FINAL DRAFT REPORT

THE EFFECT OF SILICA DISSOLUTION ON PERMEABILITY IN WATER AND ALKALINE INJECTION

by

AHMAD FURQAN BIN KHAIRUDDIN

12514

Supervised by: DR. KHALED ABDALLA ELRAIES

Dissertation submitted in partial fulfillment
Of the requirement for Bachelor of Engineering (HONS)
(Petroleum Engineering)

MAY 2013

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

THE EFFECT OF SILICA DISSOLUTION ON PERMEABILITY IN WATER AND ALKALINE INJECTION

by

AHMAD FURQAN KHAIRUDDIN

A project dissertation submitted to the
Petroleum Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
Bachelor of Engineering (HONS)
(PETROLEUM ENGINEERING)

Approved by,

____
(DR. KHALED ABDALLA ELRAIES)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own concept as specified in the references and acknowledgement, and that the original work contained in here have not been undertaken or done by unspecified sources and persons.

____
(AHMAD FURQAN KHAIRUDDIN)

ABSTRACT

Silica scale formation is one of many scales that are encounter during oil production. It can deposit in the well tubing, causing equipment failure and also within the reservoir near the production well. This will reduce the overall effective permeability and ultimately effects the total production of the well. It usually found during injection operation such as water injection and alkaline injection. This formation of scale is due to the dissolution of silica mineral such as quartz when it reacts with injected fluid. Dissolution takes place when a catalyst is introduced to them that can weaken the oxygen bond and convert insoluble silica into soluble silica. It occurs highly due to the injection fluid that causing environment parameter surrounded the silica mineral to change, thus promoting dissolution process. This paper discuss on the effect of pH value and salinity of the fluid toward the dissolution rate. Two set of experiments will be conducted to verify the factors; static and dynamics tests. The concentration of soluble silica will be measured using spectrophotometric. The data obtained will be analysis and discussed to determine its significant factor on dissolution rate.

ACKNOWLEDGEMENT

The author would like to praise to Allah, the Almighty God for giving the opportunity to accomplish this final year project as part of requirement for Bachelor of Engineering (Hons.) in Petroleum Engineering at Universiti Teknologi PETRONAS. The author also would like to thank and express his gratitude to all the persons that had helped him in completing the project. Without their help, it is impossible to complete this project. The person author like to express his utmost gratitude is to author's supervisor, Dr. Khaled Abdalla Elraies. He had guide the author from the scratch until completion of this project. To Final Year Project Coordinator, Mr M Aslam Md Yusof, a big thank you for managing the Final Year Project students. Also the author would like to express his gratitude to Mr Ahmad Fatah, the supervisor assigned for this project who is currently pursuing his master in Universiti Teknologi PETRONAS. The author would like also like to express his gratitude to the lab technologist at Block 15 and Block 14, Mr Saiful and Mr Zamdi for their continues guidance, time and patience in assisting the author throughout the project Last but not least, the author would like to thank his fellow colleagues who had going through the same challenges in completing the Final Year Project. They had given a moral support and guidance in ensuring the Final Year Project is finish within the time frame.

TABLE OF CONTENT

ABSTRACT...III

ACKNOWLEDGEMENT IV

LIST OF TABLES VII

PROJECT BACKGROUND 1

1.1 Introduction 1

1.2 Problem Statement... 2
1.2.1 Problem Identification 2
1.2.2 Significant of the Project.. 3

1.3 Objective and Scope of Study 3

1.4 The Relevancy of the Project 4

1.5 Feasibility of the Project within the Scope of Time Frame 4

CHAPTER 2..5

LITERATURE REVIEW 5

2.1 Literature Review 5

CHAPTER 3.. 14

METHODOLOGY... 14

3.1 Project Methodology 14

3.2 Key Milestone... 15

3.3 Gantt Chart... 16

3.4 Experiment Methodology... 17

CHAPTER 4.. 20

RESULT AND DISCUSSION 20

REFERENCES 38

LIST OF FIGURES

Figure 2.1: Dissolution process……………………………………………………………7
Figure 2.2: Polymerization process……………………………………………………..9
Figure 2.3: Base catalyzed reaction……………………………………………………10
Figure 2.4: Precipitation process by metal ion……………..……………………….10
Figure 3.1: Process flow of work……………………………………………………….11
Figure 4.1: Salinity effect in static test…………………………………………………21
Figure 4.2: NaHCO3 effect in static test………………………………………………..22
Figure 4.3: Glass container at 0 day…..……………………………………………...23
Figure 4.4: Measuring silica concentration using spectrophotometer…………………..24
Figure 4.5: Na2CO3 effect in static test………………………………………………...24
Figure 4.6: Permeability result for distilled water injection (AFK 4)…………………..26
Figure 4.7: Differential pressure for distilled water injection (AFK 4)………………....27
Figure 4.8: Permeability result for salinity injection (AFK 4)………………………….28
Figure 4.9: Differential pressure result for salinity injection (AFK4)………………….28
Figure 4.10: Permeability result for distilled water injection (AFK 2)…………………29
Figure 4.11: Differential pressure result for distilled water injection (AFK 2)…………30
Figure 4.12: Permeability result for 0.4% of alkaline injection (AFK 2)……………….30
Figure 4.13: Differential pressure result for 0.4% of alkaline injection (AFK 2)……….31
Figure 4.14: Permeability result for distilled water injection (AFK6)………………….32
Figure 4.15: Differential pressure result for distilled water injection (AFK 6)…………33
Figure 4.16: Permeability result for 1.0% of alkaline injection (AFK 6)………………..34
Figure 4.17: Differential pressure result for 1.0% of alkaline injection (AFK 6)……….34

LIST OF TABLES

Table 1.0: Key Milestone for Project…………………………………………………...12
Table 2.0: Gantt chart for the project implementation for both FYP I and FYP II…….16
Table 4.1: Static test for variation of salinity concentration……………………………17
Table 4.2: Result in static test for variation of NaHCO3 concentration………………..20
Table 4.3: Result of static test with variation of Na2CO3 concentration……………….22
Table 4.4: Results from Poroperm………………………………………………………34
Table 4.5: Summary of dynamic test results for all injections………………………….36

CHAPTER 1

PROJECT BACKGROUND

1.1 Introduction

Silica scale formation is common to be encountered during the implementation of injection operation. It can be seen by the drop in production with time that highly due to the silicate scale forming within the tubing. It will accumulate and causes restriction flow to the production. Its presence can also accumulate within certain downhole equipment that will cause it to breakdown. The raise of silicate scale problem is due to the mixing incompatible fluid during water and alkaline injection.

Injection well is known as a secondary recovery that is executed after primary recovery. It is a common IOR method that is done at offshore environment fields. It uses the natural energy of the reservoir in order to produce more oil. The primary principle of water injection is to increase oil production by injecting water into the reservoir that serves to maintain the reservoir pressure, thus avoiding from the reservoir pressure decline. The water injected will fill up the void spaces in the pore for pressure maintenance and displace oil toward the production well. The primary factor that will lead to the success of water injection is the ability to inject sufficient amount of water of interest into the targeted zone. However, the rate of injectivity depends on three factors:

- Inherent reservoir quality
- Contact of the pay zone of interest by injection well
- Formation damage that effects the water injection

Any water that is being injected will has its own properties that usually different from the reservoir itself. The injection will automatically interact with the reservoir that will lead to changes in most chemical properties. Moreover, even to reinject produced reservoir water for the purpose of injection will has different properties even though it comes from the reservoir itself. This is due to the break out of solution as it produced together with the hydrocarbon such as carbon dioxide. This reduction of gas will change the composition and the pH of the reservoir water. This causes problem with compatibility issues.

Ignoring this problem will cause formation damage within the reservoir. Several well-known scales that usually found during water injection are calcium carbonate, calcium sulphate and barium sulphate.

Another method is alkaline flooding. This method is an EOR type where unlike water flooding, it uses alkaline which has high pH value, to be injected into the reservoir. The alkaline will react with certain type oil in the reservoir that produce surfactant. Surfactant is an organic substance that able to reduce the interfacial tension between oil and water.

It consists of two main parts which one part is soluble in water while the other one is soluble in oil. These parts will absorb at the interfacial surface and reducing the interfacial tension between oil and water. This will trigger an increase in overall oil production. However, there are several concerns that relate with alkaline flooding due to its tendency to cause scale problem such as hydroxide precipitation from the reaction between alkaline with calcium ions.

1.2 Problem Statement

1.2.1 Problem Identification

Silicate scale is often encountered during alkaline and water flooding in sandstone reservoir. The scaling can accumulate at production tubing or any other surface equipment that will cause loss in production and require frequent well intervention. However, if the problem is severe, workover will be needed which is costly and time consuming. Silicate scale is not only subjected to precipitate at the tubing, it can also precipitate within the reservoir pore that will lead to pore plugging and loss in permeability.

The cause of silicate scale formation is complicated to explain as it depends on many factors such as pH value, silica concentration, other ions concentration, and temperature. To formulate a certain method that can tackle each of every factor will require in-depth understanding of silica scale mechanism. Unlike most of other minerals scale that solely depend on the saturation level with respect to the mineral, silicate has the ability to precipitate under several processes such as biological activities and co precipitation with other mineral.

Scale control can be done by either through using mechanical method, chemical method and inhibition method. Mechanical method refers to the removal of scale that accumulates inside the tubing by mechanical means such as jet blaster. While chemical method involves using acid treatment to soak the tubing. The acid will dissolve the scale and can be flush out afterward.

Inhibition refers to method that inhibits the scale polymerization thus keeping it soluble. For mechanical and chemical methods, they are only possible if the damages take place in or near the wellbore.

For damages that take place deep within the reservoir pore, it is best to handle it by inhibition method. However, to formulate the inhibition that will effectively control silicate scale requires further studies on the factors that affect the silicate formation.

1.2.2 Significant of the Project

There are commonly two type of reservoir bearing zones, sandstone and carbonate. For sandstone reservoir, there is a high possibility of encountering quartz which is the most abundant mineral in Earth’s continental crust. It is made up from silica and oxygen bonding together. Thus, silicate scale will be encountered when the production well is shifted to water or alkaline flooding. By having better understanding on silica behavior, we can avoid the problem at the early stage of operation, rather than spending extra cost on rectification due to silicate scale.

1.3 Objective and Scope of Study

The study will centers around the effect of water injection and alkaline flooding environment.

The objectives of this study are:

- To study the effect of pH value on silica dissolution
- To study the effect of salinity on silica dissolution
- To study the effect of alkaline concentration on silica dissolution
- To study the effect of silica dissolution on permeability

The scope of study includes:

- To investigate the effect of salinity on silica dissolution with function of time.
- To investigate the effect of pH value on silica dissolution with function of time.
- To investigate the effect of alkaline concentration on silica dissolution with function of time.
- To investigate the effect of silica dissolution on permeability with function of time.

1.4 The Relevancy of the Project

The project is related to mineral formation and reservoir behavior which is under Petroleum Engineering field of studies.

1.5 Feasibility of the Project within the Scope of Time Frame

Discussion has been done with my supervisor and gantt chart has been drafted. From the timeline and the type of experiments that are going to be conducted, it is feasible to be completed within the give time frame.

CHAPTER 2

LITERATURE REVIEW

2.1 Literature Review

Silica is one of the minerals that can form into scale during production. It can exist in various forms. One of them can be an amorphous type, a non crystalline type structure. This type of structure does not have reticular nor granular structure. They have no definite melting point, gradually become soft as temperature increase due to low binding energy compare with crystalline structure. However, it can further become a more structured order arrangement such as quart with increase in temperature for conversion purposes. There are two main mechanisms that occur during injection operation on silica deposition in permeability, dissolution and deposition

2.1.1 Scale

Scale refers to a deposit of coating that can be formed in well completion that will cause flow restriction as it thickening within the tubing. It occurs when there is disturbance in thermodynamic and chemical equilibrium state. The disturbance will alter the condition of equilibrium by several factors, mainly due to pressure drop, flow viscosity, type of metal, temperature and dissolved gas. It can start as early as during production or during water injection. Scale problem during production is due to the reservoir itself that can be controlled with pressure and temperature while as for during injection, it’s mainly due to reaction of mixing two incompatible fluid.

Scale is any inorganic, solid material that precipitates in the reservoir, wellbore or well completion during production of oil and gas. Scale deposition usually manifests itself as the rate reduction. it can also associated with changes in water cut. There are several types of scales that can be found such as carbonate, sulphates, iron scales and also halite.

2.1.2 Silica scale

Silica scale in oil and gas is complex and difficult to manage. The formation of silica scale can be illustrated in several steps.

