



University of
Stavanger

Faculty of Science and Technology

MASTER'S THESIS

| | |
|---|---|
| Study program/Specialization: MSc in Petroleum Engineering Specialization- Natural Gas Technology | Spring semester, 2016 Open access |
| Writer: Bikram Timilsina | (Writer's signature) |
| Faculty supervisor: Jann Rune Ursin | |
| Thesis title: EFFECTS OF FINES MIGRATION ON CO₂ WELL INJECTIVITY | |
| Credits (ECTS): 30 | |
| Key words: <ul style="list-style-type: none">- Carbon capture and storage- CCS- CO₂ injection and capture- Mineral precipitation- Fines migration- Colloidal transport- Sandstone rock | Pages: 61 Stavanger, 15/06/2016 Date/year |

THIS PAGE IS INTENTIONALLY LEFT BLANK

ACKNOWLEDGEMENT

First of all, I would like to thank Norwegian government state fund (Lanekassen) for awarding me Quote scholarship to study at University of Stavanger.

Special thanks goes to my supervisor, Prof. Jann Rune Ursin, for providing me an opportunity to work on this thesis. It is his supervision and constant encouragement that made this work effective.

I would also like to thank PhD candidate, Yen Adams Sokama-Neuyam, for helping me as lab supervisor. Thanks a lot for sharing your experimental skills and giving regular encouragement from beginning of the lab work to the end of writing process.

I want to appreciate help I received from Pahmi during the experiment. Thank you so much my friend.

Last but not least, I want to say thanks to Dhruvit for his help and valuable suggestions.

THIS PAGE IS INTENTIONALLY LEFT BLANK

ABSTRACT

Carbon capture and storage is considered an important way to reduce atmospheric emission of greenhouse gases such as CO₂. This technology involves capture of carbon from the source of emission, transportation to storage sites and then injection into the suitable formations, oceans and other storage options.

This paper is focused on injectivity issues related to injection of supercritical CO₂ into the formation. When CO₂ is injected into sandstone, interaction between the injected CO₂, formation brine and the rock minerals, generate fine particles inside this porous media which could affect the injection process. This paper recognizes mineral dissolution as the source of fines inside the porous media. Interaction of CO₂, formation water and rock under suitable range of temperature and pressure is cause of mineral dissolution. During CO₂ reinjection, the injected fluid could transport these fine particles into the porous media. The transported fines could bridge pore channels and consequently reduce rock permeability and hence CO₂ injectivity. Unfortunately, this phenomenon have not been well studied experimentally.

Based on literature research, the estimated amount of calcite precipitation after 100 days of CO₂ storage was found. Necessary calculations were done to inject same concentration of alumina particles into Berea sandstone core. After particle injection, CO₂ injection was done and permeability of the core was measured. In this way, laboratory approximation of CO₂ reinjection after 100 days was constructed. Significant reduction in permeability was recorded in the presence of particles.

After this, alternate brine and CO₂ injection was performed in the same core to see if brine could push fine particles out of the core and improve permeability of the core. However, there was no significant improvement in permeability after this alternate injection.

Another experiment was conducted to see the effect of salt precipitation inside the core. This experiment did not involve injection of particles. However, very high salinity of NaCl brine was injected and vaporized with dry CO₂ and then permeability was measured. Brine experiment also showed significant decline in permeability. Permeability improved when concentration of brine was reduced.

THIS PAGE IS INTENTIONALLY LEFT BLANK

TABLE OF CONTENTS

| | |
|--|-----------|
| ACKNOWLEDGEMENT | ii |
| ABSTRACT | iv |
| TABLE OF CONTENTS | vi |
| LIST OF TABLES | ix |
| LIST OF FIGURES | x |
| NOMENCLATURE | xi |
| CHAPTER 1: INTRODUCTION | 1 |
| 1.1 General Introduction | 1 |
| 1.2 Objectives of the research | 2 |
| 1.3 Outline of thesis | 2 |
| CHAPTER 2: THEORY | 3 |
| 2.1 Carbon Capture and Storage (CCS): A brief History and Future prospects | 3 |
| 2.1.1 The Importance of CCS | 3 |
| 2.1.2 Sequestration Techniques | 3 |
| 2.1.3 Knowledge gap in CCS | 9 |
| 2.1.4 Future Prospects of CCS..... | 10 |
| 2.1.5 Industrial-Scale Projects in Norway | 11 |
| 2.2 Prerequisites for CCS | 12 |
| 2.2.1 Storage Capacity..... | 12 |
| 2.2.2 Well Injectivity | 12 |
| 2.3 Well Injectivity Challenges in CCS | 13 |
| 2.3.1 Formation Dry-out and Salt Precipitation | 13 |
| 2.3.2 Mineral Dissolution and Fines Migration..... | 14 |
| 2.4 Rock and Fluid Properties | 15 |
| 2.4.1 Properties of CO ₂ and brine..... | 15 |
| 2.4.2 Solubility of CO ₂ in brine..... | 16 |
| 2.4.3 Capillary back flow pressure in CO ₂ brine interaction..... | 19 |

| | |
|--|-----------|
| 2.4.4 Rock Properties..... | 19 |
| CHAPTER 3: COLLOIDAL TRANSPORT IN POROUS MEDIA..... | 21 |
| 3.1 Definition and Characteristics of colloids..... | 21 |
| 3.2 Factors affecting transport of colloids in porous media..... | 21 |
| 3.3 Effects of colloidal transport on well Injectivity..... | 23 |
| 3.4 Reinjection of CO ₂ in CCS..... | 23 |
| CHAPTER 4: PRE-EXPERIMENTAL WORK | 25 |
| 4.1 Mineral dissolution in CCS: A laboratory approximation of the problem..... | 25 |
| 4.2 Selection of Experimental materials and conditions..... | 26 |
| 4.2.1 Sandstone Rocks..... | 26 |
| 4.2.2 Formation Brine..... | 26 |
| 4.2.3 Preparation of brines..... | 28 |
| 4.2.4 Colloidal Suspension | 29 |
| 4.3 Key Parameters | 31 |
| 4.4 Error Analysis | 32 |
| 4.4.1 Types and nature of errors | 32 |
| CHAPTER 5: EXPERIMENTS | 34 |
| 5.1 Experimental Objectives | 34 |
| 5.2 Experimental Materials and Conditions..... | 34 |
| 5.3 Experimental Setup | 35 |
| 5.4 Experimental Procedures..... | 36 |
| 5.4.1 Preparation of Core..... | 36 |
| 5.4.2 Experiment 1: CO ₂ -brine alternative injection in the core initially saturated with particle suspension..... | 36 |
| 5.4.3 Experiment 2: CO ₂ -brine alternative injection in the core initially saturated with particle suspension to study the effect of salinity..... | 38 |
| 5.4.4 Experiment 3: Experiment without particles- Brine experiment..... | 39 |
| 5.5 Analytical Methods | 39 |
| 5.5.1 Uncertainties in experimental data | 39 |
| 5.5.2 Averaging of the values | 39 |
| CHAPTER 6: RESULTS | 41 |

| | |
|--|-----------|
| 6.1 Results and Discussion..... | 41 |
| 6.1.1 Experiment1: Particles diluted with HS brine followed by HS brine injection..... | 41 |
| 6.1.2 Experiment 2: Particles diluted in HS brine followed by injection of reduced brine concentration | 47 |
| 6.1.3 Experiment 3: Brine Experiments without Particle solution | 50 |
| 6.2 Conclusion..... | 55 |
| 6.3 Limitations and Future works | 55 |
| REFERENCES..... | 56 |
| APPENDICES | 61 |
| Appendix 1 | 61 |
| Appendix 2 | 61 |
| Appendix 3 | 61 |

LIST OF TABLES

| | |
|---|----|
| Table 1 Comparison of sequestration techniques for captured CO ₂ | 8 |
| Table 2: Mineralogical composition of Berea sandstone..... | 20 |
| Table 3: Properties of core provided from manufacturer..... | 26 |
| Table 4: Composition of formation water for 2 litres of solution..... | 27 |
| Table 5: Calculation of molarity..... | 27 |
| Table 6: Properties of Colloidal Suspension..... | 29 |
| Table 7: Calculation of calcite volume and mass of high salinity brine..... | 30 |
| Table 8: Calculation of desired concentration of particles..... | 30 |
| Table 9: Calculation of Pore Volume and Porosity..... | 32 |
| Table 10: Permeability measurements at each cycle of experiment 1..... | 61 |
| Table 11: Permeability measurement in different cycles (salinity test)..... | 61 |
| Table 12: Permeability measurement during brine experiment..... | 61 |

LIST OF FIGURES

| | |
|--|----|
| Figure 1: CO ₂ injection at ocean..... | 7 |
| Figure 2: Schematic of Sleipner CO ₂ storage project..... | 11 |
| Figure 3: Phase diagram showing various phases of pure CO ₂ | 16 |
| Figure 4: Effect of pressure on CO ₂ solubility in brine..... | 17 |
| Figure 5: CO ₂ solubility versus temperature at constant pressure..... | 18 |
| Figure 6: CO ₂ solubility with different concentration of brine..... | 18 |
| Figure 7: Entrapment of fines at pore constriction (Source: Sen, 2001)..... | 22 |
| Figure 8: Calcite precipitation with time..... | 25 |
| Figure 9 Schematic of lab core flooding..... | 35 |
| Figure 10: Plot of dP versus time during injection of particles and brines..... | 41 |
| Figure 11 Formation of filter cake during particle injection..... | 43 |
| Figure 12: Injection of supercritical CO ₂ to particle suspension and brines..... | 45 |
| Figure 13: Permeability measurements at each cycle..... | 46 |
| Figure 14: General sketch of each cycle..... | 46 |
| Figure 15: Pressure profile during particle and brine injection of reduced salinity..... | 47 |
| Figure 16: Supercritical CO ₂ injection in particle suspension and brines..... | 48 |
| Figure 17: Permeability measurement in different cycles..... | 48 |
| Figure 18: General sketch for each cycle during salinity test..... | 49 |
| Figure 19: Pressure profile during injection of brines of different salinity..... | 50 |
| Figure 20: Supercritical CO ₂ injection in different cycles of brine..... | 50 |
| Figure 21: Semi log plot of supercritical CO ₂ injection..... | 51 |
| Figure 22: Permeability measurement during brine experiment..... | 51 |
| Figure 23: General sketch showing result of each cycle..... | 52 |

NOMENCLATURE

| | |
|-----------------|----------------------------|
| CCS | Carbon Capture and Storage |
| CO ₂ | Carbon dioxide |
| EOR | Enhanced Oil recovery |
| EGR | Enhanced Gas Recovery |
| FW | Formation water |
| PV | Pore Volume |
| dP | Pressure drop |
| ρ | Density |
| DOC | Dissolved Organic Carbon |
| μ | Ionic Strength |
| C | Molar Concentration |
| M | Molarity |
| Z | Valence |

CHAPTER 1: INTRODUCTION

1.1 General Introduction

Carbon capture and storage (CCS) is a process that constitutes capture of CO₂ from the sources like industries and other energy related sources, its transportation and storage to another location so that it can be isolated from the atmosphere for a long period (Working Group III of the Intergovernmental Panel on Climate Change, 2005). Capture, transport and storage are three major components of the CCS. All three components are found in industrial operations today. Capture involves separation of CO₂ from other gases and then transported to suitable storage sites. Storage sites may be far from potential sources where CO₂ is captured. CO₂ is compressed before transportation in order to convey large quantities of the gas in manageable volumes. CO₂ is then stored in ocean or underground geological formations.

Capture of CO₂ and its storage into deep formations is considered important mitigation technique to reduce atmospheric emission of CO₂. Various concentrations of particles could detach from the porous media into the flow stream during injection of CO₂. Injection of CO₂ at high rate can mobilize and redistribute these fine particles. The transported fines could clog the core and impair injectivity. Deposition of particles and decrease in permeability is a major problem faced by oil and gas fields. Fines migration inside the reservoir is influenced by various factors such as chemical and hydrodynamic conditions inside the porous media. Fines can even plug the core completely and this is in general irreversible process. Once the porous media is plugged, it is difficult to restore the permeability. In some cases, the well might be abandoned. Therefore, proper assessment of fines migration is important and initiatives should be taken to minimize the effect of fines migration in order to prevent formation damage.

When CO₂ is injected into deep saline aquifers, initial fluid equilibrium is disturbed (Fischer et al., 2010). Also, chemical reaction take place in the reservoir between injected CO₂, formation water and reservoir rock. As a result of these reactions, mineral dissolution and fines detachment which could change the chemical and physical properties of the reservoir. Mineral dissolution is identified as a major source of fines during CO₂ injection.

This research seeks to investigate the effect of particle release and mobilization due to dissolution during CO₂ injection. Decline in the injectivity is case-dependent. Particles size, particles concentration, ionic strength of carrying fluid are important parameters that affect fines migration and CO₂ well injectivity.

When CO₂ is injected into porous media saturated with brine, following things are expected to occur:

- CO₂ gets dissolved in brine and its density is increased. This brine can either sink down or react with water to form acid. Acid can react with the components of rock and precipitate mineral carbonates.
- H₂O gets dissolved or vaporized by dry CO₂. This may lead to salt precipitation in the close vicinity of injection well.

CO₂ brine rock interaction in subsurface reservoir can impose strong effect on injection operations for long term CO₂ storage. During injection, water is displaced and vaporized from brine continuously. This decreases brine saturation and when the brine reaches supersaturation, salt could be precipitated into the pores of the rock (Hurter et al., 2008).

1.2 Objectives of the research

The objectives of this thesis are stated as follows:

- i. To study the effect of wellbore dry-out and salt precipitation on CO₂ injectivity.
- ii. To study the effect of mineral dissolution and fines migration on the reinjection of CO₂ during CCS.

1.3 Outline of thesis

Chapter 2 discusses CCS and well Injectivity challenges.

Chapter 3 explains the mechanisms of colloidal transport and their importance to CO₂ injectivity and CCS.

Chapter 4 introduces the reader to the experimental design, measurement techniques, approximations and uncertainties.

Chapter 5 deals with the experimental process.

Chapter 6 sums up the result, discussions, conclusions and proposal for further research.

CHAPTER 2: THEORY

2.1 Carbon Capture and Storage (CCS): A brief History and Future prospects

2.1.1 The Importance of CCS

Use of fossil fuels as source of energy has increased carbon content in the atmosphere. Greenhouse effect and climate change has been a major concern over decades. CO₂ gas can trap heat in the atmosphere and increase temperature on earth. This effect is similar to heat trap by glass in green house. Changes in surface temperature, ocean temperature, melting of polar ice, rise of sea level are some of the effects caused by atmospheric emission of greenhouse gases.

In 1992, United Nations Framework Convention on Climate Change (UNFCCC) was formed with the objective to stabilize the concentration of greenhouse gases in the atmosphere. The International Energy Agency (IEA) is working to stabilize CO₂ concentration in the atmosphere at 450 ppm. To achieve this limit, around 1.4 GtCO₂ per year should be captured by 2030 (IEA, 2009).

CCS is important to address this major environmental concerns. However, the continual dependence of industrial and domestic activities on fossil fuel compounds the challenge. Proper implementation of CCS could reduce atmospheric CO₂ and prevent climate change.

2.1.2 Sequestration Techniques

The term CO₂ sequestration describes process that either removes CO₂ from atmosphere or diverts CO₂ from emission sources to other storage places such as deep oceans, geological formation etc. The following are potential storage techniques for CO₂ storage:

Geological Storage

Geological storage means injection of CO₂ in a dense form into a rock formation below the earth's surface for storage. Geological storage can be promising only if the trapping mechanism of CO₂ is effective. Trapping of CO₂ within geological storage sites can occur as a result of buoyancy between CO₂ and fluids present in storage sites. When CO₂ is injected deep into the subsurface, it might rise

until it is trapped. Impermeable seal or fluid above injected CO₂ can act as potential trapping source. Physical trapping mechanism by impermeable seal is similar to the trapping of oil and gas in reservoir. In case there is no physical trapping, hydrodynamic trapping is also possible if fluid migrates very slowly over a long distance. Injected CO₂ has less density compared to saline water in the formation. It rise up, displacing less dense water. It could rise to the top of the formation where it again gets trapped within structures or gets dissolved with formation water and migrates with formation water. In long term, significant amount of dissolved CO₂ migrates with formation water. Several researchers have found that hydrocarbons and other gases including CO₂ can remain trapped for millions of years (Magoon and Dow, 1994; Bradshaw et al., 2005).

With increasing density of the injected CO₂, efficiency of geological storage increases. When density of CO₂ is increased, it will go down because of buoyancy and chance of leaking to surface is minimum. According to Bachu, 2003, cold sedimentary basins, where temperature gradient is lower, are better options for CO₂ storage because density of CO₂ can be higher even at shallower depth.

CO₂ injection is done at high temperature and pressure into stable rocks that are found deep inside earth. At this temperature and pressure range, CO₂ is in supercritical state. Supercritical CO₂ behaves like liquid in the sense that it occupies less volume when it is stored inside the formation.

Trapping mechanism in geological storage

Trap refers to some type of combination of rocks which is suitable to contain fluids and sealed by some impermeable structure on the top. Basic trapping mechanisms occurs during geological storage of CO₂. Some of them are listed below:

- Stratigraphic trapping
- Structural trapping
- Residual trapping
- Solubility trapping
- Mineral trapping

Stratigraphic trapping and structural trapping mechanism are dominating mechanism to store CO₂. Cap rock can enclose the impermeable formation from the top to form stratigraphic trapping

mechanism. This is similar to empty bucket turned upside down. CO₂ can get trapped inside this formation. In structural trapping, the formation shifted by fault can act as place to store CO₂.

Long term trapping mechanism

When CO₂ injection is stopped, surrounding water starts to move towards the pores containing CO₂. Then additional pressure is given by surrounding water which makes CO₂ immobile. This phenomenon is known as residual trapping which happens in a long term. Injected CO₂ can also dissolve in saline water or oil contained in the porous media. In this case, more dense fluid is formed which may sink to the bottom of the formation. This is known as solubility trapping. Dissolved CO₂ can also react with surrounding rock under favourable temperature and pressure conditions. When this reaction occurs, stable metal carbonates are formed and stored for a long period of time, which is referred to as mineral trapping.

Generally, trapping processes may take several years if CO₂ stays for longer time underground. These trapping processes take place over many years at different rates. Generally, the longer CO₂ stays underground, the more secure its storage becomes. With the passage of time, more-secure trapping mechanisms are increasingly likely to have significant effect.

