increases.

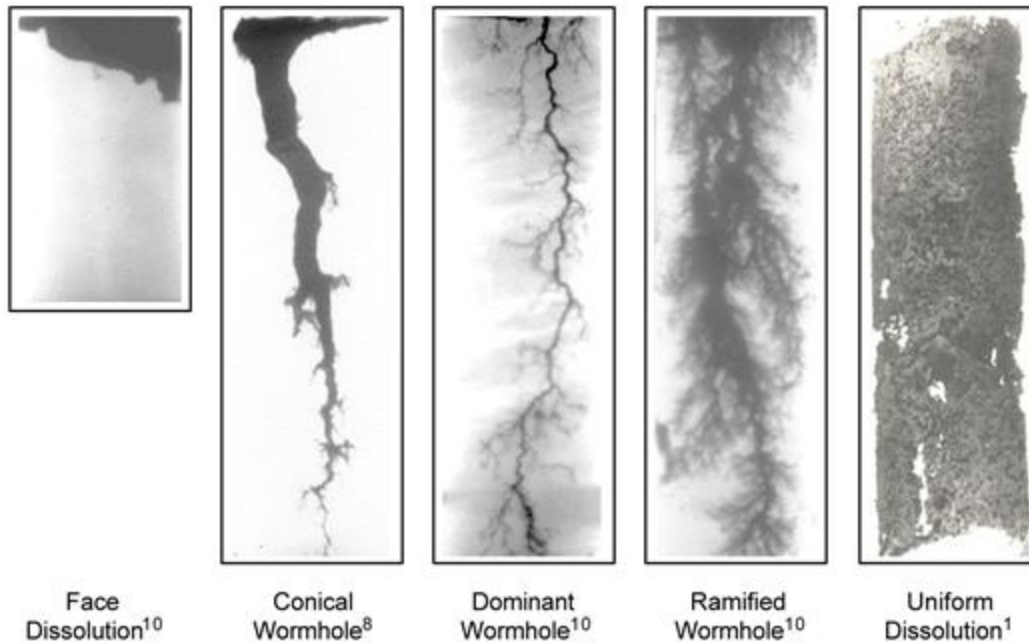


Figure 9: Injection rate impact on dissolution structures (Fredd and Fogler, 1999)

These different dissolutions structures are associated with different volume of acid consumed to create the dissolution in limestone rock. Figure 10 below shows the different efficiency curves as a function of injection rate (velocity) and Pore Volume to Breakthrough (PVBT). For each rate (velocity), there is a certain pore volume required to break through. For example, the higher rate at  $10^2 \text{ cm}^3/\text{min}$  it is required 5.3 PVBT compared to less PVBT of 2.5 when the injection rate is  $10 \text{ cm}^3/\text{min}$ .

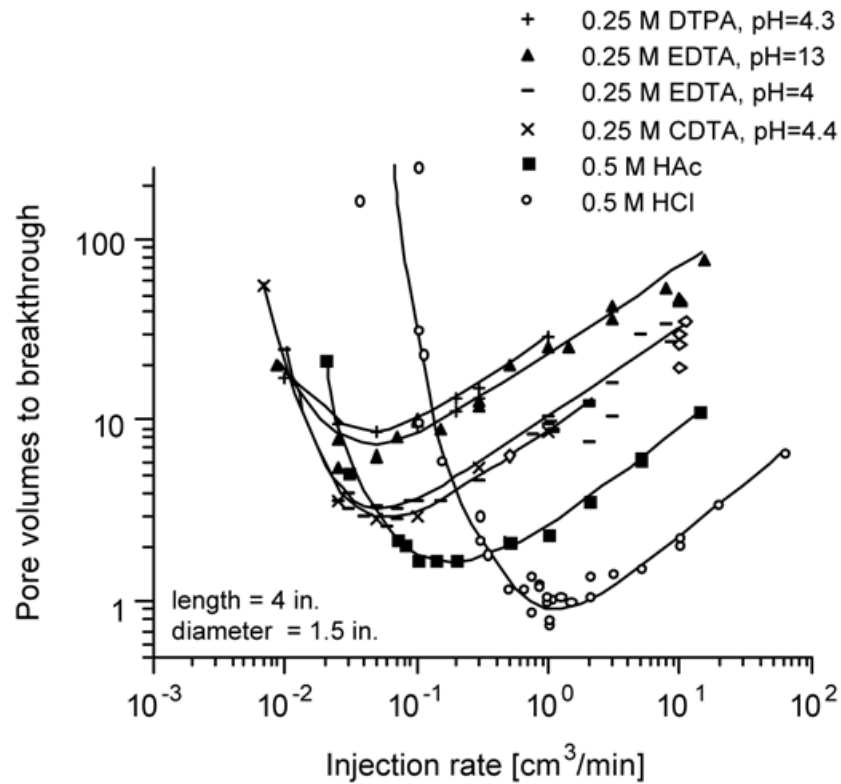


Figure 10: PVBT as a function of injection rate (velocity) (Fredd and Fogler, 1999)

Also, the dissolution of the rock is affected by the Damköhler number which is the net rate of dissolution over the rate of transport by convection. It measures the amount of reactant that is being consumed on the walls of a wormhole. For a wide range of fluid/mineral systems that were investigated, the optimum Damköhler number occurs at approximately 0.29.

[Klimentos, T., and S. Hassan \(2001\)](#) explained that along with other factors, the mechanical properties impact the sand production of a reservoir. The mechanical properties that impact the sand production are Poisson's ratio, Young's modulus and the strength of the rock. A

study of the petrophysical properties was also performed. The impact of all these properties was studied to identify the maximum fluid pressure drawdown before sand production start.

[McDuff et al., \(2010\)](#) performed a large-scale acidizing experiment on Indiana limestone. The authors performed X-ray diffraction, petrophysical analysis, thin section and micro-CT scanning for the rock before and after the acidizing job in order to understand the impact of creating the wormholes on the rock properties. The study was performed under confining pressure and a back pressure to simulate the reservoir conditions. Also, the injected acid was in radial flow to simulate the impact of the acid near the well bore.

[Joel, E. O., and M.. Pournik \(2011\)](#) have studied different correlations that estimate the rock strength after an acid job. The authors found that there are significant errors in the calculated rock embedment strength. Also, most studies showed that the rock strength will decrease with acid etching. However, the values of the embedment strength are within the measurement error limits. So, we can not get a certain conclusion on the acid effect on the rock weakening.

[Cao et al., \(2013\)](#) have studied the relationship between compressive strength (both uniaxial and triaxial) and the elasticity modulus. This was done by fitting the measured values of compressive strength and elasticity modulus using different methods such as linear function, logarithmic function, and polynomial function. Then, the formula that best

relates the two parameters (compressive strength and the elasticity modulus) was selected based on the correlation coefficient. The authors found that both the uniaxial compressive strength and triaxial compressive strength of the rock increase with the elasticity modulus. Also, they observed that the rock uniaxial compressive strength is reduced when the moisture content increases.

[Etten et al., \(2015\)](#) investigated the impact of different permeability values on a wormhole's creations using and the PVBT by using 15% HCl. They started with classifying the limestone core samples by permeability. They had four samples' groups with the permeability values of 6 mD, 11 mD, 33 mD, and 239 mD. The efficiency curves for each of the permeability curves are shown in Figure 11. The curves show that the as the permeability values decreases, the PVBT value also decreases. From the curves, we can see that this observation is more pronounced when the permeability is low.

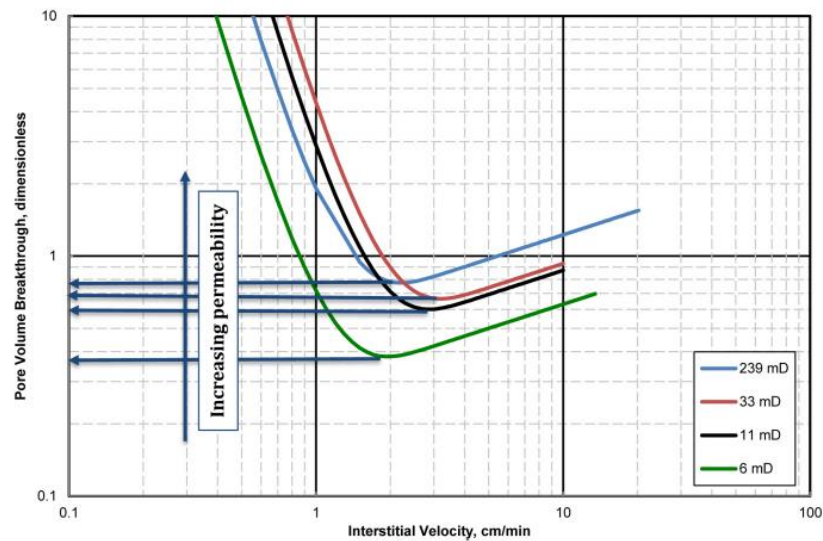


Figure 11: Efficiency curves as a function of permeability ([Etten et al., 2015](#))

Also, it is shown in Figure 12 that the increase of permeability is not proportional to the increase of optimal PVBT. The PVBT increases in a logarithmic rate.

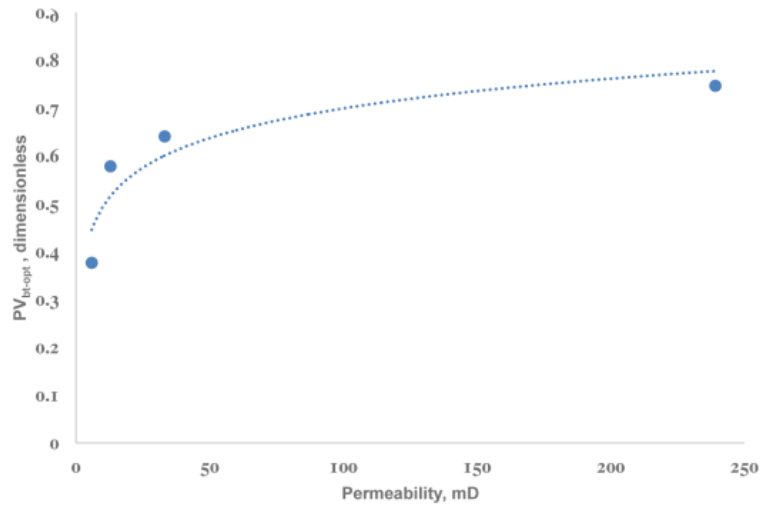


Figure 12: PVBT as a function of permeability (Etten et al., 2015)

[Wei et al., \(2015\)](#) studied the impact of CO<sub>2</sub> sequestration on the caprock by simulating the parameters that will affect the caprock integrity. Using their model, they were able to statistically classify different parameters based on their impact on the Coulomb failure stress. They found that the Young's modulus, burying depth, Poisson's ratio, friction angle, and stress field are the most important parameters when it comes to the level of Coulomb failure stress. Also, for the level of vertical deformation, only the burying depth was found the most significant.

[Agartan et al., \(2016\)](#) investigated the effects of the formation rock heterogeneity on the stability of carbon dioxide trapping when mixing it with brine for CO<sub>2</sub> sequestration. surrogate fluids were used to simulate the dissolved CO<sub>2</sub> in brine. The setup synthetic reservoir included for zones that represent the mixing section, the source zone, the caprock and bedrock for both homogeneous and heterogenous sand. Photos of the fingering of the fluid in the sand were taken at different times. They concluded that in homogeneous formations with mid or high permeability the convective mixing is the dominant. On the other hand, the diffusive mixing is more observed in the low permeability zones. This diffusive mixing will increase the amount of immobilized gas that dissolves in low permeability layers.

The difference between the deformation behavior of a rock and the compressive strength can be understood by considering an acid flood to a tight limestone. [Lai et al. \(2018\)](#) have shown that for flooding tight limestone with acid, there is almost no impact on the strength of the rock because it is hard for the acid to penetrate the tight limestone due to the low permeability. On the other hand, the Young's modulus was reduced almost by half which explain the impact of the acid on the tight limestone deformation behavior. The reaction between the acid and the tight rock will mainly occurs on the inlet of a core sample and that makes the surface pore structure loose, which leaves a large portion of the core sample without any change. When loading an axial stress, the loose surface will deform quickly, which will lead to a large strain under the same stress that was applied before the acid flood. This will cause the Young's modulus to be lower. However, the loose part will not have a big impact on the compressive strength because it will be compacted.

[Dong et al., \(2019\)](#) investigated the impact of wormhole geometry and rock strength weakening on wormhole stability that could cause a failure to the reservoir rock by using coupled hydro-chemo-mechanical simulation. The numerical simulation started with the mass conservation equation. The wormhole geometry was calculated and after that the mechanical properties of the reservoir were updated. Finally, the simulator started depleting the reservoir to find the induced stress field that was caused by the wormholes. The findings of the model are that both the face dissolution and the uniform dissolution can reduce the stability of the borehole by either making a wellbore enlargement or reducing the rock strength. Also, the model predicted that most of the wormholes are not under failure state.

[Gou et al., \(2019\)](#) have studied the impact of hydrochloric acid on a tight dolomite. The porosity and permeability did not change because the acid and the rock reaction only take place on the sample surface. Also, the increase of the reaction time between the tight dolomite and the acid will cause the dissolution to the contact surface only. On the other hand, they observed a reduction in the mechanical strength of the rock with time after the acid treatment. Also, the Young's modulus and the Poisson's ratio were reduced after the acid treatment.

[Naik et al., \(2020\)](#) Performed an acid fracturing conductivity tests on the Ratawi limestone core samples. After having the acid fracture, the permeability was measured using nitrogen and was compared with the permeability before the acid job. It was found that the rate of fracture conductivity is declining with the closure stress applied. The different closure stress was used to simulate different reservoirs conditions. Also, the wormholes were forming preferentially and rapidly along the sealed natural fractures. The minerals that are not soluble such as the clay streaks with higher mechanical properties acts as the pillars to support the fractures open as closure stress was applied. This mineralogy heterogeneous will support the with fracture conductivity sustainability.

[Xiao et al., \(2020\)](#) performed an acidizing job on limestone cores with medium-high porosity and low permeability. The cores were tested for tensile strength, uniaxial compression test at different confining pressures, and fracture toughness test before and after the acid job. The experiments were done for different rates and using two acid concentration (15 wt% HCl and 20 wt% HCl) for comparison. As the HCl concentration increases, the dissolution rate increases but with a small value. For the low permeability and medium-high porosity carbonate cores, the experiments showed that the surface of the cores is uniform dissolution and no penetrating channels formed during gelled acid reaction.

[Freni et al., \(2021\)](#) introduced a tool that evaluates the capacity of an aquifer (how much aquifer volume is needed to store a certain amount of CO<sub>2</sub>). This tool which is using Excel/VBA is based on a volumetric method used by the SPE. This tool is using a simple material balance equation which is good for an early step of a project. As a result, other physical phenomena such as CO<sub>2</sub> solubility were introduced to improve the tool predictions. Each gas volume injected is calculated and related to pressure increase. Then, the volume of the gas dissolved is deducted from the injected mass of the gas injected. The tool was validated with a 3D sector model which showed good alignment.

## **2.4. CO<sub>2</sub> impact on geomechanical and petrophysical properties**

[Barbara et al., \(2008\)](#) made a numerical model that simulate CO<sub>2</sub> injection in a heavy oil reservoir to reconstruct the chemical composition of the reservoir before the injection which includes the pH value and the boundary conditions at 62 °C and 15 MPa. Also, predicts the precipitation/dissolution processes of the brines over 100 years after injection and to validate the short-term evolution of the in situ reservoir fluids due to the CO<sub>2</sub> injection. The statistical Median Test which is used to compare measured and computed data, predicts that the geochemical model is able to describe the real behavior of most investigated variables.

[Denney \(2013\)](#) has studied the impact of the injecting carbonic acid on the mechanical properties of limestone and shale. First, he performed a laboratory tests on the shale and limestone core samples. Then, he constructed a 3D geomechanical model where he was relating the stress and strain in the model to the change in porosity. These changes in porosity lead to an increase in the permeability and the Poisson's ratio. Also, the model found that the strength and elastic properties were degraded. The laboratory tests results were used for comparison with the model results.

[Ajibola et al., \(2016\)](#) used a two dimension simulator to simulate the unstablity that might happen when CO<sub>2</sub> start mixing with aquifer brine and the rate of mixing. They found that the pattern of the fingering is affected by the different vertical and horizontal diffusivity coefficients. At Rayleigh number greater than 800, fingers are present. Also, fingers grow with the increase in mixing time, the increase in Rayleigh number and when the Rayleigh number decreases, the critical time increases. Density difference, permeability, and gravity impact are more important than the diffusion coefficient in controlling the fingering degree. This model was validated with the experimental data in the literature.

[AlAmeri et al., \(2016\)](#) studied the impact of the CO<sub>2</sub> sequestration on limestone mechanical properties and the impact of different times of sequestration on the mechanical properties. The experiment was done by soaking different types of limestone at 100 Celsius and 200 psi. These rocks were aging for different times (14, 30, or 90 days). By comparing the Young's modulus, and Poisson's ratio, it was found that these mechanical properties were

decrease after sequestration as shown in Figure 13. Also, increase of the sequestration time reduced the Young's modulus of the cap rock as shown in Figure 14.