1. Silica dissolution – high pH water react with quartz in reservoir that will change insoluble silica into soluble silica, monometric silica.
2. Silica polymerization – the soluble silica will polymerize and become colloidal silica which is bigger that monometric silica.
3. Silica deposition – if metal ions are present in solution, it can act bridge for the colloidal silica to form amorphous metal silicate. In absence of divalent cations and surface to deposit, it can continue to polymerize the colloidal silica to form bigger chain silica until it reaches a point where it is too big to be kept in suspension, thus, deposited.
4. Co-precipitated with other scale – in presence of carbonate scale, it will provide nuclei space for silica scale development. It can cause silica to deposited even though the solution is still undersaturated with silica.

Handling silica scale is not as easy as other normal scale as it does not solely depending on its saturation level. This is because there are many other reaction that can occurred to form silica scale.

1. Polymerization
2. Colloidal suspension
3. Precipitate of silica mineral
4. Biological activity.

In defining the silica, it usually can be indentified based on its characteristic such as grain size, morphology and refractive index. Silica has refractive index ranginging between 1.46 to 1.51. it occur as aggregates of fine grain of less that 5um or coarse grain more than 20 um. Its chemical composition effected its appearance such as for Aluminium-rich silica, it has dark gray colour and form of cloudy. Silica scale is rarely compared with other scale as it does not has a fixed structure which used to characterize it. Whoever, there are method that available to characterize it by using X-ray diffraction, light microscopy and SEM-EDS analysis.

Dissolution

Initially, silica is in form of quartz within the earth layers. Quartz can be found at most area of sandstone as it is the most abundant mineral within the Earth's crust. However, it undergone dissolution process that convert insoluble silica into soluble type which is a de-polymerization process via hydrolysis. In order to achieve it, it requires catalyst, the catalyst will chemisorbs to increase the coordination number and weaken oxygen bonding causing the silica atom to be discharged as soluble ions. The hydroxyl ion will act as the catalyst in alkaline solution while hydrofluoric acid in acid solution. Saneie and Yortsos in their paper, have describe the interaction of silica with alkaline that consist of two steps, a rapid formation of the complex and a slower rate that refers to bond bre akage. (Saneie and Yortsos, 1996).

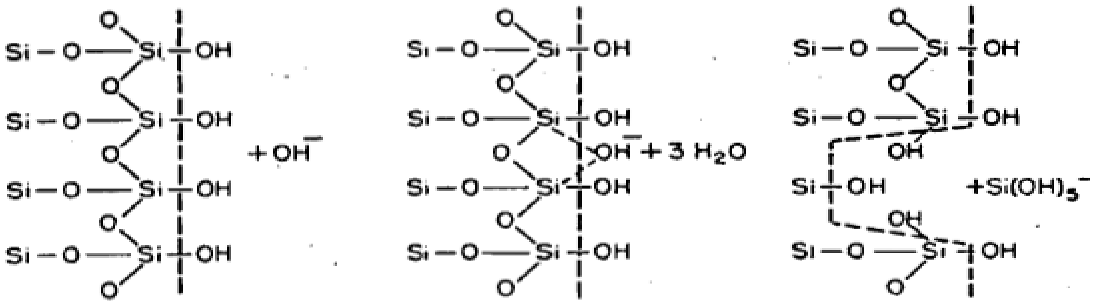


Figure 2.1: Dissolution process

For the silica and oxygen molecules, there are sufficient spaces between the ions to accommodate the hydroxyl ions. Thus, through the exposed surface, ionic charge and silica is constantly being exchange to change silicon atom into silica ion via adsorption of OH^-. However, even though hydroxyl ions and hydrofluoric acid are catalyst, they don't exhibit similar characteristics. Stober had made an observation where stishovite, a type of silica that is surrounded by six atoms, is insoluble in HF acid while soluble in weak alkaline.

HF acid will react with silica by converting it to SiF, which is hydrophobic due to absence of oxygen atom that can form bond with hydrogen atom from solution. Due to the hydrophobic properties and closely packed monolayer, water is unable to react with the surface of the silica as a result, no dissolution occur. Whereas in hydroxyl solution, it will react with silica to form SiOH that has oxygen atom to bond with hydrogen from solution, hydrophilic properties.

This enables water to react with the surface of silica even though it was tightly packed with six atoms. Thus for hydrofluoric acid to permit dissolution process, it requires less dense component to allow water reaches its surface such as quartz.

The dissolve silica will form a monomeric silica. Monometric silica has only one atom and known as $Si(OH)_4$. It is basically nonionic in neutral, weak acidic solution and does not transmit electric current unless ionized in alkaline solution.

It is the simplest form of silica and can polymerize between them to form a longer and more complex molecules known as colloidal particles. The difference between a soluble and colloid silica is measure base on dialysis membrane. Soluble silica will be able to pass through while colloids will not.

The rate of dissolution is dependence on the pH. It tends to increase its rate of dissolution in high pH value. Baumann has indicated that from pH value of 3 to 6, the rate of dissolution increase in proportional to hydroxyl ion concentration. However, it is no possible to solely depends on pH value as surface area also has effects on the rate of dissolution.

Goto has stated that the rate of dissolution is proportional with the surface are that is not less than 5 nm diameter. This is because as surface area exposed to hydroxyl ion increases, more silica can react that one time. Particles that located inside surely cannot dissolve as fast as the outer layer due to the fact of limited hydroxyl ion that reaches it. It requires the outer layer to be fully dissolved to maximize it dissolution rate.

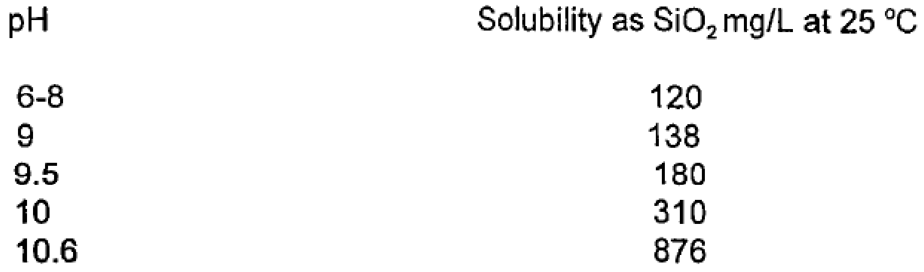
It has been reported by Dienert and Wandenbulcke that stated salt as a good catalyst for dissolution. The claimed was made based on the observation of quartz in container to be dissolve faster in presence of salt. Silica has been seen remained undissolved in a pure water while rapidly dissolve in seawater. Impurities have been noticeable for having effect on silica rate of dissolution in neutral solution.

Solubility

The dissolution process will continue to occur until the solution has reaches it saturation point, where it can no longer accept any silica ions. Saturation level of the solution is determined by the solubility that is affected by several factors such as pH value, temperature and particle size.

As discussed earlier, pH exhibit characteristic to affect the rate of dissolution. More than that, it highly influences the solubility by allowing continuous dissolution process to take place. A high pH will increase the solubility of silica and it is significantly reduced below pH 10.5.

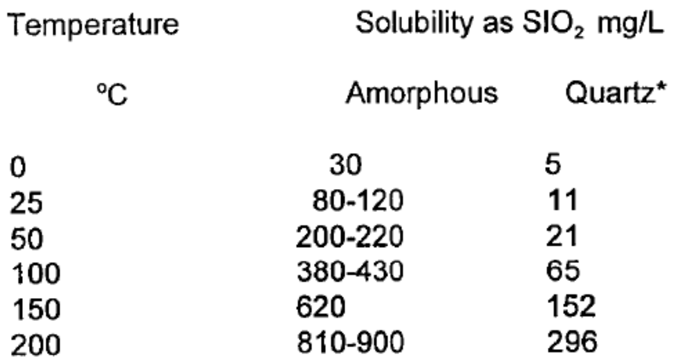
Having pH above than 11, the hydroxyl ions converting $Si(OH)_4$ to silica ions and able to keep it unsaturated, thus more silica will be dissolved in the process. Whereas, if the pH is below 11, the dissolution process can only convert silica until the solution reaches its saturation level, acting only as a catalyst.



pH	Solubility as SiO_2 mg/L at 25 °C
6-8	120
9	138
9.5	180
10	310
10.6	876

Figure 2.2: The effect of pH on solubility of amorphous silica

The effect of pH has been reported by Gill that solubility of amorphous silica remains constant at pH range 6-8 and increase as it increase to 8.5 and above. The increase of solubility is due to the formation of silicate ions. Ajmad and Zuhl have found that while other ions forming scale have inversely dependent on solution temperature, silica solubility tend to increase with increase in solubility that resulting in lower supersaturation level.(Ajmad and Zuhl, 2008) Temperature also has the same effect on the solubility with the increase in solubility at higher temperature but not significant.



Temperature	Solubility as SIO$_2$ mg/L	
°C	Amorphous	Quartz*
0	30	5
25	80-120	11
50	200-220	21
100	380-430	65
150	620	152
200	810-900	296

Figure 2.3: The effect of temperature on solubility of silica

Another factor is due to its size particle. Smaller size silica will has higher solubility when compare with the bigger size particle. However, the particle size is greatly affected by the polymerization rate, temperature, salt and silica concentration, and pH value. Gill stated that particle size that is less than 3 nanometer in diameter are extremely soluble while the bigger size particles show a large variability in solubility ranging between 120 to 60 ppm.(Gill, 1998)

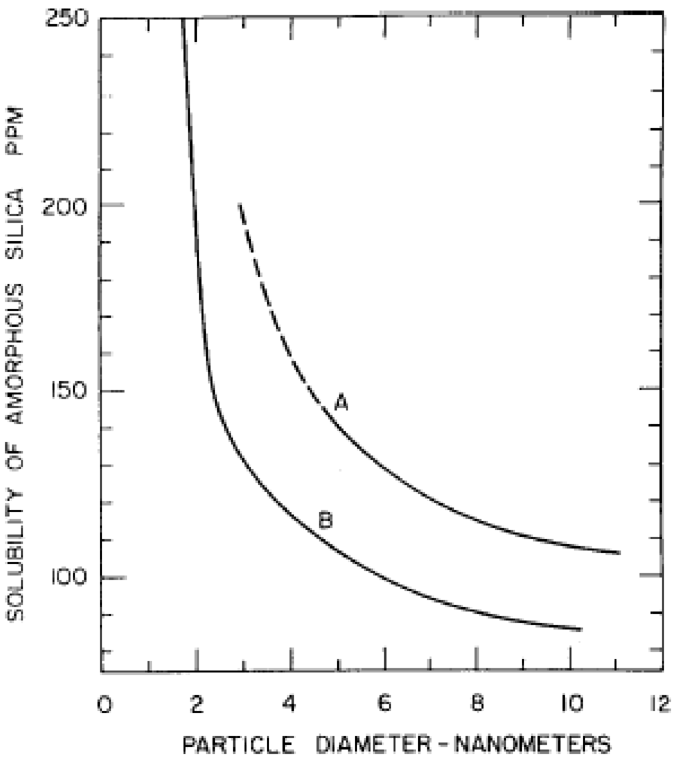


Figure 2.4: the effect of particle size on amorphous silica solubility

Deposition

After dissolution has taken place, the concentration of silica will increase until it become saturated. As the solution travel from injection well toward the production well, there will be changes within the surrounding properties that can cause the initially saturated silica become supersaturated solution due to its solubility changes.

Initial, the solution will has a specific pH value with specific solubility, however, as it moves through the reservoir, it will reacts with other water in the reservoir that will reduce it pH value by neutralization action by the connect water (Arensdorf et al., 2010). Moreover, there will be a dramatic decrease in solubility as the pH value drop below 8.5 (Amjad and Zuhl, 2008). This reduction in solubility will lead to polymerization of colloidal silica that is the first step of deposition of silicate scale.

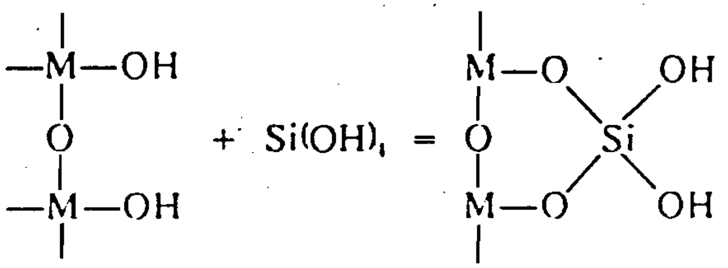


Figure 2.5: Polymerization process

Thus, when solution reach supersaturated, colloidal and monometric silica will deposited in different ways between each of them. Monometric silica polymerize out from solution in three methods. The first one is by deposit on solid surface that bears OH group that it can reacts and form silicate. As the initial surface is covered, it can extend the deposition on silica thus, forming a thicker film as time pass by. The second method takes place where there is no sufficient surface for it to deposit on.

Thus, it polymerizes between the low polymers to further build up and becomes a complex 3D polymer, colloidal particle. The last method is rarely appears and its mechanism is unknown. However, it has been studied that living organism can take away silica from extremely dilute solution and deposited as insoluble silica within the organism itself known as biogenic amorphous silica.