Potential geological formations where CO₂ can be stored are as follows:

Depleted oil and gas reservoirs

In depleted reservoirs, CO₂ is stored in those pores which were once occupied by hydrocarbons. Injection of supercritical CO₂ at high pressure inside the reservoir could lead to deformation of reservoir or cap rock. This can fracture the formation, therefore proper assessment need to be done to find maximum pressure that the formation can handle without getting damaged. Geomechanical modelling of the subsurface can help in the assessment of reservoir sustainability for higher range of pressures. Depleted oil and gas reservoirs are most promising reservoirs because of the following reasons:

- First of all, hydrocarbons were originally trapped for millions of years before production which indicates integrity and safety of trapping injected CO₂.

- Detail study of geological structures and physical properties of the reservoir have been done during exploration of oil and gases.
- Different models have been developed to observe movement and behavior of hydrocarbons which can be applied to predict behavior of injected CO₂.
- Depleted fields will not be affected significantly by CO₂ since it was previously occupied by hydrocarbons.

Deep saline formations

Deep saline formation consists of porous rock with water of very high salinity. Such saline formations are widely spread throughout the world which meets criteria for long term storage of CO₂. In these formations fluids are already trapped in the rock. Injecting CO₂ adds more fluid inside the rock. CO₂ can dissolve into saline water and chemically react with the rock to produce stable carbonates for storage.

Unmineable coal seams

CO₂ could be injected into the micropores within the coal. CO₂ is held tightly within the coal matrix and cannot come out even in the absence of cap rock.

Ocean Storage

Ocean has covered most portion of the earth, therefore CO₂ storage in ocean can be done in vast amount. Injection of liquid CO₂ into North Atlantic Ocean was proposed by Marchetti (1977) in order to isolate CO₂ from atmosphere for centuries. Overall aim in ocean storage is to store CO₂ for long period of time and isolate it from the atmosphere. Over centuries interaction between CO₂ and ocean results in mixing and affect atmospheric CO₂ concentration (Working Group III of the Intergovernmental Panel on Climate Change, 2005). CO₂ could be stored as liquid, solid or hydrate form. All of these phases can dissolve into sea water in a long term. CO₂ dissolves into sea water until its density increases and then sinks more deeply. This phenomenon is more likely in near fields where CO₂ is injected. In far field, concentration of injected CO₂ is low and there is no significant increase in density of CO₂ mixed water. CO₂ can be transported by ocean currents and continuously mix with ocean water. This behavior can affect greater volume of ocean water.

Figure 1 shows schematic of injection of CO₂ in ocean at larger depth and dispersing of CO₂.

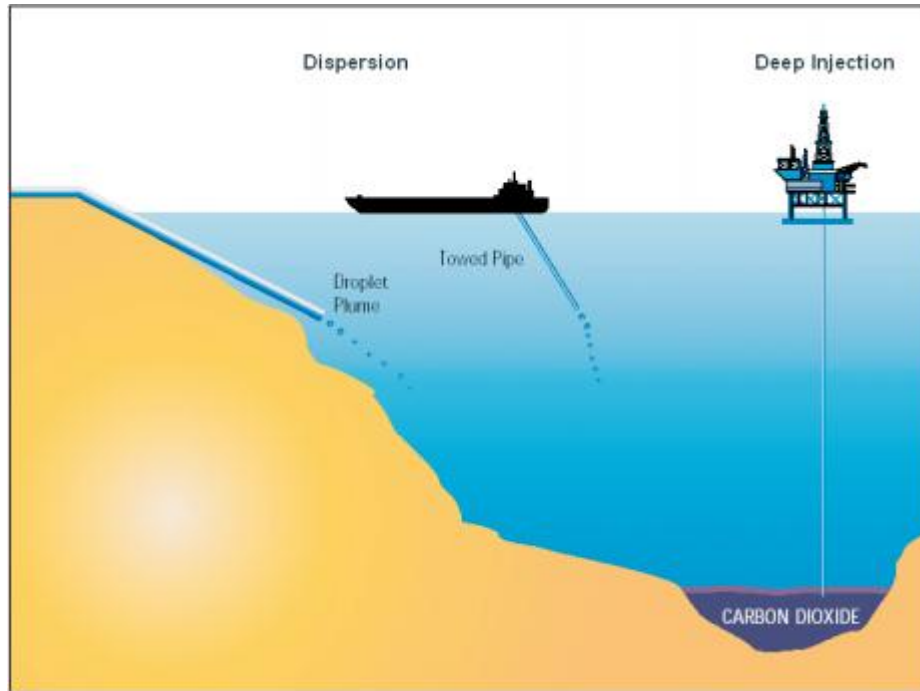


Figure 1: CO₂ injection at ocean

(Source: IEA Greenhouse Gas R&D Programme, 1999)

Surface water of oceans, which are relatively warm, are saturated with CO₂ but colder deep waters are unsaturated. These cold waters have huge capacity to dissolve CO₂. CO₂ should be injected at depth of at least 1500 m in order to minimize the environmental impact in the productive surface waters of the ocean (IEA Greenhouse Gas R&D Programme, 1999). Subsea pipeline technology already has capacity of this depth. Injection of CO₂ at depth deeper than 3000m can increase retention time of CO₂ in the ocean. At greater depth, dissolution of CO₂ into overlying water will be reduced since hydrate is formed which can further migrate within the sea. For deep injection, a vertical pipe is required which is attached to the platform as shown in figure 1.

Mineral Storage

Due to injection of CO₂ into ocean, acidity increases in a long term. This acidity can be neutralized to a larger extent by natural dissolution of minerals. This is a slow process which occurs in the sea-floor sediments and on land. According to Archer et al., 2008 ocean can absorb more CO₂ with less change in ocean PH and concentration of carbonate ion because of this neutralization process. Carbonate minerals are considered as primary alkaline minerals that can neutralize CO₂ acidity (Rau et. al, 2001).

Different researchers have done experiments and observations for mineral dissolution and precipitation in fresh water as well as in sea water under different range of temperature and pressure conditions. Assayag et al., 2009 have studied extent of mineral dissolution and precipitation induced by water-rock-CO₂ interaction. These researchers found that rate of carbonate mineral dissolution is higher than silicate minerals. Kheshgi, 1995 said that 0.8 mole of additional CO₂ can be stored in sea water per mole of CaCO₃ dissolved. From their result, it can be suggested that injected CO₂ will be converted to solid carbonate minerals in a long term.

Table 1 shows comparison of different sequestration techniques on the basis of storage potential, availability of technology, cost, and environmental issues.

Table 1 Comparison of sequestration techniques for captured CO₂

Source: IEA Greenhouse gas R&D Programme, 2000.

| Storage Option | Potential Magnitude (GtCO ₂) | Availability and applicability | Environmental and safety issues | Storage Cost (US\$/tCO ₂) |
|------------------------|--|--|--|---------------------------------------|
| 1) Deep Ocean | | | | |
| Deep Ocean | >4000 | Proximity to deep ocean required. Questions about duration of storage. Concerns about legality | Local environmental issues. | 1-5 |
| 2) Underground | | | | |
| Deep saline reservoirs | >800 | Widely distributed; existing offshore application being monitored | Integrity of store has to be demonstrated | 1-2 |
| Diffused gas fields | 800 | Localized; largely based on existing technology | Relatively minor concern if original seal is sound | 2-3 |
| Diffused oil fields | 130 | Localized; uses existing technology | Relatively minor leakage concerns | Can be a net benefit |

| | | | | |
|---------------------------------|--|--|--|--------|
| Unmineable coal seams | >15 | Regional availability; development of existing technology required | Relatively minor leakage concern | 60-100 |
| 3) Terrestrial | | | | |
| Mineral Carbonates | Large-potential not estimated | Widely applicable; R&D on sequestration required | Relatively minor concerns | 60-100 |
| Bulk storage of CO ₂ | Large in principle but constrained by cost | Little restriction; existing technology can be used | Concern about potential for accidental release | 160 |

2.1.3 Knowledge gap in CCS

CCS is operating with limited knowledge and with a lot of uncertainties. There are uncertainties related to cost of CCS systems and storage potential. Lack of exploration and appraisal works has compounded the risk associated with storage. Inadequate knowledge on trapping mechanism and reservoir condition results in storage integrity risk. In general, technical uncertainty in CCS is still high. CCS could attract investors if the link between CCS technology and major carbon emitters is established and improved. New business models can be developed based on experience and geological data of oil and gas industries. Lack of proper legal and regulatory framework have made CCS challenging for industries. During exploration of oil and gas, risk associated with seal is proven during discovery phase. On the contrary, seal risk is continued during injection and post injection process (Senior et al., 2010).

There are some issues regarding public opinion on storage projects. In some countries, the public have not accepted CO₂ storage which is causing barriers for storage projects. Business risk for private sector is even high due to public issues and lack of legal regulatory frameworks. According to Senior et al., 2010, uncertainty for storage projects are greater than oil and gas fields. There are gaps in knowledge regarding the costs of retrofitting existing power plants with CO₂ capture. Research shows if existing plants are retrofitted with CCS, there could be significant increase in cost and overall efficiency of plant will be reduced (Working Group III of the Intergovernmental Panel on Climate Change, 2005).

2.1.4 Future Prospects of CCS

CCS could be a plausible mitigation technique for global warming and climate change. It is very promising as it can reduce emissions directly from source and prevent the release of CO₂ into the atmosphere. Oil and gas industries might be attracted to CCS technology because of the following reasons:

Enhanced Oil Recovery (EOR)

Large quantity of CO₂ is injected into depleted oil reservoirs. CO₂ dissolves in oil and reduces viscosity of oil in the process. About 10 to 12 % of oil reserves could benefit from this process (APEC Energy Working Group, 2012). A part the injected CO₂ could remain in the bottom of the reservoir as pressure support for depleting reservoirs. This technique however need to be weighed against cost of other gas injection for oil recovery. Martin and Taber, 1992; Moritis, 2003 suggested that CO₂ could be used for EOR, with an incremental oil recovery of 7–23% (average 13.2%) of the original oil in place. Several researchers have studied CO₂ storage in relation to EOR (Klins, 1984; Taber et al., 1997; Kovscek, 2002; Shaw and Bachu, 2002). They suggested that, for CO₂-EOR, the gas should be injected into the reservoir with a depth of more than 600 m.

Enhanced Gas Recovery (EGR)

CO₂ injected into depleted gas reservoirs could aid both the displacement and mobilization of oil. In the reservoir, the CO₂ front mixes with other natural gas present through diffusion and dispersion. EGR is more pronounced in those reservoirs where there is no aquifer water encroachment. In such reservoir, injected gas could provide pressure support from the bottom and enhance production.

Enhanced Coalbed Methane Recovery (ECBM)

Unconventional gas reserves such as coal beds have large amount of methane gas held by adsorption in the coal. CO₂ could be injected into the coal bed matrix, which then gets adsorbed. Due to CO₂ adsorption, methane gas in the rock matrix is released and methane production could be increased.

2.1.5 Industrial-Scale Projects in Norway

Sleipner

The Sleipner project is owned by Statoil in North Sea. It is the world's first commercial scale project launched for geological storage of CO₂ in a saline formation. This project uses CO₂ gas from Sleipner West Gas Field which is injected into a saline formation 800 m below seabed as shown in figure 2. From 1996 this project started to inject CO₂ and by 2005 more than 7 MtCO₂ has been injected into the formation (Working Group III of the Intergovernmental Panel on Climate Change, 2005). They further added that this saline formation has a large storage capacity of about 1-10 Gt CO₂. Lindeberg and Bergmo, 2003, have performed simulations covering thousands of years, and found that CO₂ will dissolve in the pore water and become heavier, sinking down to minimize the chances for leakage in a long term.

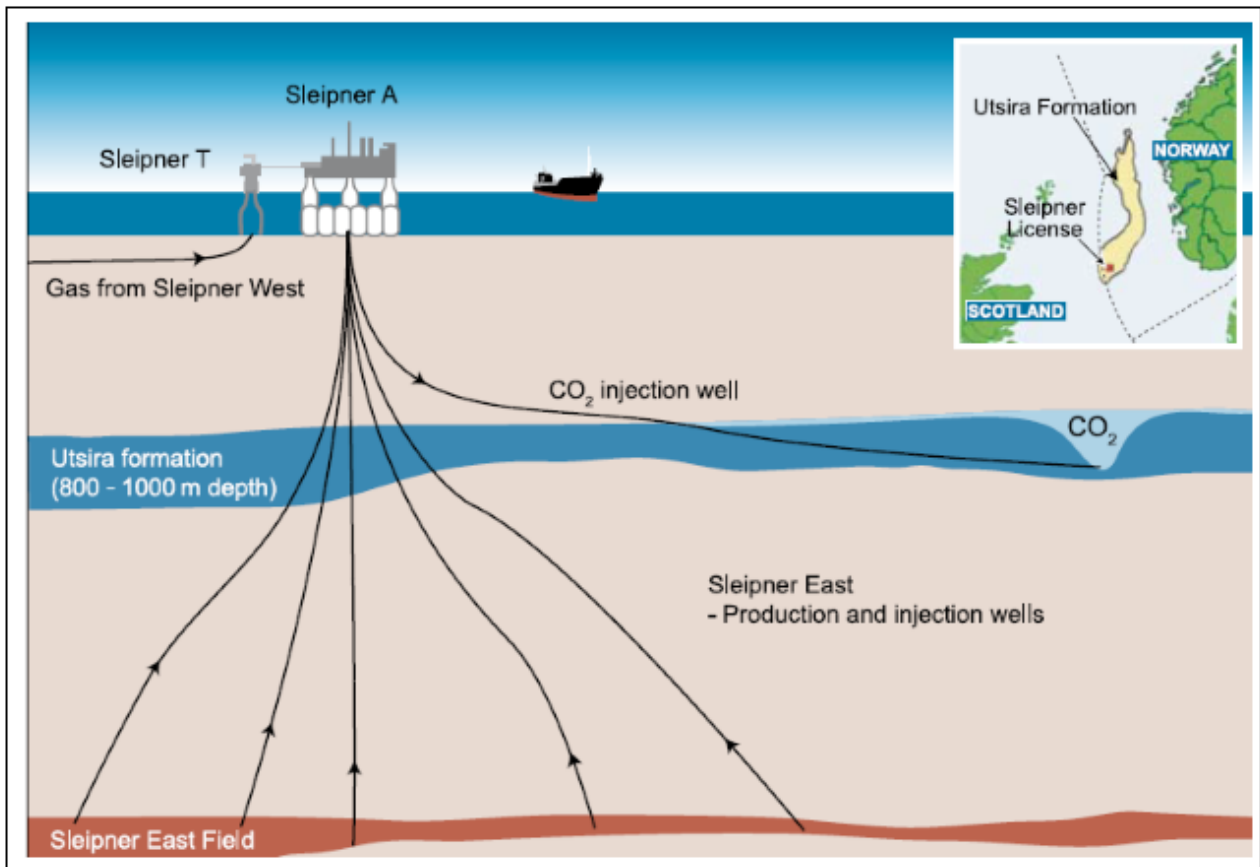


Figure 2: Schematic of Sleipner CO₂ storage project

(Source: Working Group III of the Intergovernmental Panel on Climate Change, 2005).

Snøhvit

This CCS project was started in 2008. In this field, natural gas produced is first sent for carbon capture. Captured carbon is injected into sandstone formation at depth of 2400m below seabed (Roels, 2015). It is then stored in a geological layer of porous sandstone called Tubåen formation. According to (Hosa et al., 2011; Michael et al., 2010) total storage capacity of this field is estimated to be 23 Mt. By September 2010, 0.8 million tons of CO₂ had been injected into the formation (Eiken et al., 2011). Monitoring techniques are implemented in this project to investigate the behavior of injected CO₂. Seismic surveys in different time intervals, monitoring of reservoir pressure, gravimetric surveys, reservoir simulation etc are done to monitor the system.

2.2 Prerequisites for CCS

2.2.1 Storage Capacity

Storage capacity refers to the total amount of CO₂ that can be stored in a reservoir in a fixed period of time. From economical point of view, storage capacity must be good enough to attract potential investors. The unit cost of operation could be lowered if storage capacity is large i.e. same amount of investment can be utilized for developing the site and large volume of CO₂ can be stored. Properties of oil and gas fields are always studied during exploration and production phases. These studies are also combined with computer modelling and extensive research have been done previously. Thus, storage capacity could be better estimated in depleted oil and gas fields. CO₂ could be stored in that formation which was previously occupied by hydrocarbons. Storage capacity depends on geological properties of reservoir such as porosity, thickness, and permeability. With increasing depth, the degree of compaction and cementation increases, resulting in the decrease of porosity. This reduces storage capacity and efficiency. The formation should be sealed by overlying shale, salt or anhydride beds so that CO₂ can be stored safely without being leaked into the upper parts of the reservoir.

2.2.2 Well Injectivity

CO₂ well injectivity refers to capacity of injection well to receive CO₂ without getting fractured. If injection pressure is kept below fracture pressure in that particular well, fracture is not likely to occur. Well injectivity is an important prerequisite for CCS. To inject CO₂ for a long time, there should be

sufficient injection wells with better injectivity. Well injectivity changes with time during CO₂ injection. Injectivity may be affected by a lot of physical and chemical process during injection and post injection. Parameters such as fracture pressure of cap rock, reservoir properties have made restriction in the ability of both injection wells and reservoirs to accept limited amount of CO₂ in a given time (Miri, 2015). Injection rate could be fixed after considering the wellhead pressure, permeability of reservoir rock, tubing size and other parameters (Filip Neele et. al, 2011). A pilot test could be run to measure injectivity directly. However, this pilot give limited information since all well and reservoir cannot have the same properties. Results from pilot test may vary from the overall result because of heterogeneity (Bachu, 2015).

2.3 Well Injectivity Challenges in CCS

Well Injectivity challenges impose technical and economic constraints to CCS. The two major well Injectivity challenges that will be considered in this study are effect of salt precipitation and fines migration.

2.31 Formation Dry-out and Salt Precipitation

When dry supercritical CO₂ is injected into the injection well, thermal and dehydration effect comes into play which can lead to precipitation of salt from formation brine. Experimental studies revealed that permeability is reduced significantly due to salt precipitation during CO₂ injection (Bacci et al., 2011; Pruess and Müller, 2009a). In some CCS projects such as Snøhvit and InSalah, there was significant injectivity loss when dry CO₂ was injected (Eiken et al., 2011; Hansen et al., 2013). Grude et al., 2013, did experiment on core samples from Snøhvit and found that solid salt was precipitated during CO₂ injection. They further added that most of this solid salt was at pore throat and caused significant impact on injectivity. According to (Scherer, 2004), larger pores can drain at lower entry pressures than smaller pores, and evaporation increases the concentration inside the pores, salt is more likely to precipitate in the smaller pores. This precipitation of salt is the known cause of formation damage. However, in the presence of low salinity brine, permeability is enhanced due to interaction with dry CO₂ (Hurter et al., 2008).