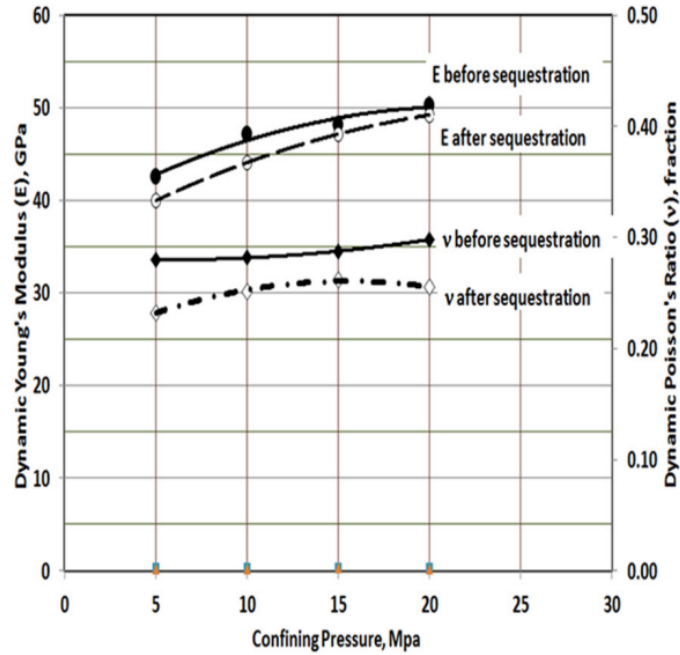


Figure 13: Reduction in Young's modulus and Poisson's ratio (AlAmeri et al., 2016)

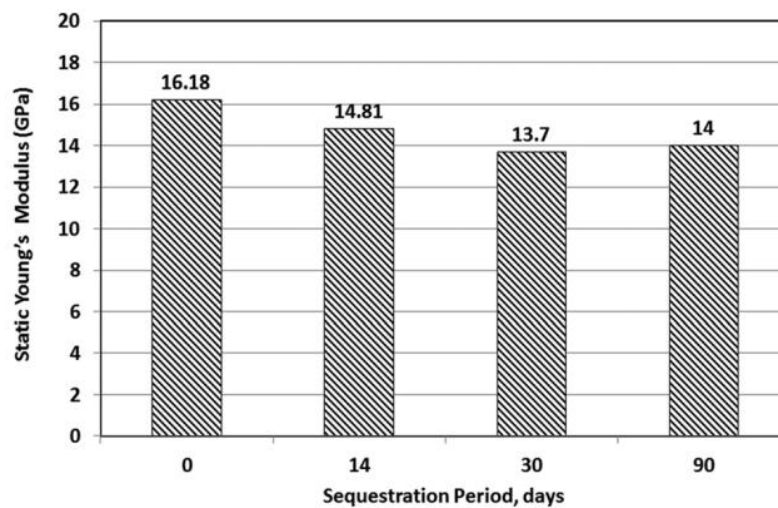


Figure 14: Sequestration time impact Young's modulus (AlAmeri et al., 2016)

[Temitope et al., \(2016\)](#) built a simulation model to assess the potential of having CO<sub>2</sub> sequestration in saline aquifer. Before building the model, the candidate site was selected based on the costs, long term storage capacity, sealing efficiency, distance from cities (risks), permeability, and the available knowledge of the reservoir continuity. As a result, a saline aquifer that surround an oil field structure was selected which is the Shuaiba formation in Abu Dhabi.

After building the static model and upscaling, the dynamic model was run for different scenarios such as the run time that varied from 100 years to 6000 years to study the movement of the CO<sub>2</sub> plume and know if and when the plume lateral movement will get to the surrounding oil fields. Also, five wells were used in the gas injection and the different locations of these wells was studied to understand the positioning impact on the objectivity at the bottom of the aquifer.

The injection of the gas lasted for 140 years, and the simulation ran for 9000 years. At the initial injection period, the dissolution trapping dominated and after the injection, the residual trapping mechanism increased but still the domination was for the dissolution trapping. The model predicted the time required (if any) for CO<sub>2</sub> plume to reach the top of the aquifer for different trapping mechanisms. As a result, and because of the CO<sub>2</sub> mobility, the seal will play an important part in the injected gas containment. Also, the model predicted that the movement of the gas to the surrounding oil fields is very slow. The salinity of the formation water is 100000ppm, the pressure is 5000 psi, and the temperature is 200 F.

[Zhang et al., \(2016\)](#) studied the impact of carbonic acid on limestone mechanical properties. They selected 4 core samples with similar properties to conduct the experiments. Each of the core samples was in a core holder under a pressure of 10 MPa and a temperature of 323 K. Then, the cores were saturated with the dead brine of 5wt% NaCl. After that, the supercritical CO<sub>2</sub> was injected with a rate of 0.5 ml/min into the cores. Then, the dead brine was injected again to measure the permeability. An example of one of the cores pressure difference verse pore volumes to breakthrough (PVBT) is shown in Figure 15.

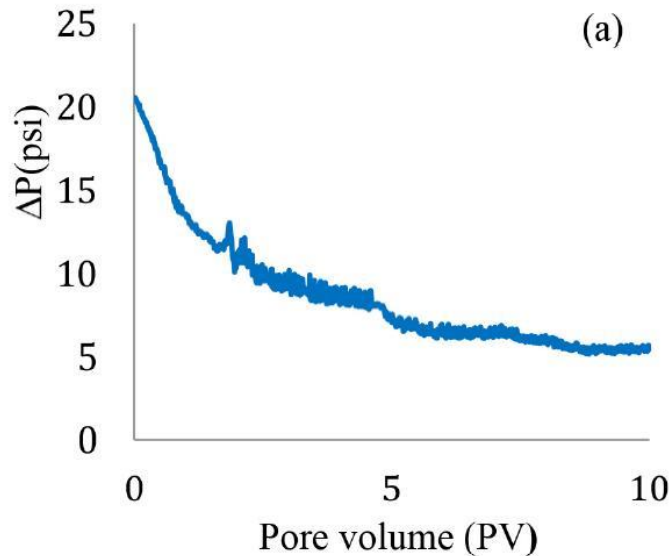


Figure 15: Pressure difference vs. pore volume to breakthrough ([Zhang et al., 2016](#))

The permeability of the cores and the roughness of the cores increase significantly. The increase in the porosity was little. The Bulk modulus, Poisson's ratio, Young's modulus, and Shear modulus were all significantly decreased after the CO<sub>2</sub> injection as shown in Table 1.

| Sample ID | Bulk modulus K (GPa) | Poisson's ratio $\nu$ | Young's modulus E (GPa) | Shear modulus G (GPa) |
|-----------|----------------------|-----------------------|-------------------------|-----------------------|
| A         | 17.40 (↓19.96%)      | 0.30 (↓11.76%)        | 20.38 (↓4.32%)          | 7.81 (↓2.01%)         |
| B         | 17.97 (↓12.60%)      | 0.30 (↓6.25%)         | 21.26 (↓4.75%)          | 8.16 (↓3.55%)         |

Table 1: Mechanical properties after the carbon dioxide injection [Zhang et al., \(2016\)](#)

[Al-Yaseri et al., \(2017\)](#) have studied the impact of injecting CO<sub>2</sub> in reservoir on the permeability of sandstones. They started the experiment by injecting the dead brine in the cores under a certain pressure and temperature to simulate the reservoir conditions. Then, the live brine was injected and followed with the injection of the supercritical CO<sub>2</sub>. The injection was at different rates. During these floods, the permeability was measured at each time for comparison. As a result of these experiments, they concluded that there is no impact of the different injection rates on the change of permeability. On the other hand, it was found that the acidity, salt type & concentration, and structure/distribution of the rock clay minerals are the main controlling factors that affect the change in permeability and/or porosity. Also, the study found that the clay minerals structure in the skeleton of the rock is very important since that dispersed clay minerals will be detached and move into the bulk fluid. On the other hand, the structurally imbedded clay minerals in the rock matrix will not be detached.

[Zhang et al., \(2020\)](#) investigated the deterioration that might happen to limestone rocks after the injection of CO<sub>2</sub> for CO<sub>2</sub> sequestration. The cores samples were divided into three groups. All cores were saturated with 5 wt% NaCl brine before the flood. These limestone samples flooded with dead brine, supercritical CO<sub>2</sub>, and live brine separately. The temperature and pressure applied of the cores are 50 °C temperature, 10 MPa back (pore) pressure and 15 MPa confining pressure. The cores were CT scanned before and after the flooding. After that, the segmented images of the cores were used in the DEM (Discrete Element Method) to simulate the changes in the core's mechanical properties.

The supercritical CO<sub>2</sub> caused some damage to the limestone, but the live brine caused much more damage. This damage affected the mechanical properties of the rock which resulted in a reducing the maximum compressive stress from 17.2 MPa, to 14.8 MPa for the supercritical CO<sub>2</sub>, and to 7.9 MPa for the live brine. Also, the porosity of the rock that was 8% increased to 14% after the supercritical CO<sub>2</sub> injection and 20% after the live brine flooding.

[Hussein et al., \(2021\)](#) investigated the modification coal surface and coal pore structure by inserting other materials to improve the coal adsorption of CO<sub>2</sub>. This material is methyl orange which is also causing pollution. This resulted in an increase in the CO<sub>2</sub> adsorption dramatically.

[Kou et al., \(2022\)](#) performed core flooding experiments to see the impact of the carbonic acid on rocks considering the heterogeneous geochemical reactions due to the different rock components. They found that the core permeability and porosity increased scientifically which indicates that the carbonate minerals dissolution dominated over mineral precipitation. The authors attributed these changes in porosity and permeability to the carbonate mineral dissolution. The evidence for this change is by observing the pore-throat size distribution, effluent brine geochemistry, and Brunauer-Emmett-Teller surface area. However, for the more permeable section of core samples that contains the larger pore size, the permeability increase is due to the dissolution of the dolomite mineral grains and cements. On the other hand, for the section of the core with lower permeability that corresponds to the smaller pore size, mineral precipitation lessened dissolution effects which does not lead to a big change in the petrophysical properties.

[Montoya, and Hoefner \(2022\)](#) constructed a model to study injecting and storing CO<sub>2</sub> in a saline aquifer in LaBarge field area which is in the southwestern corner of Wyoming state. They started the gas injection by using 2 wells and they are planning to drill a third injection well to expand their carbon storage project. They started by constructing the static model that was derived from the extensive structural interpretations based on 3D seismic over the gas field, limited regional 2D seismic data and subregional well control. Then, the dynamic model was run to history match the gas production and gas injection disposal, to evaluate the impact of key parameters affecting CO<sub>2</sub> injection rates with time, and to predict the size and location of CO<sub>2</sub> plumes through time in both Madison and Bighorn reservoirs.

The volume-weighted average gas saturation at various time steps was calculated to determine the CO<sub>2</sub> gas plume expansion for the new CO<sub>2</sub> disposal well. The model was run forward more than 80 years to increase confidence in maintaining a maximum injection rate. The results predicted that the injection rates of around 70 MCFD and there is no interference between the new well and the existing gas injection wells.

Different Scenarios were run to test the uncertainty of different variables such as kh, expected skin and relative permeability on maintaining CO<sub>2</sub> injection rates over time. The model will be calibrated after the new injection well be drilled to refine the prediction of CO<sub>2</sub> injection rates, plume sizes, and the potential for interference between wells over time.

[Wilson, et al., \(2022\)](#) tested the effect of injecting CO<sub>2</sub> in limestone that is saturated with brine to construct a model that predicts the impact of the injection of CO<sub>2</sub> for different parameters. The experiments were done for different rates and permeability values. Also, the effluent data was collected for each experiment to track the dissolution and as a result study the pore enlargement and the time to create a wormhole for each case. Each core was CT scanned after the injection. Porosity and permeability relation also was used to construct the model. The model is using all these information to calculate the amount of dissolved mineralize in each time step. Also, by history matching the data from the experiments with the model results, the simulator can predict other scenarios with different parameters.

## 2.5. Temperature impact on CO<sub>2</sub> solubility and reactivity

[Portier et al, \(2005\)](#) was studying the impact of salinity, pressure, and temperature on the solubility of CO<sub>2</sub> in the aquifer. They measured the differences in solubility by changing the values in each parameter. Also, they generated a thermodynamic model to validate the available experimental observations, the calculation results with the experimental measurements, and the other models of CO<sub>2</sub> solubility results. An example of the results that they have is shown in Figure 16. The curves show that the solubility decreases as the temperature increases.

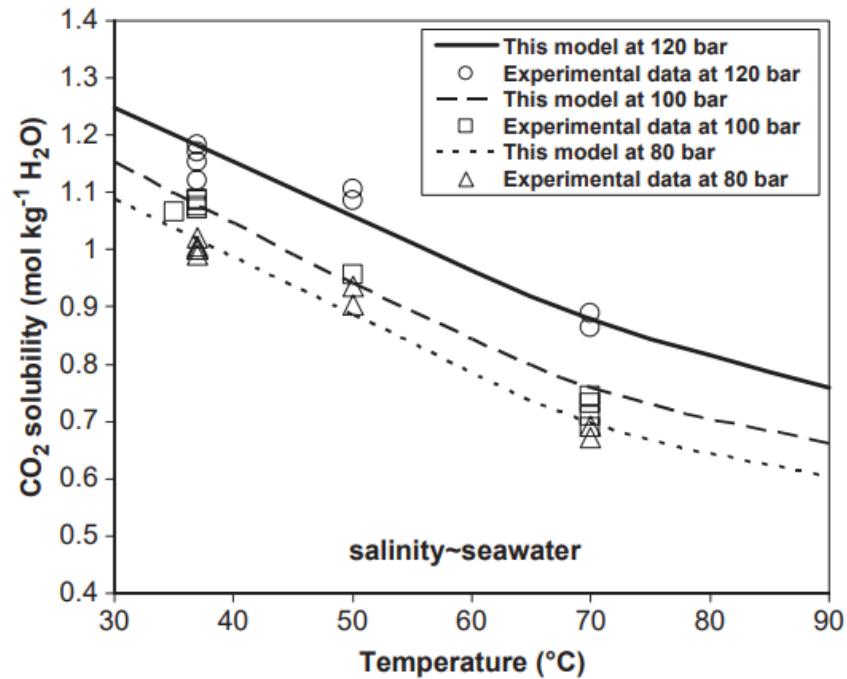


Figure 16: CO<sub>2</sub> solubility as a function of temperature ([Portier et al, 2005](#))

[Merete et al., \(2006\)](#) tested the impact of injecting CO<sub>2</sub> and carbonate water on the mechanical stability of chalk rocks at different temperature. For a certain pressure, the decrease in salinity and temperature will increase solubility of CO<sub>2</sub>. Also, the impact of salinity is lowered as the temperature increases.

CaCO<sub>3</sub>(s) solubility increases with the increase in pressure and decreases with the increase in temperature. Even though that chalk dissolution rate should increase with the decrease pH value, but the amount of chalk going into solution is related to the concentration of dissolved CO<sub>2</sub>. As a result of the injection of the carbonate water, the average yield point and deformation modulus are lowered. For a certain pressure, the increase temperature to 90 °C improved chalk stability.

[P.N.K. De Silva et al., \(2011\)](#) Discussed in their paper the methodologies for estimating the capacity of carbon dioxide storage in saline aquifers such as the mathematical models, dimensional analysis, and analytical investigations. The different trapping mechanisms were also discussed for better estimation of the capacity of carbon dioxide storage. The trapping mechanisms are mineral trapping, structural and stratigraphic trapping, solubility trapping, residual gas trapping, and hydrodynamic trapping. Also, different parameters were discussed in the paper that have an impact on estimating the storage capacity such as permeability, pressure, temperature, injectivity, and compressibility. The authors found several techniques that can increase the capacity of the storage such as using g horizontal injection wells instead of vertical injection wells. Also, the capacity can be increased by making hydraulic fractures in the acid injection wells and transport the produced brine to another.

In the laboratory, [Shariat et al., \(2012\)](#) measured the interfacial tension (IFT) between CO<sub>2</sub> and formation brine. The effectiveness of the structural trapping depends on the capillary pressure which is a function of the IFT. The pressure of the experiment is between 1000 and 18000 psia, and the temperature is up to 4000 F. The findings of the study are as follow:

- The temperature is a big factor in determining the CO<sub>2</sub> – H<sub>2</sub>O IFT (IFT decreases with temperature increase)
- CO<sub>2</sub> - H<sub>2</sub>O will not be fully miscible at all the pressure and temperature applied.
- CO<sub>2</sub> saturated water density is strongly dependent on the pressure and temperature.
- For a certain temperature, CO<sub>2</sub> - H<sub>2</sub>O IFT is relatively insensitive to pressure.

[Cheng et al., \(2013\)](#) evaluated the pH value of CO<sub>2</sub> saturated water at different temperature and pressure. It was found that the pH value will increase with the increase of temperature and decreases with the increase of pressure. The decrease in the pH value initially is rapid with the increase in pressure but much slower at high pressure.

[Fulai et al., \(2017\)](#) studied the thermodynamic stability of dawsonite after injecting CO<sub>2</sub> and the impact of different temperature on this stability. The study was done by allowing the interaction between the rock water and CO<sub>2</sub> which created carbonic acid. By doing that they were able to distinguish between the temperature where the dawsonite is stable and other temperature. At a temperature of 120<sup>0</sup> C and above the dawsonite was found unstable and below the temperature of 120<sup>0</sup> C, dawsonite is found stable. Also, they found that the

dissolution and corrosion degrees of the unstable minerals in the sandstone will increase when the temperature increases.

[Kumar et al., \(2020\)](#) has constructed a compositional model that simulate the impact of injecting KCl and HCl in limestone. The model has 152 X 25 X 25 cells in the I, J, K coordinates where the corners and edges of the rectangle were nullified to model a cylindrical core. One of the aqueous phases is the carbon dioxide which is a result of the limestone and HCl interaction. The different fluids variables were calculated using the standard literature correlations such as the viscosity values as a function of temperature as in Figure 17.

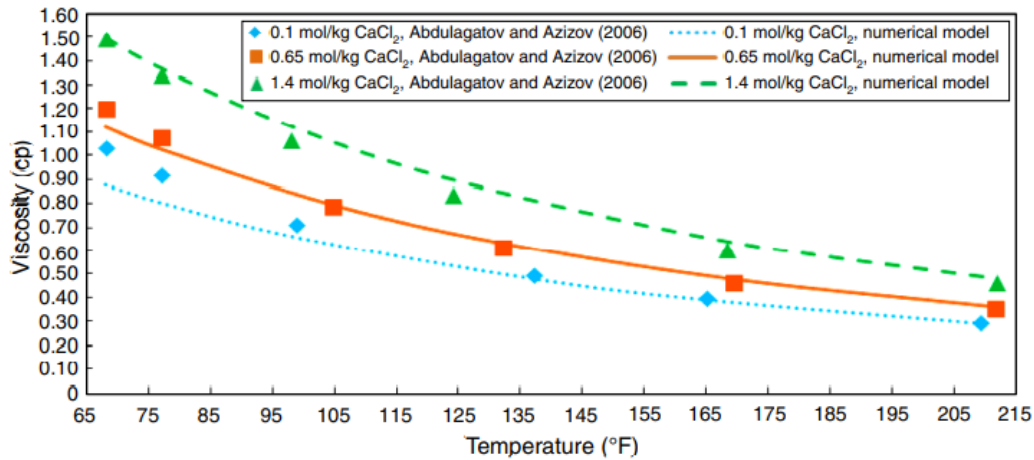
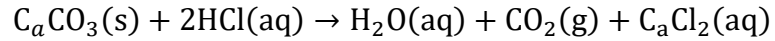


Figure 17: The change in viscosity as a function of temperature ([Kumar et al., 2020](#))

One of the cells at I = 152 is where the injection point and at I = 1 is where the producer with no flow boundaries across all the peripheral cells. The fluid entry and exit is allowed

through cells that are perforated. The reaction between the limestone and HCl is modeled as shown in the equation below.