As for colloidal particles, it can deposits in two processes. An adherent coating can be build up by alternate wetting of a dilute solution and drying it. Particles will be bonded on a surface one it has dry up. This can be seen along the waterline at hot spring. The second process is coagulation between colloidal particles due to solution condition that cause it to be close with each others.

For a solution to reach supersaturated, it can be done by increasing the concentration in solution, decreasing the temperature and lowering the pH level. When the solution reaches supersaturated solution, soluble monomeric silica will form colloidal silica since it exceeds the maximum solubility that is can accept. However, it has been reported that presence of other ions can cause the silica to precipitate. Silica is able to precipitate with the presence of calcium carbonate as it provides a crystalline matrix that can trapped the silica.

$$\mathrm{Si(OH)_4 + OH^-} \longrightarrow \mathrm{(OH)_3SiO^- + H_2O}$$

$$\mathrm{Si(OH)_3^- + Si(OH)_4} \longrightarrow \underset{\text{(dimer)}}{\mathrm{(OH)_3Si - O -- Si(OH)_3}} \mathrm{+ OH^-}$$

$$\text{Dimer} \longrightarrow \text{Cyclic} \longrightarrow \text{Colloidal} \longrightarrow \text{Amorphous Silica (scale)}$$

Figure 2.6: Base catalyzed reaction

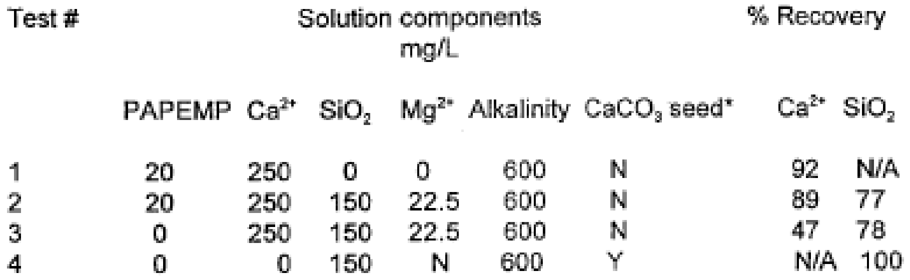
Magnesium also has shown the scaling trend by providing the hydroxide ion that will act as catalyst and cause magnesium silicate when pH is greater than 8.5 (Arensdorf et al, 2010). The problem with magnesium and silica is a difficult situation due to the converse solubility of magnesium silicate and colloidal silicate. Colloidal silicate solubility increase with increase of pH while magnesium solubility increase with decrease in pH. If the polyvalent metal ions are absence, amorphous silica can continue to polymerize between them and deposit as silica scale.

$$\mathrm{OFeOH.H_2O + Si(OH)_4 \rightarrow Fe(OH)_3.SiO_2 + 2H_2O}$$

$$\mathrm{Fe^{2+} + H_2O + Si(OH)_4 \rightarrow Fe(OH)_3.SiO_2 + 2H^+ + 1/2\ H^0}$$

Figure 2.7: Precipitation process by metal ion

Midkiff and Foyt had found that hard silica occurred when calcium carbonate precipitate and it will provide a crystalline matrix which silica can be found. Gill reported that in an environment where calcium carbonate or other precipitations are absence, higher concentration can be used compare with the environment where calcium carbonate is presence. This scenario does the same with temperature effect.(Gill, 1998)



Test #	Solution components mg/L						% Recovery	
	PAPEMP	Ca^{2+}	SiO_2	Mg^{2+}	Alkalinity	$CaCO_3$ seed*	Ca^{2+}	SiO_2
1	20	250	0	0	600	N	92	N/A
2	20	250	150	22.5	600	N	89	77
3	0	250	150	22.5	600	N	47	78
4	0	0	150	N	600	Y	N/A	100

Figure 2.8: Effect of calcium carbonate precipitation on silica precipitation

Silica Polymerization Inhibition Using Polymer

Polymers have been introduced to counter the silica scaling problem. It was generally effective acting as inhibitor and dispersants under normal operating condition. However, its performance dropped under thermal stress. Under different concentration, results show very little increase in inhibition effectiveness with increase of concentration.

Squeeze treatment

Rectifying silica scale problem required well intervention. It is an operation that involves entering a live well for improve its performance. Scale can be manage by many methods and one of it is squeeze treatment. It involve pumping chemical into the well bore that will inhibit silica scale.

The operation works by changing the solution condition such as pH value, temperature and metal ions. However, to ensure that the inhibitor works as predicted is difficult.

CHAPTER 3

METHODOLOGY

3.1 Project Methodology

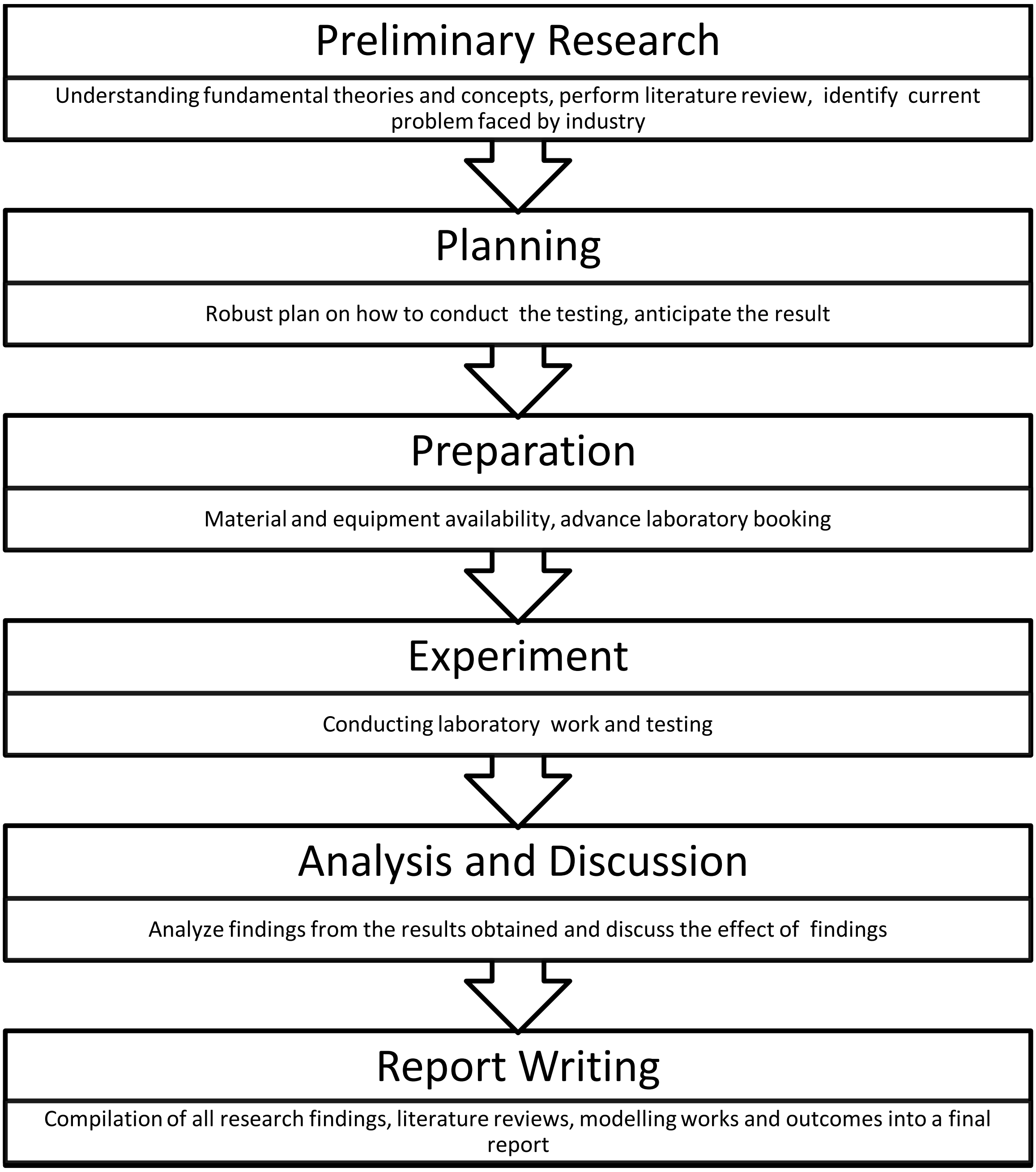


Figure 3 Process flow of work

3.2 Key Milestone

Table 1. Key Milestone for Project

Week	**Objectives**
FYP I	
5	Completion of preliminary research work
6	Submission of extended proposal
9	Completion of proposal defence
12	Confirmation on lab material and equipment for conducting experiment
13	Submission of Interim draft report
14	Submission of Interim report
FYP II	
5	Finalized the experiment procedure
6	Conducting experiment
7	Result analysis and discussion
8	Submission of progress report
9	Preparation for Pre-SEDEX
11	Pre-SEDEX
12	Submission of draft report
13	Submission of technical paper and dissertation
14	Oral presentation
15	Submission of project dissertation

3.3 Gantt Chart

Table 2. Proposed Gantt chart for the project implementation for both FYP I and FYP II.

TOPIC	PROJECT ACTIVITIES	WEEKS																											
		Final Year Project 1														Final Year Project 2													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Project Scope Validation	■																											
	Project Introduction		■	■	■	■	■																						
	Submission of Extended Proposal						■																						
	Identify material and equipment						■	■																					
	Training on how to conduct experiment							■	■	■																			
	Proposal Defence									■																			
	Detail Study									■	■	■	■	■	■														
	Submission of Interim Draft Report														■														
	Finalized Procedure														■	■	■												
	Conducting Experiment															■	■	■	■	■									
	Result analysis and discussion																		■	■	■	■							
	Submission of progress report																						■						
	Preparation for Pre-SEDEX																						■	■	■	■			
	Pre-SEDEX																									■			
	Submission of draft report																									■	■		
	Submission of technical paper and dissertation																										■		
	Oral presentation																											■	
	Submission of project dissertation																												■

Proposed Gant chart for the project implementation for both FYP I and FYP II. Based on the Gant Chart, the project is feasible to be completed within the given amoun of time.

3.4 Experiment Methodology

In this project, two types of experiments will be conducted. The motive behind this is to ensure that the data collected is more reliable and can support the final conclusion. The two experiments are Static Test and Dynamic Test.

3.4.1 Static Test

The static test experiments at which quartz will be in contact with solution are used to study the mechanism of silica dissolution. The experiments will be set up based on two parameters that influence the dissolution process, salinity and pH value. This experiment is made up based on the assumption that fluid flow has no effect on chemical reaction between the solution and the quartz, thus no stirring action will be done. This experimental approach is to determine the changes in soluble silica concentration and solution with increase in time in static.

This experiment will be done by repeating it by changing its parameter in pH value and salinity level within distilled water. It is important that the solutions remain free from any impurities that can affect the silica dissolution process. 5 batch of solutions that have different pH value, ranging from 0.2%, 0.4%, 0.6%, 0.8% and 1% of alkaline. 5 batch of solution with different salinity level that is 5,000 ppm, 10,000 ppm, 15,000 ppm, 20,000 ppm, and 25,000 ppm, based on the percentage of the salinity in the solution will be prepared and stored in bottle test. All of the batch will have the same volume for this experiment and kept at a constant temperature at 50 C^O.

16 g of quartz will be prepared for every 80ml batch and it will be soak in each of the solution for 10 days. The solution will be check for reading at Day 3, Day 7 and Day 10 when it reaches it equilibrium point. The solution will be left until it reaches it equilibrium point, where no more silica is further dissolved. The soluble silica will be checked by the silicomolybdate method. All data will be record and analyze.

3.4.2 Dynamic Test

The dynamic test experiments are done be flowing silica solution into the core sample to study the mechanism of dissolution effect on permeability. The experiments will be conducted based on two changing parameters, salinity and pH value. These experiments are made up based on the assumption of changing parameter in the solutions' pH and salinity as it flow into the core. The experimental approach is to determine the change of permeability of the core with increase of time.

This experiment is done by using core flooding technique. Brine solutions will be prepared with different pH value. 3 types of brine solutions will be prepared at 0%, 0.4% and 1.0% at 25 000 ppm of salinity for all of the solution. It will be flow into the core with a constant rate of 0.3 mL/min and temperature at ambient.

The dry core will first be measured its initial porosity and permeability using gas. Then, the core will be flooded where the differential pressure between inlet and outlet will be monitor to determine any changes in permeability within the core. Permeability test will be stopped when the pressure has stabilized. The core will be dried for a day before it will be measured for any changes in porosity and permeability using gas. The experiment will be repeated by using other initially prepared solution by using other cores.