Giorgis et al., 2007 studied about relative decrease in permeability when CO₂ is injected into movable and immovable brine. They found that there is uniform distribution of precipitated salts in immobile

brine and it has negligible effect on permeability loss while in case of movable brine, there was significant reduction in permeability. If evaporation rate is increased capillary pressure gradient becomes high and flow of brine towards inlet increases. On the other hand, injection pressure gradient also increases with injection rate that acts against capillary back flow (Giorgis et al., 2007).

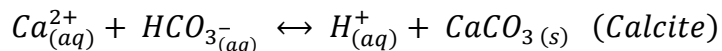
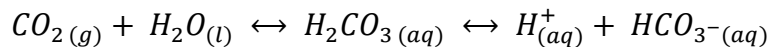
Miri, 2015 reached interesting conclusions about salt precipitation during CO₂ injection. They are listed below:

- Salt has a hydrophilic nature which gives massive capillarity to the salt aggregates to imbibe water.
- Salt grows as porous aggregates in the gas phase enhancing the distribution of brine, and increasing the surface area for evaporation, and therefore increasing the evaporation rate.
- Evaporation induces nucleation and precipitation which induces further capillary transport i.e., salt aggregates imbibe more water to compensate the increased evaporation.

In summary, there is massive salt precipitation which is self-enhancing, causing significant impact upon permeability.

2.32 Mineral Dissolution and Fines Migration

Interaction between CO₂, host rock and aquifer is responsible for mineral dissolution and precipitation. Extent of mineral dissolution and precipitation depends on temperature, pressure, availability of CO₂ etc. First, CO₂ dissolves in water to form weak carbonic acid and then form bicarbonates. Bicarbonates could react with cations to form stable carbonates. Feldspars, clays in sandstone reservoir could act as source of cation. The reaction is summarized as shown:



Nagy et al., 1992 did experiment to determine mineral dissolution and precipitation of kaolinite at 80 °C. Based on experiment and numerical modelling, these researchers determined precipitation rate laws for silicate and calcite. Their research was limited to equilibrium state and precipitation rates were not determined for wide range of saturation states. Lebron and Suarez, 1996 conducted

experiment to determine mechanism of calcite precipitation in the presence of Dissolved Organic Carbon (DOC) and found significant decrease in precipitation rate of calcite when DOC was higher.

Reaction between CO₂ and water is dependent on solubility of CO₂. Hangx, 2005 performed experiment to determine the effect of temperature, pressure and salinity in the solubility of CO₂. He found that solubility of CO₂ increases with increase in temperature above 100°C while it decreases with temperature below 100 °C. Solubility of CO₂ increases with increasing pressure while increasing salinity decreases solubility.

Regardless, mineral precipitation is inevitable in CO₂ injection and storage. These precipitated minerals, if smaller in size, cannot be held down by gravity and could be transported in the flow stream during CO₂ injection.

Factors affecting rate of dissolution

Temperature: Rate of mineral dissolution is highly affected by temperature. Small increase in temperature can enhance the reaction and increase dissolution rate. Hangx, 2005 quantified the effect of temperature in the dissolution rate of anorthite. He found that increasing temperature from room conditions to 100 °C, dissolution increased 1.5 times; at 200 °C it increased 2.75 times and at 300 °C magnitude of dissolution increased by 3.5 times.

Pressure: Effect of pressure of CO₂ in mineral dissolution has not been well investigated. Formation of carbonic acid and its reaction with host rock is more or less not dependent on CO₂ pressure.

Salinity: Increase in salinity has negative effect on mineral dissolution. As concentration of ions such as Na⁺ increases, less concentration of hydrogen ions will be available to react with feldspar. This results in decrease in dissolution rate with increase in salinity (Hangx, 2005).

2.4 Rock and Fluid Properties

2.4.1 Properties of CO₂ and brine

CO₂ is a chemical compound consisting of 1 atom of carbon and two atoms of oxygen. Physical properties of CO₂ changes with change in temperature and pressure. It is a solid at temperatures below

-56.5 °C (dry ice). If this ice is heated at pressure below 5.1 bar, it directly sublimates into vapour. For temperature above 31.10 °C and pressure above 73.9 bar CO₂ reaches a supercritical state. If temperature is below 31.1 °C and pressure above 73.9 bar liquid CO₂ is formed. Density of supercritical CO₂ is less than density of liquid CO₂. Figure 3 shows phases of pure CO₂ as function of temperature and pressure.

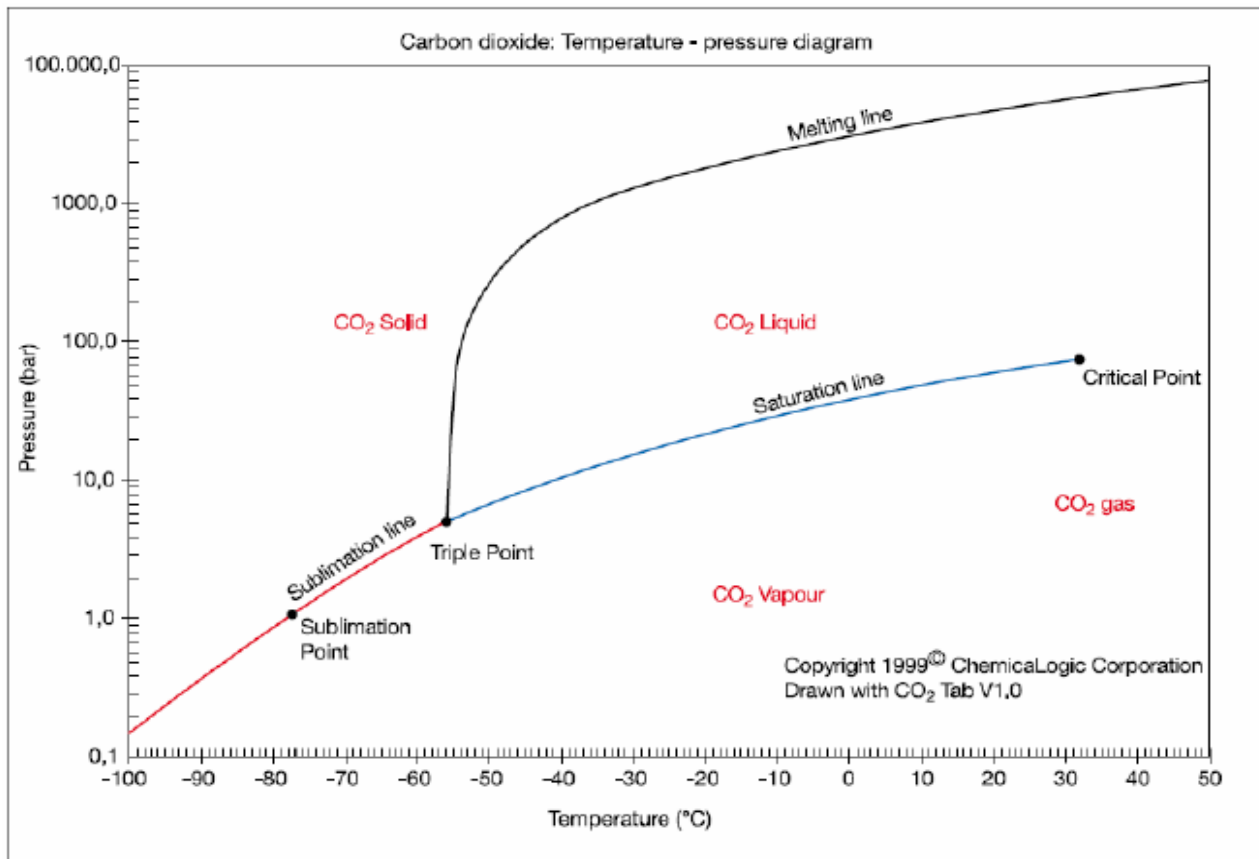


Figure 3: Phase diagram showing various phases of pure CO₂

(Source: ChemicalLogic Corporation, 1999)

2.4.2 Solubility of CO₂ in brine

Mineral dissolution and precipitation is strongly dependent on the solubility of CO₂ in the brine. Injected CO₂ from injection well is dry and it dissolves in formation brine to form acid. If more CO₂ gets dissolved, more acid is formed and more precipitation is likely. Solubility of CO₂ in brine is affected by factors such as temperature and pressure.

Effect of Pressure: CO₂ solubility in brine increases significantly with increase in pressure. Figure 4 shows that solubility increases up to pressure of 10 MPa and then it increases slowly afterwards. This graph was plotted by Duan and Sun, 2003 at the temperature of 323 K and brine salinity of 1 mol NaCL/kg brine.

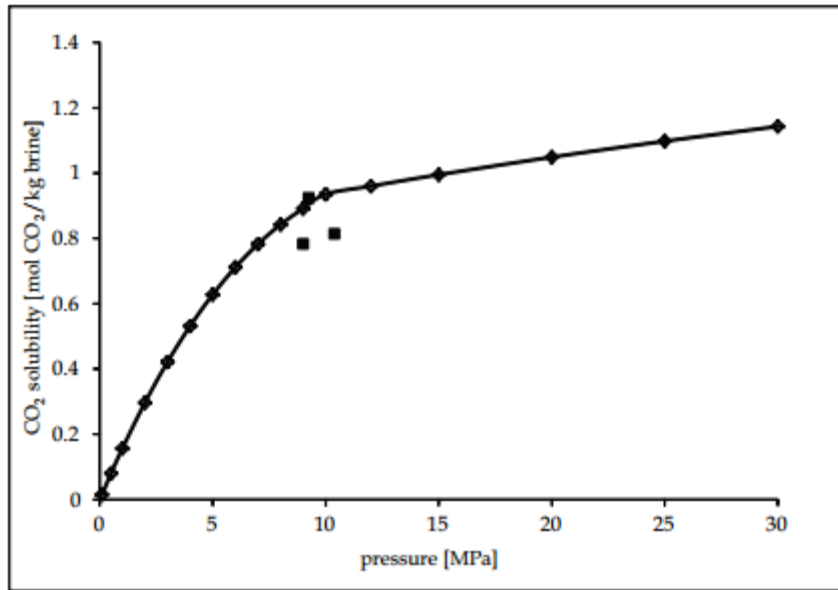


Figure 4: Effect of pressure on CO₂ solubility in brine

(Source: Duan and Sun, 2003)

Effect of Temperature: Increase in temperature decreases the solubility of CO₂ in brine as shown in figure 5. Experiments done by various researchers confirm this effect. Curve with open diamonds was prepared by Duan et al., 2003, 2006.

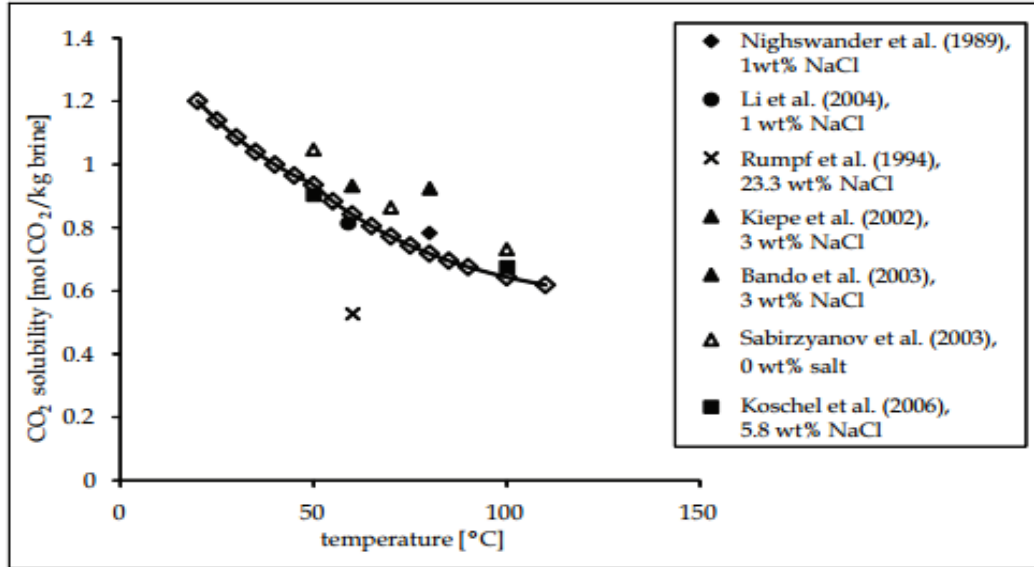


Figure 5: CO_2 solubility versus temperature at constant pressure

(Source: Duan and Sun, 2003)

Effect of brine salinity: solubility of CO_2 decreases when concentration of brine is increased. Figure 6 shows findings of different researchers. Curve with open diamonds represents research done by Duan et al., 2003, 2006.

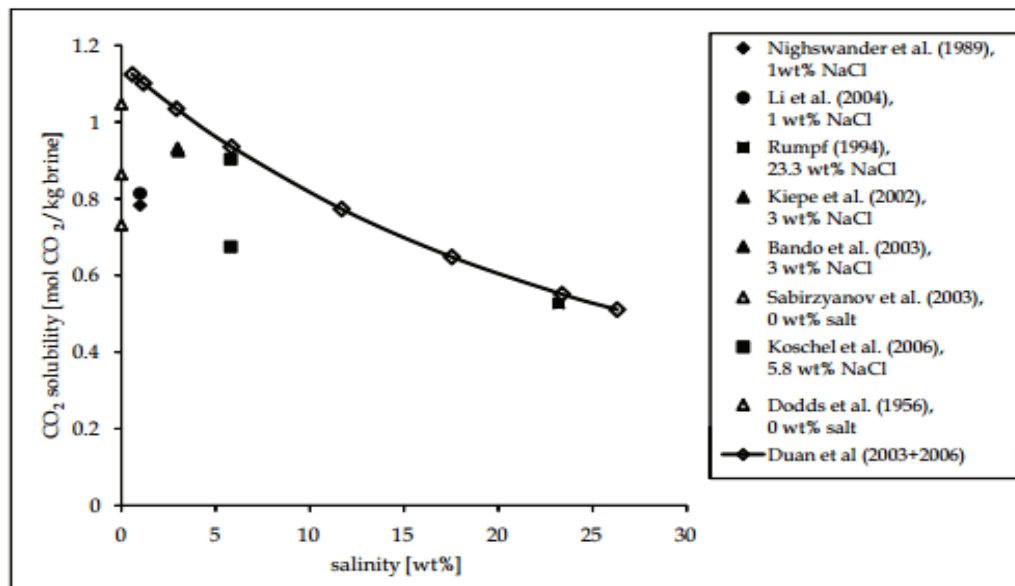


Figure 6: CO_2 solubility with different concentration of brine

(Source: Duan and Sun, 2003)

2.4.3 Capillary back flow pressure in CO₂ brine interaction

When CO₂ is injected into the saturated core and mixes with brine, the equilibrium of CO₂ is disturbed. Flow of CO₂ inside the pore is dependent on capillary backflow pressure. Pressure difference created between CO₂ and brine interface is capillary back flow pressure during CO₂ brine interaction.

Mathematically it can be represented by Laplace-Young equation:

$$P_c = 2\sigma \cos \theta / r$$

Where,

P_c is capillary backflow pressure; σ is the interfacial tension between CO₂ and the aqueous phase, θ is the contact angle; r is the radius of the pores.

Capillary back flow increases if pore throat is small as it is inversely proportional to the radius of the pore. Muller et al. (2009) and Peysson et al. (2014) found that capillary back flow leads to salt precipitation near inlet and decreases injectivity. However, the exact conditions for capillary-driven backflow have not been understood and experimental proof is very limited.

2.4.4 Rock Properties

Sandstone are sedimentary rocks formed by the compaction of sand grains under pressure for many years. Sand grains carried by rivers, lake deposits etc can get accumulated under pressure for millions of years. Cement gets precipitated and it binds those sand grains to form compact sandstone rocks.

Sedimentology of sandstone:

Matrix: It consists of fine materials that are present inside the pore spaces between the grains.

Cement: Cement comes as a result of mineral precipitation which then binds the grains together to compact it.

Mineralogy:

Quartz and feldspar are main mineral constituents forming sandstone rock. Quartz is physically hard and insoluble in nature. Quartz is found in abundant quantity in sandstone rock. Table 2 shows mineral composition of Berea sandstone provided by Chevron Oil Field Research Company.

Table 2: Mineralogical composition of Berea sandstone

| Mineral | Berea sandstone |
|--------------|-----------------|
| Quartz | 86 |
| K-feldspars | 5 |
| Calcite | 1 |
| Dolomite | 1 |
| Clays | 7 |
| Total | 100 |

CHAPTER 3: COLLOIDAL TRANSPORT IN POROUS MEDIA

3.1 Definition and Characteristics of colloids

Fine particles are those particles having size of the order of 1 micron which can be inorganic, organic or biological in origin (Khilar and Fogler, 1998). Group of these fine particles having charge is termed as colloids. These colloids could be found in large range in subsurface environment (McCarthy and Zacchara, 1989). Due to various factors such as hydrologic, geochemical, and microbiological processes these particles can be released (Nyhan et al., 1985; Gschwend and Reynolds, 1987; McCarthy and Zacchara, 1989; Ryan and Gschwend, 1990; Ouyang et al., 1996).

Typical characteristics of colloids are listed below:

- Colloids are mixture of solvent and suspended particles.
- Particles are difficult to see with naked eyes, but they are larger than molecules.
- Colloids remain in suspension against force of gravity.
- They have good absorption capacity since finely divided particles have larger surface area exposed.
- Colloids have the ability to scatter light.

Colloids can be classified into sol, emulsion, foam and aerosol.

1. **Sol:** If solid particles are suspended in a liquid.
2. **Emulsion:** Suspension between two liquids.
3. **Foam:** Foam consists of gas particles trapped in a solid or liquid suspension.
4. **Aerosol:** Solid or liquid particles dispersed in gas.

3.2 Factors affecting transport of colloids in porous media

Transportation of colloids is mainly affected by physical and chemical processes such as advection, diffusion, dispersion etc. Depending on size and distribution of pores, size and concentration of colloid entrapment or piping occurs (Khilar and Fogler, 1998). Colloidal transport may occur in larger pores,

and colloid retention may occur at pore throat. Colloids that are retained in smaller pore throats decrease effective pore size and contribute to permeability impairment (Bradford et al., 2002).