The model was validated by repeating acidizing experiments that were described in the published literature and also by doing laboratory tracer injection experiment experiments of carbonate acidizing on Indiana limestone cores. The model was able to predict the efficiency curve of ([Fredd and Fogler 1999](#)).

The study mentioned the importance of the understanding the CO<sub>2</sub>-aqueous system phase diagram that will allow knowing the pressure and temperature at which the CO<sub>2</sub> is evolve and not be dissolved in the solution. The separate phase of CO<sub>2</sub> will reduce the efficiency of the acid.

## 2.6. Salinity impact on CO<sub>2</sub> solubility and reactivity

[Abba et al., \(2017\)](#) studied the impact of salinity on the displacement efficiency when injecting CO<sub>2</sub> in the sandstone rocks. The salinity reduced the dispersion coefficient compared to experiments with the distilled water or experiments with the dry cores samples.

[Temizel et al., \(2017\)](#) modeled the injection of CO<sub>2</sub> in the aquifer and evaluated the geochemical trapping. The model simulated the injection of 25 years and run the simulation for another 225 years. The geochemical trapping includes the solubility trapping (when CO<sub>2</sub> dissolves into the brine) and the mineral trapping (when the supercritical CO<sub>2</sub> reacts with the rock minerals). It was noted that the solubility of CO<sub>2</sub> in the brine will increase with the increase in pressure and the decrease of temperature. Also, the increase in salinity of the brine will decrease the solubility. The salinity impact is lower than the impact of the temperature, rock density and conductivity but still salinity is an important factor that should be studied.

[Stefan \(2018\)](#) discussed the optimum depth where the maximum mass column of CO<sub>2</sub> can be stored without percolating through the aquifer caprock. To do so, the author derived the equation of the gas column height. The height of the column of the gas can be found by equating the capillary pressure equation with the buoyancy pressure equation as shown below.

$$P_b = \Delta\rho gh$$

$$P_c = \frac{2\gamma\cos\theta}{r}$$

$$h = \frac{2\gamma\cos\theta}{\Delta\rho gr}$$

The model considers the change in the density deference that is governed mainly by the change in the gas density which is a function of depth since the gas has a big compressibility. Also, the contact angle increases with depth. On the other hand, the interfacial tension decreases with pressure. Knowing the maximum height  $h$  will allow knowing the maximum mass of CO<sub>2</sub> that the formation can hold. The model was validated by comparing it with datasets observed and studied from the literature. The limitations of the model come from the assumptions that the formation has a typical geothermal and hydrostatic gradient and from the assumption that the formation has an average brine salinity.

[Tohidi and Sadeghnejad \(2021\)](#) developed a model that predicts the impact of injecting acid in a high salinity formation water and the impact of different salinity values on the fluid properties at different pressures. The model started with the continuity equation and developed the equation that calculate the impact of salinity on the density and viscosity as a function of temperature and pressure. Also, the change in rock properties were predicted by considering the most influential factors. The change in porosity that is caused by minerals precipitations and dissolutions were quantified by determining the variation of mineral volumes per grain Volume Fractions (VFI). Also, the correlation between the

permeability and porosity was considered. It was found that salinity has much more impact on the density of the fluid compared to the impact of salinity on viscosity. On the other hand, the temperature will reduce both the viscosity and density of the fluid. But the reduction in the viscosity due to the temperature is much more than the reduction in the density. Also, the Damköhler number (Da) was used to evaluate the model behavior of the core flooding at reservoir conditions. When the Damköhler number is low, the convective flow term is more dominant than the reaction term. The validity of the developed model was evaluated using experimental literature data.

[Alzayer et al., \(2022\)](#) discussed the process of modeling CO<sub>2</sub> sequestration. They used a giant synthetic anticline model. They consider the different trapping mechanisms of CO<sub>2</sub> sequestration in deep saline aquifer such as the structural trapping, solubility trapping, residual trapping, and mineral trapping. For example, the solubility mechanisms depend on the salinity and temperature of the aquifer water. Also, the three requirements of the aquifer were considered which are the adequate storage capacity which is impacted by the both the porosity and the thickness of the formation, the good injectivity of the CO<sub>2</sub>, and the seal that will trap CO<sub>2</sub> from migrating from the formation. Since the injection of CO<sub>2</sub> will increase the pore pressure, the model considered a larger area to allow larger volume of CO<sub>2</sub> to be injected. The model modeled both the live brine (liquid phase) and the CO<sub>2</sub> (gas phase). When CO<sub>2</sub> contacts water at high pressure, CO<sub>2</sub> will start dissolving in water making carbonic acid. This acid will be a little denser than water and as a result will start fingering as shown in the simulation model. As a result, more and more CO<sub>2</sub> will be dissolving in water and more carbonated water will migrate to the bottom of the aquifer.

This means that the free gas mass will be decreasing in time as shown by the model. The running time of such simulation models should be for a thousand years as in the recommended industry standards. Also, because the CO<sub>2</sub> trapping mechanisms will take a long time before they happen.

From studying the researchers' work, we could see that there is much research on the impact of salinity and temperature on CO<sub>2</sub> solubility in water and the impact of salinity and temperature on acid reactivity with limestone and wormhole generation. However, the literature is lacking studies about the impact of salinity and temperature on wormhole generation due to the carbonic acid interaction with limestone. Also, the salinity and temperature impacts on the rock's petrophysical and geomechanical properties due to CO<sub>2</sub> storage in deep saline limestone aquifers is missing. Therefore, this study provides screening criteria to select the optimum aquifer salinity and temperature that ensures safe CO<sub>2</sub> storage.

## **CHAPTER 3**

### **PROBLEM STATEMENT AND RESEARCH OBJECTIVES**

The knowledge we have from studying different types of acid is vast. However, the researches that have been done to study the impact of the CO<sub>2</sub> sequestration in saline aquifer formation is limited. The reaction between the CO<sub>2</sub> gas and the aquifer saline water will create carbonic acid that will react with the formation rock and will change the rock mechanical properties. The uncertainties that we have regarding the impact of carbonic acid on the rock are significant in avoiding the risk of formation rock failure due to excessive reaction at reservoir scale that could lead to CO<sub>2</sub> leakage.

Therefore, the goal for this study is to discover the impact of carbonic acid injection on the rocks mechanical properties after creating wormholes. This study will focus on the conditions of the formation rock that will reduce or increase the impact of carbonic acid. The conditions that will be studied are the formation temperature and the salinity of the formation water. So, the specific goals of this study are:

- 1) To study the impact of temperature and salinity on wormholes generation due to CO<sub>2</sub> sequestration.
- 2) To study the impact of temperature and salinity on the rock mechanical and petrophysical properties due to CO<sub>2</sub> sequestration.

## CHAPTER 4

### RESEARCH METHODOLOGY AND EQUIPMENT

To accomplish the research objectives mentioned in Chapter 3, our study will be divided into three parts. First, we measured the rock samples' properties. The properties that will be measured are porosity, permeability, hardness, Young's modulus, and Poisson ratio. Also, all samples will be medical-CT-scanned. Then, the mixer of brine and carbon dioxide (carbonic acid) will be injected into the core samples. The experiments conditions will be different for each sample by changing the parameters. The two parameters that will be changed are going to be the water salinity and the temperature of the injected mixer. After that, all samples' properties will be measured again, analyzed, and reported.

The study steps can be summarized in Figure 18.

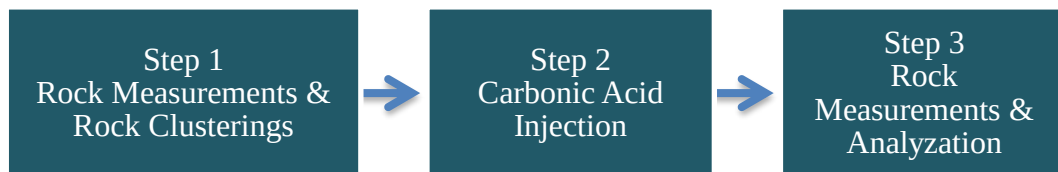


Figure 18: Research Methodology

The research procedure is as follows:

- 1) Creating carbonic acid by mixing CO<sub>2</sub> with the desired brine.
- 2) Measuring the mechanical and petrophysical properties of the rock samples before the carbonic acid injection, which are.
  - a. Porosity.
  - b. Permeability.
  - c. Rock hardness.
  - d. Young's modulus.
  - e. Poisson ratio.
- 3) Creating wormholes by injecting carbonic acid at different temperatures and different water salinity.
- 4) Repeat the measurements of the mechanical and petrophysical properties of the rock samples after the carbonic acid injection and medical-CT-scanned each core sample to analyze the impact of the carbonic acid injection.

## 4.1. Rock Measurements & Selections

### 4.1.1. Cores cutting

The rock type that was selected for this study is Indiana limestone. The cutting machine that was used to cut the rock is Mecatome ST310 Figure 19. All core samples diameter is 1.5 inch and the length of all cores samples is 3 inches.



Figure 19: Core cutting machine (Mecatome ST310)

#### 4.1.2. Cores weight and Porosity measurements

The rock samples porosity was measured using the Helium Porosimeter Figure 20. The device is using Boyles Law to measure the effective porosity of the rock samples at ambient conditions. The law states that under the same conditions where the quantity and temperature of gas is the same, the multiplication of the gas volume and pressure is the same.



Figure 20: Helium Porosimeter for porosity measurements

Also, the weight of each sample is measured using the scale shown in Figure 21. After measuring the rock samples weights, porosity, and dimensions, we could calculate the grain volume, and density. The measurements of the core samples are shown in Table 2.



Figure 21: Cores weight measurements

| Sample No | Sample name | Sample Dia (mm) | Sample Length (mm) | Dry Weight (g) | Bulk Vol (ml) | Grain Vol. (ml) | Pore Vol. (ml) | Porosity (%) | Grain density (g/ml) |
|-----------|-------------|-----------------|--------------------|----------------|---------------|-----------------|----------------|--------------|----------------------|
| 1         | IL-1        | 37.94           | 77.13              | 196.70         | 87.20         | 73.84           | 13.36          | 15.32        | 2.664                |
| 2         | IL-2        | 37.96           | 76.82              | 197.88         | 86.94         | 74.34           | 12.60          | 14.49        | 2.662                |
| 3         | IL-3        | 38.1            | 76.8               | 196.48         | 87.56         | 73.43           | 14.13          | 16.14        | 2.676                |
| 4         | IL-4        | 38              | 67.67              | 195.21         | 87.05         | 73.59           | 13.46          | 15.46        | 2.653                |
| 5         | IL-5        | 38.1            | 76.9               | 197.61         | 87.67         | 73.71           | 13.96          | 15.92        | 2.681                |

Table 2: Core samples dimensions, weight, volumes, and porosity

#### 4.1.3. Hardness measurements

Each of the rock core samples hardness was measured using the non-destructive AutoScan scanner shown in Figure 22 & Figure 23. The hardness measurements were taken from the top and bottom of each sample.

The rock hardness is measured at the core faces using the impulse hammer technique. On each of the faces twelve measurements points are taken. These measurements represent the surface property of the rock.



Figure 22: Hardness measurements using a non-destructive AutoScan scanner

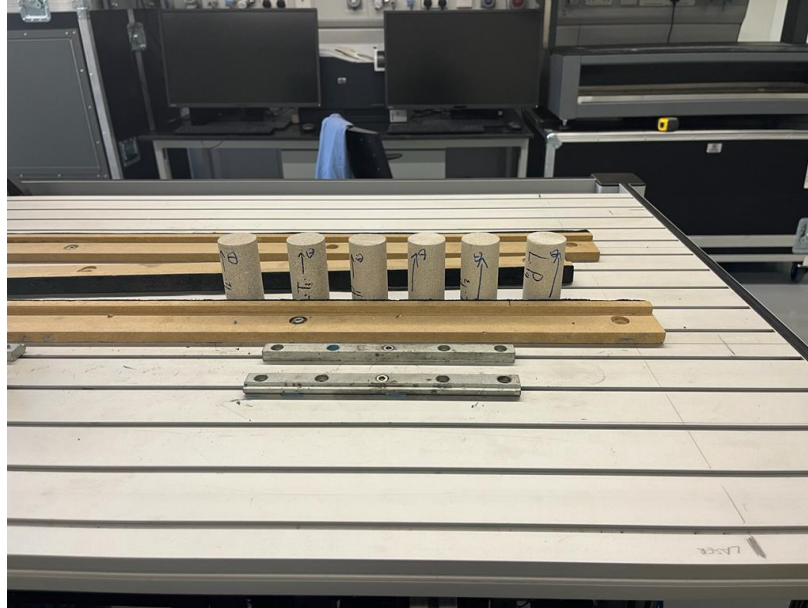


Figure 23: Measurements for core hardness

#### 4.1.4. Acoustic measurements

Acoustic measurements to each of the rock samples will be taken to measure the compressional velocity ( $V_p$ ) and shear-wave velocity ( $V_s$ ). These measurements will be taken under different confining pressures (7 MPa, 14 MPa, 21 MPa, 28 MPa). Figure 24 shows the acoustic measurements machine. Then,  $V_p$  and  $V_s$  will be converted to dynamic Young's modulus ( $E$ ), and Poisson ratio ( $\nu$ ) using the following equations.

$$G = \rho V_s^2$$

Where  $G$  is the shear-modulus and ( $\rho$ ) is the rock density,

$$\nu = \frac{V_p^2 - 2V_s^2}{2(V_p^2 - V_s^2)}$$

$$E = 2G(1 + \nu)$$



Figure 24: Acoustic measurements machine

#### 4.1.5. Medical CT-Scan

Medical CT scanning will be performed on each of the rock samples after injecting the carbonic acid to visualize the structure of the rock. A Medical CT scanner is shown in Figure 25.



Figure 25: Medical CT scanning scanner

#### 4.1.6. Cores samples clustering

The core samples were clustered based on permeability. The samples with the permeability of 1 – 4 mD were selected for the experiments. These samples will be used to study the impact of changing the values of the two parameters (Temperature, and Salinity). The different parameters values are shown in Table 3.

|                              | <b>Low</b> | <b>Mid</b> | <b>High</b> |
|------------------------------|------------|------------|-------------|
| <b>Temperature (Celsius)</b> | 35         | 60         | 85          |
| <b>Salinity (ppm)</b>        | 40,000     | 120,000    | 200,000     |

Table 3: Low, mid, and high values of the tested parameters (Temperature, & Salinity)

## 4.2. Carbonic Acid Injection

Before we started injecting the mixer of brine and CO<sub>2</sub>, the setup of the experiments was made. A draw of the setup is shown in Figure 26.

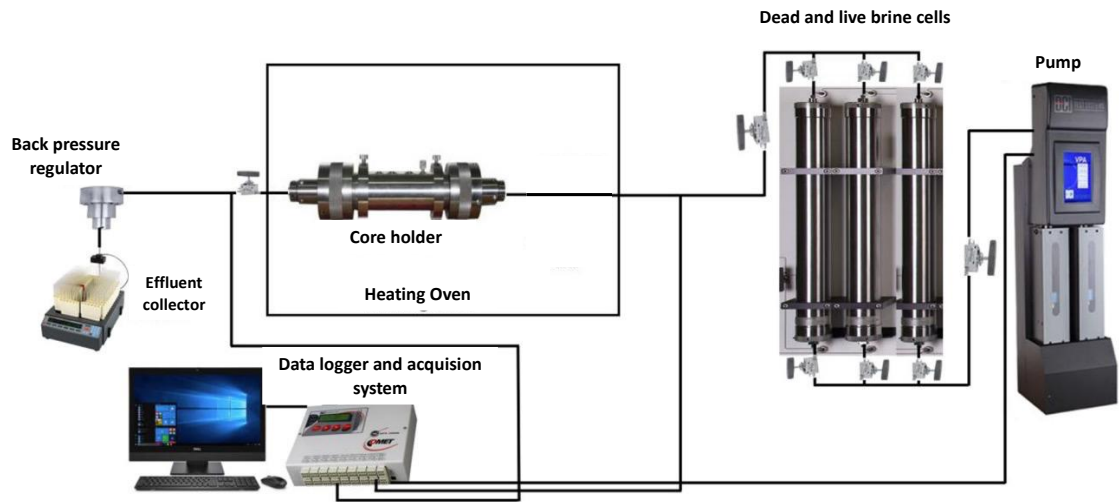


Figure 26: Carbonic acid coreflooding system

In the setup, CO<sub>2</sub> and brine were mixed in the cell at pressure of 1200 psi. The ratio of the mixer was 70% brine and 30% CO<sub>2</sub>. After that, the cell was placed in the oven to reach the desired temperature. The injection started when the cell pressure reaches 2000 psi. The cell was attached to a pump which is responsible for pumping the mixer through the setup lines to the core holder where the core sample is placed. The pump was operated at a constant rate of 1 milliliter per minute. The core holder was under a confining pressure of 2500 psi during the entire experiment. The core holder had a sleeve inside it that surrounds the core sample under the confining pressure. In addition to the sleeve, the core sample was placed in a shrinking tube that prevented the flow from passing over the core sample and as a result forced the flow to pass through the

core sample. The back of the core holder was connected to a back pressure regulator which allowed the flow when it reached a pressure of 2000 psi or higher. The pressures before and after the core holder were recorded using the data logger and acquisition system. All the experiments were stopped after all the live brine was injected. Within the setup, we added a line that was connected to a cylinder that had a brine to be used to measure the permeability of the core sample before and after the experiment. Actual photos of the setup can be seen in Figures 27, Figures 28, and Figures 29.



Figure 27: The core holder attached to the live brine accumulator inside the oven.