3.4.3 Silicomolybdate Spectrophotometric Method

This method will be used to measure any soluble silica in solution using a spectophotometric method. The method is based on the principle of ammonium molybdate reacts with reactive silica that will yield yellow color. The oxalic acid will destroy the molybdophosphoric acid and leaving silicomolybdate only. This will eliminate any interference from phosphates. This method will measure the soluble silica that not only limited to monomer silica, but also aligomer species such as dimmers, trimmers and tetramers. It can measure up until 100mg/mL.

Procedure

1. Prepared a 10-ml sample
2. Add one content of Molybdate Reagent Powder Pillow for High Range Silica. Stir until completely dissolved.
3. Add a content of Acid Reagent Powder Pillow for High Range Silica. Stir until completely mixed. Leave for 10 minutes reaction.
4. Add a content of Citric Acid power, stir until dissolved. Leave for 2 minutes.
5. Set the instrument to zero by using blank solution.
6. Insert prepared solution, and record reading in the instrument.

3.5 Tools Required

Static Test	Dynamic Test
Chemicals • Sodium Carbonate • Sodium Bicarbonate • Sodium Metaborate • Sodium Chloride	Chemicals • Sodium Carbonate • Sodium Bicarbonate • Sodium Metaborate • Sodium Chloride
Tools • Beakers • Measuring cylinder • Weighting scale • Spatula • Glass containers	Tools • Beakers • Measuring cylinder • Weighting scale • Spatula
Equipments • pH meter • Spectophotometer	Equipements • Glass dessicator • Poroperm • Benchtop permeability system

CHAPTER 4

RESULT AND DISCUSSION

This chapter will review and discuss on the results from the static and dynamic test that had been done.

4.1 Results on Static Testing

4.1.1 Salinity

Salinity experiment was conducted by varying 5 solutions with salinity concentration. The solutions were kept at a constant temperature of 50°C throughout the whole session.

Ppm	3 day	7 days	10 days
5 000	4.3	6.3	8.3
10 000	4.8	7.8	9.7
15 000	5.5	8.7	11.1
20 000	6.2	9.2	12.1
25 000	7.8	10.8	11.8

Table 4.1 – Static test for variation of salinity concentration

From the **Table 4.1**, it shows the changes in silica concentration with increasing time for different concentration of sodium chloride. The readings were taken three times starting from day 3, 7 and day 10. The graph was made to see any pattern by varying the salinity concentration on the silica dissolution.

Based on the graph at **Figure 4.1**, the sodium chloride has be seen to effect on silica dissolution process by speeding up its process. The graph shows an increasing of silica concentration with increasing time and the gradient for each line indicates the dissolution rate. Thus, the highest gradient was recorded at 25 000 ppm and the lowest was at 5 000 ppm. This indicates that the increase in salinity concentration will increase the silica dissolution rate.

Even the salinity concentration increases, it does not has significant effect on the solubility of the solution. When comparing between the trend of silica dissolution gradient, it was seen to decline as the time goes. This is due to the solubility of the solution, where it will gradually decreases as it reaches its equilibrium point. Salinity does not increase the pH value, thus, all of the concentration exhibit similar solubility of the silica. It can be seen between 25 000 ppm and 20 000 ppm, where a wide gap that was initial presence in earlier reading, was lost at the final reading.

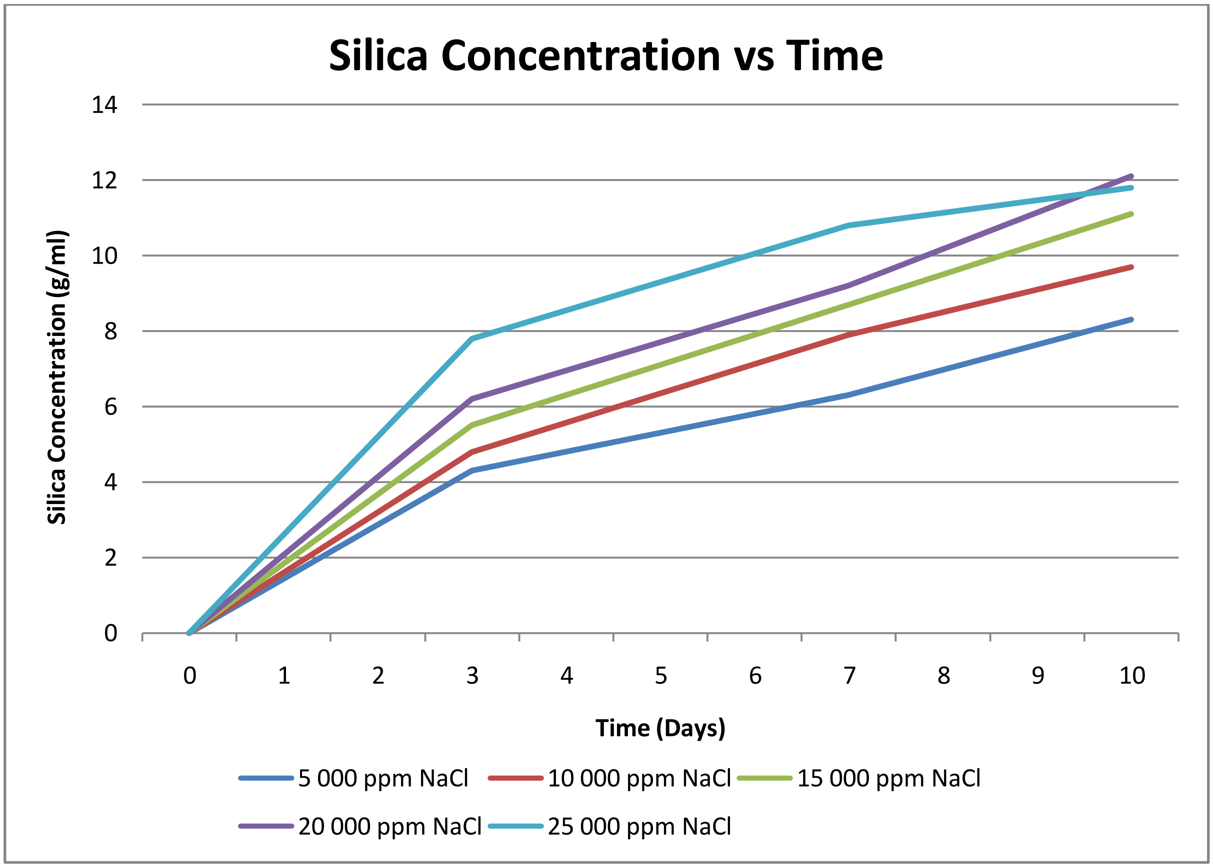


Figure 4.1 – Salinity effect in static test

4.1.2 Alkaline

In alkaline experiment, it was conducted by using two type of alkaline that different in terms of its pH value, sodium bicarbonate and sodium carbonate. Both of the alkaline are prepared in difference concentration but are placed at the same temperature, 50^{o}C.

Based on **Figure 4.2** below, it shows the silica concentration versus time in days for sodium bicarbonate. The temperature for each of concentration was held constant at 50°C throughout the experiment. At the first three days, all of the reading indicated high gradient from the initial stage. This is due to the rapid process of dissolution has taken place in dissolving quartz into soluble silica. After 7 days, the reading shows decreasing in dissolution rate for all of the solution. It continues to decrease at Day 10.

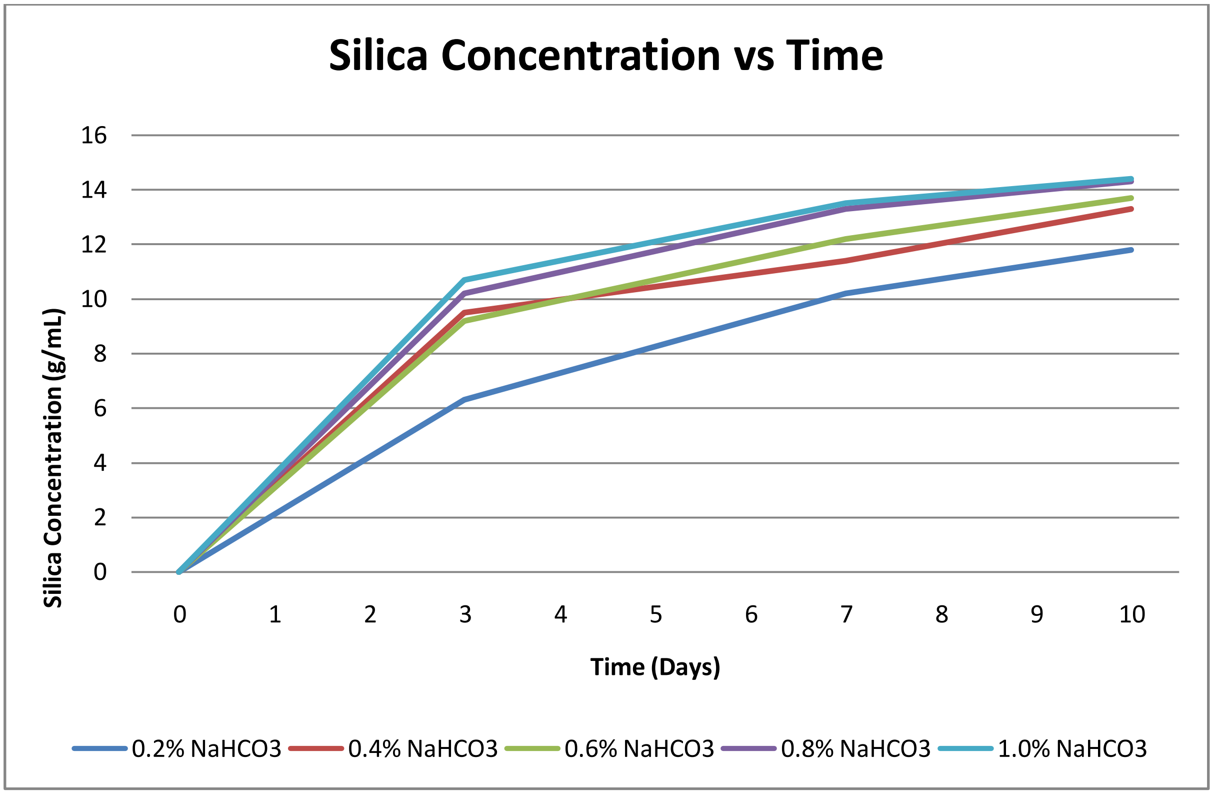


Figure 4.2 – NaHCO3 effect in static test

This is because initially, the silica concentration in the solution was none, thus, dissolution process can occurs at the highest rate that it can. However, as the concentration increases, as it reaches nearer to its equilibrium point, where the solution is unable to hold any more soluble silica, it will started to decline and ultimately, stop as it has reaches the equilibrium point. This can be seen at the graph, where the final reading for 0.8% and 1.0% were around 14 g/mL.

Concentration	**pH**	**3 days**	**pH**	**7 days**	**pH**	**10 days**	**pH**
0.2	8.74	4.3	8.54	6.3	5.5	8.3	8.50
0.4	8.75	4.8	8.59	7.9	8.51	9.7	8.53
0.6	8.78	5.5	8.65	8.7	8.59	11.1	8.55
0.8	8.81	6.2	8.74	9.2	8.63	12.1	8.60
1.0	8.84	7.8	8.76	10.8	8.68	11.8	8.69

Table 4.2 – Result in static test for variation of NaHCO3 concentration

On table 4.2, the reading of pH for every concentration at every time is record for monitoring. From 0.2% to 1.0%, there has been little increase in the pH and most of it can be considered around 8.7 to 8.8 only. Thus there will be little difference in its solubility. It can be seen where most of the reading are increasing and tend to flatten out as it getting near with 14 g/mL.

However, one another hand, by observing the graph for each of the concentration, it shows that the higher the concentration will result in higher rate of dissolution. This might be likely due to increase of Na+ with the increase in concentration that lead to more dissolution process taken place in one time.

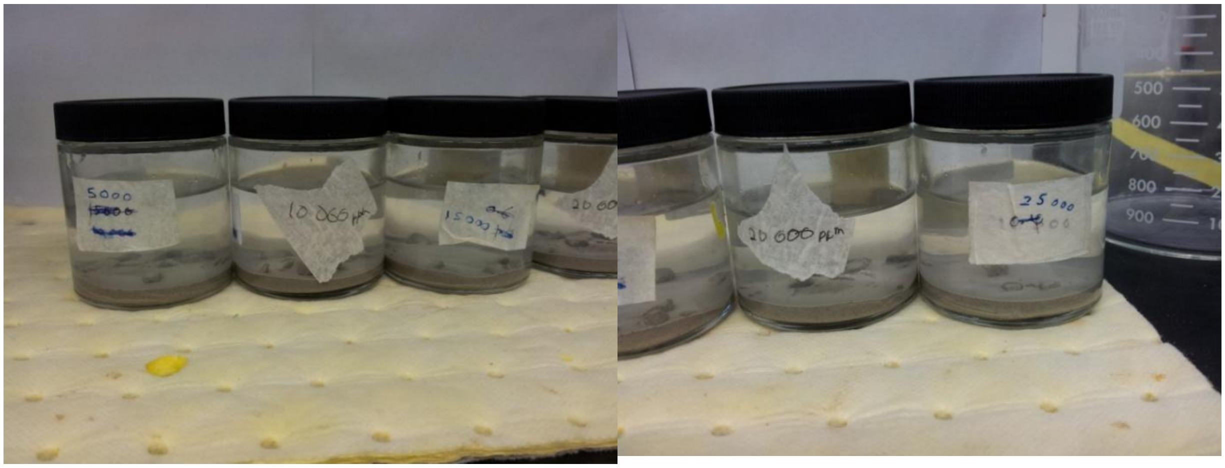


Figure 4.3 – Glass container at 0 day.