If porous media have small pore constriction size and low coordination numbers, there is high probability of entrapment of fines (Khilar and Fogler, 1998). This phenomenon is likely in consolidated porous cores such as Berea sandstone. Size of colloids should be smaller than pore constriction to avoid plugging. Piping can occur if size of colloids is much smaller than pore throats. Herzig, 1970; Gruesbeck, 1982 found mechanism for plugging, piping or other possible deposition based on ratio of size of fines to size of pore constrictions. Figure 7 shows entrapment of fines due to surface deposition, multiparticle bridging and size exclusion. From this figure, we can infer that surface deposition reduces cross sectional area of the pore throat. Multiparticle bridging and size exclusion results in complete plugging of the pore throat.

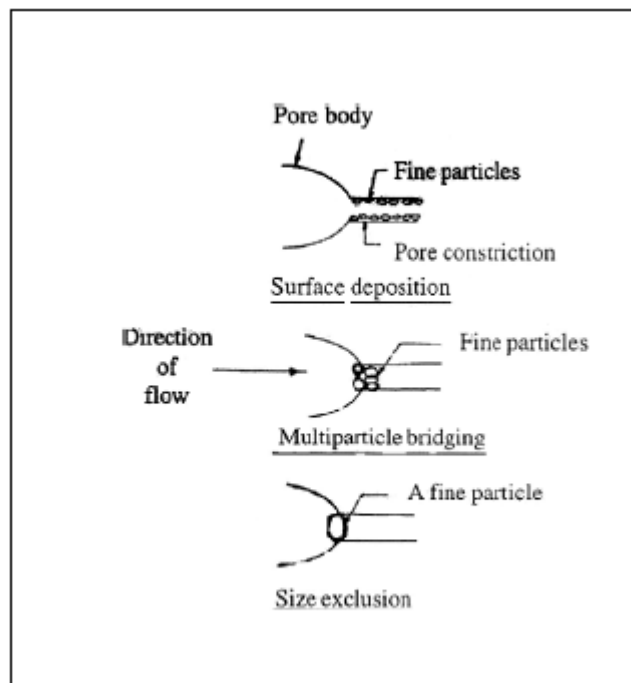


Figure 7: Entrapment of fines at pore constriction (Source: Sen, 2001)

Concentration of fines can affect transport in porous media. According to Khilar and Fogler, 1998, if ratio of size of fines to size of pore constriction is in between 0.01 to 0.1 then concentration of fines is considered important parameter for fines migration.

Flow velocity also plays an important role during migration of colloids in porous media. Muecke, 1979 said that small particles can easily form bridges at pore constriction. If flow rate is higher, force acting on these bridges is also higher and consequently there is higher probability of breaking of these bridges.

Nature of colloids can affect transport mechanism. Colloids may coagulate with each other and increase in size which can plug the pore throat. Wettability alteration can occur inside porous medium during injection of different brines and gases and can affect transport of colloids. Ionic strength of salt systems, charges carried by colloids are the colloidal conditions that can affect fines migration (Khilar and Fogler, 1998). Magal et al., 2011 studied impact of salinity on colloid transport and found that colloidal transport decreases with increasing ionic strength of the natural saline solutions. They also found that for single salt systems, rate of colloid deposition is constant above certain value of ionic strength.

3.3 Effects of colloidal transport on well Injectivity

Colloidal transport in porous media can cause drastic change in permeability of the reservoirs (Cerdeira 1987). Several researchers have studied implications of colloidal transport on natural porous media (Ochi et al., 1998). Many of these are concerned with permeability reduction due to fines migration. Researches from Khilar and Fogler, 1998 have reported that during this transport, there is retention of particles near injection and production wells. Particles retained can block the way of injected fluid and cause permeability decline. If concentration of colloids is very high, it can form filter cake inside the porous media. Deep bed filtration model has been topic of extensive research to quantify the effect coming from the formation of internal filter cake. Filter cake can also be formed outside the porous media just in front of inlet. This filter cake can act as barrier in the transport of smaller particles as well. In CCS there is combined effect of permeability reduction due to salt precipitation and colloidal transport. As explained previously there is salt precipitation near inlet in CCS resulting in injectivity loss which is again combined to injectivity loss due to colloidal transport.

3.4 Reinjection of CO₂ in CCS

CCS system needs cost and advanced technology to be implemented. There are some fields where CCS was decided to be implemented and failed later on. After years of delays and due to high costs,

plan to capture 1 million tonnes of CO₂ per year was halted in Mongstad, Norway. Snøhvit field where CO₂ injection carried out also experienced problem with leakage of CO₂, however it came into operation after technical improvements.

There are two main reasons that CO₂ capture can be halted for some years. Technical and Market issues. Once CO₂ injection is started, industries start to experience technical difficulties. In this context, there are some fields where CO₂ was injected and now it is halted. One example is In Salah Oil field in Algeria where CO₂ injection was started in 2004 and was suspended in 2011 due to issue about seal. These fields are potential sites for CO₂ reinjection in future with technological improvements.

Oil and gas industries can suffer in poor market conditions which motivate them to halt CCS technology. When market becomes better industries can be motivated to invest in CCS technology. If industries decide to use new field for CO₂ injection in future, they have to do work from initial level i.e from seismic survey. If they decide to use those fields which were abandoned in past, they already have a lot of geological and other relevant information.

CO₂ reinjection is not popular these days however it is likely to be possible in future. Before starting CO₂ reinjection, proper assessment of geological conditions of storage site, effect of fines and mineral present in the reservoir is important. This paper focuses on creating scenario for CO₂ reinjection after time period of 100 days.

CHAPTER 4: PRE-EXPERIMENTAL WORK

4.1 Mineral dissolution in CCS: A laboratory approximation of the problem

A lot of research has been conducted to study mineral precipitation after CO₂ injection. Many of them are limited to low pressure and temperature range. However, in real reservoir system low temperature and pressure is not likely to be favourable. Hangx, 2005 conducted experimental research to find the amount of calcite precipitation in calcite rich sandstone rock as shown in figure 8.

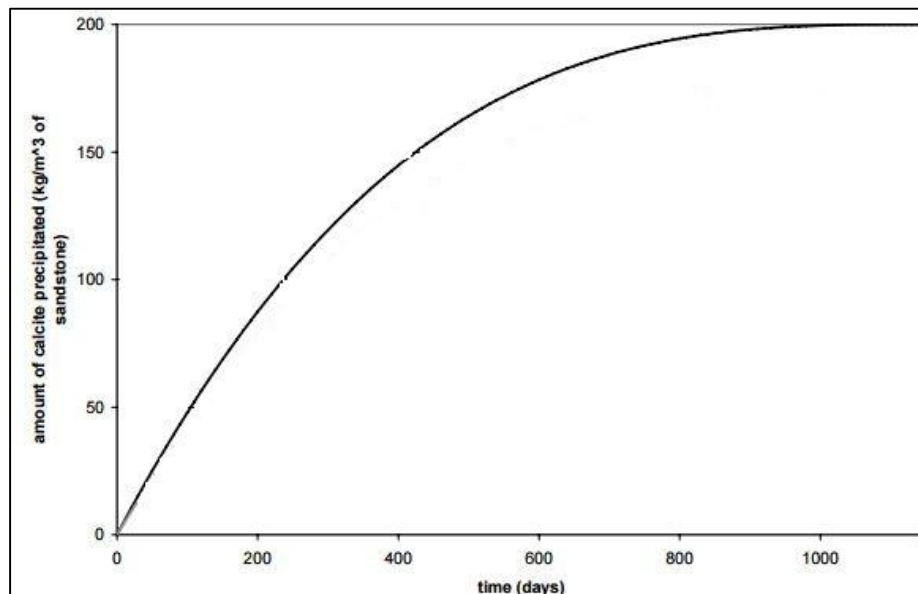


Figure 8: Calcite precipitation with time

(Source: Hangx, 2005)

Figure 8 shows amount of calcite precipitated with time due to subsurface mineralization. This result is based on reaction between sandstone rock containing 20 % Anorthite by volume at a temperature of 50 degree and CO₂ pressure of 100 bar. According to this figure, maximum 200 kg of calcite can be formed after 1000 days of CO₂ storage and then a plateau is reached. Reaction between host rock and CO₂ continues as long as CO₂ and Anorthite is available. During CO₂ injection, CO₂ is available in sufficient amount so it is not rate limiting factor. On the contrary, Anorthite content in the rock starts

to decrease slowly with time after reaction with injected CO₂ and it can be rate limiting factor in a long term. This results amount of calcite precipitation to be constant as shown in figure 8.

For CO₂ reinjection scenario, 100 days was taken as reinjection period. According to figure 8, after 100 days 49kg/m³ of calcite is precipitated in this reservoir. If it is decided to reinject CO₂ in reservoir after 100 days, calcite particles present in the reservoir will come into the flow stream and affect CO₂ injectivity. All these precipitated calcite may not be fines and cannot come into flow stream. But if all these particles are fines and come to flow stream during CO₂ injection, maximum injectivity loss could be determined. This paper focuses on maximum injectivity loss possible during CO₂ reinjection. So, all precipitated calcites are considered fines which can affect CO₂ injection.

This reinjection scenario created is bounded by certain limitations. Berea sandstone core used in this experiment have different mineral properties and may not precipitate exactly same amount of calcite as calculated by Hangx, 2005. So for the purpose of reinjection scenario, Berea core is only considered a porous media.

4.2 Selection of Experimental materials and conditions

4.2.1 Sandstone Rocks

Berea grey core having length of 20 cm and diameter of 3.81 cm bought form Kocurek Industries, USA was used during the experiment. This core was selected as it is homogenous and are used in different experimental research. Characteristics of this core is presented in table 3.

Table 3: Properties of core provided from manufacturer

| | |
|--------------------|------------|
| Brine Permeability | 105 mD |
| Gas Permeability | 280-350 mD |
| Porosity | 18% |

4.2.2 Formation Brine

Salt with composition given in table 4 was used to make 2 litres of formation water.

Table 4: Composition of formation water for 2 litres of solution

| Salt | Weight(gram) |
|--------------------------------------|--------------|
| NaCl | 154.8 |
| Na ₂ SO ₄ | 0.26 |
| KCl | 0.84 |
| MgCl ₂ .6H ₂ O | 7.12 |
| CaCl ₂ .2H ₂ O | 43.5 |
| SrCl ₂ .6H ₂ O | 4.5 |

When particle suspension was diluted with formation water, particles aggregated and reacted with formation water. Reaction occurred due to the presence of sulphate ion in formation water. As a result it was problem to push particle suspension into the core. To reduce this complexity, NaCl brine with same ionic strength of formation water was used to dilute particle suspension in this experiment. Calculation is as shown:

Table 5: Calculation of molarity

| Salt | Weight(gram) | Mol. Weight (g/mol) | Molarity (M)= n/litre |
|--------------------------------------|--------------|---------------------|-------------------------|
| NaCl | 154.8 | 58.44 | 1.3244 |
| CaCl ₂ .2H ₂ O | 43.5 | 146.98 | 0.1479793 |
| KCl | 0.84 | 74.55 | 5.634*10 ⁻³ |
| MgCl ₂ .6H ₂ O | 7.12 | 203.211 | 17.519*10 ⁻³ |
| SrCl ₂ .6H ₂ O | 4.5 | 266.53 | 8.442*10 ⁻³ |
| Na ₂ SO ₄ | 0.26 | 142.04 | 0.915*10 ⁻³ |

We know,

Ionic Strength,

$$(\mu) = \frac{1}{2} \sum_{i=1}^n C_i Z_i^2$$

Where C = Molar concentration of salts and Z is its valence.

Substituting the values, we get,

$$\mu = 1.8545179 M$$

NaCl Brine with same ionic strength: -

$$\mu = 1.8545179 M$$

Valence = 1

Concentration = x molar (supposed)

$$\text{So, } 1.8545179 = \frac{1}{2} (2x)$$

$$\therefore x = 1.8545179$$

Then, number of moles in litres = 1.8545179

Therefore,

$$\text{Weight required} = n * \text{Molar Weight}$$

$$= 58.44 * 1.8545179$$

$$= 108.378 \text{ gram in 1 litre}$$

$$\therefore \text{Weight required in 2 litres} = 216.756 \text{ grams}$$

4.2.3 Preparation of brines

216.76 g of NaCl was weighed and poured into a conical flask containing 2 litres of distilled water. Solution was stirred with magnetic stirrer for about 1 hour and then filtered using 0.22 micron filter paper. This is NaCl brine whose ionic strength is same as ionic strength of formation water. In this way 108.38 g/l brine was prepared. It is named high salinity brine in this work.

Other concentration of brines was prepared using same process. For salinity test, brine of lower concentration was prepared using similar method. Concentration was reduced by half i.e. 54.19 g/l NaCl brine is called lower concentration brine in this work.

4.2.4 Colloidal Suspension

AERODISP W640ZX from Evonic Industries (Germany) containing Al_2O_3 particle suspension with properties shown in table 6 was used in this experiment.

Table 6: Properties of Colloidal Suspension

| Properties | Value | Unit |
|--|--------------|-------------|
| Al ₂ O ₃ content | 39-41 | % |
| pH value | 6-9 | |
| Density at 20 degree | 1.39 | g/cc |
| Particle size | 80 | Nm |
| Colour of particle suspension | Milky white | |

Considering only physical properties, this alumina particle was used instead of calcite. However, volume of colloidal suspension required was calculated on the basis of required amount of calcite. This replacement of calcite by alumina was done ignoring possible interaction between core, fluid and injected CO₂.

Calculation was done to find required volume of colloid to be diluted. According to the calculation, if core is fully saturated with 85.85 ml colloidal suspension diluted with high salinity brine to make 1 litre solution, then core will contain 49 kg/m³ (0.049 g/cc) of alumina particle.

Required calcite precipitation = $49 \text{ kg/m}^3 = 0.049 \text{ g/cc}$

To make 1 litre suspension mass of calcite required = $0.049 * 1000 = 49 \text{ g/litre}$

Using density and mass of calcite, volume of calcite was calculated to be 18.081 ml. Then volume of brine was calculated to be 981.918 subtracting volume of calcite from 1000 ml. Density of brine was measured in lab by densitometer. From this mass of brine was calculated to be 1053.206 g. These calculations are shown in table 7.

Table 7: Calculation of calcite volume and mass of high salinity brine

| | Calcite | Brine |
|-----------------------|---------------------------------|--|
| Mass (gm) | 49 (used from precipitation) | 1053.206 (calculated) |
| Density (g/ml) | 2.71 | 1.0726 (measured) |
| Volume (ml) | 18.081 (calculated) | 981.918 (total volume – volume of calcite = 1000 – 18.081) |

Now,

$$\text{Concentration of calcite particles } \left(\frac{w}{W}\right) = \frac{\text{mass of calcite}}{(\text{mass of calcite} + \text{mass of brine})} = 4.45$$

Table 8: Calculation of desired concentration of particles

| | |
|--|--------|
| Density of colloidal solution measured (g/ml) | 1.39 |
| % composition of particles(provided) | 40 |
| Measured density of brine (g/ml) | 1.0726 |
| Calculated desired % W/W of particles in brine | 4.45 |
| Desired Volume of solution (ml) | 1000 |

Required volume of colloidal solution (ml) to be diluted

$$= \frac{\left(\text{Desired volume of solution} * \text{Density of brine} * \left(\frac{\text{Desired \% } \frac{w}{W} \text{ of particles in brine}}{100} \right) \right)}{\left(\frac{\% \text{ Composition of particles}}{100} * \text{Density of colloidal solution} \right)}$$

=85.85 ml

Thus 85.85 ml of colloidal suspension was diluted in high salinity brine to make total volume of 1 litre. Diluted suspension was well stirred in magnetic stirrer for more than 12 hours to make stable suspension. After that it was immediately used and new suspension was prepared for another set of experiment. According to calculation above, if core is saturated with this suspension, core will be representative like containing 0.049 g/cc of calcite particles. 0.049 g/cc calcite represents calcite precipitation after 100 days of CO₂ injection.

4.3 Key Parameters

Density: Density is defined as mass of solute per unit volume of the solution. Density of formation water, NaCl brine was measured using densitometer.

Pore Volume and Porosity

Porosity is the measure of ratio of volume occupied by pores to the total volume of the porous media. It gives a measure of the space in the rock where fluids can be stored.

Permeability measures the ability of the rock to allow the fluid to pass through it. Permeability of any rock depends on the porosity. In addition to that connection of the spaces inside the porous media is an important factor that can affect permeability.

Average pore volume and porosity of Berea core was calculated as:

Density of formation water (ρ) = 1.0662 g/cc

Length of core = 20 cm

Diameter = 3.81 cm

Therefore, Total Volume (V) = 228.0183656 cm³

Pore Volume (PV) = Wet mass - Dry mass / Density of formation water

Porosity (ϕ) = PV / Total Volume

Table 9: Calculation of Pore Volume and Porosity

| | Berea 1 | Berea 2 | Berea 3 | Average |
|-----------------|---------|---------|---------|---------|
| Wet mass (g) | 520.55 | 524.1 | 520.05 | |
| Dry mass (g) | 472.75 | 476.22 | 472.36 | |
| PV(cc) | 44.832 | 44.907 | 44.729 | 44.823 |
| Porosity | 0.1966 | 0.1969 | 0.1962 | 0.197 |

4.4 Error Analysis

Errors are introduced during measurement. True value of a quantity is never known, so this term is replaced by most probable value (MPV) which is an estimate of true value. Difference between MPV and measured value is known as error. Errors are inevitable during measurements (Taylor, 1982) so it is necessary to do error analysis during measurements.

4.4.1 Types and nature of errors

Personal Errors: Personal errors or blunders occurs due to carelessness or limitation of observer during experiments or calculations. These errors can be of larger magnitude which has high influence in final result. These errors should be exposed by repeating experiments with carefulness and having some cross check during experiment.

Systematic Errors: Systematic errors can occur due to personal, instrumental reasons. This type of error follow some mathematical or physical law and can be exposed by some functional relationship. It tends to remain constant in magnitude and tends to accumulate, so it is also known as cumulative error. Proper calibration of instruments and using better techniques during measurement are treatment procedure of systematic errors.

Random Error: Random errors are small errors which still remain in measurement data after systematic and personal errors are removed from data. Random error follows law of statistics and probability. They cannot be avoided entirely in measurements, but can be minimised by taking redundant observations.

Accuracy and Precision: Accuracy is the degree of closeness of measured value to the true value. Accuracy is affected by both random and systematic errors. Precision refers to degree of closeness of repeated measurements. Precision is affected only by random errors. Measurement may be precise without being accurate, thus both accuracy and precision are needed for reliable measurement.