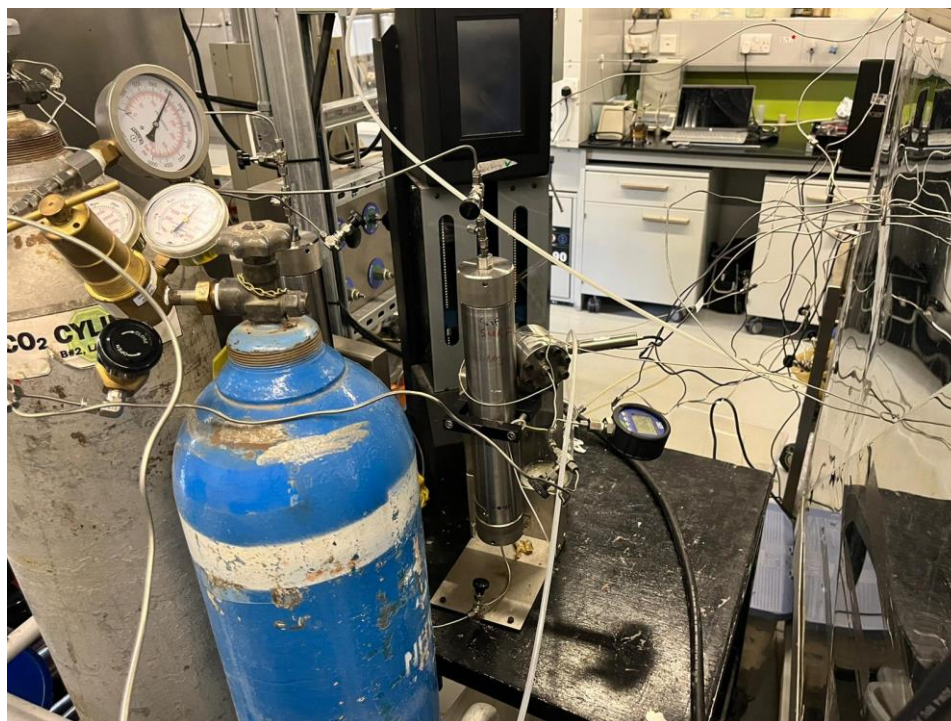


Figure 28: Back pressure regulator

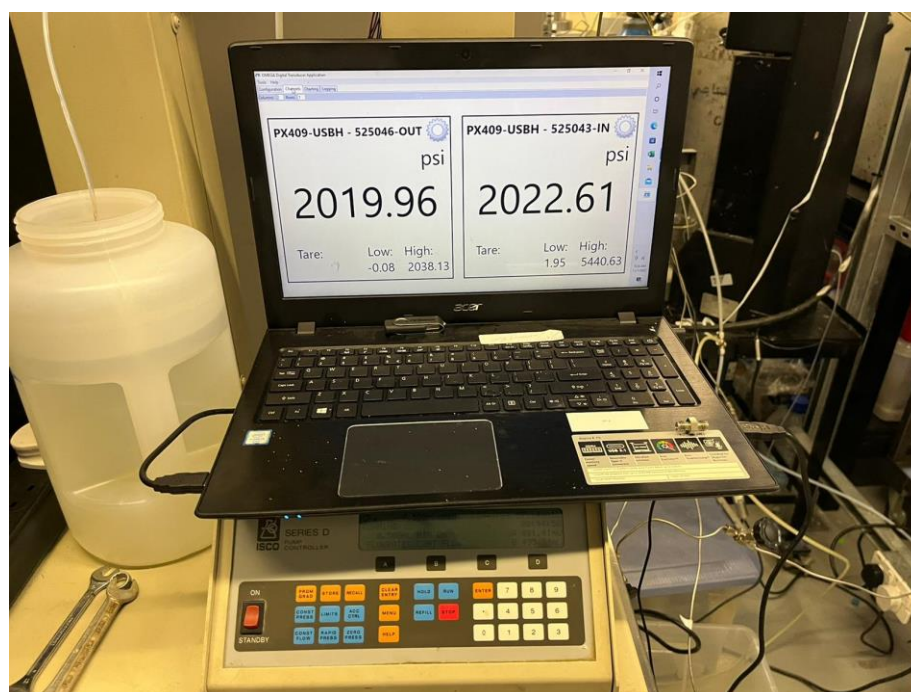


Figure 29: Data logger and acquisition system

The chemical composition of the synthetic formation brine used in this research is provided in Table 4. These compositions were converted to weight. The conversion of the composition of the brine to weight is shown in Table 5.

| <b>Ions</b>                       | <b>FW (ppm)</b> |
|-----------------------------------|-----------------|
| Na <sup>+</sup>                   | 59,491          |
| Ca <sup>2+</sup>                  | 19,040          |
| Mg <sup>2+</sup>                  | 2,439           |
| SO <sub>4</sub> <sup>2-</sup>     | 350             |
| Cl <sup>-</sup>                   | 132,060         |
| HCO <sub>3</sub> <sup>-</sup>     | 354             |
| <b>Total Dissolved Salt (TDS)</b> | <b>213,734</b>  |

Table 4: The chemical composition of the synthetic formation brine

| <b>Salt</b>                     | <b>Weight (g/L)</b> |
|---------------------------------|---------------------|
| NaHCO <sub>3</sub>              | 0.485               |
| Na <sub>2</sub> SO <sub>4</sub> | 0.51                |
| NaCl                            | 150.34              |
| MgCl <sub>2</sub>               | 9.55                |
| CaCl <sub>2</sub>               | 52.72               |

Table 5: The weight of the brine chemical composition

### **4.3. Rock Measurements & Analyzation**

After injecting all the volume of the live brine and the creation of a wormhole, the core samples were cleaned using methanol. The measurements that were performed on the core sample prior to the live brine injection were repeated to all the core samples for comparison and analysis.

## **CHAPTER 5**

### **RESULTS AND DISCUSSION**

The goals of this research are to study the impact of temperature and salinity on wormholes generation and to study the impact of temperature and salinity on the rock mechanical and petrophysical properties due to CO<sub>2</sub> sequestration. This was achieved by performing live brine flooding to limestone core samples that have similar permeabilities.

The flooding was performed to the core samples under different temperature values and different salinity values as shown in Table 6. To study the impact of temperature and salinity, the core samples porosity, permeability, Young's modulus, Poisson's ratio, and hardness were measured before and after the flooding. In addition, the generated wormholes were medical CT scanned to study the shape of the generated wormhole.

The results will be discussed in two sections. The first section will discuss the salinity impact on the limestone petrophysical and mechanical properties after generating the wormholes. The second section will discuss the temperature impact on the limestone petrophysical and mechanical properties after generating the wormholes.

| Sample | Temperature | Pore Pressure | Salinity           | Velocity |
|--------|-------------|---------------|--------------------|----------|
| IL-1   | 85°C        | 2000 PSI      | 120,000 ppm        | 1 cc/min |
| IL-2   | 60°C        | 2000 PSI      | <b>120,000 ppm</b> | 1 cc/min |
| IL-3   | 35°C        | 2000 PSI      | 120,000 ppm        | 1 cc/min |
| IL-4   | 60°C        | 2000 PSI      | <b>40,000 ppm</b>  | 1 cc/min |
| IL-5   | 60°C        | 2000 PSI      | <b>200,000 ppm</b> | 1 cc/min |

Table 6: Different experiments conditions (Salinities and Temperatures)

## 5.1. Salinity Impact

To study the impact of salinity on the rock petrophysical and mechanical properties, three limestone core samples with permeability values between 1 – 4 mD were selected. All core samples dimensions are 1.5 inch in diameter and 3 inches long. The pore volume of each sample was measured, and permeability measurements were performed using dead brine before the flooding.

For all the samples, 700 ml of the brine was mixed with CO<sub>2</sub> to make the live brine. After that, the mixer was injected at a rate of 1 ml/min. The curve of the pressure difference between the cores inlet and outlet was plotted Vs. the pore volume at different salinities is shown in Figure 30.

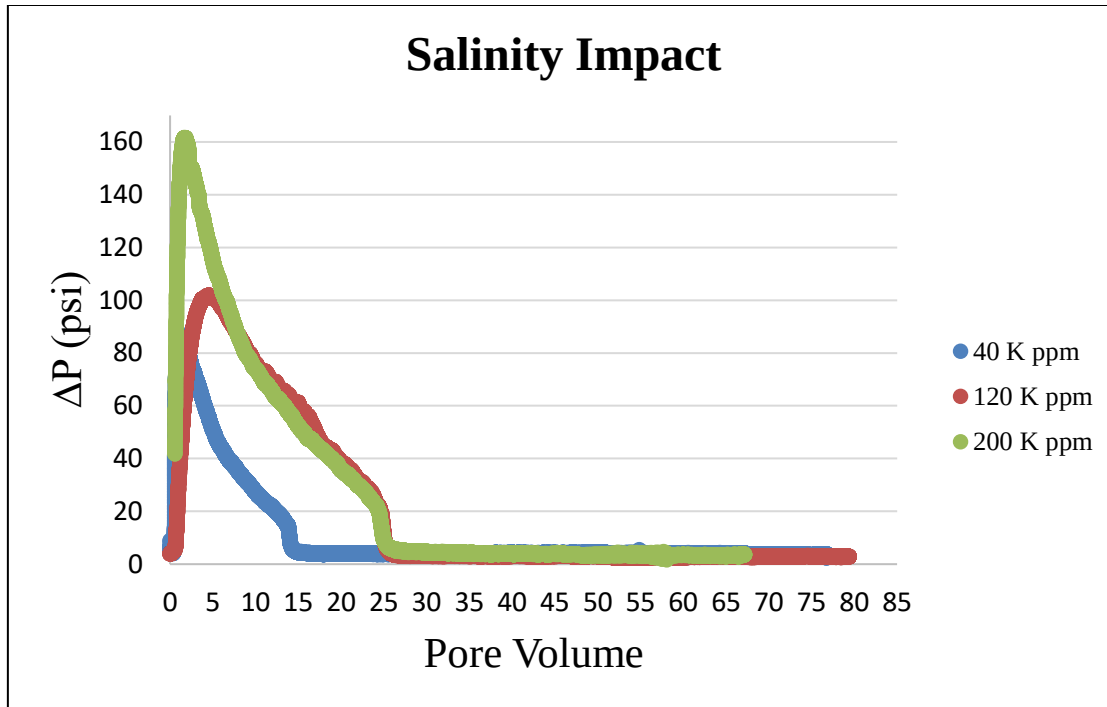


Figure 30: Cores pressure difference Vs. Pore volume

In Figure 30, the indication to creating the wormhole is when the pressure difference suddenly drops to almost zero. From the curves, we can see that the case of the 40,000-ppm live brine required less volume to generate the wormhole than the 120,000-ppm live brine case. Also, the 120,000-ppm live brine case required less volume to generate the wormhole than the 200,000 ppm case.

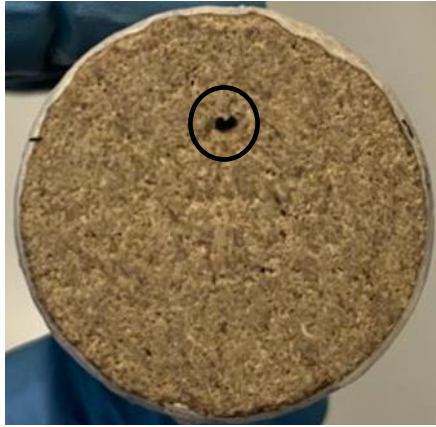
The PVBT is the live brine volume required to generate a wormhole divided by the core sample pore volume. The PVBT for the 120,000 ppm case and the 200,000 ppm case are similar because the pore volume of the 120,000 ppm rock sample is smaller than the 200,000 ppm rock sample pore volume.

This means that the time required to generate the wormhole decreases as the salinity of the solution decreases. The time and volume (PVBT) of live brine required to generate the wormholes for each of the cases can be seen in Table 7.

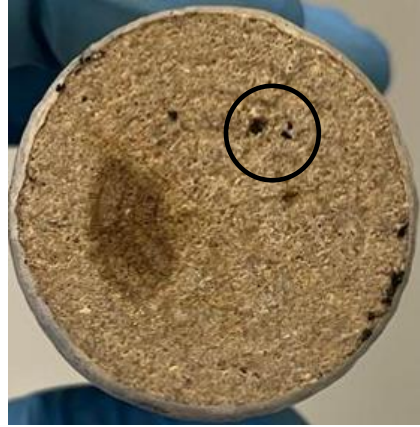
As the salinity of the brine decreases, the solubility of CO<sub>2</sub> in water increases. As a result, the live brine becomes more acidic which will increase the reaction between the live brine and the rock. Because of that we see faster time to breakthrough and as a result less volume to breakthrough as the salinity decreases. Also, Figure 31 shows the inlet and the outlet of each of the cores after the flooding. The radius of the wormholes increases as the salinity of the brine decreases. After generating the wormhole, the rest of the injected live brine will react with the wormhole wall which results in increasing the wormhole thickness and increasing the wormhole volumes. The wormhole volumes of the 40,000 ppm case, 120,000 ppm case, and 200,000 ppm case are 603 mm<sup>3</sup>, 506 mm<sup>3</sup>, and 273 mm<sup>3</sup> respectively. This can also be seen from the medical CT scan of the core samples in Figure 36 after the wormholes were generated.

| <b>Name</b> | <b>Salinity (ppm)</b> | <b>Time to Breakthrough (hours)</b> | <b>PVBT</b> |
|-------------|-----------------------|-------------------------------------|-------------|
| IL-4        | 40,000                | 3.2                                 | 14.3        |
| IL-2        | 120,000               | 5.2                                 | 24.8        |
| IL-5        | 200,000               | 5.9                                 | 25.6        |

Table 7: Generated wormholes time & PVBT for different salinities



40K ppm Inlet



40K ppm Outlet



120K ppm Inlet



120K ppm Outlet



40K ppm Inlet



40K ppm Outlet

Figure 31: Cores samples inlet and outlet of wormholes for different salinities

### 5.1.1. Impact of Salinity on Porosity

Table 8 shows the porosity of the samples before and after generating the wormholes and the change in porosity for different salinities.

| <b>Name</b> | <b>Salinity (ppm)</b> | <b>Before (%)</b> | <b>After (%)</b> | <b>average relative increase</b> |
|-------------|-----------------------|-------------------|------------------|----------------------------------|
| IL-4        | 40,000                | 15.46%            | 16.92%           | 9.4%                             |
| IL-2        | 120,000               | 14.49%            | 15.18%           | 4.8%                             |
| IL-5        | 200,000               | 15.92%            | 16.09%           | 1.1%                             |

Table 8: Change in porosity after the wormholes generation

All samples' porosities increased after generating the wormhole. The change in porosity increases as the salinity of the brine decreases. Figure 32 shows the trend of the porosity change for all the samples. The relationship between the change porosity and salinity is linear.

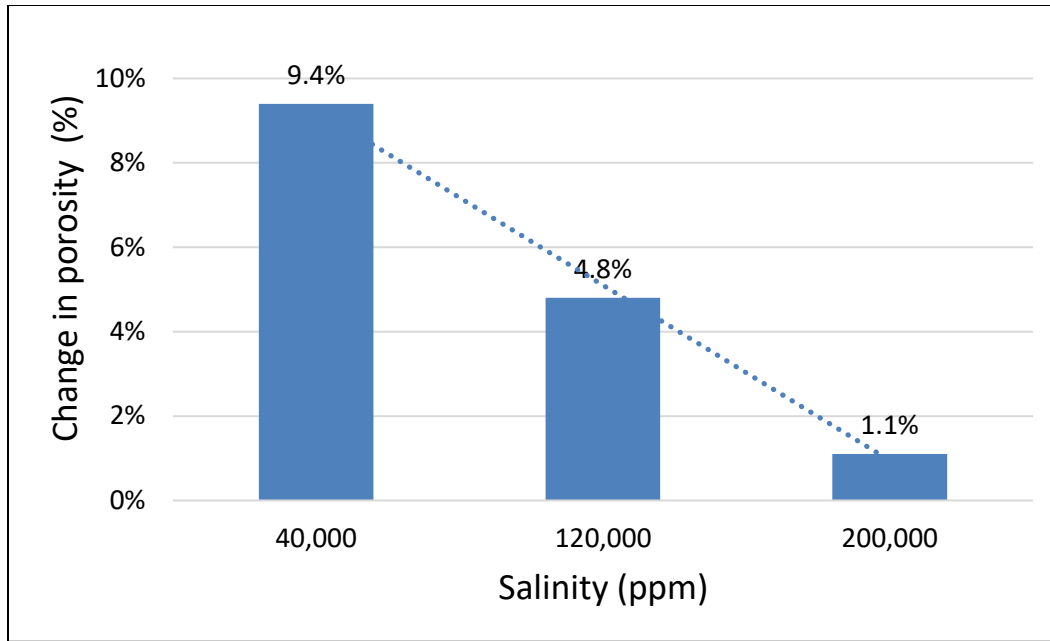


Figure 32: The linear relationship between the change porosity and salinity

In Figure 33, the amount of the live brine and wet CO<sub>2</sub> injected after breakthrough was calculated and plotted with the change in porosity for each salinity. The change in porosity has a strong relation with the amount of live brine injected after breakthrough. As the volume of live brine injected after breakthrough increases, the change in porosity increases. This is due to the reaction between the live brine and the wormhole wall after breakthrough. This explains the importance of the time required to breakthrough and as a result the condition at which the live brine is injected. During CO<sub>2</sub> sequestration, a specific volume of the gas must be stored regardless of whether the wormhole was generated or not. After generating wormholes, the injection of CO<sub>2</sub> will continue, and the time required to generate these wormholes will be a big factor in determining the amount of increase in the rock porosity. The wormholes volumes for

different salinity are shown in Table 9. As the salinity decreases the wormholes volume increases.