As for the sodium carbonate at **Figure 4.5**, the trend for its graph is the same as sodium bicarbonate, where the concentration of silica tends to increase with time. All of the reading increase until Day 10 and each higher concentration indicates greater dissolution rate when comparing with the lower concentration.

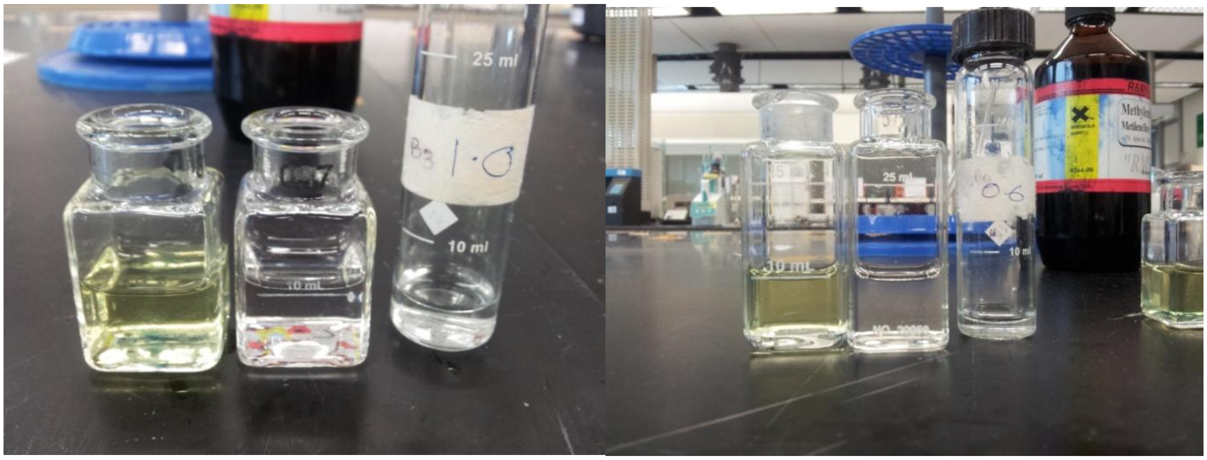


Figure 4.4 – Measuring silica concentration using spectrophotometer at Day 3

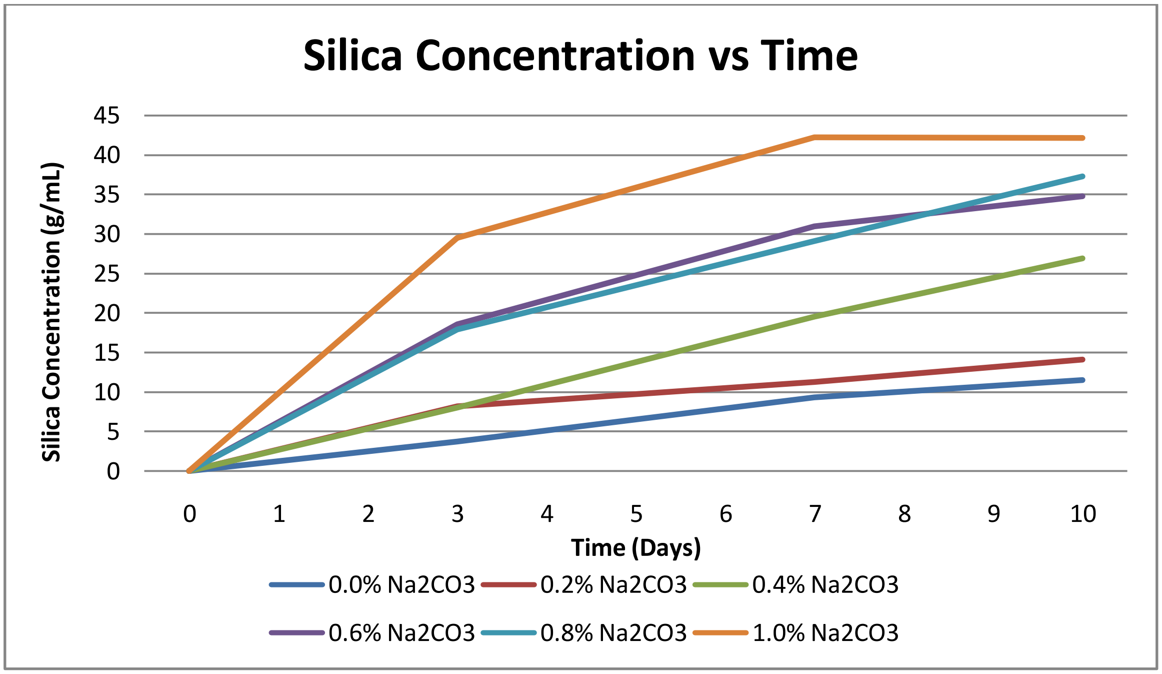


Figure 4.5 – Na2CO3 effect in static test

However, a significant difference that can be seen is the gradient of its graph is steeper than in sodium bicarbonate. This indicates that the rate of dissolution that occurred in sodium carbonate is much higher compare with sodium carbonate. This is due to the difference in the pH between the two of them. Sodium carbonate has pH value around 11 while sodium bicarbonate only at 8. The high pH was seen to ease the dissolution process that allows more silica to be dissolved even at the same concentration.

Concentration	**pH**	**3 days**	**pH**	**7 days**	**pH**	**10 days**	**pH**
0.0	9.30	3.7	8.83	9.3	8.50	11.5	8.27
0.2	10.99	8.2	10.86	11.3	10.16	14.1	9.86
0.4	11.14	8.0	10.91	19.5	10.31	26.9	10.10
0.6	11.21	18.6	11.13	31.0	10.60	34.8	10.26
0.8	11.23	17.9	11.17	29.1	10.58	37.3	10.32
1.0	11.26	29.5	11.19	42.2	10.65	43.1	10.38

Table 4.3 – Result of static test with variation of Na2CO3 concentration

Moreover, pH value affects the solubility where, it will increase in higher pH. Thus, more silica can be dissolved in the solution. It can be seen at the graph where sodium carbonate solutions were able to dissolve silica up to 40 g/mL, while only 14 g/mL was the highest reading in sodium bicarbonate.

Another point to highlight is all of the initial pH value for each of the alkaline solutions decreases in time. This is likely due to the reaction in dissolution processes in converting insoluble silica into soluble silica, involve in reaction with Na+ that lead to reduction in pH. The pH value is expecting to stabilize and remain unchanged once it reaches its equilibrium point. At this state, no dissolution occur and no reaction with the Na+ ions. Furthermore, as soluble silica is being introduced into the solution, the solution will re-adjust its properties due to new molecules.

4.2 Dynamic Test Result and Discussion

4.2.1 Salinity Dynamic Test

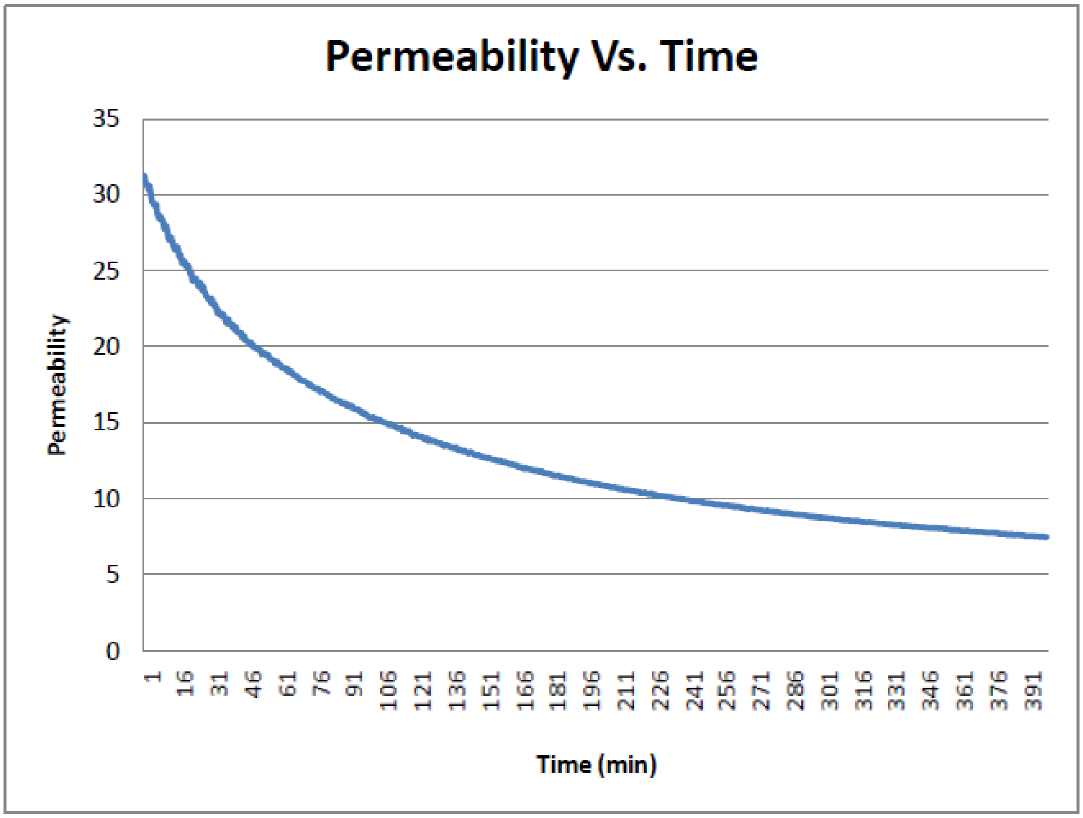


Figure 4.6 – Permeability result of dynamic test for distilled water injection (AFK 4)

From **Figure 4.6**, the graph on permeability versus time for distilled water. Distilled water was injected during the initial stage to check its permeability before the introduction of salinity into the core, AFK 4. The core was injected at a rate of 1.0 cc/m while temperature was kept constant. The experiment ended when the differential pressure has been stabilized. The differential pressure changes is shown at **Figure 4.7**, where initially, it started to increase until it reaches at certain value that it will start to stabilize and no longer increase. Since the permeability is calculated based on the differential pressure, it will stay constant at 7.51 mD when the differential pressure stays constant after flowing for 400 min.