CHAPTER 5: EXPERIMENTS

5.1 Experimental Objectives

Experiment was conducted with the following objectives:

- To study the effect of calcite precipitation on CO₂ reinjection using external monodisperse colloidal solution.
- To investigate the possibility of mitigating the colloid-impaired core through alternate injection of brine and CO₂.
- To study the effect of brine salinity on the resident colloids within the rock.

Overall objective of this experiment was to study the feasibility of CO₂-brine alternate injection in the core which contains fine particles and in the core without particles.

5.2 Experimental Materials and Conditions

- Weighing device was used to measure weight of salt and magnetic stirrer was used to dissolve salt during brine preparation.
- Filtration of brine was done using filter paper of 0.22 micron. Pump was used as an aid during filtration process.
- CO₂ gas from Yara Praxair company was used. According to company information purity of gas is 99.7%.
- Pump: Quiziz pump was used to inject brine and particle suspension to the core.
- ISCO pump was used to inject CO₂. Both supercritical and liquid CO₂ was injected from same pump set at 80 bar. Temperature was maintained at 20° C for liquid CO₂ while it was increased to 60° C for injecting supercritical CO₂.
- 36 cm long core holder was used to mount the core inside, oven was used to maintain temperature.
- Long coiled tubing was used in the inlet and it was fixed inside oven so that fluid passing through it can attain temperature of oven.
- Back pressure valves were connected for both brine and CO₂ injection so that experiment can run in set pressure.

- Piston cells were used during brine and particle injection and to collect effluent after CO₂ injection.
- Pressure gauges were connected to measure differential pressure, confinement pressure, pore pressure at outlet.
- LabView software was installed in computer to record data in real time. All datas were collected in excel and analysis was done by making relevant plots and tables.

5.3 Experimental Setup

Experimental setup was done in laboratory core flooding apparatus.

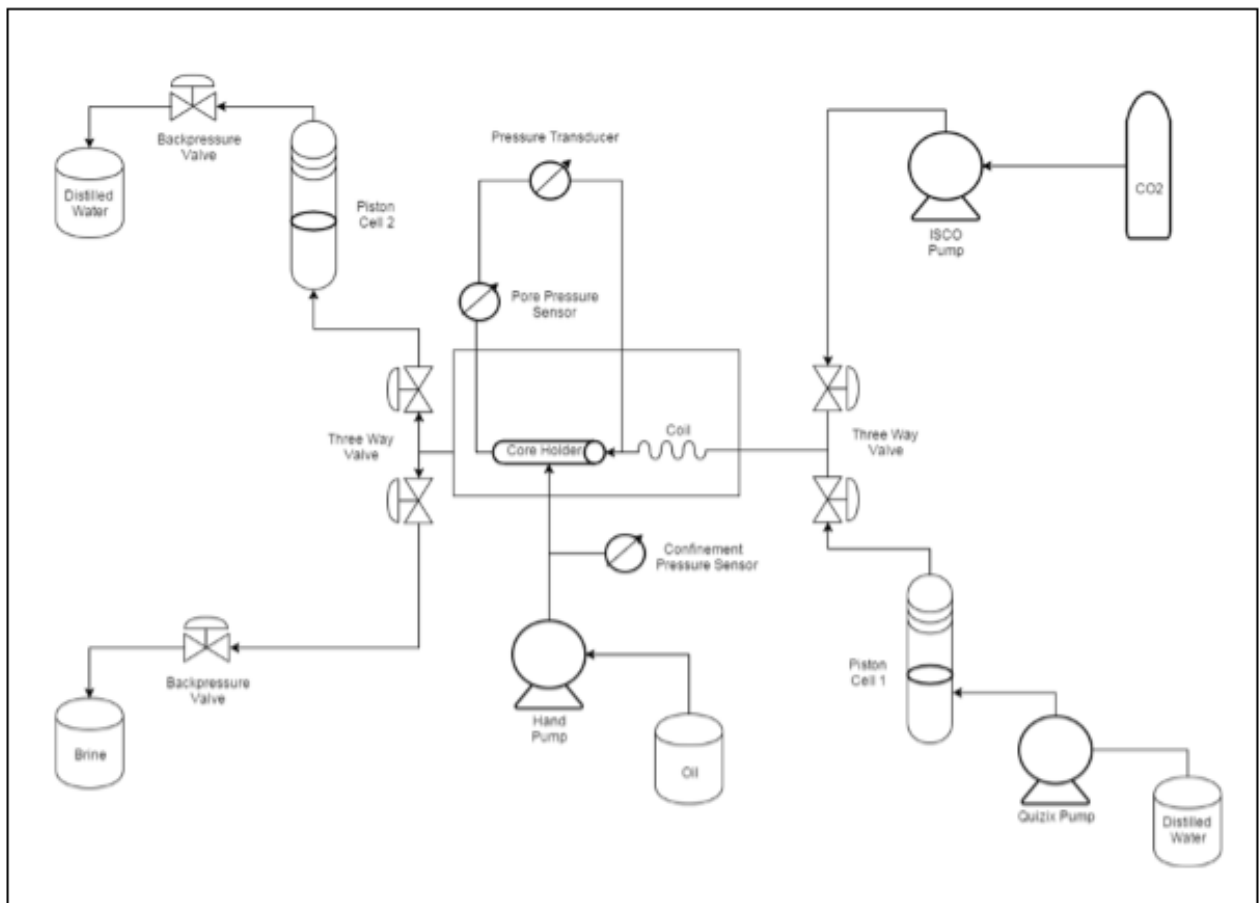


Figure 9 Schematic of lab core flooding

Figure 9 shows core flooding apparatus and setup used in this research. Quizit pump takes distilled water and delivers to bottom of piston cell 1. Brine or particle suspension kept in upper end of piston

inside piston cell then comes out of piston cell and goes to the core. Core is kept inside core holder in enclosed oven to provide necessary temperature. There is long coiled tubing near to inlet to ensure that fluid inside tubing will get enough time to attain oven temperature. Confinement is given by pumping oil from hand pump and confinement pressure is recorded by the sensor. Fluid can come out from outlet which is regulated by back pressure regulator at 7 bar. Pore sensor measures pore pressure at outlet and Pressure transducer measures pressure drop, dp across the core.

ISCO pump receives CO_2 gas from the bottle and delivers it to the core at set pressure. CO_2 from outlet of the core is sent to piston cell 2 and stored there. Piston cell 2 is initially filled with distilled water and this water goes outside when CO_2 starts to come and fill the piston cell. ISCO pump is set to operate at 80 bar.

5.4 Experimental Procedures

5.4.1 Preparation of Core

Berea grey sandstone core was first wrapped with Teflon tape. It was then covered by plastic sleeve so that CO_2 cannot leak from the core during experiment. This core holder was kept inside an oven and then connected to inlet and outlet tubing and corresponding pressure sensor tubing. Hand pump was used to provide required confinement pressure. After preparation of core the following methodology was used in lab to run the experiments:

5.4.2 Experiment1: CO_2 -brine alternative injection in the core initially saturated with particle suspension

- 1) First of all liquid CO_2 was injected through the core mounted inside core holder at 5 ml/min and permeability of core with liquid CO_2 was measured. This is initial permeability of the core where there is no particle and brine invasion.

Cycle 1

- 1) One piston cell of colloidal suspension prepared with high salinity brine was then injected at 2ml/min for about 4 hours at the pressure of 7 bar. This step was done to saturate the core with particles.

- 2) Supercritical CO₂ was injected at 10 ml/min for about 3 hours at temperature of 60° C and 80 bar.

Injection of supercritical CO₂ was done to move all producible brines out of the core and to vaporize it. As a result, core was dry and it contain fine solid particles and salt precipitated from the brine.

- 3) Core holder was disassembled and core was taken out. Filter cake was formed in the inlet of the core. This filter cake was removed and core was prepared and kept inside core holder again.
- 4) Liquid CO₂ was then injected at 5 ml/min at temperature of 20° C and pressure of 80 bar, and permeability of core was measured. This gives permeability of core which contains particles and precipitated salt.

Cycle 2

- 1) One piston cell of high salinity brine was injected at 2 ml/min into the same core.
- 2) Vaporization of this brine was done by injecting supercritical CO₂ as explained in cycle 1.
- 3) Injection of liquid CO₂ was done to measure permeability of core after brine vaporization.

Cycle 2 was done to see if brine could push out the particles and precipitated salts from the core and show some changes in the permeability.

Cycle 3

It is repetition of all steps in cycle 2. During vaporization in cycle 2, more salts are precipitated because high salinity brine was injected in first step of cycle 2. Cycle 3 was done to see if this brine could carry out those precipitated salts and improve permeability.

Cycle 4

In this cycle reduced concentration of brine was used in first step. This is half the concentration of high salinity brine.

Step 2 and 3 were vaporization of brine and permeability measurement respectively as explained in cycle3.

Reduced concentration of brine was injected to see the effect of brine salinity during CO₂ injection.

5.4.3 Experiment 2: CO₂-brine alternative injection in the core initially saturated with particle suspension to study the effect of salinity

New Berea core was prepared and kept inside core holder as explained before.

- 1) First of all liquid CO₂ was injected through the core mounted inside core holder at 5 ml/min and permeability of core with liquid CO₂ was measured. This is initial permeability of new core where there is no particle and brine invasion.

Cycle 1

- 1) One piston cell of colloidal suspension diluted with high salinity brine was then injected at 2ml/min for about 4 hours at the pressure of 7 bar. This step was done to saturate the core with particles.
- 2) Supercritical CO₂ was injected at 10 ml/min for about 3 hours at temperature of 60 ° C and 80 bar.
Core holder was disassembled and core was taken out. Filter cake was formed in the inlet of the core. This filter cake was removed and core was prepared and kept inside core holder again.
- 3) Liquid CO₂ was then injected at 5 ml/min at temperature of 20 ° C and pressure of 80 bar, and permeability of core was measured. This gives permeability of core which contains particles and precipitated salt.

In this cycle all procedures are same as done in first cycle of experiment 1.

Cycle 2

- 1) One piston cell of brine (reduced concentration) was injected at rate of 2 ml/min for about 4 hours.
- 2) Supercritical CO₂ was injected to vaporize this brine at 10 ml/min.
- 3) Liquid CO₂ was injected to measure the permeability after all brines were vaporized.

Cycle 3

All process were repetition of cycle 2.

5.4.4 Experiment 3: Experiment without particles- Brine experiment

- 1) First of all liquid CO₂ was injected through the new core mounted inside core holder at 5 ml/min and permeability of core with liquid CO₂ was measured. This is initial permeability of the core where there is no particle and brine invasion.

Cycle 1

- 1) Very high concentration of NaCl brine (300g/l) was injected to the core at 2 ml/min.
- 2) Vaporization was done injection supercritical CO₂ at 10 ml/min.
- 3) Permeability measurement was done by injection liquid CO₂ at 5 ml/min.

In **cycle 2** high salinity brine was injected and all steps of cycle 1 was repeated.

In **cycle 3** reduced concentration of brine was injected and all steps of cycle 1 was repeated.

Salt experiment was done to see effect coming from various concentration of salts. Here is no particle invasion and final permeability reading depends only on salt precipitation during brine vaporization.

5.5 Analytical Methods

5.5.1 Uncertainties in experimental data

In this experimental work, several experiments have been repeated to ensure accuracy in work. Proper care was taken during experimental setup and instrument handling. Core was carefully set inside core holder and was never touched with bare hands. Tubing connected to pressure gauge were cleaned after each experiment so that there is no pressure taping. In this way differential pressure gauge could give precise reading during experiment. Sensitivity of this pressure gauge was 0.0009 bar.

Despite these efforts, uncertainty in experimental data is inevitable. Repeated experiments of same quantity showed that there was approximately **10% uncertainty** in experimental data.

5.5.2 Averaging of the values

Averaging gives better result only when the variance is small. For experimental values for example 10, 11, 11.5, 20, averaging will not give better approximation since 20 is then an outlier. To reduce

the uncertainty, average values were taken after repetition of experiments. For example: Three different experiments were done to calculate pore volume and porosity of Berea core and average value was taken after calculation as shown in table 9.

Averaging technique was also used to find initial rock permeability. Initial permeability shown in result and discussion section is average of three values determined from three different experiments.

CHAPTER 6: RESULTS

6.1 Results and Discussion

6.1.1 Experiment1: Particles diluted with HS brine followed by HS brine injection

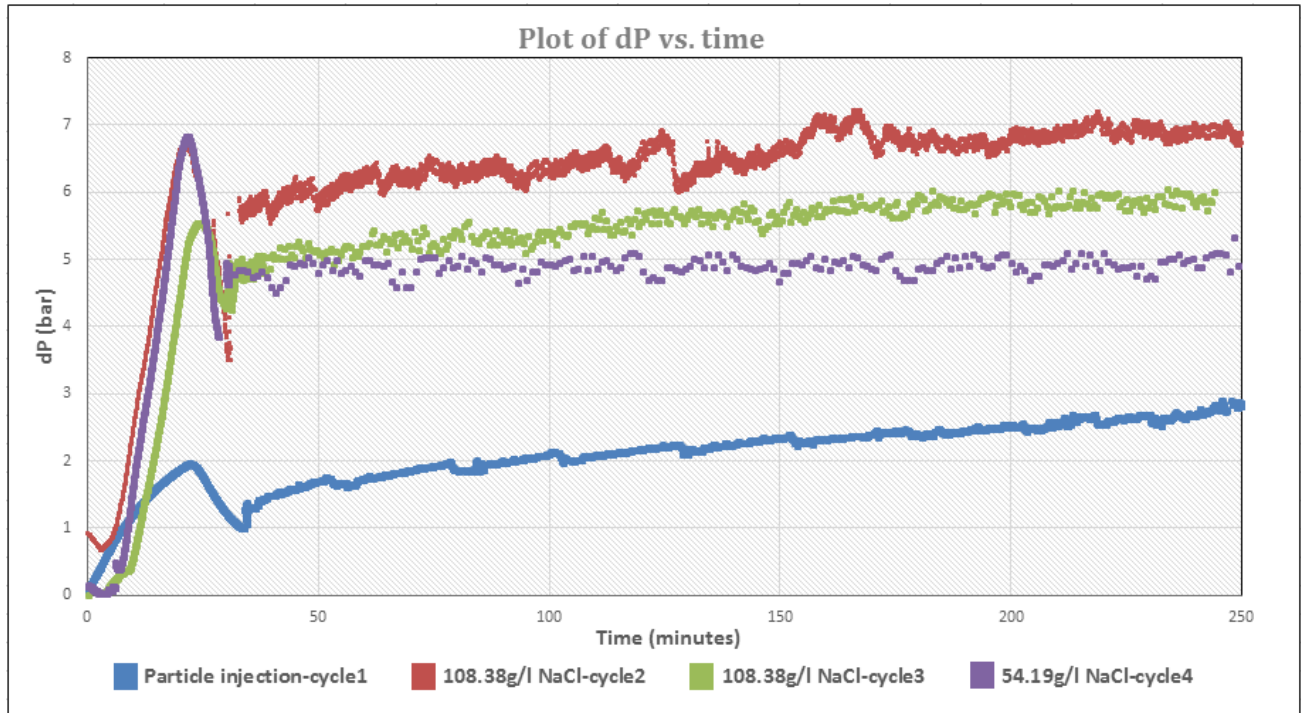


Figure 10: Plot of dP versus time during injection of particles and brines

Cycle 1

Blue curve in figure 10 represents injection of colloids diluted in HS brine. Pressure drop increases up to 2 bar and then comes down after about 1 PV was injected. After this there was breakthrough and then flow of suspension was observed at outlet. During this time, particles pass from pore body and pore throat. When particle reached to pore throat, it needs more energy to get out of the throat and to reach to another pore body. If particles are stuck at one pore throat, it will have to find an alternative way to travel and reach the pore body. During this process, particle need more energy as a result of which dp is increased. Once particle start to come out from core, dp again gets lowered. After this there is continuous injection of particles inside the core. As more and more particles are injected,

particle deposition occurs inside core which is explained by increasing nature of dp till 10 PV of suspension was injected.

Interaction between supercritical CO₂ and brine saturated porous media:

When dry supercritical CO₂ is injected inside saturated porous media, following three things are expected to occur:

- i. Displacement of brine out of the porous media
 - ii. Capillary back flow of brine towards the inlet
 - iii. Vaporization of immobile brine
-
- i. First, dry gas starts to give pressure to brine inside porous media. It then starts to push pore water out of porous media. This is similar to piston pushing water out of the cylinder. During this process, most of the water gets pushed towards outlet of the core.
 - ii. Interaction between dry CO₂ and brine creates saturation gradient before evaporation front. When capillary pressure overcomes injection pressure gradient, remaining brine inside core starts to move towards evaporation front. Water saturation inside the core is re-equilibrated as a result of this process. During this process there is also little evaporation. However it is not enough for oversaturation and thus salt does not precipitate (Peysson et al., 2014).
 - iii. When water saturation in the core reaches to irreducible water saturation, Darcy flow of brine is not dominant any more so vaporization starts. Salt gets accumulated near the inlet and gets precipitated. Vaporization process occurs near inlet and it may lead to major injectivity loss.

In figure 12 (cycle 1), it was expected that dP profile will go down significantly during movement of brine out of the core. However, in this experiment, particle was also moving with the brine. Particles can get attached to pore throat during movement which is explained previously. As a result, dP can increase for some time and then again it starts to decrease. Due to particle movement inside core, we were unable to see flat curve which was expected in the middle of the experiment. So all curves during supercritical CO₂ injection is not showing expected pressure behavior. To see pressure behavior during supercritical CO₂ injection, one experiment was done in the absence of particles which is explained later.

Permeability measurement shown in figure 13 (cycle 1) shows that core lost permeability significantly due to presence of particles.

Cycle 2

When particle injection was done in cycle1, filter cake was formed in front of the core inlet. Particle suspension of higher concentration (4.45% W/w) as shown in table 7 at the rate of 2 ml/min inside consolidated sandstone core was responsible for formation of filter cake. Filter cake formed is shown in figure 11. Because of filter cake, we were unable to saturate the core completely during particle injection. Vaporization in cycle 1 caused movement of particles along with movement of brine. That means, in this step, all other pore throats were occupied with particles which was unsaturated before. Cycle 2 started with this same core containing particles. When brine was injected (figure 10), curve of dP in cycle 2 increased to maximum value than any other curves which is result of vaporization in cycle 1. Initial rise in dP is because of rearrangement of particle inside core during brine injection which occurs until flow starts from outlet which is explained preciously. In later part of this curve, we can see horizontal pattern. At this point, concentration of particles coming as effluent was significantly reduced. Effluent looked like clear water which indicates that particles coming out of the core as effluent is now less and dominant phenomena inside core is movement of brine. This explains the horizontal nature of curve at later part.