Also, the impact of the wormhole volume is obvious in changing the porosity. Figure 34 shows the strong relation between the wormhole volume and the change in the rock porosity.

| Sample Name | Salinity (ppm) | Wormhole Volume (mL) |
|-------------|----------------|----------------------|
| IL-4        | 40,000         | 603                  |
| IL-2        | 120,000        | 506                  |
| IL-5        | 200,000        | 273                  |

Table 9: Wormholes volume for different salinity values

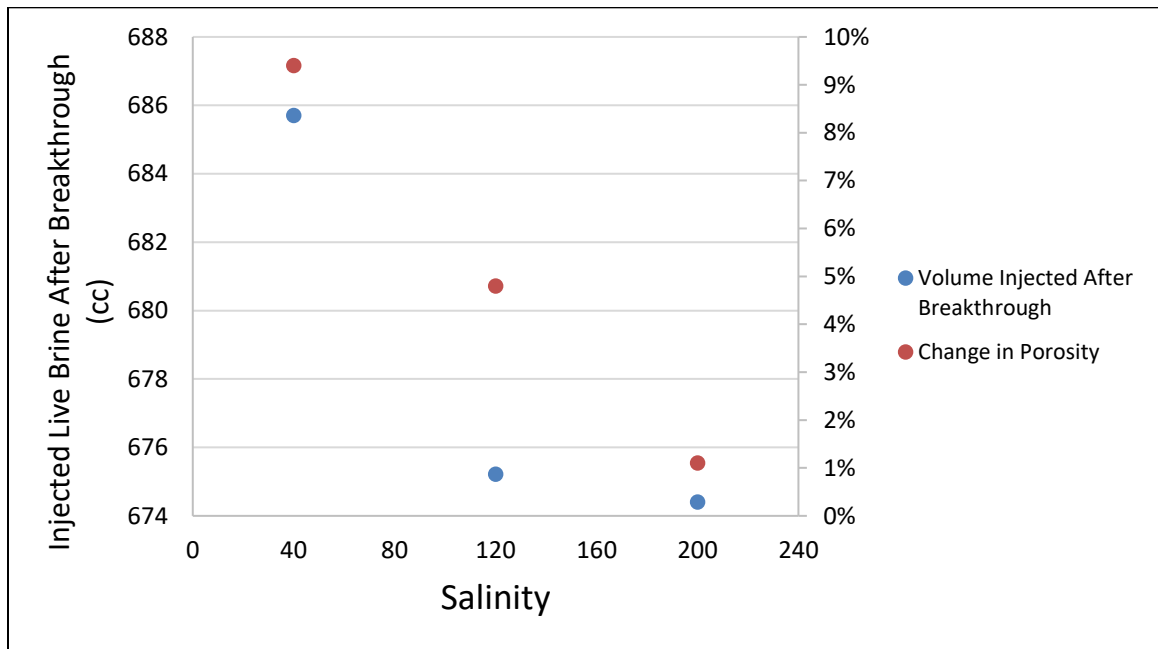


Figure 33: Injected live brine after breakthrough & change in porosity relationship

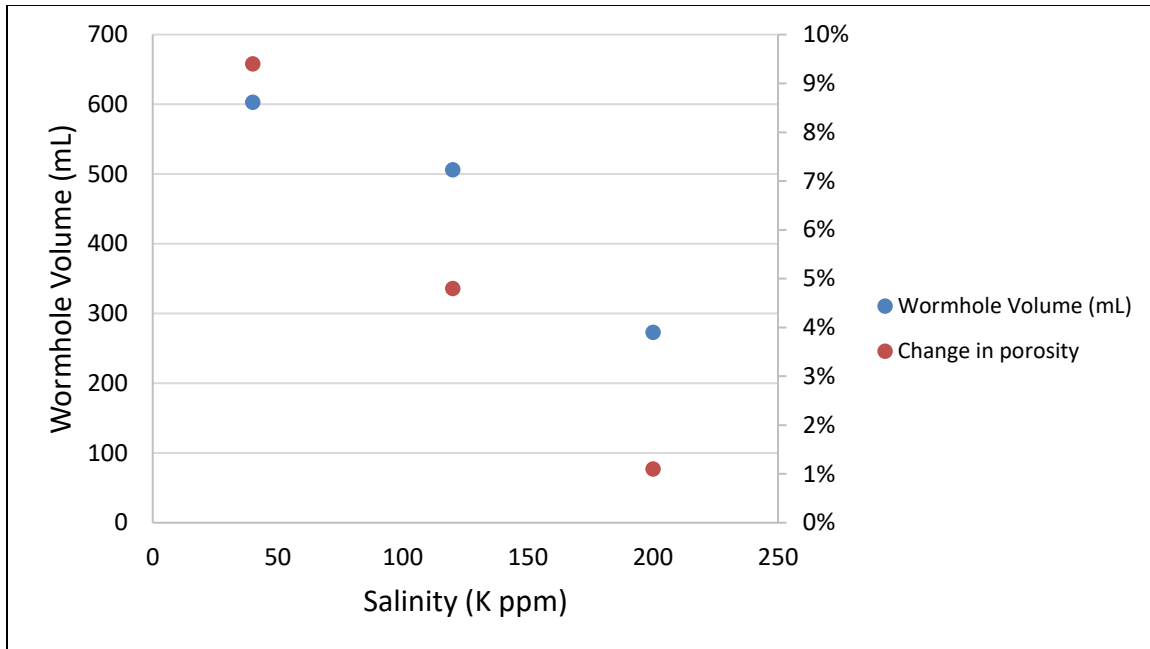


Figure 34: Relationship between the wormhole volume and the change in porosity

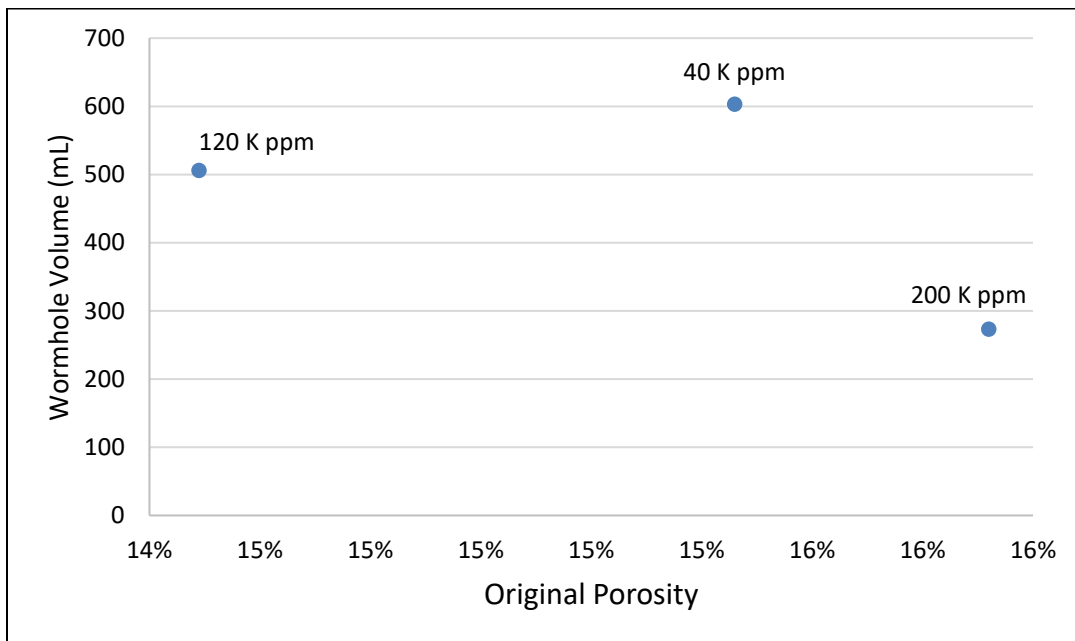


Figure 35: Relationship of wormhole volume & original porosity at different salinities

Figure 35 shows the relationship between the core's original porosity and the wormhole volume for different salinities. We can see that there is no clear relationship between wormhole volume and the original porosity. On the other hand, the wormhole volume is mainly affected by the salinity of the live brine. As the salinity decreases, the wormhole volume increases. This shows that the salinity of the live brine is the dominant factor that impacts the wormhole volume regardless of the porosity value.

By generating the wormholes through the cores, the values of the permeability increased from (1 – 4 mD) to Darcy values. The medical CT scan of all the cores is shown in Figure 36. The size of the wormholes increases as the salinity decreases.

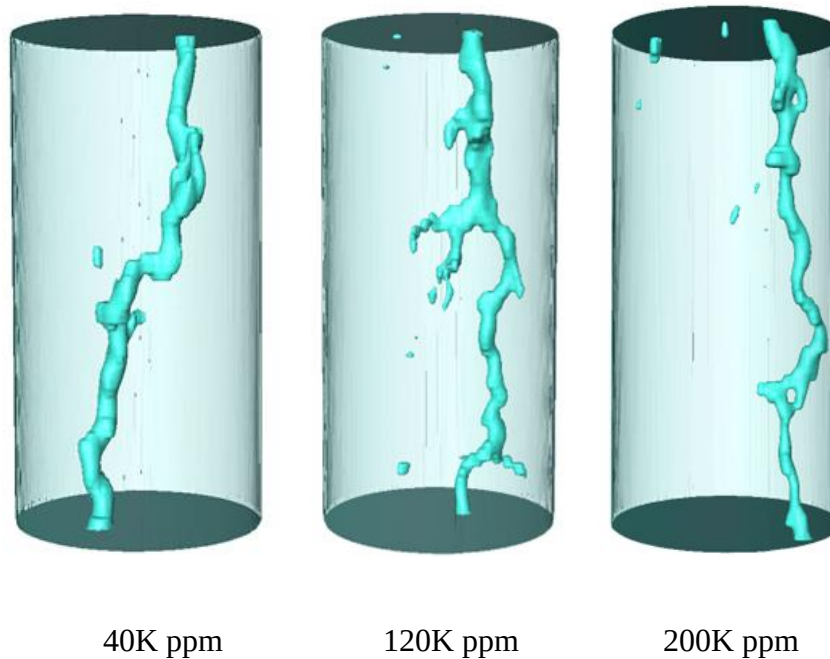


Figure 36: Medical CT scan of the wormholes at different salinities

### 5.1.2. Impact of Salinity on Young's Modulus and Poisson's Ratio

The dynamic Young's modulus was measured for all the samples before and after the flooding under the different confining pressures (7 MPa, 14 MPa, 21 MPa, 28 MPa) as shown in Figure 37, Figure 38, and Figure 39. For all the samples, the Young's modulus decreased after injecting the live brine. The reduction in the Young's modulus was calculated for further analysis.

In all cases, the Young's modulus increases as the confining pressure increases. As the confining pressure increase, the compression on the core sample increases and as a result the pore space becomes smaller. This will result in a reduction in the rock porosity. The stress is not applied at the pore's positions but at the solid portion of the rock. So, as the porosity decreases because of the confining pressure the Young's modulus increases ([Ridengaoqier, and Hatanaka, 2021](#)).

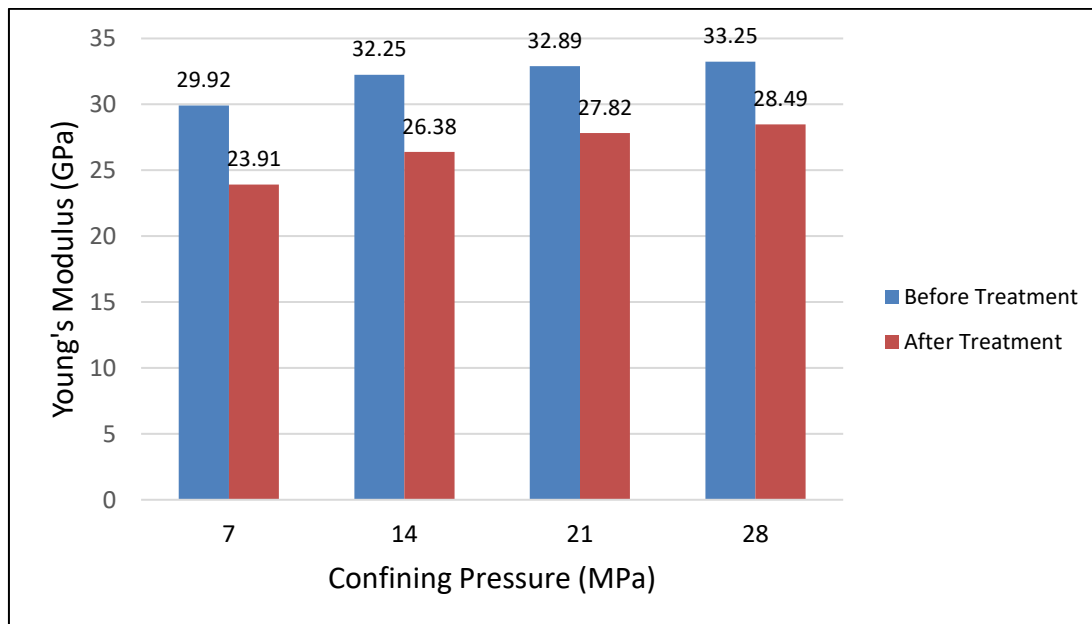


Figure 37: The reduction in dynamic Young's modulus for (40,000 ppm) case

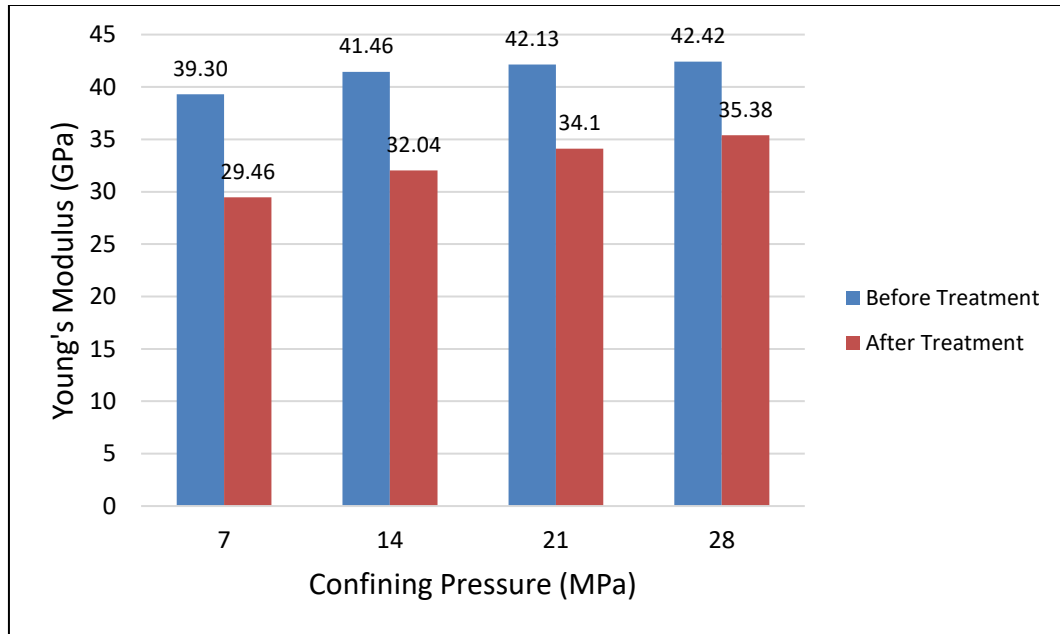


Figure 38: The reduction in dynamic Young's modulus for (120,000 ppm) case

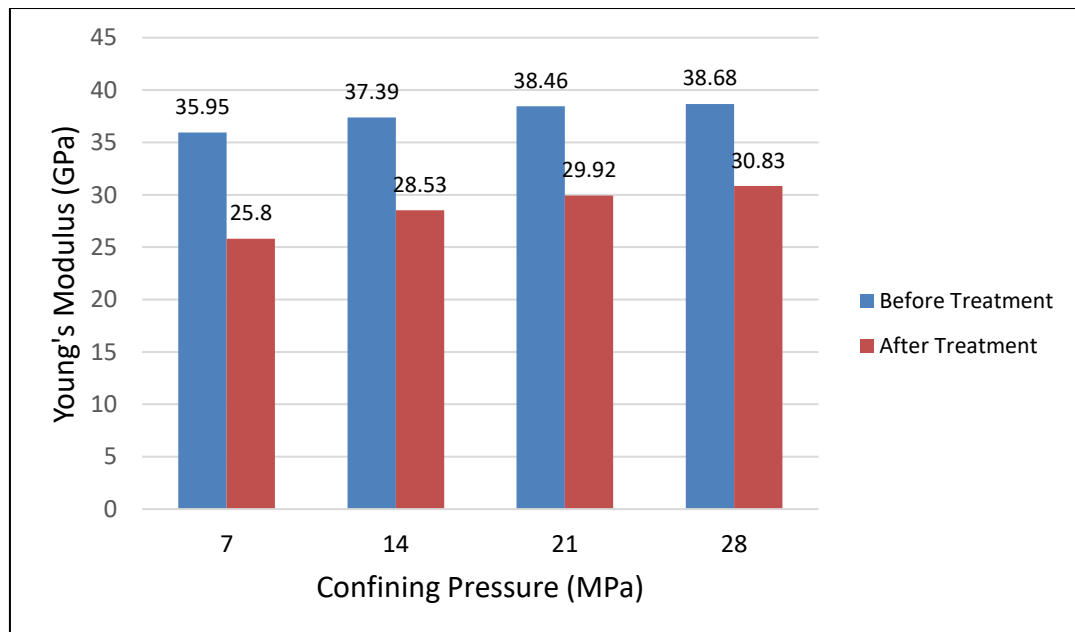


Figure 39: The reduction in dynamic Young's modulus for (200,000 ppm) case

As a result of generating the wormholes and opposite to the reduction in the Young's modulus, the Poisson's ratio increased for all the core samples as shown in Figure 40.

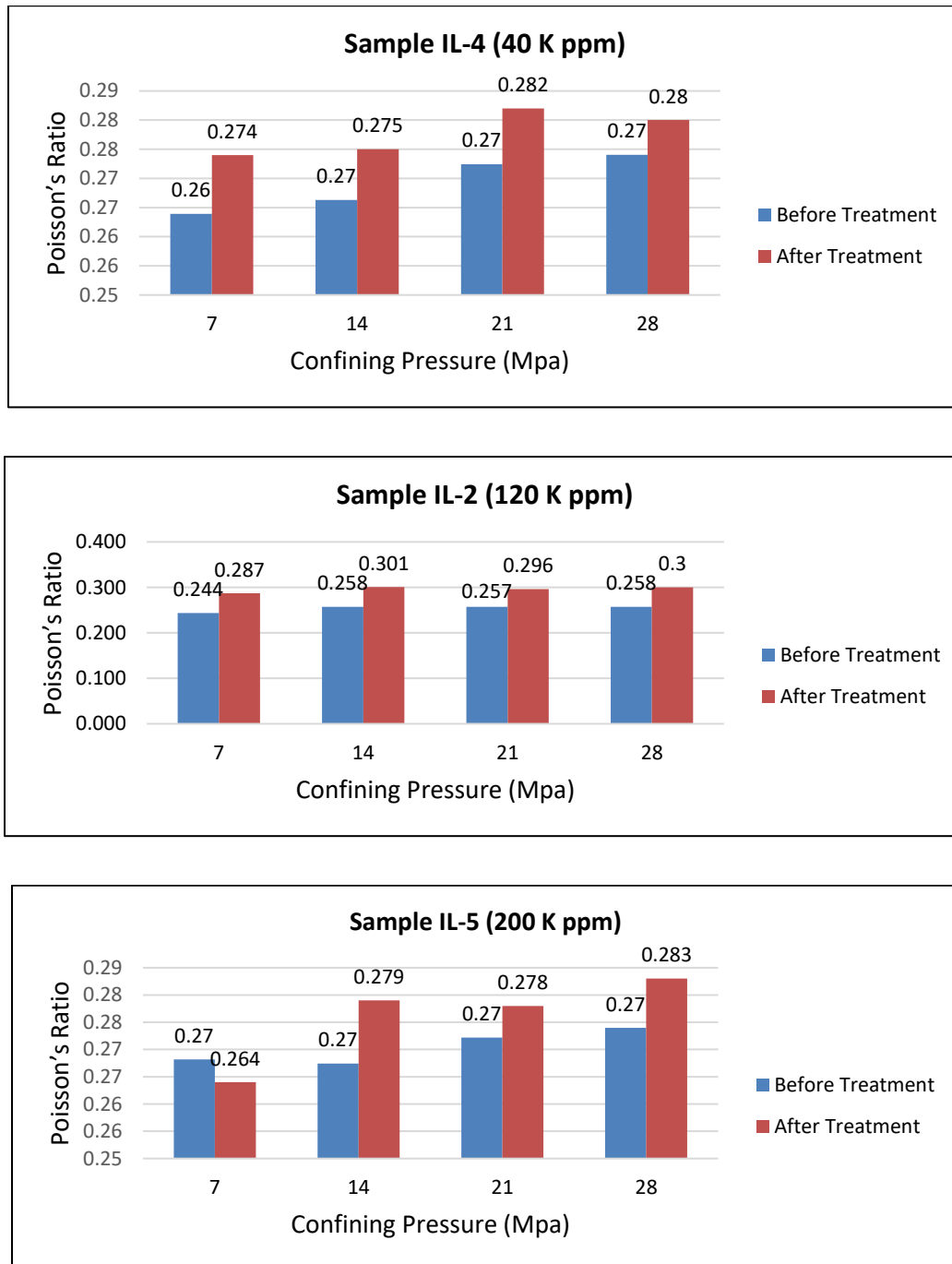


Figure 40: Increase in Poisson's ratio for different salinity values.