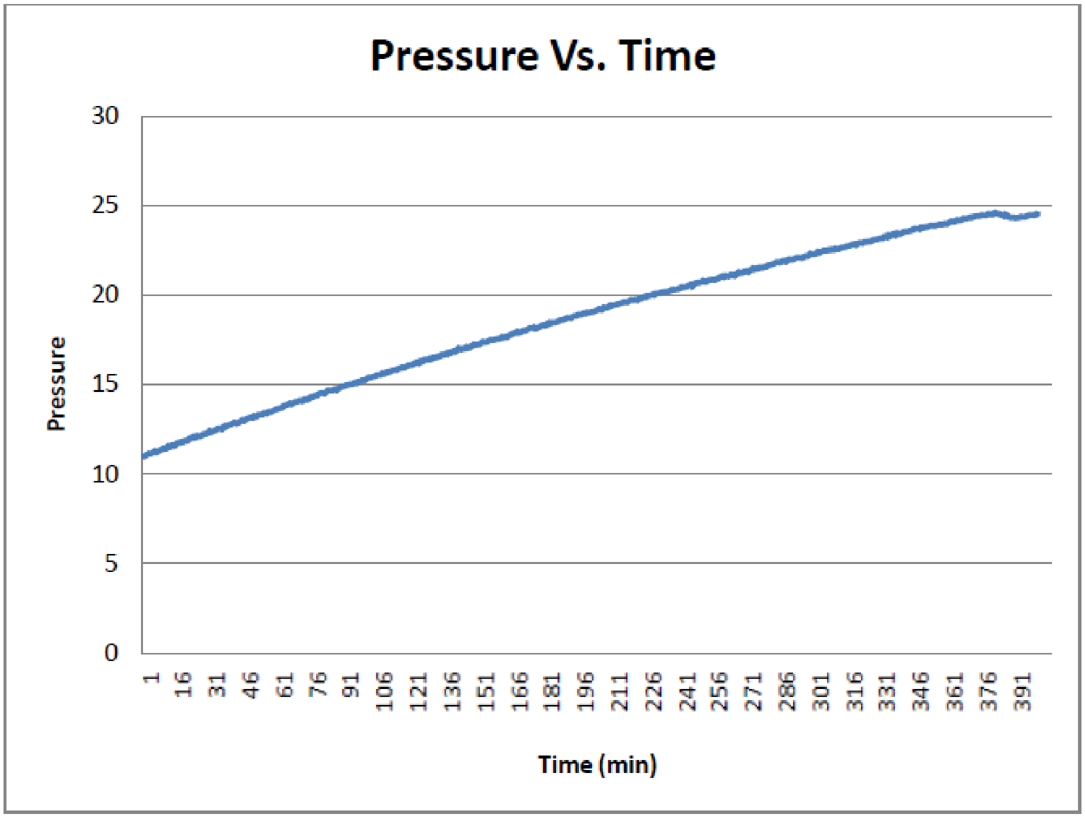


Figure 4.7 – Differential pressure result of dynamic test for distilled water injection (AFK 4)

After the pressure has been stabilized, the equipment is stop from pumping and change the injection solution to 25 000 ppm salinity solution. The rate was injection at 0.3 cc/min as studies showed that the movement of fluid within the reservoir is within that rate. It will illustrate the movement of fluid within the actual reservoir. **Figure 4.8** shows the final permeability for core AFK 4 is 8.99 mD after injection with the salinity solution. The increase from initially 7.51 mD indicates that dissolution process had taken place that causes the improvement in its interconnecting pore space, measured as permeability. The equipment had been left operating for 1000 min but reached its stabilized pressure at around 150 min of pumping with differential pressure around 8 psi.

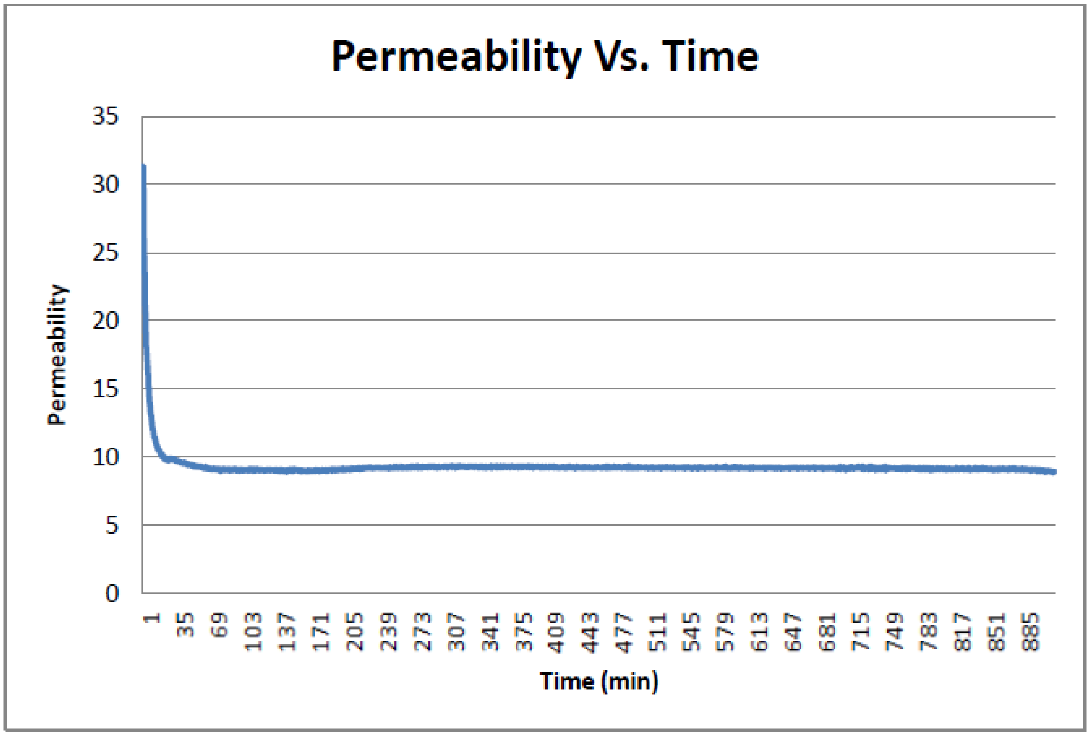


Figure 4.8 – Permeability result of dynamic test for salinity injection (AFK 4)

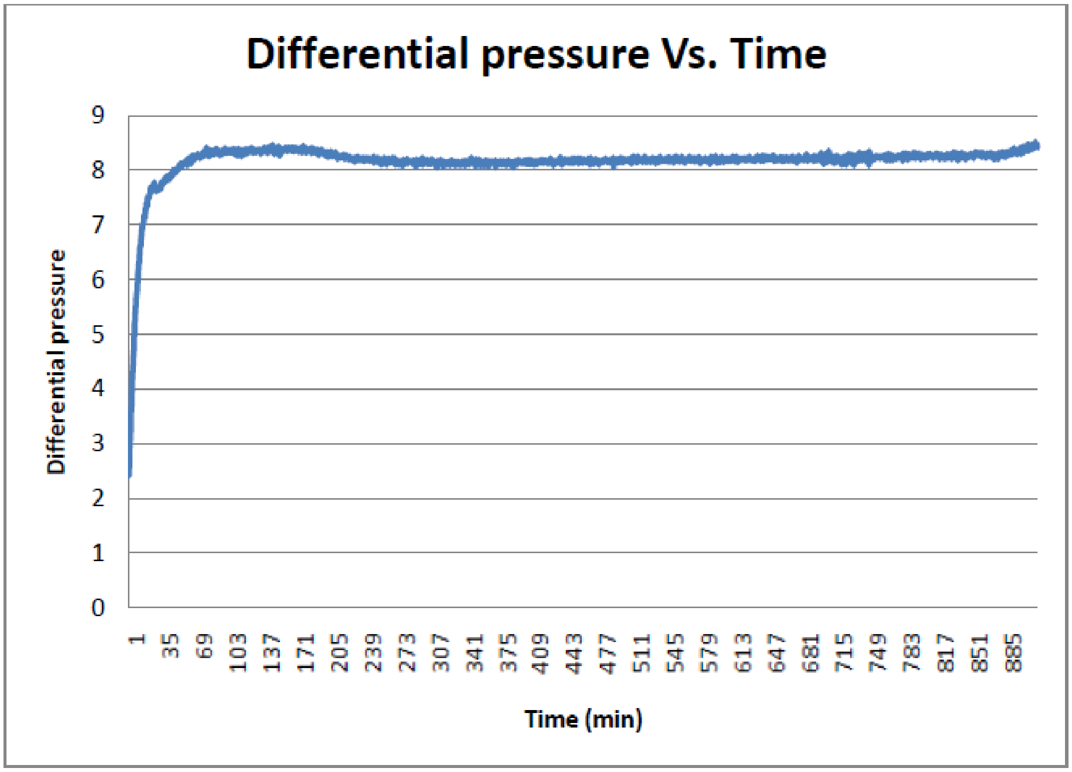


Figure 4.9 – Differential pressure result of dynamic test for salinity injection (AFK 4)

4.2.2 Alkaline Dynamic Test

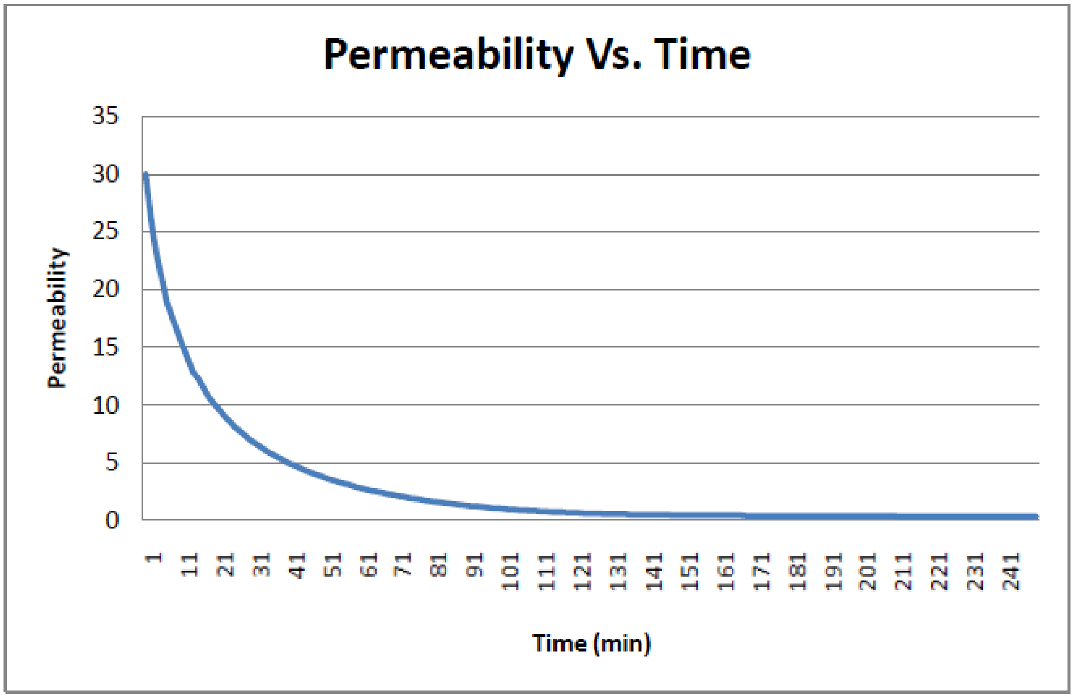


Figure 4.10 – Permeability result of dynamic test for distilled water injection (AFK 2)

Alkaline dynamic test begin by injecting the core with distilled water get the permeability value of the core. The injection was at 1.0 cc/min to speed up the process of reaching stabilized pressure state. **Figure 4.10** shows the changes in permeability with time when injecting with distilled water at rate of 1.0 cc/min. The permeability reduced with time until the differential pressure has been stabilized in **Figure 4.11**. The permeability reading for the distilled water was 0.24 mD with differential pressure around 140 psi.

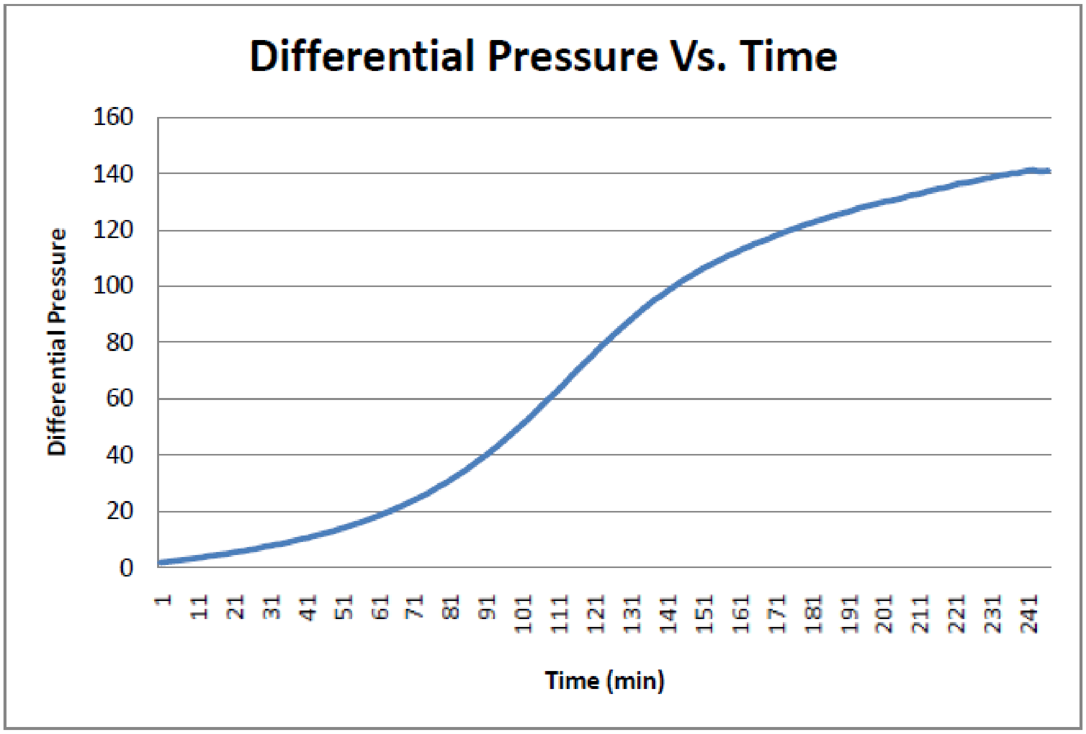


Figure 4.11 – Differential pressure result of dynamic test for distilled water injection (AFK 2)