Figure 11 Formation of filter cake during particle injection

Permeability measured after cycle 2 was 46.63 mD which is more than permeability measured after particle injection in cycle 1. During supercritical CO₂ injection in cycle 2, CO₂ was able to wash out some particles that were suspended on the wall.

According to Sbai and Azaroual, 2011, when external particles are injected into a porous medium, some particles get attached to the walls. They further added that this suspended particles remain there until electrostatic forces acting is more than hydrodynamic and gravitational force. Supercritical CO₂ injection at 10 ml/min created enough hydrodynamic force to move suspended particles from wall and bring it to the flow stream. However it was not able to wash those particles which were attached to the wall. HS brine was unable to detach particles since same salinity of brine was used to dilute particle suspension.

During vaporization in cycle 2, some more salt was deposited because HS brine was injected prior to vaporization. Permeability measurement in cycle 2 has combined effect coming from wash out of some particles and deposition of more salt inside the core. As a result there was some improvement in permeability compared to permeability reading in cycle 1 as shown in figure 13.

Cycle 3

Pressure behavior during brine injection shows similar trend in the beginning until flow begins from outlet which is explained previously. After cycle 2, some more particles are removed from core which results in lowering of dP in cycle 3 (figure 10). When supercritical CO₂ was injected, there was no washing out of particles since all hanging particles were removed during cycle 2. Instead, there was more precipitation of salt during vaporization process. This led to decrease in permeability at cycle 3 as shown in figure 13.

Cycle 4

dP is more initially than any other curves in cycle 4 (figure 10). It is because more salts were precipitated in inlet during vaporization of cycle 3 (figure 12). Since reduced concentration of brine was injected, this brine was able to deposit some salt which was precipitated in previous cycle. Continuous injection of brine led to deposition of more salt from the core. During supercritical CO₂ injection, first movable brine was pushed out of the core. That means salt concentration inside core is

reduced more during this stage. Finally vaporization starts and precipitation of salt happens near inlet. However, more salt was already pushed out of the core during first phase of supercritical CO₂ injection. As a result, permeability measurement reached to 58.09 mD in this cycle.

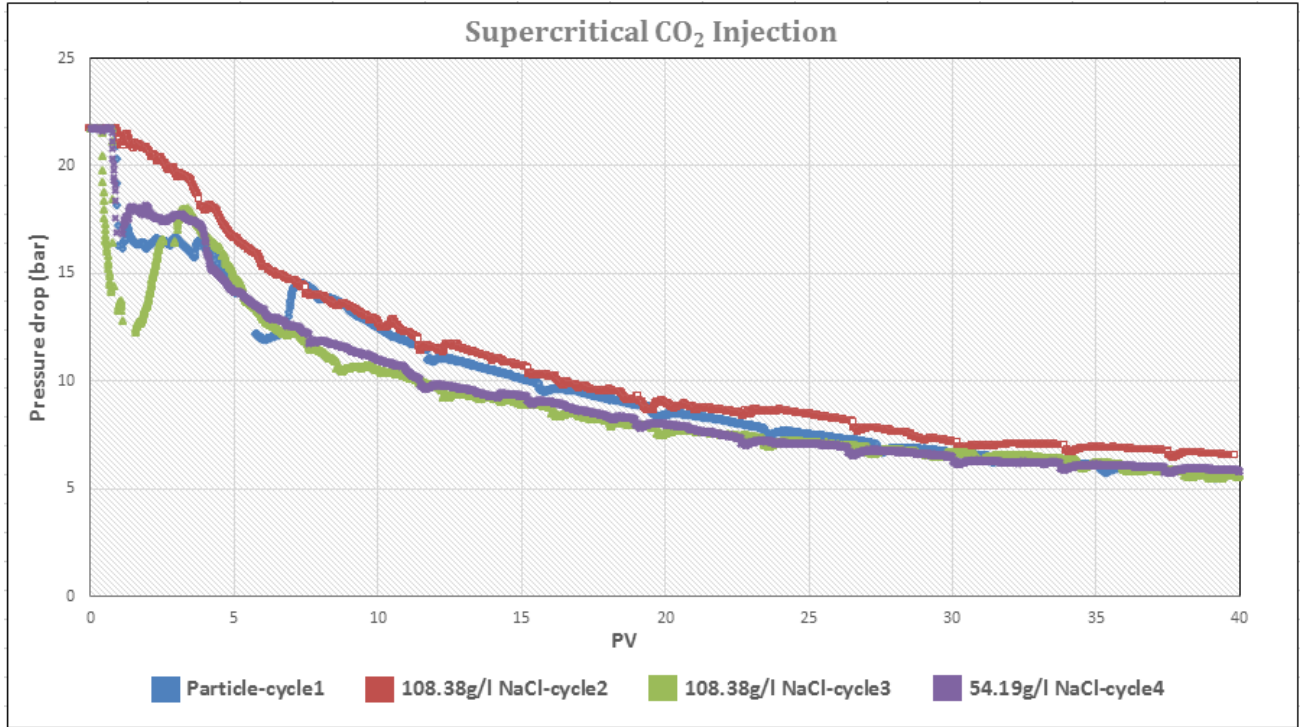


Figure 12: Injection of supercritical CO₂ to particle suspension and brines

Initial Permeability of the Core was measured with liquid CO₂ before injecting particles. Average initial permeability of the core was found to be 1300.792 mD.

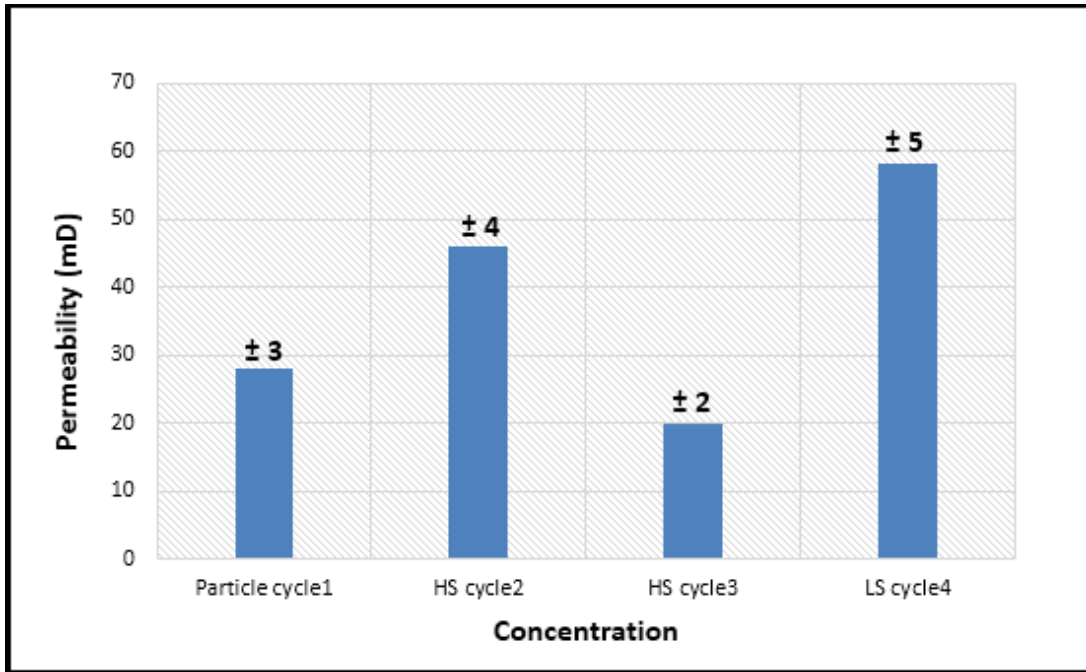


Figure 13: Permeability measurements at each cycle

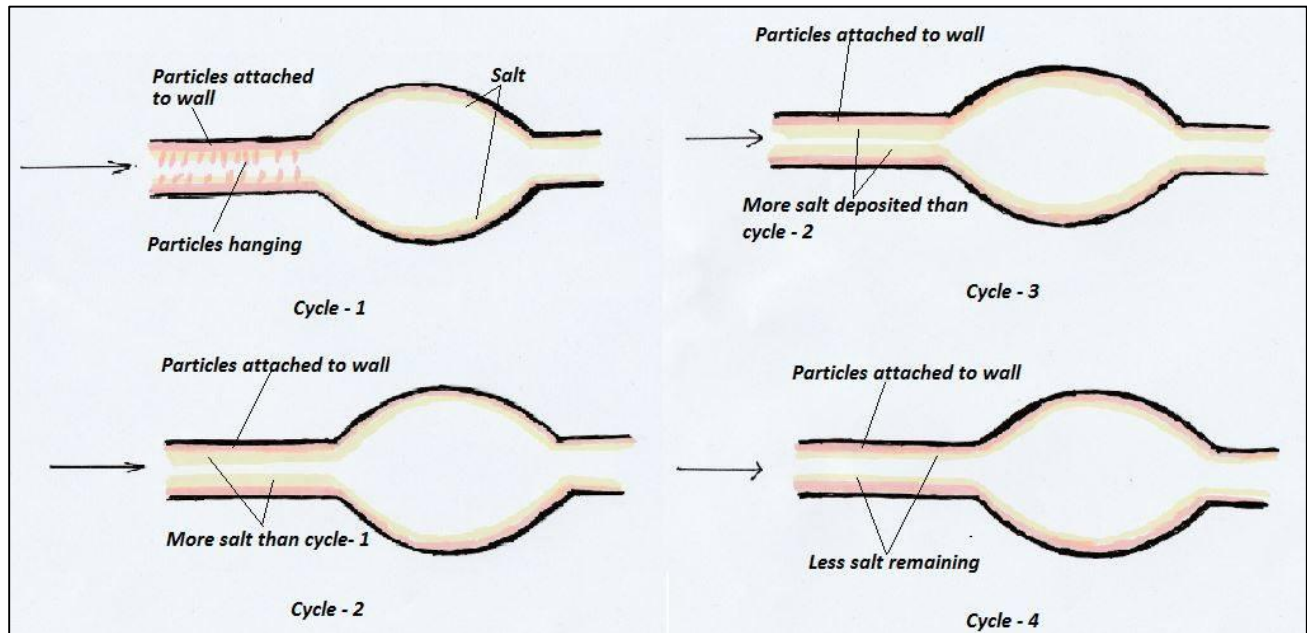


Figure 14: General sketch of each cycle

Figure 14 gives overview of particles and salt deposited after each cycle. Particles and salt concentration were changing at each cycle that was responsible for change in permeability readings. Phenomenon of deposition is already explained previously.

6.1.2 Experiment 2: Particles diluted in HS brine followed by injection of reduced brine concentration

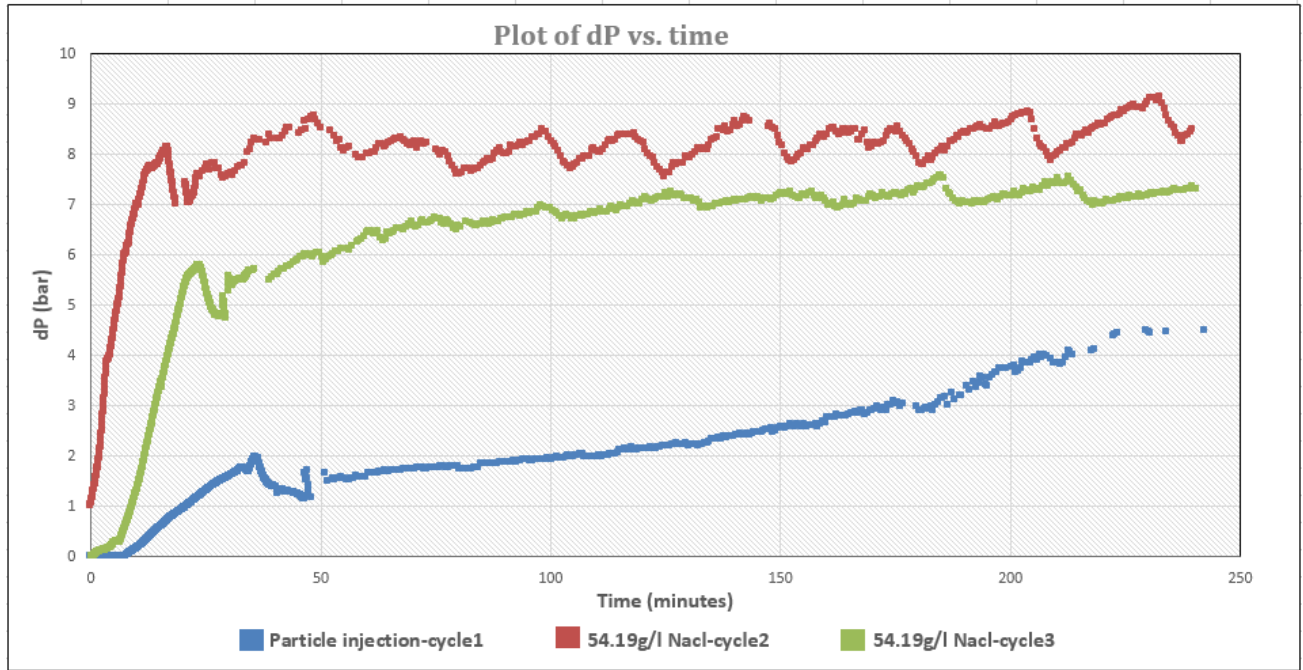


Figure 15: Pressure profile during particle and brine injection of reduced salinity

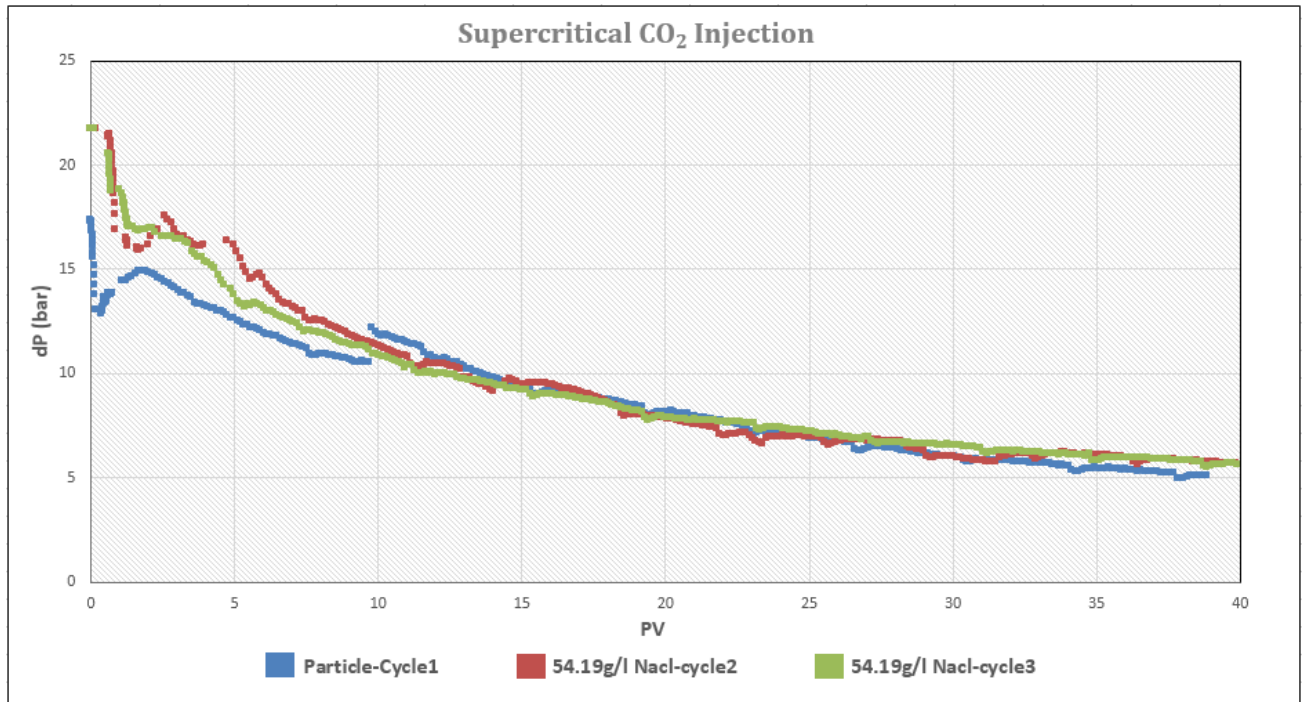


Figure 16: Supercritical CO₂ injection in particle suspension and brines

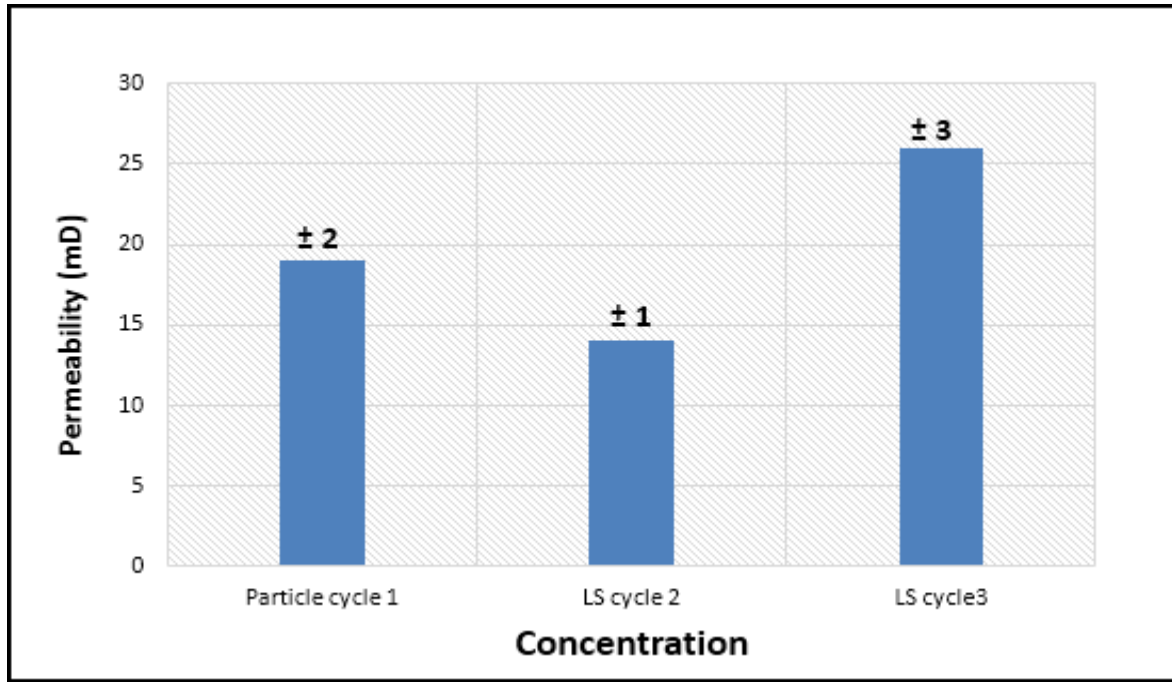


Figure 17: Permeability measurement in different cycles

Cycle 1

Particle injection, supercritical CO₂ injection and permeability measurement in cycle 1 was like repetition of cycle 1 in experiment 1. All results in cycle 1 have similar pressure behavior as explained previously in cycle 1 of experiment 1.