A comparison between the reduction in Young's modulus at different confining pressure for each of the different live brine salinity is shown in Figure 41. The reduction in the Young's modulus increases as the salinity increases. As the salinity increases, the live brine becomes less acidic and as a result, it will spend more time to generate the wormholes. The more time required to generate the wormhole, the more time live brine will react with the bulk of the core. As the time of the reaction between the live brine increases, the reduction in Young's modulus increases.

On the other hand, live brine with the least salinity is more acidic and will generate a wormhole faster. After generating the wormhole, the rest of the live brine will travel through the channel and will not have the chance to interact with bulk and reduce the Young's modulus as in the case of the high salinity live brine.

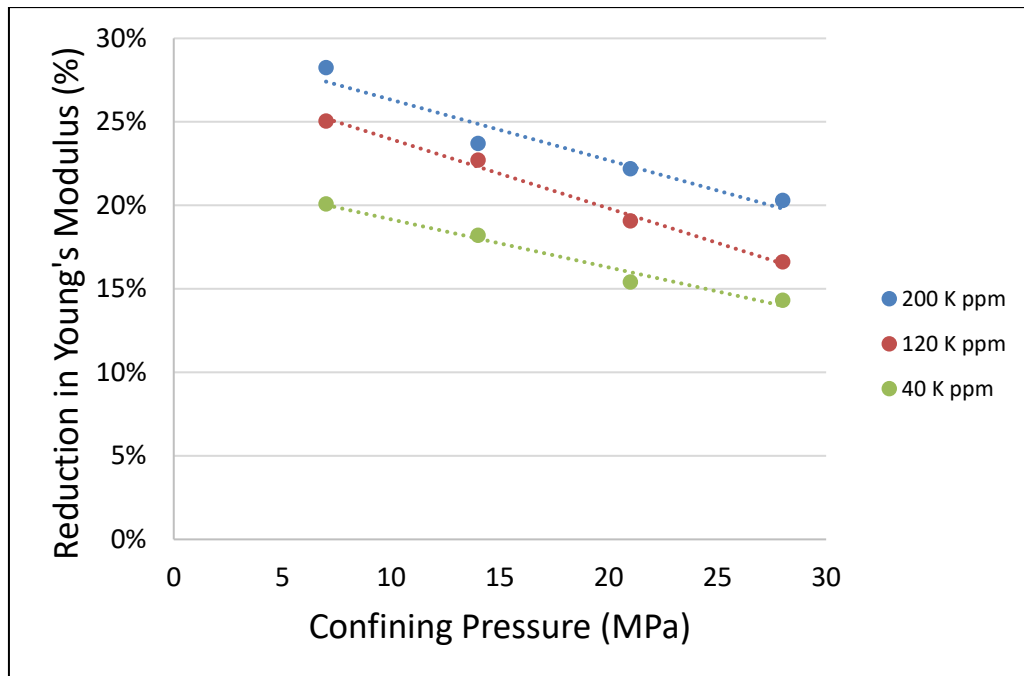


Figure 41: Reduction in Young's modulus for different live brine salinity

### 5.1.3. Impact of Salinity on the Rock Hardness

The rock hardness was measured on the surface of the core samples inlet and outlet using the auto-scan before and after the live brine injection. The core samples average hardness (Inlet and Outlet) was calculated and plotted as shown in Figure 42. The average hardness of all the samples was reduced after the live brine flooding.

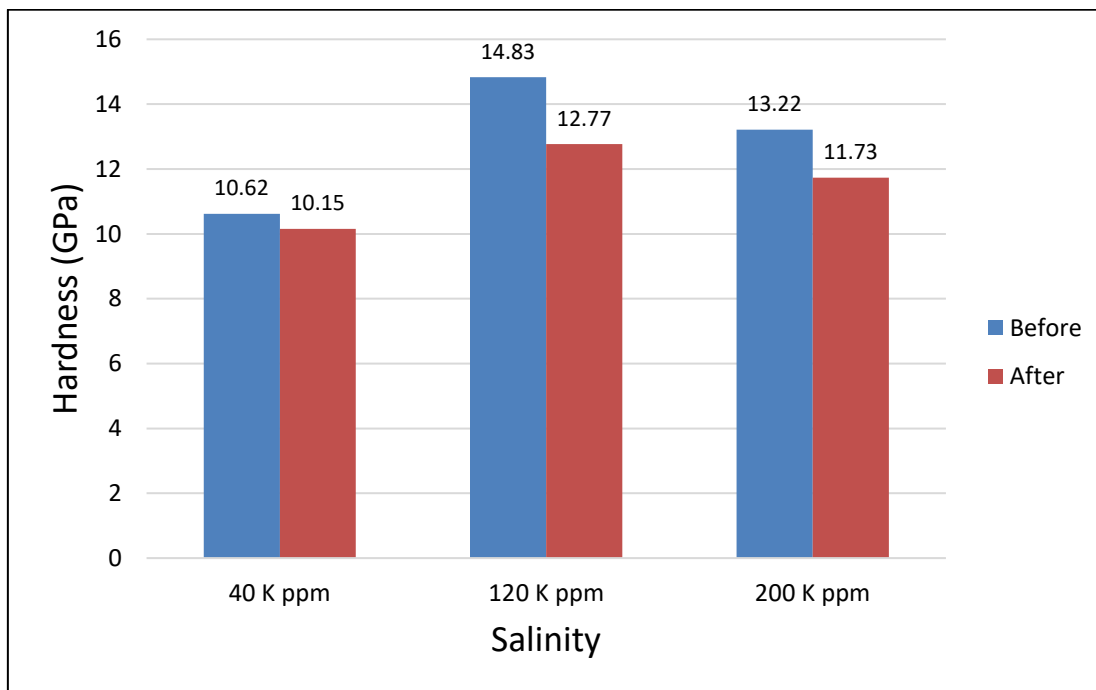


Figure 42: Rock hardness before and after live brine injection for different salinities

The reduction in the core inlet hardness was related to the salinity of the live brine. The reduction in the core samples inlet hardness increases as the salinity of the live brine decreases as shown in Figure 43. The rock hardness is a surface property of the rock. As the salinity decreases, the live brine becomes more acidic. Live brine with different salinities will interact with the core inlet for similar time. In this case, the biggest factor that impacts the reduction in the rock hardness is the acidity of the live brine.

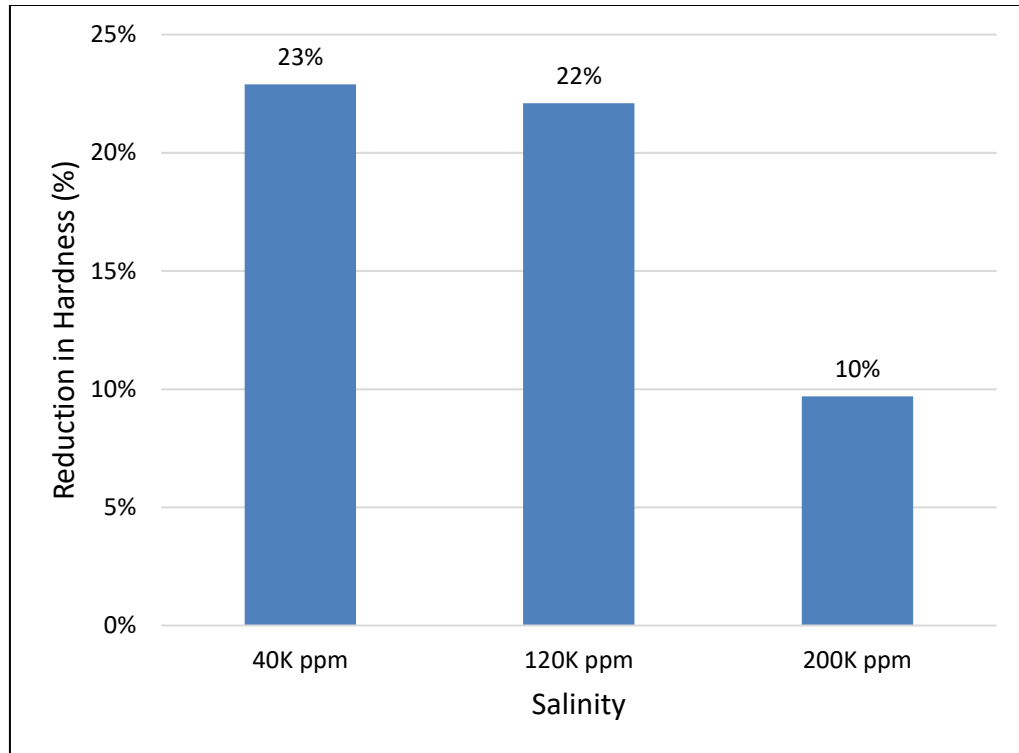


Figure 43: Reduction in core inlet hardness for different salinities

## 5.2. Temperature Impact

To study the impact of temperature on the rock petrophysical and mechanical properties, three limestone core samples with permeability values between 1 – 4 mD were selected. All core samples dimensions are 1.5 inch in diameter and 3 inches long. The pore volume of each sample was measured, and permeability measurements were performed using dead brine before the flooding.

For all the samples, 700 ml of the brine was mixed with CO<sub>2</sub> to make the live brine which was injected at a rate of 1 ml/min. The curve of the pressure difference between the cores inlet and outlet was plotted Vs. the pore volume at different temperatures is shown in Figure 44.

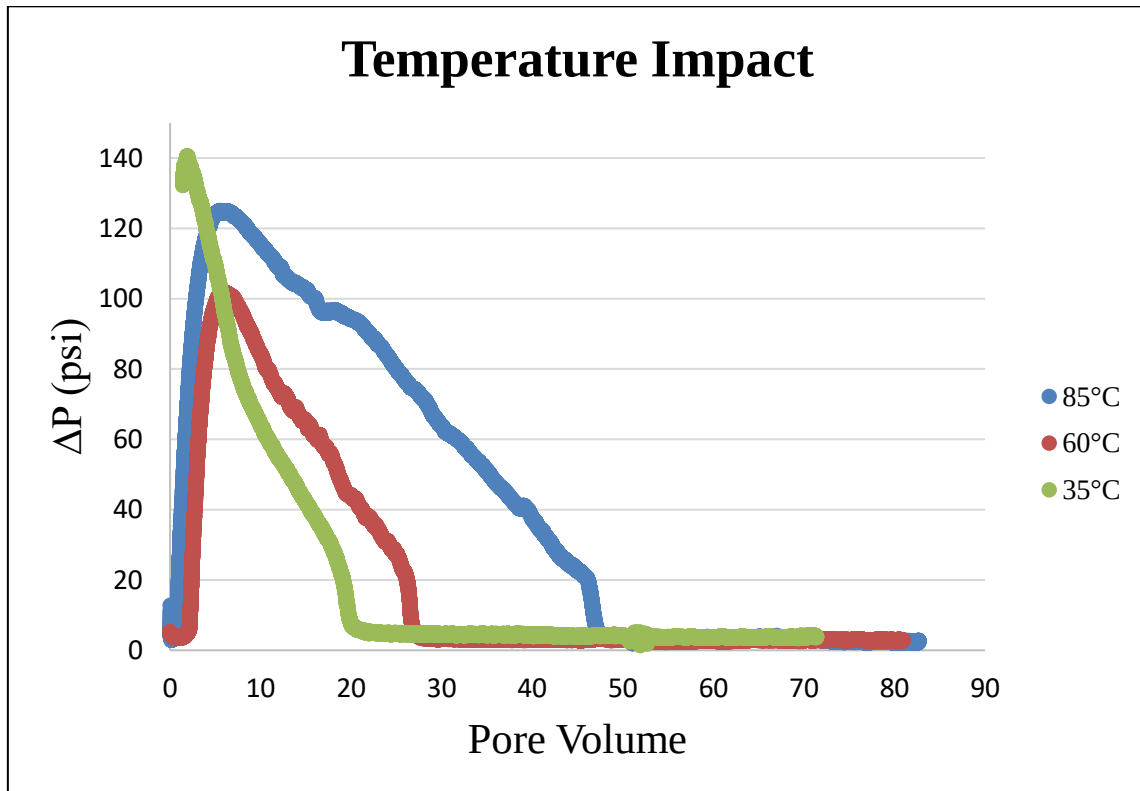


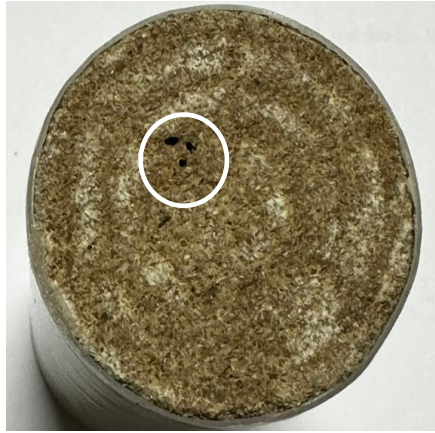
Figure 44: Cores pressure difference Vs. Pore volume

In Figure 44, the indication to creating the wormhole is when the pressure difference suddenly drops to almost zero. From the curves, we can see that the live brine at 35°C required less volume to generate the wormhole than at 60°C. Also, at 60°C it required less volume of live brine to generate the wormhole than at 85°C. This means that the time required to generate the wormhole decreases as the temperature decreases. The time and volume (PVBT) of live brine required to generate the wormholes for each of the cases can be seen in Table 10.

As the temperature decreases, the solubility of CO<sub>2</sub> in water increases. As a result, the live brine becomes more acidic which will increase the reaction between the live brine and the rock. Because of that we see faster time to breakthrough and as a result less volume to breakthrough as the temperature decreases. Also, Figure 45 shows the inlet and the outlet of each of the cores after the flooding. Also, Figure 50 shows the medical CT scan of the wormholes. As the temperature increases the wormholes become more branched.

| <b>Name</b> | <b>Temperature<br/>(°C)</b> | <b>Time to Breakthrough<br/>(hours)</b> | <b>PVBT</b> |
|-------------|-----------------------------|-----------------------------------------|-------------|
| IL-3        | 35                          | 4.6                                     | 19.7        |
| IL-2        | 60                          | 5.4                                     | 25.7        |
| IL-1        | 85                          | 10.4                                    | 46.9        |

Table 10: Generated wormholes time & PVBT for different salinities



Inlet (35°C)



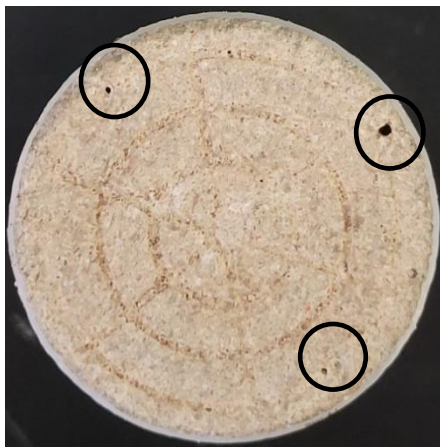
Outlet (35°C)



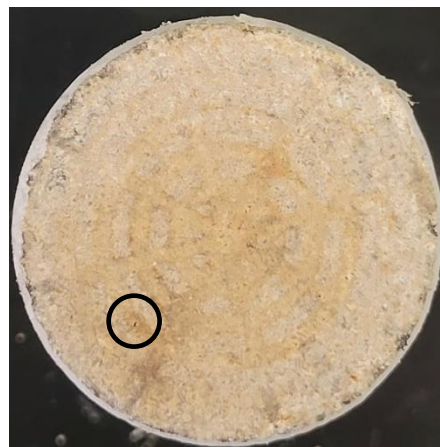
Inlet (60°C)



Outlet (60°C)



Inlet (85°C)



Outlet (85°C)

Figure 45: Cores inlet and outlet of wormholes generation for different salinities

### 5.2.1. Impact of Temperature on Porosity

Table 11 shows the porosity of the samples before and after generating the wormholes and the change in porosity at different temperatures.

| Name | Temperature (°C) | Before (%) | After (%) | average relative increase |
|------|------------------|------------|-----------|---------------------------|
| IL-3 | 35               | 16.14%     | 16.37%    | 1.4%                      |
| IL-2 | 60               | 14.49%     | 15.18%    | 4.8%                      |
| IL-1 | 85               | 15.32%     | 15.92%    | 3.9%                      |

Table 11: Change in porosity after the wormholes generation

All samples' porosities increased after generating the wormhole. However, the change in porosity did not increase as the temperature decreased. Temperature has two opposite impacts on the reaction. As the temperature decreases the solubility increases which results in more acidic solution. On the other hand, decreasing the temperature will slow the reaction kinetics according to the Arrhenius equation. Figure 46 shows the trend of the porosity change for all the samples.

