# Study of Static Adsorption Test for Investigating Barium Sulphate Inorganic Scaling

by

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# CERTIFICATION OF APPROVAL

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UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
MAY 2011

# 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 except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

HASYIMAH GHAZALI

# ABSTRACT

Barium sulphate is one of the inorganic scaling that exists in this world. This scaling has lead to problems to the production system not only on the rate of production but also the completion components. It is crucial for the industrial men to handle this problem by not only overcome it but also prevent. The various inhibitors that available in the market may have contributed to the prevention of the scaling problems; however the need of environmental friendly chemicals as inhibitor is crucial to ensure the sustainability development in oil and gas industry. This study is about the evaluation of the commercial inhibitor and the green inhibitor to prevent the deposition of barium sulphate in the field. One of the experimental works for testing the inhibitor for scaling is static adsorption test. This report explains the background study of this project, objectives, literature review, methodology, results that have been obtained as well as the analysis of the results that has obtained from this project. The test has been run on 22 samples with different parameters which includes the concentration of scale inhibitors both conventional and green inhibitors, the pH of the solutions and the test temperatures. The analysis had concluded that the green inhibitor has positive promising effects to overcome the barium sulphate scale problem that occurs in the industry.

# ACKNOWLEDGEMENTS

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

Inorganic scales are the common problem faced in the wells either production wells or injection wells. Inorganic scales are basically the deposits of minerals that form from the mineral aqueous solution due to interruption in chemical equilibrium and thermodynamic which lead to the supersaturation. It can be classified to two major groups which are the carbonate and sulphate scales.

The barium sulphate, $BaSO_4$ formed when the alkaline earth metal, barium, Ba which present as positive ion dissolve in water with the sulphate which present as negative ion. The scales develop due to the deposition of these substances.

The scale deposition will lead to various problems such as formation and perforation blockage, scale build-up inside the tubing, pipeline and surface facilities, restriction to the movement of sliding sleeves, closure of downhole safety valve and wireline intervention tools. Barium sulphate scale mostly occurs in the field at the North Sea.

There are various ways available to treat and prevent the scale problems. There are namely by using the chemical modeling prediction, surface treatment, high polish surface, plug water producing zones, sulphate treatment, sulphate removal from seawater prior to injection, injection of aquifer water with limited sulphate content and scale inhibitor. This study will focus on the evaluation of two types of scale inhibitors which is green inhibitors and conventional inhibitors to prevent the barium sulphate deposition as a scale.

There are many experimental procedures that can be used to evaluate the efficiency of scale inhibitors. There are namely static bottle tests, tube blocking test compatibility tests, thermal ageing static adsorption test and also dynamic adsorption tests. For this study the static adsorption test will be conducted to evaluate the selected inhibitors.

## 1.2 Problem statement

Barium sulphate is one of the most complex scale type occurs which cannot be resolved in water or hydrochloric acid (HCl). There are many ways present nowadays to prevent and overcome the scale problems. There are namely using the scale inhibitors and removal techniques such as mechanical as well as chemical methods. This study is about finding the best inhibitors to avoid the deposition of barium sulphate.

The efficiency of scale inhibitors may varies accordingly, but it is important for the industries to commercialize the usage of green inhibitors as to protect the environment. Thus, the study of static adsorption for inhibitors of barium sulphate is to determine the efficiency of several types of inhibitors which are conventional inhibitors and green inhibitors will be conducted during this project.

## 1.3 Objectives & Scope of Study

Objectives:

- To conduct static adsorption test for barium sulphate inorganic scale
- To evaluate the efficiency of inhibitors used in the experiment in delaying nucleation process
- To compare the performance of inhibitors for barium sulphate scaling with previous study

Scope of study:

- Literature review- research & data gathering
- Analyzing test subjects, variables and parameters
- Identifying test procedures and mechanism

## 1.4 Relevancy of Project

This project is to study about the chemicals that are potentially being used as inhibitors. The study is to evaluate the efficiency of various inhibitors in order to choose the best and most efficient that should be used in the industry with no environmental effect. It will not only focusing on the effect of work itself, but also will be considering the economical feasibility.

## 1.5 Feasibility of Study within the Scope and Time Frame

This study is expected to be very much feasible as the followings are considered:

- All equipments and tools are readily available at the university labs and the chemicals needed can be purchase easily.
- The static adsorption experiment is well understood thus a smooth work procedure while conducting this experiment is expected.
- The variables for this experiment will be tested based on reasonable parameters range. Thus, it is easy to conduct.
- As the experimental work expected a result within a short time frame, this study should finish within the allocated time.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Barium Sulphate Inorganic Scaling

Inorganic scaling is actually the deposition of sparingly soluble inorganic salts from the aqueous solution. There are many types of scales encountered in the industry namely calcium carbonate, sulphate scale, sulfide scales as well as sodium chloride. Sulphate scales formed when there is a mixture between the formation water and injected sea water. Barium is in the group II metal ions, which its sulphates solubility decreases as going down the group thus explains why the barium sulphate is most insoluble and hardest to control.

$$Ba^{2+} + SO_4^{2-} \text{->} BaSO_4 \text{ (ppt)}$$

When the precipitation occurs near the wellbore region, the sulphate scale will causes the formation damage. Sulphate scale typically happens in the seawater-flooded reservoir (Taylor and Francis, 2009). Only the best dissolver at reasonable rate would be able to dissolve the barium sulphate as it is very stubborn and insoluble in the water and hydrochloric acid as mentioned earlier. The formation water usually does not require high concentration of barium ion for the barium sulphate scale to deposit due to its high insolubility.