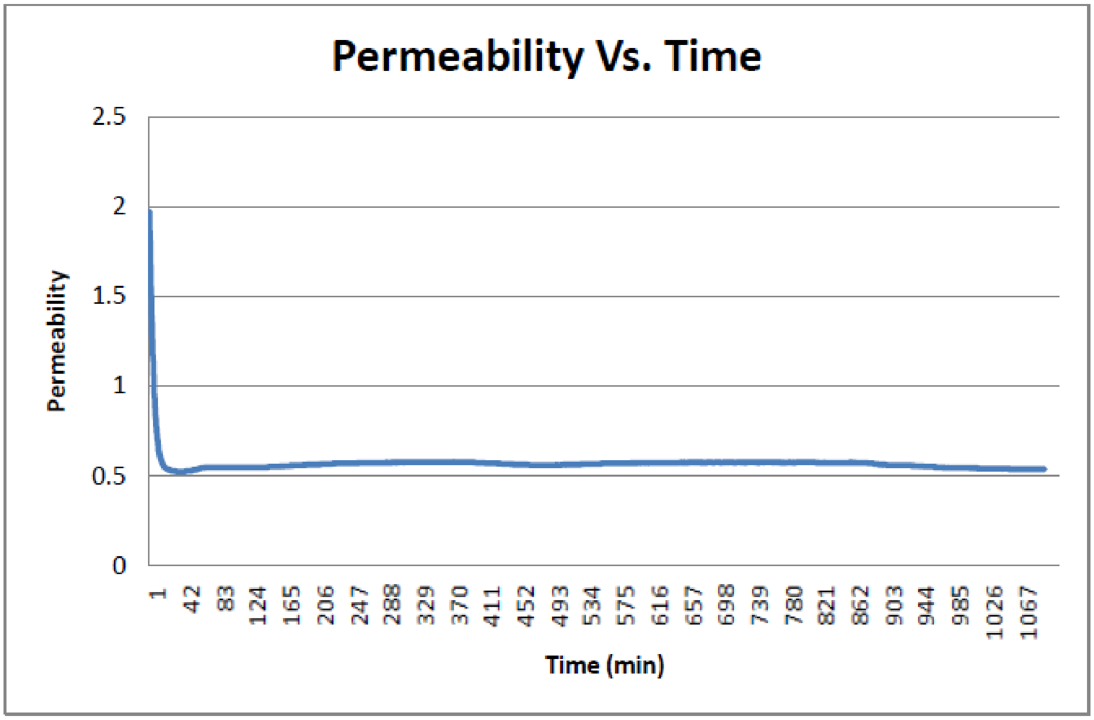


Figure 4.12 – Permeability result of dynamic test for 0.4% of alkaline injection (AFK 2)

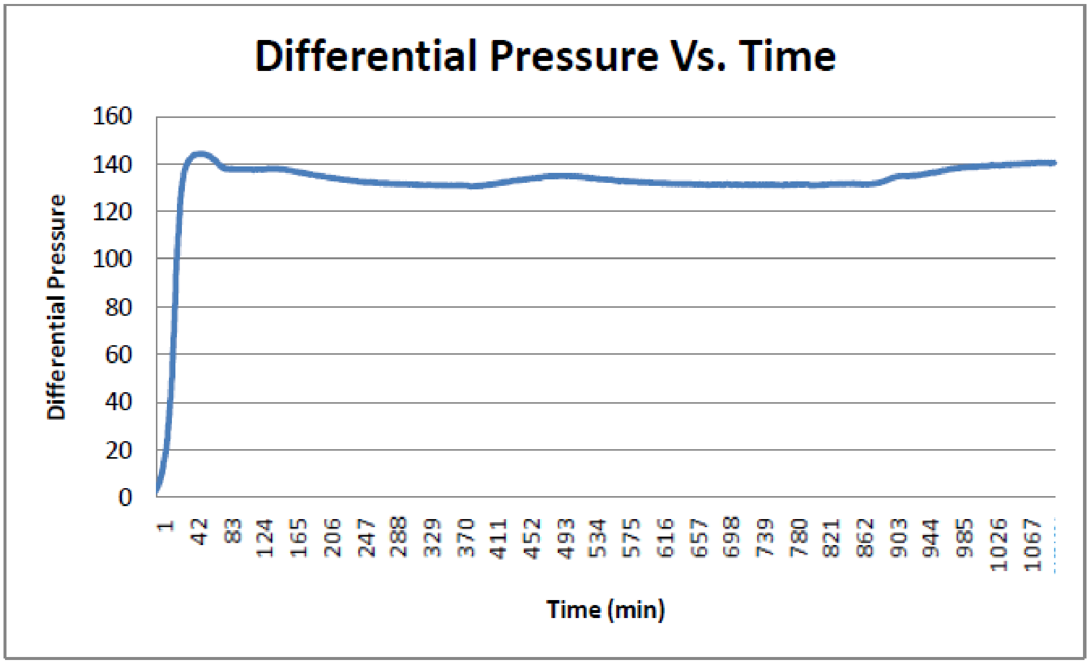


Figure 4.13 – Differential pressure result of dynamic test for 0.4% of alkaline injection (AFK 2)

The core was then flooded with 0.4% of sodium carbonate with salinity of 25 000 ppm, until the differential pressure stabilize. The injection rate was reduced to 0.3 cc/min match the fluid movement with the reservoir. In **Figure 4.12**, the permeability reduces until 0.35, when the differential pressure had stabilized (**Fig. 4.13**) and the permeability remain constant. From there, an increase in permeability was seen at around 0.11 mD.

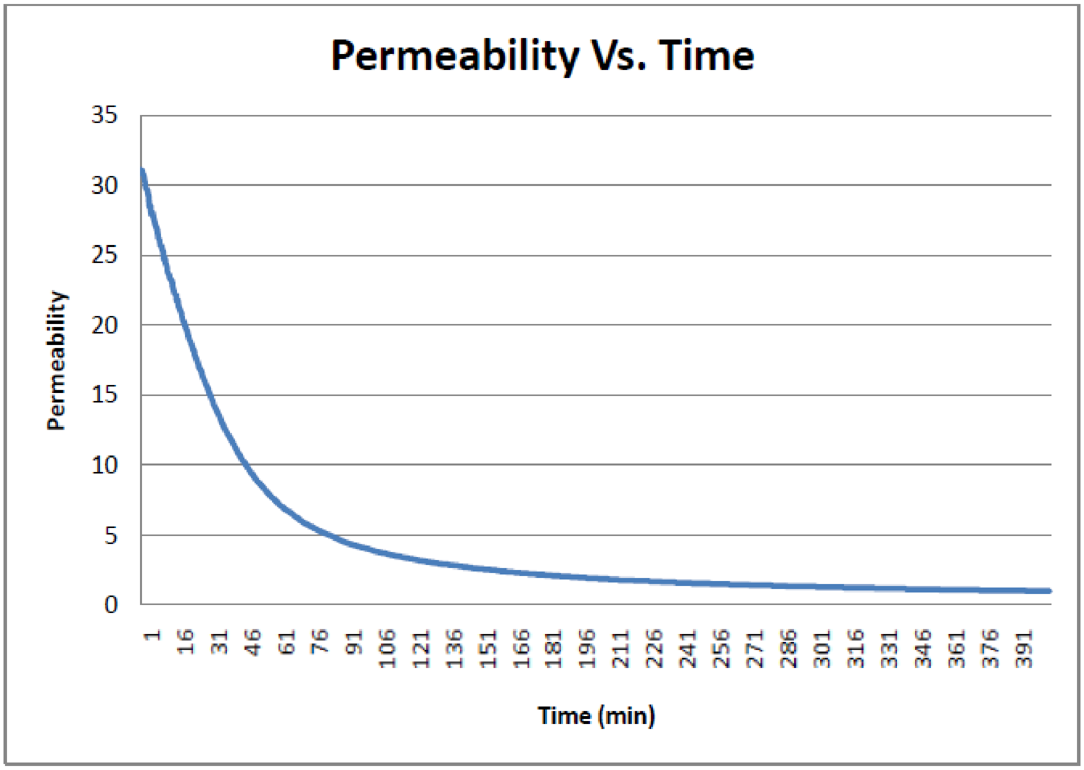


Figure 4.14 – Permeability result of dynamic test for distilled water injection (AFK 6)

Figure 4.14 shows the injection graph for AFK 6 during the distilled water injection. As in salinity test, the temperature was kept constant during the whole experiment. The reading for the permeability was taken when it pressure has stabilize. **Figure 4.15**, shows the changes in differential pressure. It increased and began to stabilize at around 400 min of injection. The reading of permeability shows at 0.98 mD. The experiment is then continue by injecting 1.0% of sodium carbonate with 25 000 ppm of salinity into the core. The injection rate was also reduced to 0.3 cc/min to match the fluid movement within the reservoir, as done in earlier experiment.

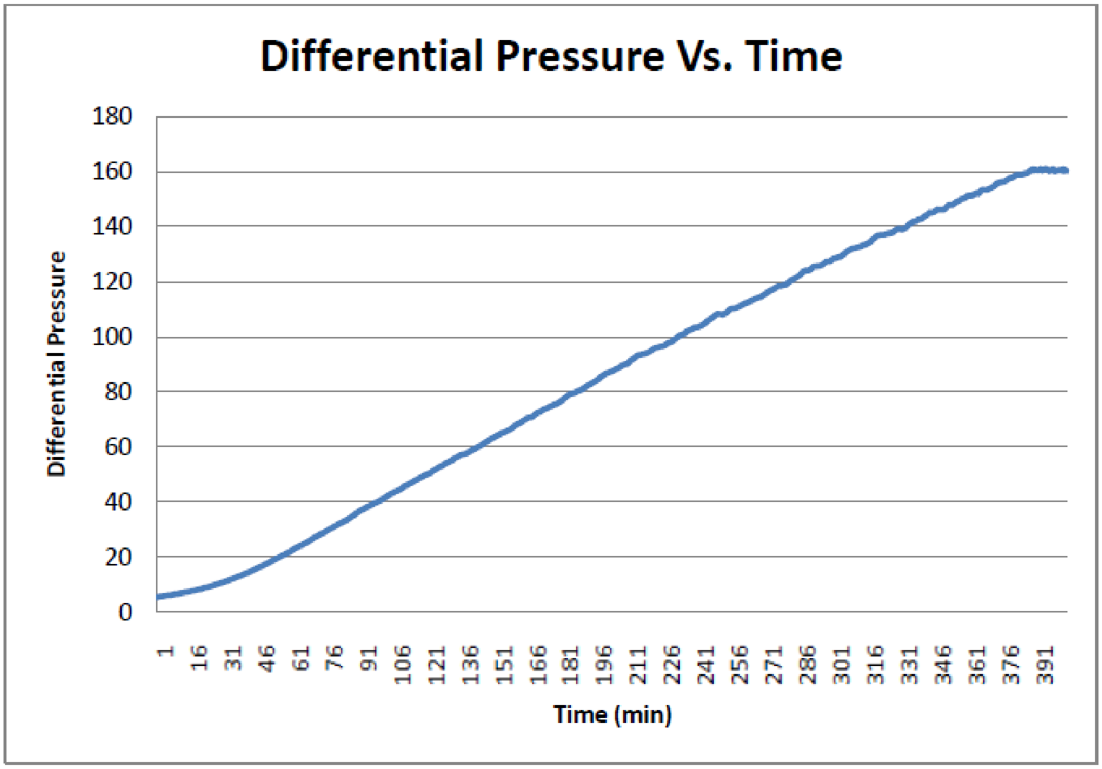


Figure 4.15 – Differential pressure result of dynamic test for distilled water injection (AFK 6)

The pressure began to stabilize after 300 min of injection and it stays until the equipment is put to stop after 900 min of running. The final permeability reading was 1.62 mD with differential pressure of 45 psi. The increase of permeability suggested that there has been improvement in interconnecting pore space. This is highly due to the dissolved of silica from quartz due to dissolution process.