Cycle 2

Brine of reduced salinity i.e 54.19 g/l was injected in first part of cycle 2. This brine was carrying particle suspension out of the core as in experiment 1. However dP is increased more than in cycle 1 and it follows some different pattern (figure 15). Some salts were precipitated during vaporization of particle suspension diluted with HS brine in cycle 1. Reduced concentration of brine in cycle 2 dissolve those salts in cycle 2. Pressure behavior during brine injection in cycle 2 has combined effect of carrying particles and salts inside the core. Because of this, dP was higher and fluctuating all over during the whole experiment which was not observed in experiment 1. Effluent was clear in cycle 2 which means particles were not pushed out of the core. During injection of supercritical CO₂, particles hanging on the wall were detached since lower concentration of brine was injected previously. So

more particles came to flow stream with additional salt which plugged the pore throat and it was not displaced out of the core. As a result permeability measurement in cycle 2 was 13.90 mD which is lower than permeability measurement in cycle 1 (figure 17).

Cycle 3

Brine of same salinity used in cycle 2 was injected. As concentration of brine is not changed, it did not dissolve additional salt. When supercritical CO₂ was injected, then displacement of salt and particles started but it was not significant. During vaporization, some salt were deposited again (figure 16). Since some particles were pushed out of the core and more salt was precipitated, permeability improvement was not significant. However, it reached to 26.32 mD which is almost double as compared to permeability in cycle 2.

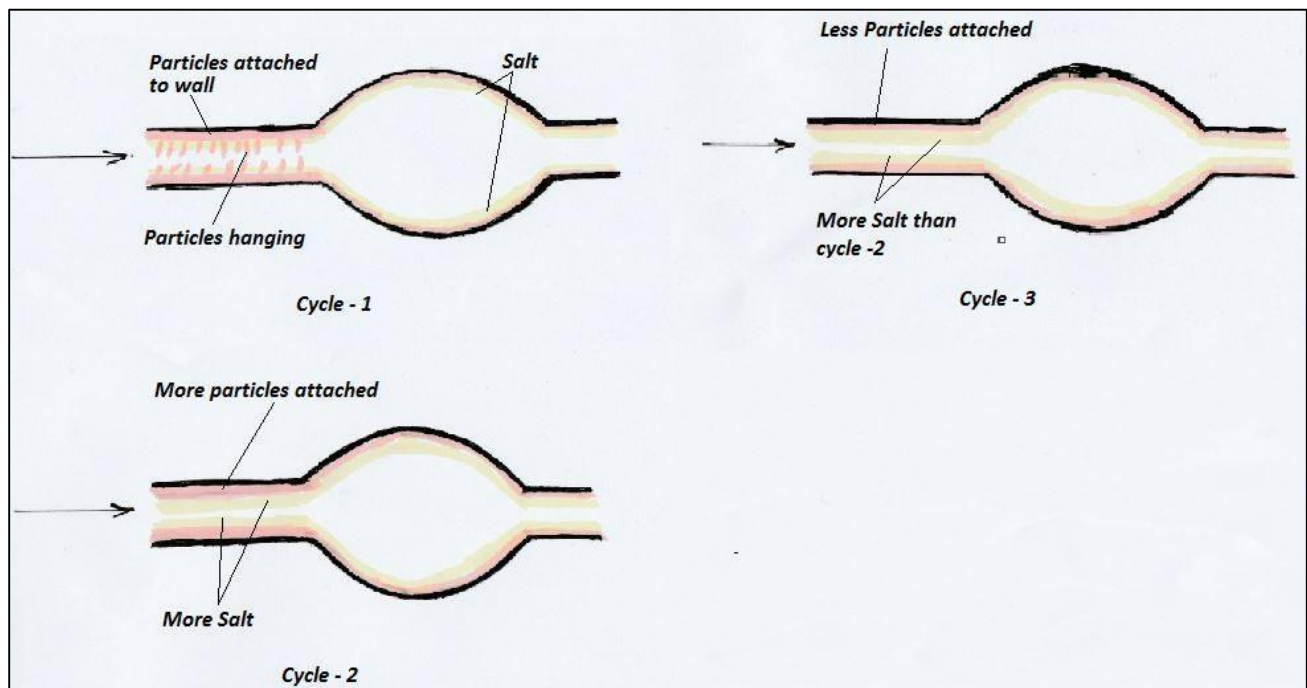


Figure 18: General sketch for each cycle during salinity test

Figure 18 shows general trend that particles and salt followed inside the core after completion of each cycle.

6.1.3 Experiment 3: Brine Experiments without Particle solution

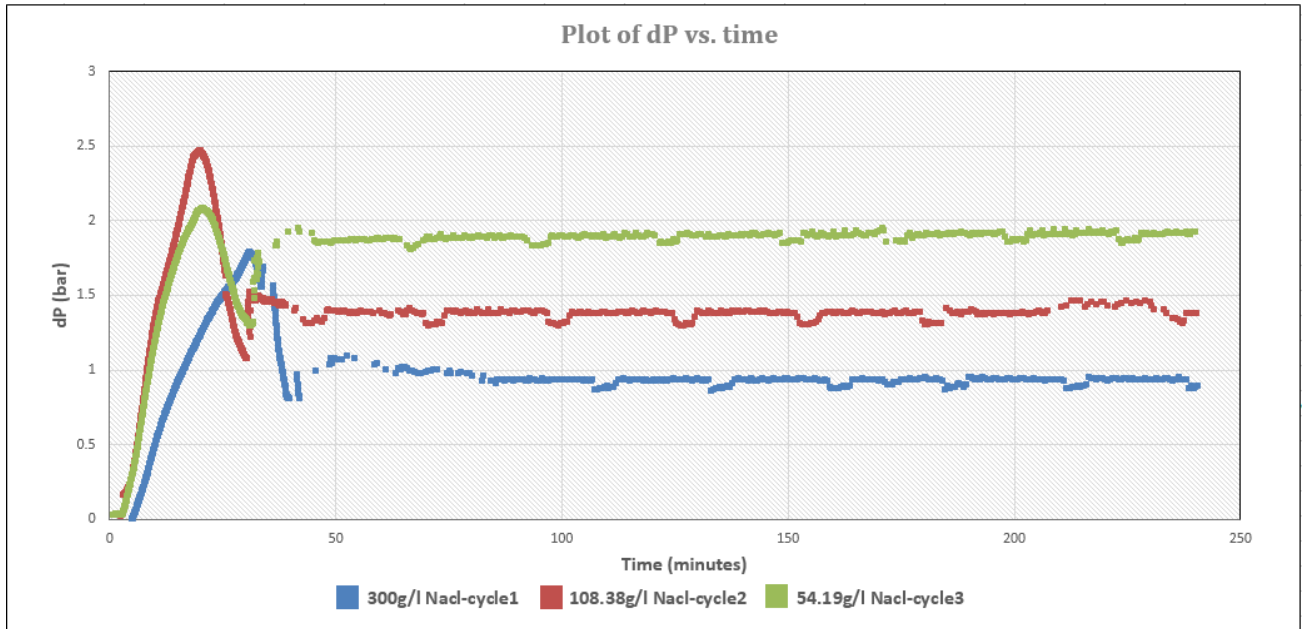


Figure 19: Pressure profile during injection of brines of different salinity

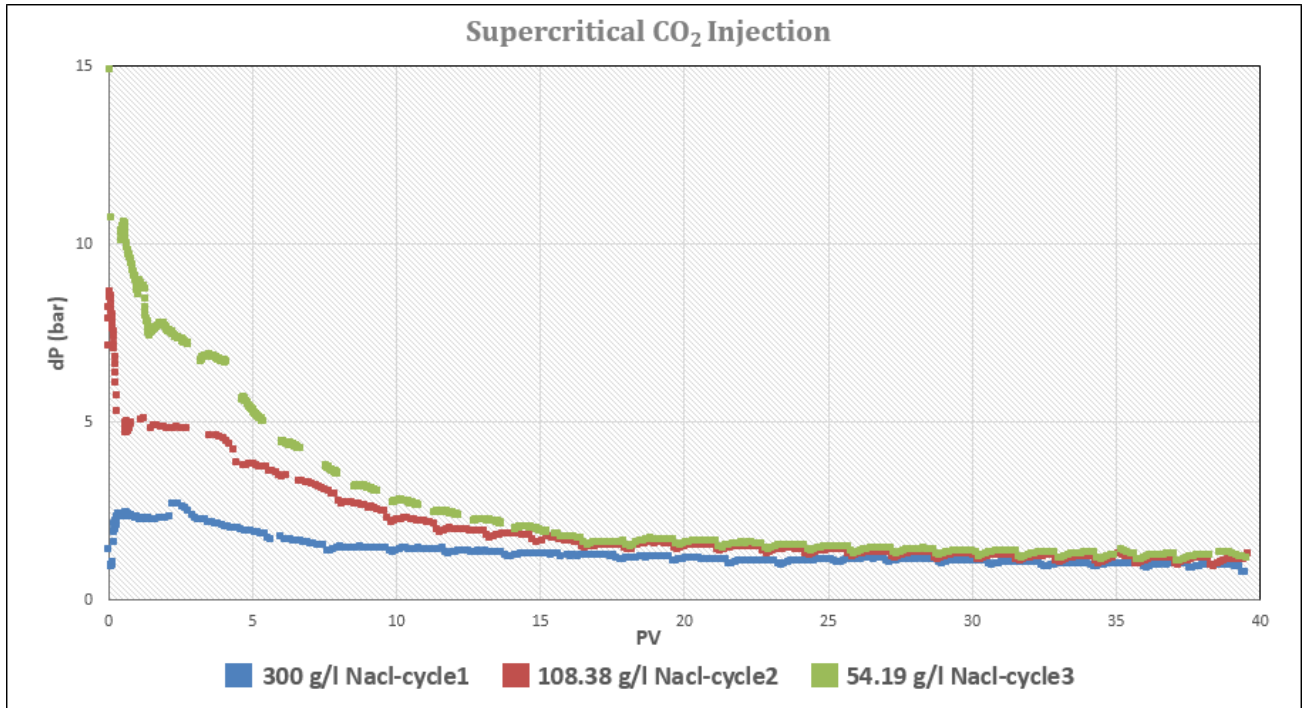


Figure 20: Supercritical CO₂ injection in different cycles of brine

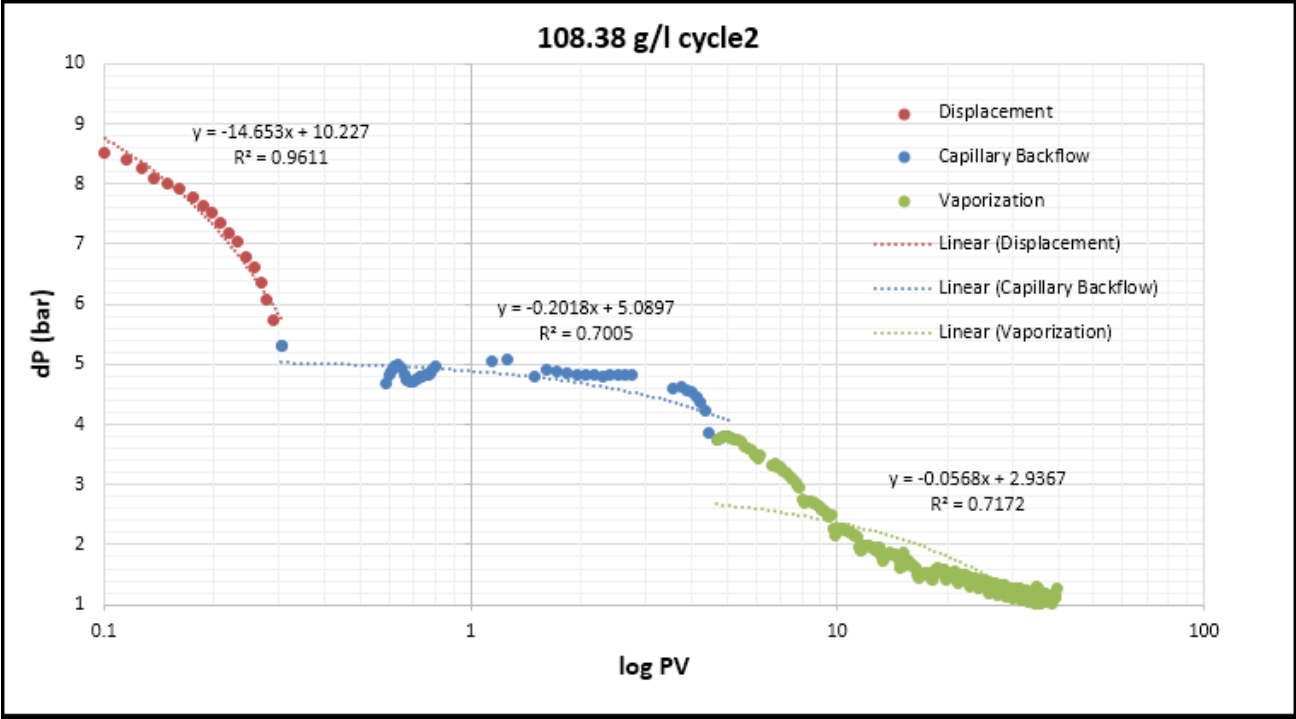


Figure 21: Semi log plot of supercritical CO₂ injection

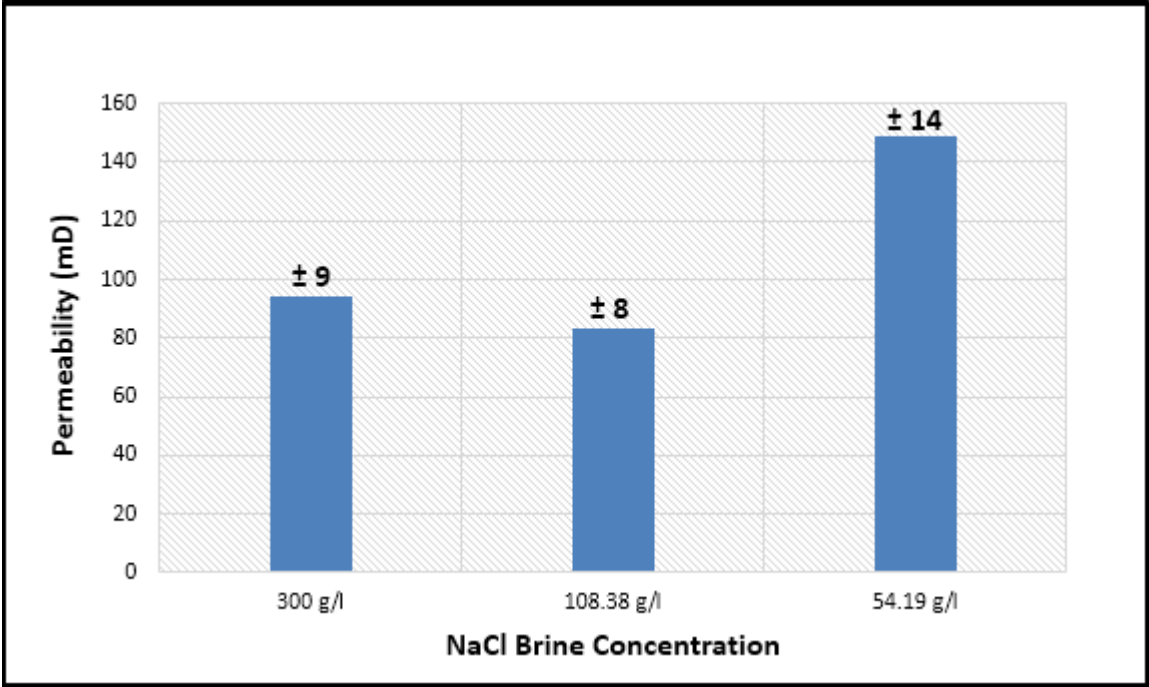


Figure 22: Permeability measurement during brine experiment

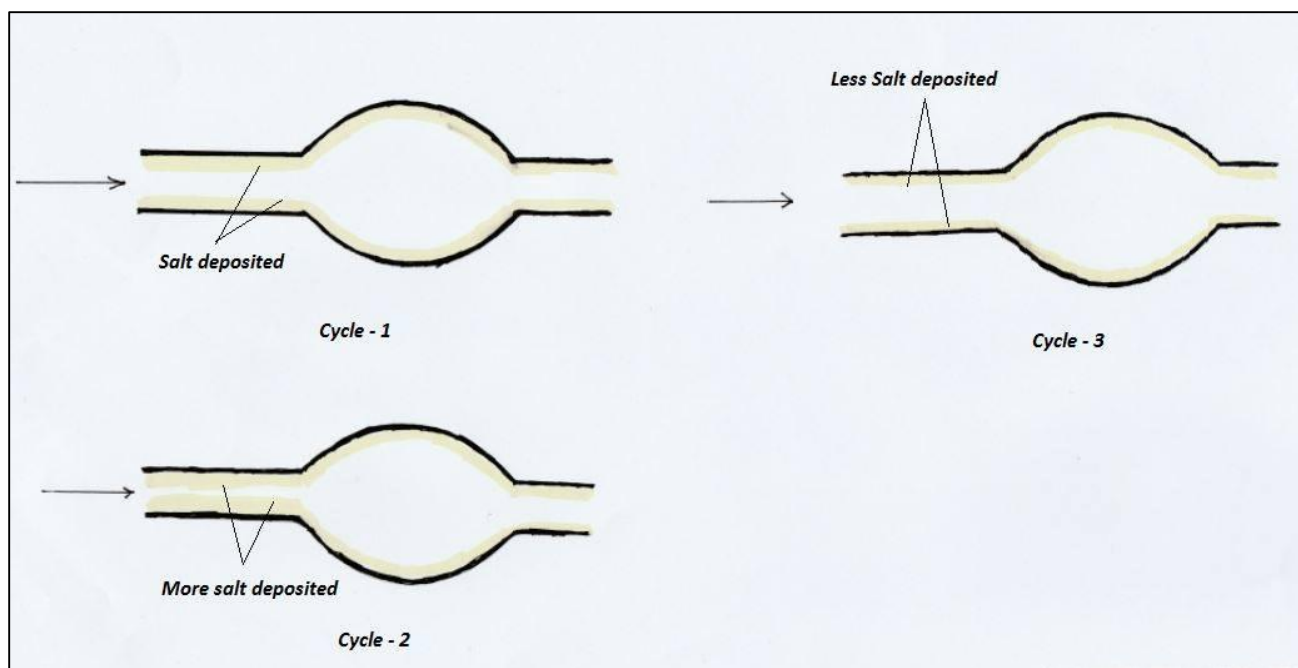


Figure 23: General sketch showing result of each cycle

Figure 23 shows concentration of salt deposited after each cycle. This figure helps to explain pattern observed at the end of injection of brine of various salinity. Explanation provided is coming below:

Cycle 1

300 g/l NaCl brine was injected to core at 2 ml/min. dP increased initially and it again came down, this was time period when brine was passing through the core (figure 19). Due to higher brine salinity, it need some energy to pass through the pre throat because of which dP was fluctuation initially. Since there is no particles, dP reached up to 1.8 bar and came down which is lower than dP seen during particle injection in previous experiments. After that pressure profile was horizontal till the end of brine injection. This indicates that brine do not need additional energy to move inside core once the flow was observed from outlet of the core. After brine injection, supercritical CO₂ was injected at 10 ml/min. Interaction of supercritical CO₂ with brine inside core followed the pressure behavior as explained previously (figure 20). There was significant pressure drop in first part which was movement of brine out of the core. dP initially was more than 22 bar and it suddenly drop down to about 2 bar after some time. This is in agreement with research done by Bacci et al., 2011, who found that most of the brine is produced in the beginning when first pore volume of dry CO₂ is injected. However, our

sensor was not designed to read higher values of dP than 22 bar and we missed to record it. In the middle part of experiment there was capillary back flow and curve went flat and salt precipitation started in last part. Only 40 PV of CO₂ injected at higher rate was not able to move all salt and plug the core completely. So, with liquid CO₂ permeability of 93.73 mD was measured in cycle 1 (figure 22).