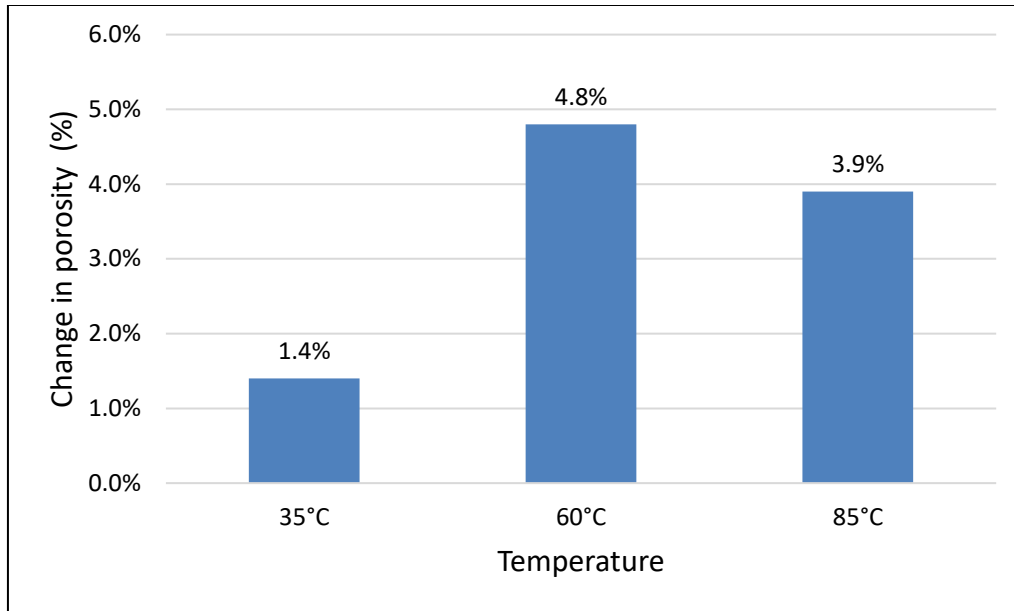


Figure 46: The relationship between the change porosity and temperature

In Figure 47, the amount of the live brine and wet  $\text{CO}_2$  after breakthrough was calculated and plotted with the change in porosity for each temperature. For the samples with temperatures of 60°C and 85°C, the change in porosity increases as the volume of live brine injected after breakthrough increases. On the other hand, the 35°C case does show a similar trend as it is affected also by the low temperature that reduces the reaction between the volume of live brine injected after breakthrough and the wall of the wormhole. The wormhole volume of 35°C case is very small compared with higher temperature wormholes volumes as shown in Table 12.

Also, the impact of the wormhole volume is obvious in changing the porosity. Figure 48 shows the strong relation between the wormhole volume and the change in the rock porosity.

| Sample Name | Temperature | Wormhole Volume |
|-------------|-------------|-----------------|
| IL-1        | 85°C        | 479             |
| IL-2        | 60°C        | 506             |
| IL-3        | 35°C        | 294             |

Table 12: Wormholes volume for different salinity values

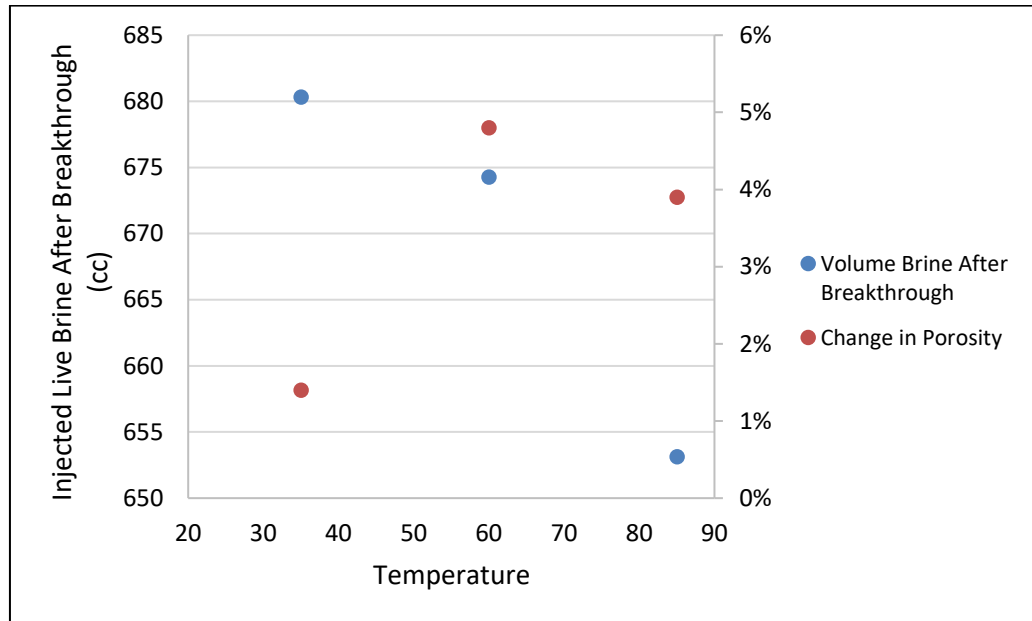


Figure 47: Injected live brine after breakthrough and change in porosity relationship.

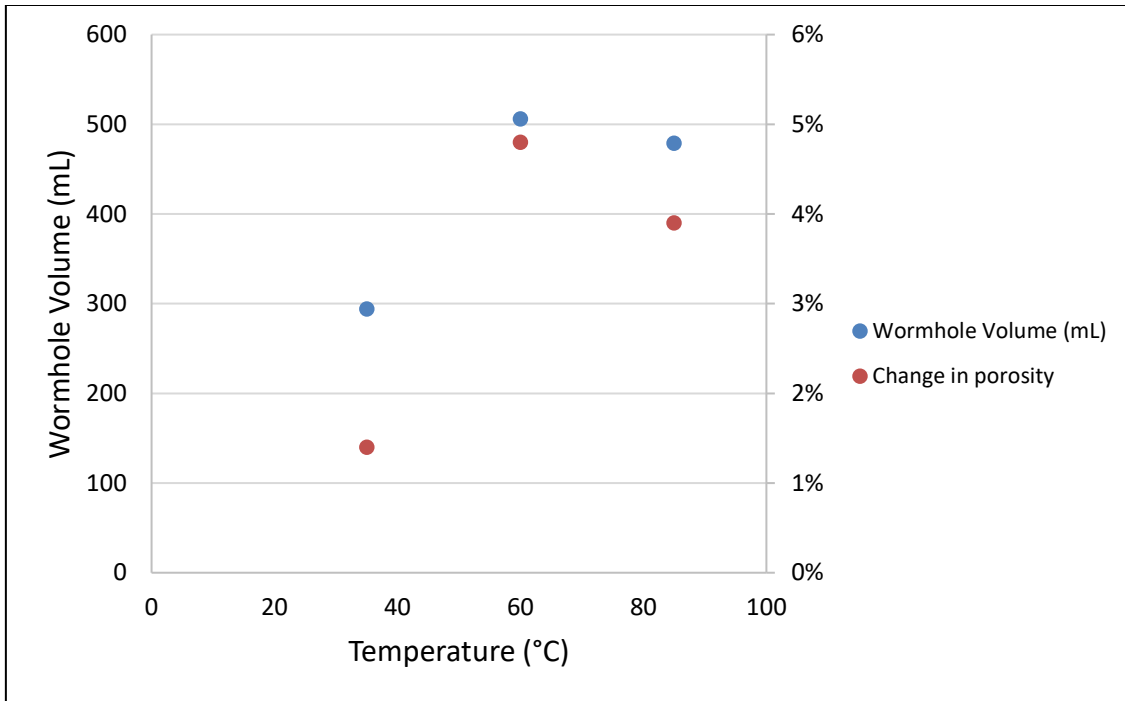


Figure 48: Relationship between the wormhole volume and the change in porosity

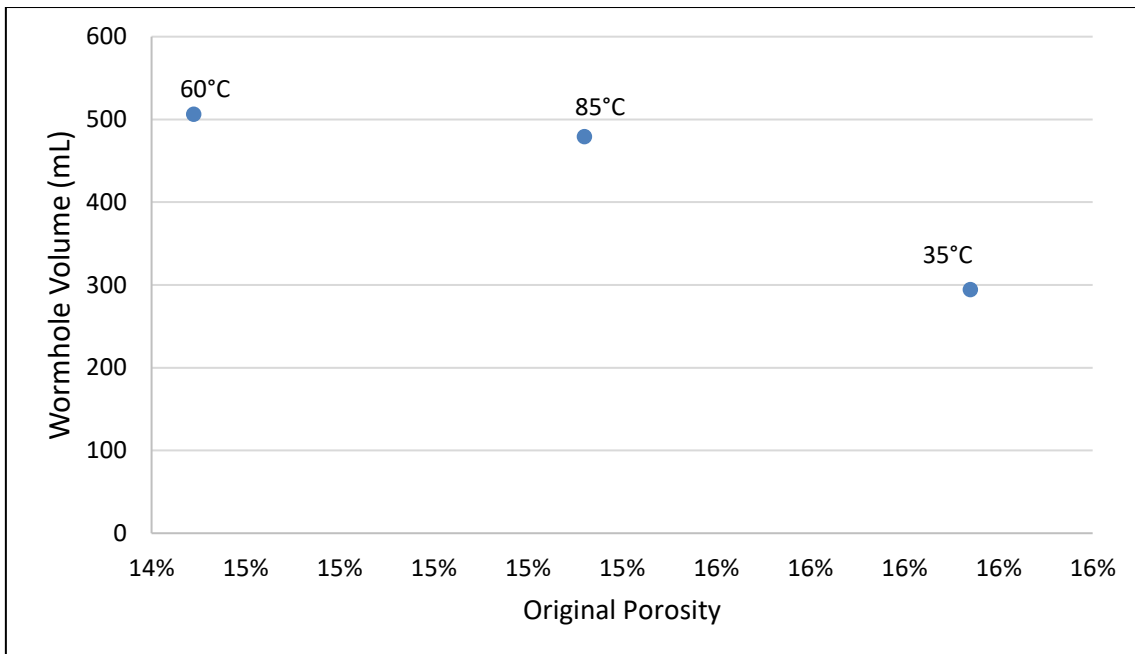


Figure 49: Wormhole volume & original porosity relation at different temperatures

Figure 49 shows the relationship between the core's original porosity and the wormhole volume at different temperatures. We can see that there is a relationship between wormhole volume and the original porosity. As the porosity decreases, the wormhole volume increases.

By generating the wormholes through the cores, the values of the permeability increased from (1 – 4 mD) to Darcy values. The wormholes become more branched as the temperature increases. The CT scan of all the cores is shown in Figure 50.

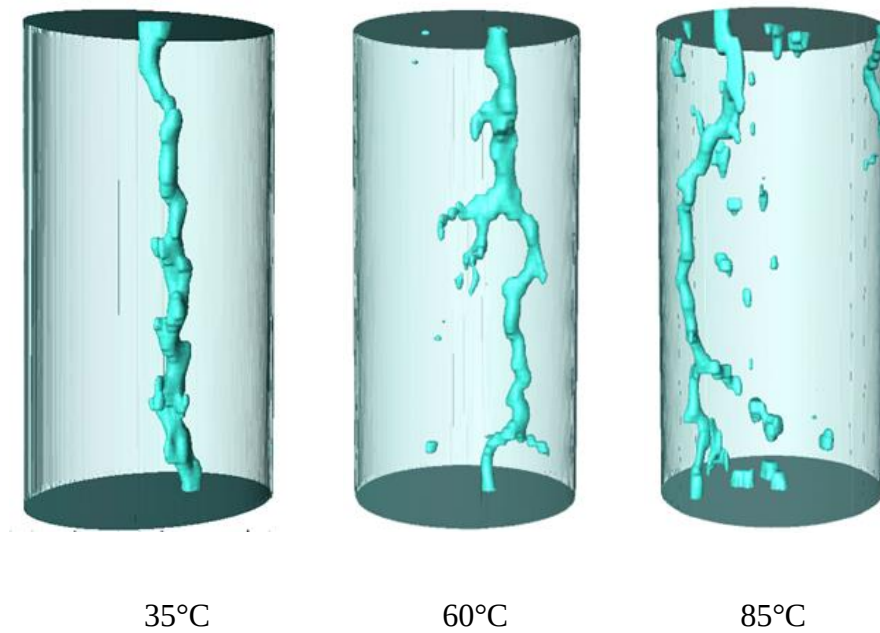


Figure 50: Medical CT scan of the wormholes at different temperatures

### 5.2.2. Impact of Temperature on Young's Modulus and Poisson's Ratio

The dynamic Young's modulus was measured for all the samples before and after the live brine injection under the different confining pressures as shown in Figure 51, Figure 52, Figure 53. For all the samples, the Young's modulus decreased after injecting the live brine. The reduction in the Young's modulus was calculated for further analysis.

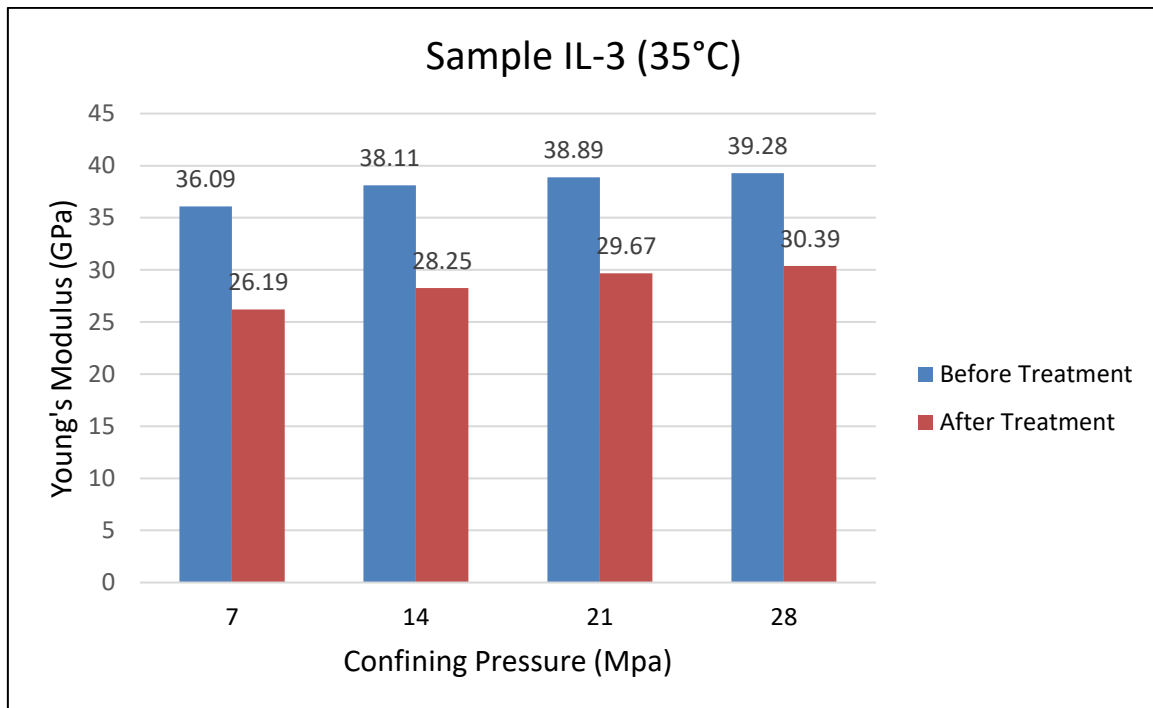


Figure 51: The reduction in dynamic Young's modulus for (35°C) case

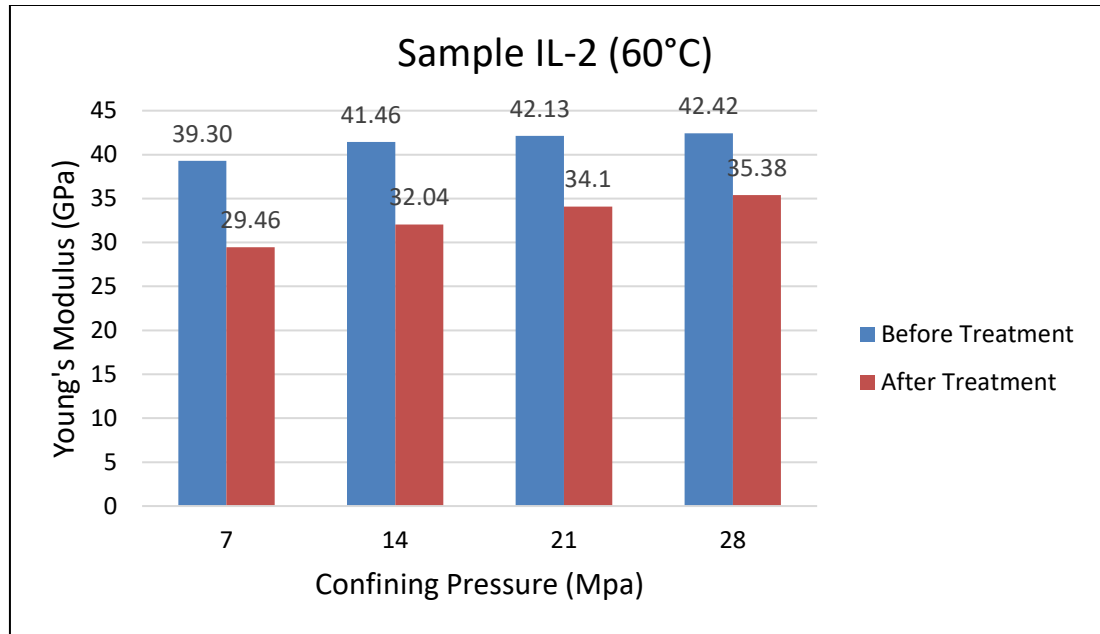


Figure 52: The reduction in dynamic Young's modulus for (60°C) case

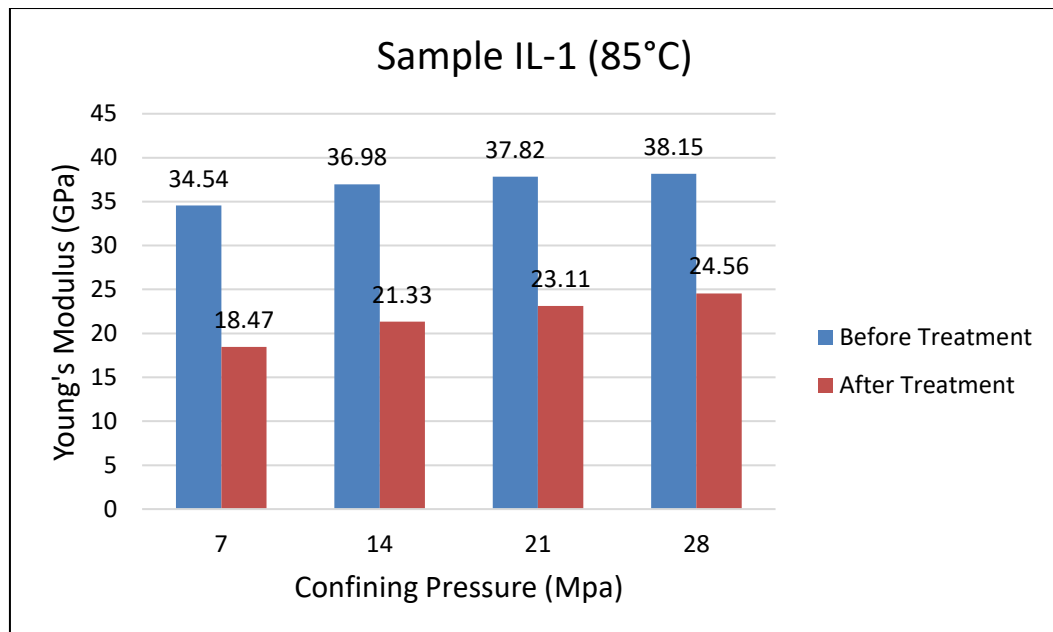


Figure 53: The reduction in dynamic Young's modulus for (85°C) case

As a result of generating the wormholes and opposite to the reduction in the Young's modulus, the Poisson's ratio increased as shown in Figure 54.