Core Sample	K_{air}	Pore Volume	Bulk Volume
AFK 4	184.601	17.392	20.153
AFK 2	184.789	16.74	19.464
AFK 6	174.149	17.151	19.379
AFK 4 (Salinity)	107.988	16.304	18.892
AFK 2 (0.4% Alk)	31.741	16.511	19.198
AFK 6 (1.0% Alk)	61.407	17.115	19.338

Table 4.4 – Results from Poroperm

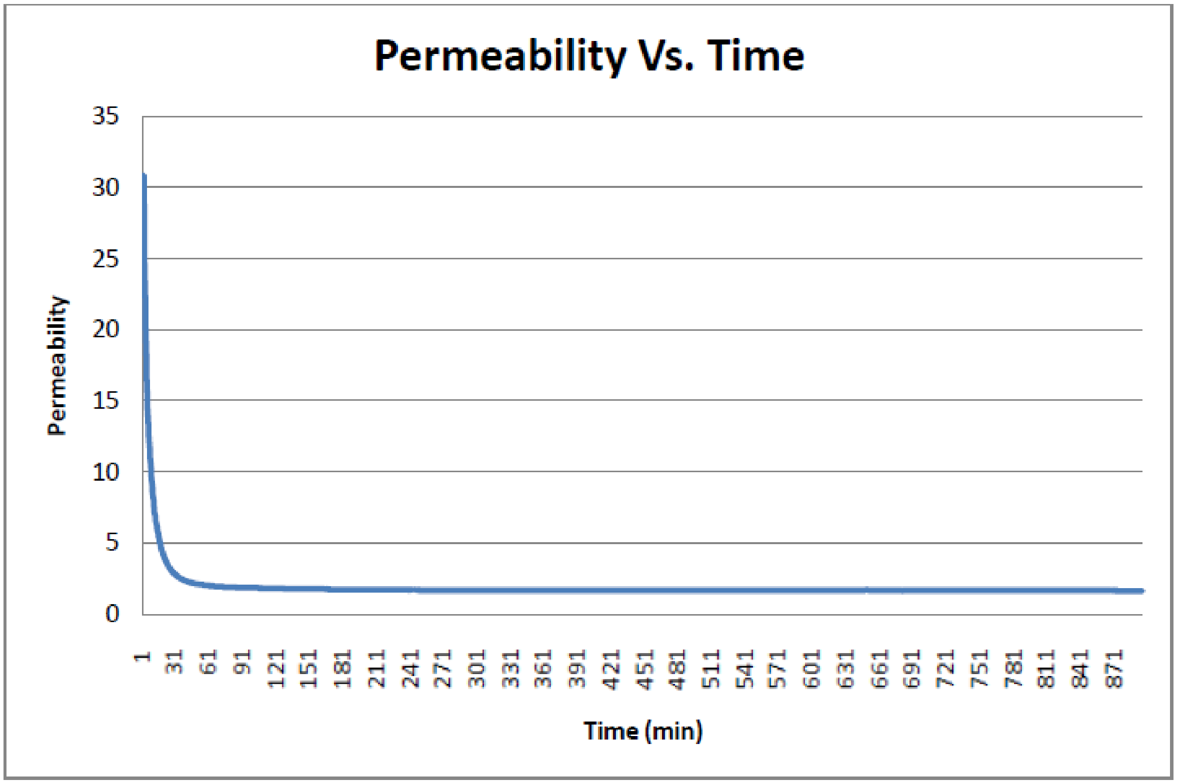


Figure 4.16 – Permeability result of dynamic test for 1.0% of alkaline injection (AFK 6)

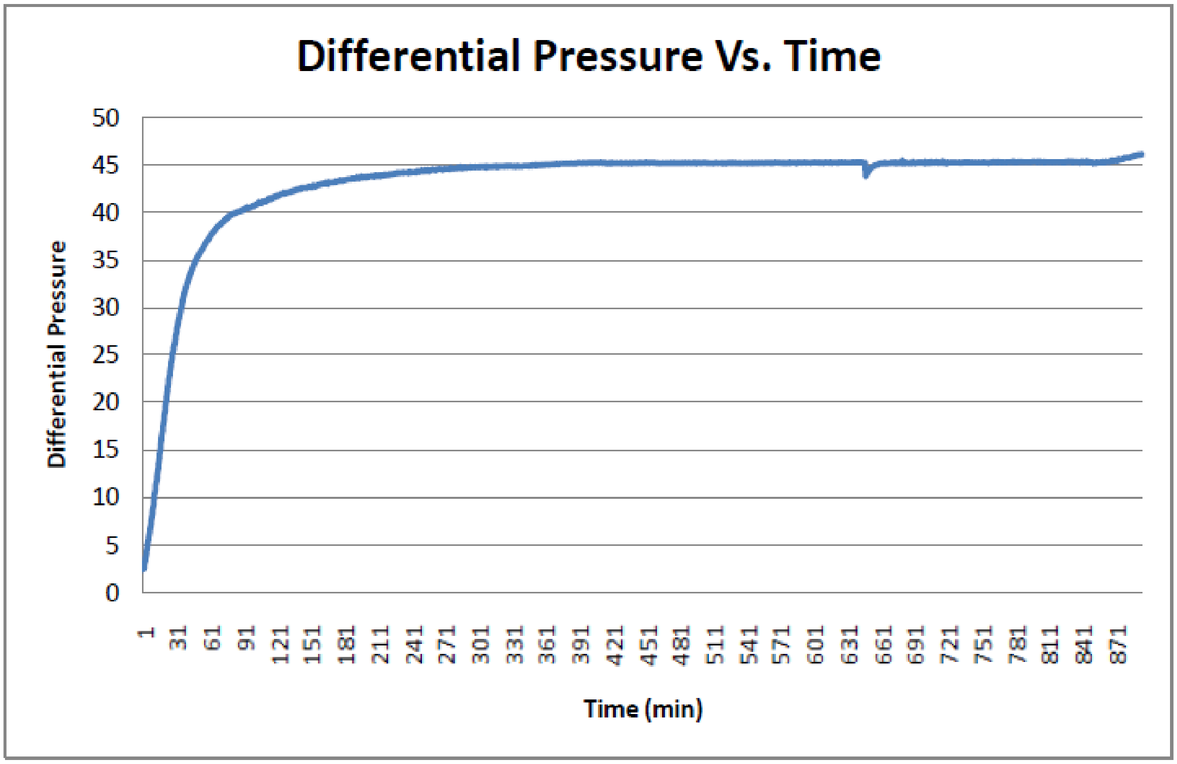


Figure 4.17 – Differential pressure result of dynamic test for 1.0 % of alkaline injection (AFK 6)

When comparing the salinity results with the alkaline results, it shows that salinity recorded a higher increase of permeability, 1.48 mD while alkaline results only increase at 0.64 mD. However, this does not mean that salinity cause higher rate of dissolution when comparing with the alkaline. This is because the parameter is not the same. The higher permeability shows higher interconnecting pore space, thus leading to bigger surface area expose to the dissolution process. Since alkaline has lower initial reading for permeability, it has lower surface area exposed when comparing with the salinity test.

Brine	Perm with Distilled Water	Perm with Brine	Differences	Percentage of Differences
0.0% Na_2CO_3, 25 000 ppm NaCl	7.51	8.99	+1.48	+19.71
0.4% Na_2CO_3, 25 000 ppm NaCl	0.24	0.35	+0.11	+51.42
1.0% Na_2CO_3, 25 000 ppm NaCl	0.98	1.65	+0.67	+63.30

Table 4.5 – Summary of dynamic test results for all injections

To make it at a parameter that can be compared with the same parameter, the percentage of increase were done to compare the result where it will be depending with its initial permeability. Based on **Table 4.5**, brine with only salinity concentration shows an increase in permeability at 1.48 mD, with 19.71% of increase in overall permeability. While brine with presence of 1.0% of Na_2CO_3 shows 0.64 mD of increase of permeability, with 63.30% on increase in overall permeability. Based on earlier static test, the results indicate that alkaline has higher dissolution rate when compare with salinity result. When comparing the result on dynamic test, it shows that the higher silica dissolution rate will cause higher increase in permeability. When comparing between 1.0% Na_2CO_3 with 0.4% Na_2CO_3 results, 1.0% Na_2CO_3 recorded higher percentage of permeability changes at 63.30% while 0.4% Na_2CO_3 only at 51.42%.

This is because lower silica dissolution has taken place in 0.4% Na_2CO_3, thus, causes lower silica to be dissolved when compare with 1.0%. Na_2CO_3. The trend follows when comparing between 0.4% Na_2CO_3 and brine with only salinity presence. Since salinity recorded lower silica dissolution rate, it will has lower increase in percentage of permeability.

This indicates that with higher silica dissolution rate taken place, more silica were able to be dissolved thus causes higher increase in permeability. Increase in permeability, although is favorable to allow more production in oil, in this case is different. This increase in permeability will be seen near the injection well where the water and alkaline were initially injection. This soluble silica will moves through the reservoir, following the path of the fluid moves which is toward the production well. As it flows toward the production well, it will react with the reservoir fluid that will alter its initial properties such as pH and composition. This reaction can decrease its solubility and prompt for silica polymerization that will lead to silica deposition. Thus, having a high increase in permeability is not very favorable since more silica will be dissolved in the solution.

As for the results measured using gas, all of the cores recorded lower permeability reading compared with the initial run. This is highly due to the reaction from injecting distilled water into the core. The distilled water causes the core to be damaged during its injection. This can be seen when cloudy solution was collected at the end of the outlet section.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The static experiment was to study the effect of salinity and alkaline to the silica dissolution process. From the result obtained, the salinity and alkaline do have effect on the silica dissolution, resulting in an increase in dissolution rate as its concentration increases. However, while salinity can affect the dissolution process, it cannot alter the solubility that highly effected due to the pH value. Hence, a high pH value alkaline such as sodium carbonate or sodium hydroxide, will has the greatest impact on silica dissolution as it not only increase the dissolution rate but also the solubility that will lead to more soluble silica to be transported. In the dynamic experiment, the results indicated that the higher the rate of silica dissolution will cause more silica to be dissolved in the solution. This can be seen with the increase in permeability.

5.1 Recommendation for Static Test

1. For better analysis, the concentration should be varied at a greater range to get reliable overview parameters.
2. Use a higher pH value to further study on the effect of pH on silica dissolution
3. Increase the experiment time period further than just 10 days to see the equilibrium for each of the concentration.

5.2 Recommendation for Dynamic Test

1. For better initial permeability reading, it is proposed to start injecting at the same 0.3 cc/min as the flow will allow the fluid to enter the core smoothly.
2. It is proposed to start injecting the core with brine as distilled water is found to be damaging for the core thus affecting the experiment.
3. It is proposed to measure the waste water from the injection for silica concentration to verity the silica dissolution has taken place.

REFERENCES

1. R.K. Iler, The Chemistry Of Silica, John Wiley & Sons, New York, 1979.
2. J.S. Gill, Silica Scale Control, Paper NACE 98226 presented at the NACE International Corrosion 1998, San Diego, California, March 22-27.
3. Amjad, Z. And R.W. Zuhl. 2008. An Evaluation of Silica Scale Control Additives for Industrial Water Systems. Paper NACE 08368 presented at the NACE International Corrosion 2008, New Orleans, Lousiana, March 16-20.
4. Arensdorf, J., Hoster, D., McDougall, D., Yuan, M. 2010. Static and Dynamic Testing of Silicate Scale Inhibitor. Paper SPE 132212 presented at the CPS/SPE International Oil & Gas Coference and Exhibition, Beijing, China, 8-10 June 2010.
5. Sonne, J., Kerr, S., Miner, K. 2012. Application Of Silicate Scale Inhibitors For ASP Flooded Oilfields: A novel Approach To Testing and Delivery. Paper SPE 154332 presented at the SPE International Conference and Exhibition on Oilfield Scale, Aberdeen, UK, 30-31 May 2012.
6. Demadis, K.D., Stathoulopoulou, A., Ketsetzi, A. 2007. Inhibition and Control of Colloidal Silica: Can Chemical Additives Untie the “Gordian Knot” of Scale Formation? Paper NACE 07058 presented at the NACE International, Houston, Texas.
7. Arensdorf, J., Kerr, S., Miner, K., Ellis-Toddington, T. 2011. Mitigating Silicate Scale in Production Wells in an Oilfield in Arberta. Paper SPE 141422 presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, USA, 11-13 April 2011.
8. Amjad, Z., Zuhl, R.W. 2010. The Role of Water Chemistry on Preventing Silica Fouling in Industrial Water Systems. Paper NACE 10048 presented at the NACE International, Houston, Texas.
9. Saneie, S., Yortsos, Y.C. 1996. Paper SPE 17409 presented at SPE California Regional Meeting, Long Beach, California, 23-25 March 1996.
10. Sheikholeslami, R., Al-Mutaz, I.S., Koo, T., Young, A. Desalination. 139. 2001. 83-95.

11. Bremere, I., Kennedy, M., Mhyio, S., Jaljuli, A., Witkamp, G., Schippers, J. Desalination. 132. 2000. 89-100.
12. Demadis, K.D., Stathoulopoulou, A. Ind. Eng. Chem. Res. 2006. 45. 12. 4436-4440.
13. Bohlmann, E.G., Mesmer, R.E., Berlinski, P. 1979. Paper SPE 7889 presented at SPE 1979 International Symposium on Oilfield and Geothermal Chemistry, Houston, Texas, 22-24 January 1979.