If vaporization was done for more time, probably more salt would get precipitated and we could get even less permeability reading. Since our injection rate was higher, there was small time for evaporation. There was more displacement and less vaporization.

Cycle 2

HS brine (108.38 g/l) injected for 4 hours was not able to wash much salt out of the core. Salt was accumulated inside the core after vaporization in cycle 1. As a result pressure profile in this cycle was higher compared to pressure profile in cycle 1 (figure 19). Once outlet flow started in brine injection, pressure profile was horizontal but again it is higher than pressure profile in cycle 1. When supercritical CO₂ was injected, there was significant decrease in dp initially. This is because of brine displacement out of the core. After that there is flat part of the curve due to capillary pressure which favored back flow of brine towards inlet (figure 20). Accumulation of more salt in first cycle led to increase in capillary back flow since salt occupied pore throat and reduces size of pore throat. Capillary back flow increases when size of pore throat decreases which is explained earlier in the literature. So, precipitation increased in this phase and permeability of the core decreased to 82.73 mD.

Figure 21 is similar to cycle 2 of figure 20, but it is analysis done in semi log plot. This plot shows three different pressure gradients for three stages- brine displacement, capillary backflow and vaporization. Semi log plot can give estimation of duration of each stages during injection of supercritical CO₂ injection.

Cycle 3

Lower salinity of brine injected in cycle 3 dissolve more salt when it was passing through the core. So dP was increased than cycle 2 during the brine injection process and was stable around 2 bar (figure 19). Pressure profile during supercritical CO₂ injection started from higher value but it went to match with other curves in later part of the experiment (figure 20). During brine displacement, most of the brine which has now dissolved additional salt, was displaced out of the core which is seen by sharp

decrease in dP. After capillary back flow in middle part, there was vaporization of brine. When permeability was measured, we found significant recovery in permeability (figure 22). This is because lower salinity brine moved out more salt out of the core.

From this experiment we found that salt precipitation occurs in close vicinity of the injection well. Less value of permeability during high salinity brine injection shows that effect increases with increase in salinity of the brine. This result is in agreement with Andre et al., 2007 who found that there is more pronounced well injectivity loss in the vicinity of the injector in the presence of high salinity brine.

Giorgis et al., 2007 did simulations at very high rate of CO₂ injection and found that CO₂ can be injected with limited loss of injectivity. When rate of injection is high, evaporation process is not balanced by flow of brine. Inlet pressure gradient can overcome capillary back pressure and precipitation of salt near inlet is minimized. In this way injection loss can be minimized. This simulation result, however, has not back up from other experimental works. Our lab is not designed to inject CO₂ at such a high rate. So, injection of supercritical CO₂ at very high rate like in simulation rate as explained is still subject to research.

6.2 Conclusion

Listed below are the conclusion of this research:

- Presence of particles inside porous media can have significant impact on the permeability which can be related to maximum loss in injectivity.
- Salt precipitation occurs during the vaporization of brine present inside porous media and can affect permeability.
- Alternate injection of brine and CO₂ cannot wash out the particles present inside porous media and thus it cannot improve permeability.

6.3 Limitations and Future works

This research was carried out on the basis of literature review on mineral precipitation. Calcite precipitation used in this research was not calculated for Berea sandstone rock, but for another type of rock which have different mineralogy than Berea sandstone rock. So, this research is not representative of mineral precipitation in Berea core. We were unable to saturate the core with calculated volume of colloids since filter cake was formed during particle injection. Effluent collected was disposed without having studied the concentration of particles coming out in the effluent. So, this research is unable to calculate the amount of particles retained inside the core. Observed pressure behaviour only indicates the presence of particles but they were never quantified.

Study of different phases in the interaction of supercritical CO₂ and brine can be interesting research topic. This new research might include behaviour of brine displacement, time period of capillary back flow, study of injection pressure that can minimize effect of capillary back flow, maximum injection pressure possible during CO₂ injection without creating fractures inside the formation.

REFERENCES

- Aji, K. 2014. *The Experimental and Theoretical Study of Fines Migration in Porous Media under Particle-rock Repulsion and Attraction*. PhD Thesis. K. Aji. The University of Adelaide. Australia.
- Andre, L., Audigane, P., Azaroual, M., Menjot, A. 2007. *Numerical Modelling of fluid-rock chemical interactions at the supercritical CO₂-liquid interface during supercritical CO₂ injection into a carbonate reservoir, the Dogger aquifer (Paris Basin, France)*. Energy Conversion and Management 48, 1782-1797.
- Archer, D., Brovkin, V. 2008. *The millennial atmospheric lifetime of anthropogenic CO₂*. Climate Change, Open Access, 4 June.
- Assayag, N., Matter, J., Ader, M., Goldberg, D., Agrinier, P. 2009. *Water-rock interactions during a CO₂ injection field-test: Implications on host rock dissolution and alteration effects*. Elsevier journal, Chemical Geology, 12 February.
- Bacci, G., Korre, A., Durucan, S. 2011. *Experimental investigation into salt precipitation during CO₂ injection in saline aquifers*. Elsevier journal, Energy Procedia.
- Bradford, S., Yates, S., Bettahar, M., Simunek, J. 2002. *Physical factors affecting the transport and fate of colloids in saturated porous media*. Water Resources Research, Vol. 38, NO. 12, 1327, 31 December.
- Bacci, G., Korre, A., Durucan, S. 2011. *Experimental investigation into salt precipitation during CO₂ injection in saline aquifers*. Energy Procedia 4, 4450-4456.
- Bachu, S. 2003. *Screening and ranking of sedimentary basins for sequestration of CO₂ in geological media*. Environmental Geology, 44(3), 277–289.
- Bachu, S. 2015. *Review of CO₂ storage efficiency in deep saline aquifers*. International Journal of Greenhouse Gas Control.
- Bachu, S., Chalaturnyk, R., et al. 2012. *Building Capacity for CO₂ Capture and Storage in the APEC region*. A training manual for policy makers and practitioners, APEC Energy Working Group, June.
- Bradshaw, J., Boreham, C., Pedalina, F. 2005. *Storage retention time of CO₂ in sedimentary basins: Examples from petroleum systems*. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 541-550.

- Eiken, O., Ringrose, P., Hermanrud, C., Nazarian, B., Torp, T., Høier, L., 2011. *Lessons learned from 14 years of CCS operations: Sleipner, In Salah and Snøhvit*. Energy Procedia 4, 5541-5548.
- Fischer, S., Liebscher, A., Wandrey, M. 2010. *CO₂-brine-rock interaction- First results of long-term exposure experiments at in situ P-T conditions of the Ketzin CO₂ reservoir*. Elsevier journal, Chemie der Erde, 1 June.
- Giorgis, T., Carpita, M., Battistelli, A. 2007. *2D modeling of salt precipitation during the injection of dry CO₂ in a depleted gas reservoir*. Energy Conversion and Management, Elsevier, 2 March.
- Grude, S., Dvorkin, J., Clark, A., Vanorio, T., Landrø, M. 2013. *Pressure effects caused by CO₂ injection in the Snøhvit Field*. First break 31.
- Gruesbeck, C., Collins, R. 1982. *Entrainment and deposition of fine particles in porous media*. Soc. Pet. Engin. J., Dec., 847-856.
- Gschwend, P., Reynolds, M. 1987. *Monodisperse ferrous phosphate colloids in an anoxic groundwater plume*. J. Contam. Hydrol. , 1, 309– 327.
- Hangx, S. 2005. *Behaviour of the CO₂-H₂O system and preliminary mineralization model and experiments*. Submitted to Shell International Exploration and Production (leader CATO), December.
- Hansen, O., Gilding, D., Nazarian, B., Osdal, B., Ringrose, P., Kristoffersen, J., Eiken, O., Hansen, H. 2013. *Snøhvit: The History of Injecting and Storing 1 Mt CO₂ in the Fluvial Tubåen Fm*. Energy Procedia 37, 3565-3573.
- Herzig J., Leclerc, D., Legoff, P. 1970. *Flow of suspension through porous media - Applications to deep bed filtration*. Ind. Engin. Chem., 62(5), 8-35, 1970.
- Hosa, A., Esentia, M., Stewart, J., Haszeldine, S., 2011. *Injection of CO₂ into saline formations: Benchmarking worldwide projects*. Chemical Engineering Research and Design 89, 1855-1864.
- Hurter, S., Labregere, D., Berge, J., Desitter, A. 2008. *Impact of Mutual Solubility of H₂O and CO₂ on Injection Operations for Geological Storage of CO₂*. Schlumberger Carbon Services, Paris, 8-11 September.
- IEA Greenhouse R&D programme, 2000. *CO₂ Storage as Carbonate Minerals*. PH3/17, February.
- IEA Technology Roadmap. 2009. *Carbon capture and storage*. October.
- Iglauer, S. *Dissolution Trapping of Carbon Dioxide in Reservoir Formation Brine – A Carbon Storage Mechanism*. Curtin University, Department of Petroleum Engineering, ARRC Building, Australia.
- IPCC. 2005. *IPCC Special Report on Carbon Dioxide Capture and Storage*. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., O. Davidson, H. C. de

Coninck, M. Loos, and L. A. Meyer]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp.

Kheshgi, H. 1995. *Sequestering atmospheric carbon dioxide by increasing ocean alkalinity*. Energy, 20, 915-922.

Khilar, K., Fogler, H. 1998. *Migration of Fines in Porous Media*. Dordrecht/London/Boston: Kluwer Academic Publishers.

Klins, A., 1984. *Carbon Dioxide Flooding*, D. Reidel Publishing Co., Boston, MA, 267 pp.

Kovscek, A., 2002. *Screening criteria for CO₂ storage in oil reservoirs*. Petroleum Science and Technology, 20(7-8), 841-866.

Lebron, I., Suarez, D. 1996. *Calcite nucleation and precipitation kinetics as affected by dissolved organic matter at 25°C and pH > 7.5*. Geochimica et Cosmochimica Acta, Vol. 60, No. 15, pp. 2765-2776, 15 April.

Lindeberg, E., Bergmo, P. 2003. *The long-term fate of CO₂ injected into an aquifer*. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6).

MacCarthy, J., Zachara, J. 1989. *Subsurface transport of contaminants*. Environ. Sci. Technol., 23, 496- 502.

Magal, E., Weisbrod, N., Yechieli, Y., Sharon L., Walker, S., Yakirevich, A. 2011. *Colloid transport in porous media: Impact of hyper-saline solutions*. Elsevier journal, Water Research, 22 April.

Magoon, B., Dow, W. 1994. *The petroleum system*. American Association of Petroleum Geologists, Memoir 60, 3-24.

Marchetti, C., 1977. *On Geoengineering and the CO₂ Problem*. Climatic Change, 1, 59-68.

Martin, D., Taber, J. 1992. *Carbon dioxide flooding*. Journal of Petroleum Technology, 44(4), 396-400.

Michael, K., Golab, A., Shulakova, V., Ennis-King, J., Allinson, G., Sharma, S., Aiken, T., 2010. *Geological storage of CO₂ in saline aquifers—A review of the experience from existing storage operations*. International Journal of Greenhouse Gas Control 4, 659-667.

Miri, R. 2015. *Effects of CO₂-Brine-Rock Interactions on CO₂ Injectivity – Implications for CCS*. PhD Thesis. R. Miri. University of Oslo, 10 August.

Moritis, G., 2003. *CO₂ sequestration adds new dimension to oil, gas production*. Oil and Gas Journal, 101(9), 71-83.

Nagy, K., Steefel, C., Blum, A., Lasaga, A. *Dissolution and Precipitation Kinetics of Kaolinite: Initial Results at 80°C with Applications to Porosity Evolution in a Sandstone*. Department of Geology and Geophysics, Yale University.

Neele, F., Nepveu, M., Hofstee, C., Meindertsma, W. 2011. *CO₂ storage capacity assessment Methodology*. TNO report, 29 April.

Nyhan, J., Brennon, B., Abeele, W., Wheeler, M., Purtymun, W., Trujillo, G., Herrera, W., Booth, J. 1985. *Distribution of plutonium and americium beneath a 33-yr-old liquid waste disposal site*. J. Environ. Qual., 14, 501– 509.

Ocean Storage of CO₂. 1999. Produced by IEA Greenhouse Gas R&D Programme, February.

Ochi, J., Vernoux, J. 1998. *Permeability Decrease in Sandstone Reservoirs by Fluid Injection: Hydrodynamic and Chemical Effects*. J. of Hydrology 208 (3): 237-248.

Ouyang, Y., Shinde, D., Mansell, R., Harris, W. 1996. *Colloid-enhanced transport of chemicals in subsurface environments*. A review, Crit. Rev. Environ. Sci. Technol., 26, 189– 204.

Peysson, Y., Andre, L., Azaroual, M. 2014. *Well injectivity during CO₂ storage operations in deep saline aquifers—Part 1: Experimental investigation of drying effects, salt precipitation and capillary forces*. International journal of Greenhouse Gas Control 22, 291-300.

Pruess, K., Müller, N. 2009. *Formation dry-out from CO₂ injection into saline aquifers: 1. Effects of solids precipitation and their mitigation*. Water Resources Research 45, W03402.

Rau, G., Caldeira, K., Knauss, K., Downs, B., Sarv, H. 2001. *Enhanced Carbonate Dissolution as a means of Capturing and Sequestering Carbon Dioxide*. Institute of Marine Sciences, University of California, Santa Cruz, CA 95064, 14-17 May.

Roels, S. 2015. *Formation dry-out and injectivity impairment during CO₂ storage in saline aquifers*. Research conducted as part of the Dutch National Program of CCS: CATO-2. 2 September.

Ryan, J., Gschwend, P. 1990. *Colloid mobilization in two Atlantic coastal plan aquifers: Field studies*. Water Resour. Res., 26, 307– 322.

Sbai, M., Azaroual, M. 2011. *Numerical modeling of formation damage by two-phase particulate transport processes during CO₂ injection in deep heterogeneous porous media*. Advances in Water Resources, Elsevier, 34 (1), pp.62-82.

Scherer, G. 2004. *Stress from crystallization of salt*. Cement and Concrete Research 34, 1613-1624.

Sen, T. 2001. *Studies on colloidal fines-associated contaminant transport in porous media*. PhD Thesis, Department of Chemical Engineering, Indian Institute of Technology, Bombay, Mumbai, India.

Senior, W., Bradshaw, J., Chikkatur, A., Wright, M. 2010. *Planning saline reservoir storage developments – the importance of getting started early*. Elsevier journal, CO₂ Geological Storage Solutions Pty Ltd. Proceedings of 11th International Conference on Greenhouse Gas Technologies, Amsterdam.

Shaw, J., Bachu, S. 2002. *Screening, evaluation and ranking of oil reserves suitable for CO₂ flood EOR and carbon dioxide sequestration*. Journal of Canadian Petroleum Technology, 41(9), 51–61.

Taber, J., Martin, F., Seright, R. 1997. *EOR screening criteria revisited - part 1: introduction to screening criteria and enhanced recovery fields projects*. SPE Reservoir Engineering, 12(3), 189–198.

APPENDICES

Appendix 1

Table 10: Permeability measurements at each cycle of experiment 1

| | Permeability(mD) |
|-----------------------|------------------|
| Particle-cycle1 | 27.85 ± 2.79 |
| 108.38g/l NaCl-cycle2 | 46.63 ± 4.66 |
| 108.38g/l NaCl-cycle3 | 20.03 ± 2 |
| 54.19/l NaCl-cycle4 | 58.09 ± 5.81 |

Appendix 2

Table 11: Permeability measurement in different cycles (salinity test)

| | Permeability(mD) |
|----------------------|------------------|
| Particle-cycle1 | 19.42 ± 1.94 |
| 54.19g/l NaCl-cycle2 | 13.90 ± 1.39 |
| 54.19g/l NaCl-cycle3 | 26.32 ± 2.63 |

Appendix 3

Table 12: Permeability measurement during brine experiment

| | Permeability(mD) |
|-----------------------|------------------|
| 300g/l NaCl-cycle1 | 93.73 ± 9.37 |
| 108.38g/l NaCl-cycle2 | 82.73 ± 8.27 |
| 54.19g/l NaCl-cycle3 | 149.51 ± 1.5 |