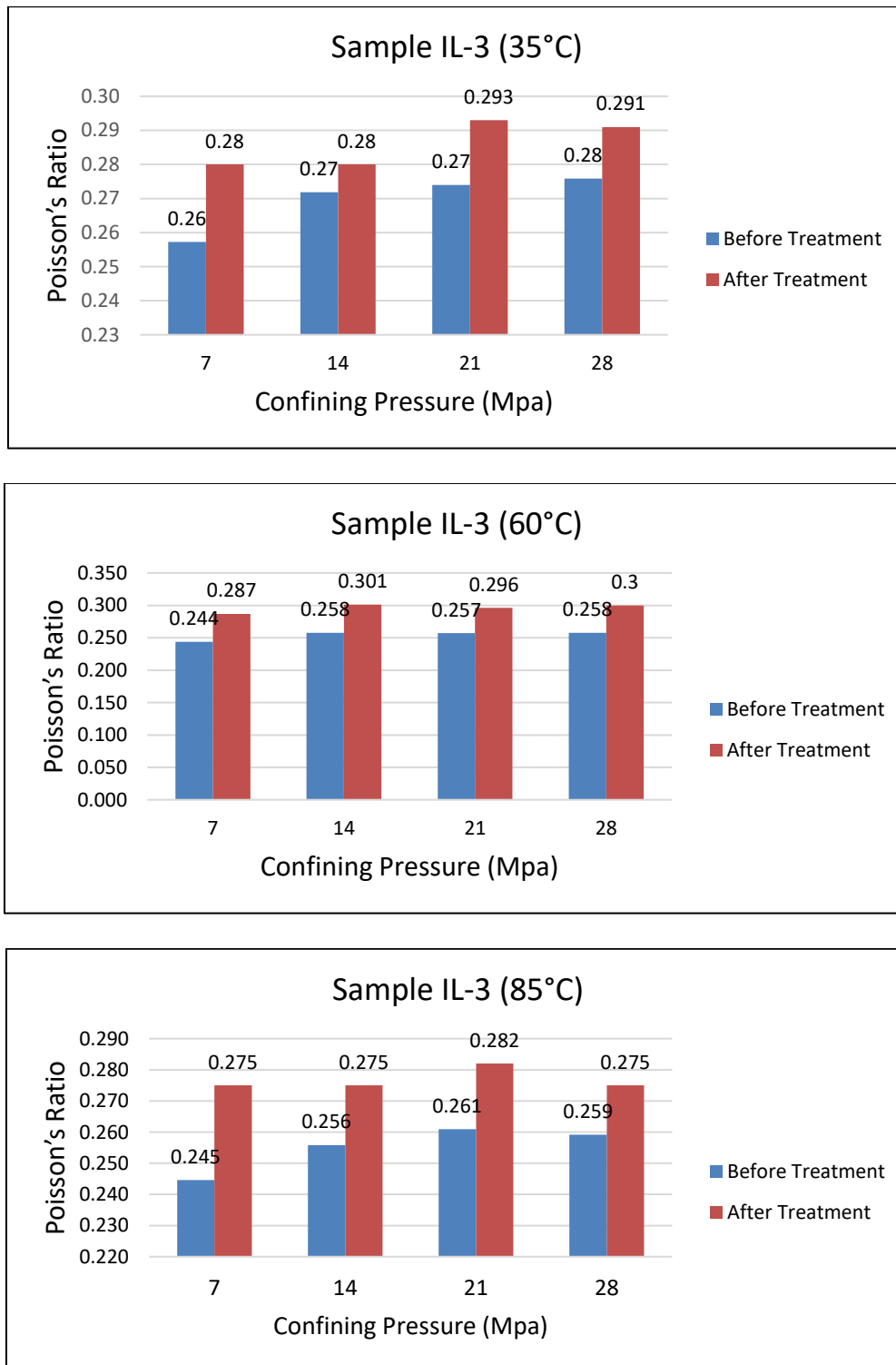


Figure 54: Increase in Poisson's ratio for different temperature values.

A comparison between the reduction in Young's modulus (YM) at different confining pressure for each of the different temperature is shown in Figure 55. The reduction in the Young's modulus was the highest at 85°C because at this temperature the live brine becomes least acidic and had to spend more time (10.5 hours) to generate the wormhole and hence mostly reacted on the bulk of the sample.

The 35°C case and the 60°C case generated wormholes in 4.6 hours and 5.4 hours respectively. There are two factors that impact the reduction in the YM, the time to generate the wormhole and the acidity of the solution. If a live brine generates the wormhole faster than another live brine, then it will not have enough time to reduce the YM as the slower live brine. However, if the time that requires two acidic solutions to generate a wormhole is close to each other, then the acidity of these solutions will be the dominant factor in determining which core sample YM will be reduced more. Even that the 60°C case was slower in generating the wormhole than the 35°C case, but this time different was not enough to cause more reduction in the YM. Because of that, the 35°C case more acidic live brine was more able to reduce the YM more than the 60°C case.

We can conclude that the fast generation of a wormhole has a positive impact on the rock integrity. Also, the acidity of the solution plays an important part and can be the dominant factor when the time of generating the wormholes by two different solution is close.

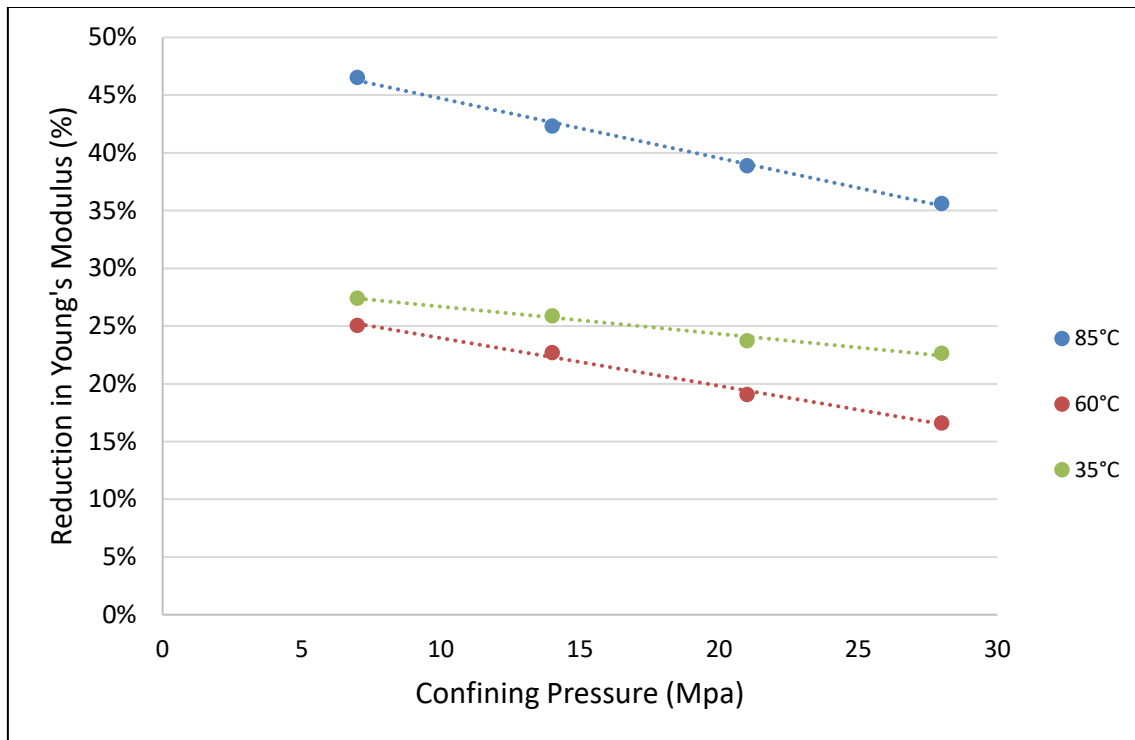


Figure 55: Reduction in Young's modulus for different temperature

### 5.2.3. Impact of Temperature on the Rock Hardness

The hardness was measured on the surface of the core samples inlet and outlet using the auto-scan before and after the live brine injection. The core samples average hardness (Inlet and Outlet) was calculated and plotted as shown in Figure 56. The average hardness of all the samples was reduced after the live brine injection.

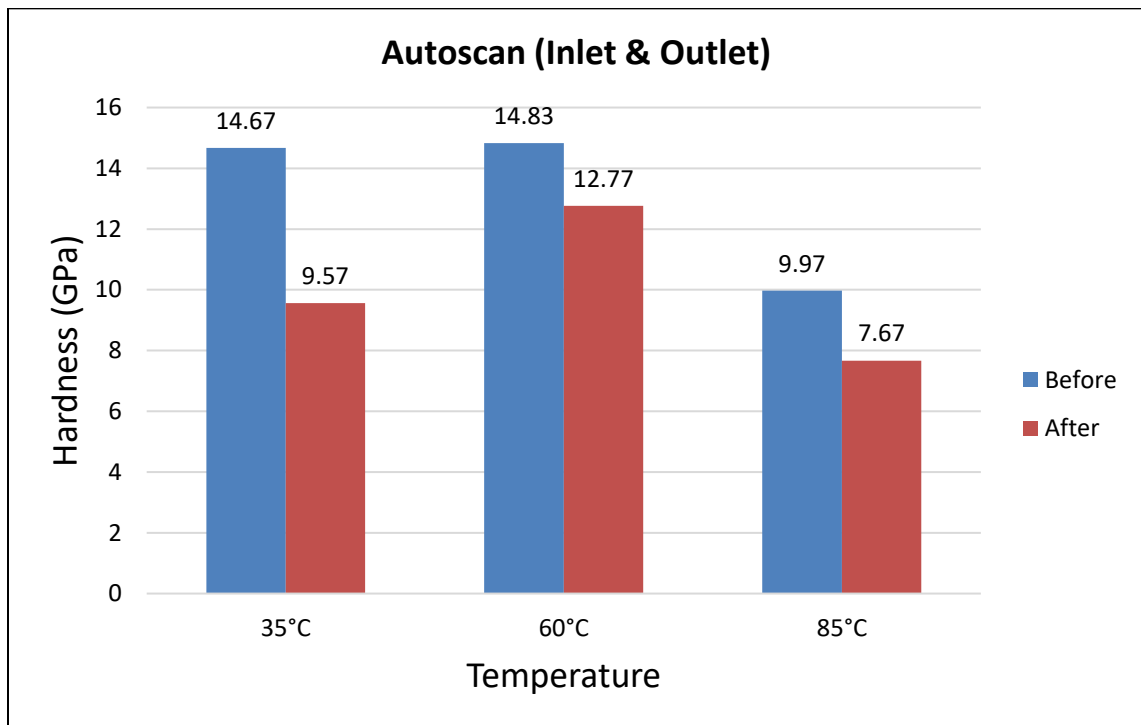


Figure 56: Rock hardness before & after live brine injection for different temperature

The reduction in the core inlet hardness was related to the temperature. The reduction in the rock hardness increases as the temperature decreases as shown in Figure 57. The rock hardness is a surface property of the rock. As the temperature decreases, the live brine becomes more acidic. Live brine with different temperature will interact with the core inlet for similar time. In this case, the big factor that impacts the reduction in the rock hardness is the acidity of the live brine.

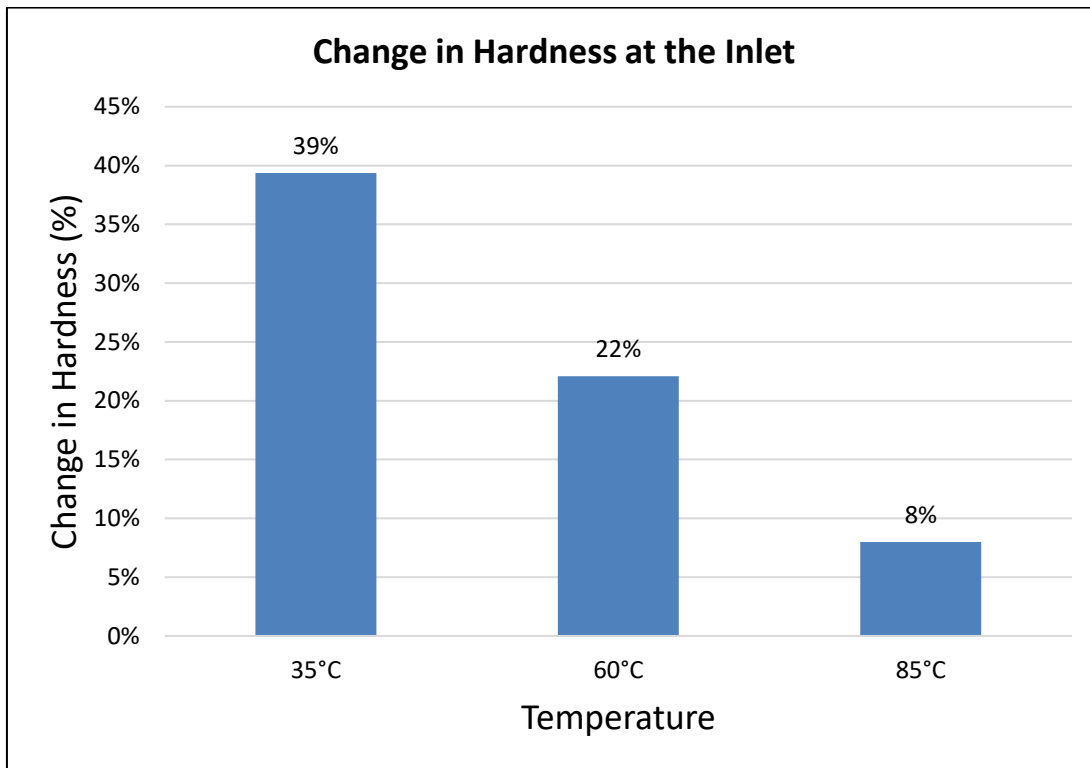


Figure 57: Reduction in core inlet hardness for different temperature

## CHAPTER 6

### CONCLUSION

Based on the research results, the following conclusions can be made for both salinity and temperature:

#### 6.1. Salinity

The impact of salinity was tested by having three salts concentrations of the live brine (40,000 ppm, 120,000 ppm, and 200,000 ppm). In all cases, the injection of the live brine resulted in generating wormholes. The time required to generate the wormholes has a positive relation with salinity. As a result, the amount of live brine required to generate the wormhole increases with salinity.

After injecting all the live brine and the wet CO<sub>2</sub>, the porosity of all the core samples increased. There is a negative linear relation between salinity and the change in porosity. As the salinity increases, the reduction of porosity decreases. Also, the reduction of porosity has a strong relationship with volume of live brine injected after generating a wormhole. After generating the wormhole, the remaining live brine and wet CO<sub>2</sub> will continue the reaction and the enlargement of the wormhole. This was observed by measuring the wormhole volume. The wormholes volumes for the 40,000 ppm, 120,000 ppm, and 200,000 ppm are 603 mm<sup>3</sup>, 506 mm<sup>3</sup>, and 273 mm<sup>3</sup> respectively.

For all the cases, the Young's modulus (YM) reduced after the live brine and wet CO<sub>2</sub> injection. There is a positive relationship between the reduction in the dynamic YM and salinity. This is due to the fact that as the salinity increases, the live brine becomes less acidic which will require more time to generate the wormhole. As a result, the bulk of the core sample will be exposed more to the live brine and that will reduce the YM more. On the contrary, when the live brine is more acidic, the time to generate the wormhole is short. The remaining of the live brine and wet CO<sub>2</sub> will go through the channel without reacting with the bulk of the core.

The average hardness of all the core samples was reduced after injecting the live brine and wet CO<sub>2</sub>. There is a negative relation between the core inlet hardness and salinity. The live brine interaction with the core inlet is independent of the wormhole generation time. The live brine with different salinities will interact with the surface of the core sample for similar time and rate. As a result, the big factor that will reduce the hardness of the rock is how acidic is the solution. On the other hand, and at the core outlet, there is no clear relation between the reduction in hardness and salinity.

The fast generation of wormholes due to the more acidic live brine has a positive impact on the rock Young's modulus. This is counterintuitive because someone might think that the more acidic is the live brine, the more damage that occurs to the rock mechanical properties.

## 6.2. Temperature

The impact of temperature was tested by performing the live brine injection under three different temperatures (35°C, 60°C, and 85°C). In all cases, the injection of the live brine resulted in generating wormholes. The time required to generate the wormholes has a positive relation with temperature. As a result, the amount of live brine required to generate the wormhole increases with temperature.

After injecting all the live brine and the wet CO<sub>2</sub>, the porosity of all the core samples increased. There is no clear trend between the change in porosity and the live brine temperature. There is a linear relationship between the change in porosity and the wormhole volume. Also, the wormholes become more branched as the temperature increases.

The reduction in the YM is very high at the highest temperature compared to the mid and least temperature. It is associated with the time to breakthrough as the 85°C case has the highest breakthrough time. The 35°C case and 60°C have a close time to breakthrough where the difference is less than one hour. Because of the 35°C case brine higher acidity, the YM of the 35°C case was reduced more than the 60°C case.

The average hardness of all the core samples was reduced after injecting the live brine and wet CO<sub>2</sub>. There is a negative relation between the core inlet hardness and temperature. The live brine interaction at the core inlet is independent of the wormhole generation time. The live brine at different temperatures will interact with the surface of the core sample for similar time and rate. As a result, the big factor that will reduce the hardness of the rock is

how acidic is the solution. On the other hand, and at the core outlet, there is no clear relation between the reduction in hardness and temperature.

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