The ratio of formation water to seawater breakthrough plays an important role to rigorousness of the deposition of sulphate scale. Besides that, the severity of sulphate scale also depends on the degree of supersaturation.

## 2.2 Scale Inhibitors

To prevent the supersaturation of barium sulphate, an agent that has the ability to avert or retard the nucleation or crystal growth of inorganic scales called scale inhibitors are used. Non-polymeric and polymeric inhibitors are commonly used to adsorb onto the crystal surfaces, which then consumed in lattice thus slowing the growth and nucleation. Such inhibitors are categorized into two groups namely green inhibitor (biodegradable and environmental friendly) and non-green inhibitor.

The inhibitors are believed to work based on the two mechanisms which are firstly is the nucleation inhibition where the scale crystals that formed disrupted or redissolved by the action of inhibitor molecules. The other mechanism is crystal growth restrain where the inhibitor is adsorbing or interacts with the active crystal growing edges or spirals consequently retarding or stopping the crystal growth process (K.S Sorbie, et al, 2004).

### 2.2.1 Diethylenetriaminepenta; Methylene-phosphonic Acid (DTPMPA)

Diethylenetriaminepenta; methylene-phosphonic acid (DTPMPA) is the conventional inhibitor which is accepted widely due to its simplicity and commercial viability at low cost (Taylor and Francis Group, 2009).

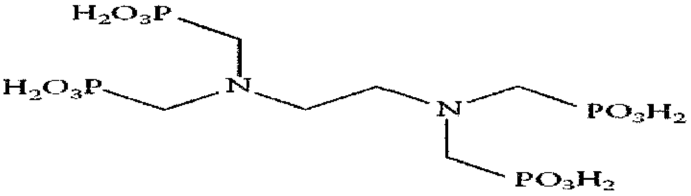

*Figure 1: Molecular structure of methylenephosphonic acid (DTPMPA)*

DTPMPA is the non-polymeric phosphonate molecules where it is known that the small molecular phosphonate work primarily as crystal growth inhibitors. This agent is innocuous and can be easily dissolved in acid solution. Besides that DTPMPA has excellent scale and corrosion inhibition and good thermal tolerance ability. It also works effectively in the alkaline and high temperature environment better than other organophosphines (Quicerwater, 2011).

*Table 1: Specification of DTPMPA*

| Specifications | |
|---|---|
| **Molecular formula** | $C_9H_{28}N_3O_{15}P_5$ |
| **Molar mass** | 573.20 |
| **Appearance** | Brown transparent liquid |
| **Active acid** | 48.0 – 52.0% |
| **Phosphorus acid (as PO33-)** | 3.0% max |
| **Chloride (as Cl-)** | 12 – 17% |
| **Density (20 centigrade)** | 1.35 – 1.45 g/cm$^3$ |
| **pH (1% solution)** | 2.0 |
| **Fe ppm** | 35 max |
| **Specific gravity** | 1.420 at 20°C |
| **pH** | < 2 at 25°C |
| **Freezing point** | None |

### 2.2.2 Phosphino Polycarboxylic Acid (PPCA)

It is a one type of conventional inhibitor that works through a balance between nucleation inhibition mechanism and crystal growth retardation mechanism (C.E. Inches, et al, 2006). It contains a single phospino group attached to two polyacrylic or polymaleic chains. PPCA contains phosphorus atom that makes it easier to analyze compared to polycarboxilic acids and results in better performance in handling barium sulphate, calcium compatibility and rock adsorption. The productions of phosphinicosuccinic acid oligomers together with smaller molecules form the reaction of hypophosphite ions with maleic acid are useful for carbonate scale squeeze inhibitors (Taylor and Francis, 2009).

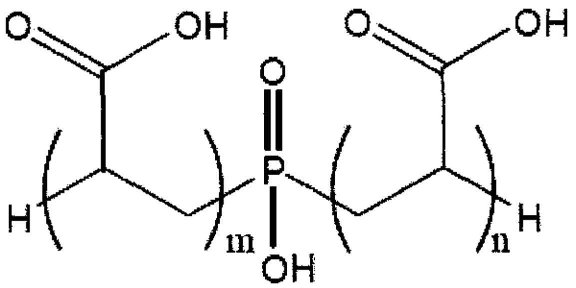

*Figure 2: Molecular structure of phospino polycarboxylic acid (PPCA)*

### 2.2.2 Carboxy Methyl Inuline (CMI)

It is a multipurpose scale inhibitor that has unique combination of anti scaling, sequestration and dispersing properties. Carboxymethylation of inulin chemical derivativation has produced the CMI. This green inhibitor has the inulin which is a reserve plant polysaccharide, extracted from chicory root. The inulin is the β poly-fructoside with a glucose unit at the reducing end. Its raw material is renewable. CMI which is high in calcium tolerance has high solubility in water and also low viscosity is the threshold scale inhibitor for calcium carbonate ($CaCO_3$), calcium sulphate ($CaSO_4$), barium sulphate ($BaSO_4$) and strontium sulphate ($SrSO_4$) scaling.

The introduction of carboxylate groups into the polysaccharide by carboxymethylation with sodium monochloro acetate is a reagent in alkaline medium. Degrees of substitution (DS) of the carboxymethyl inulin are made at different level and products are available with DS range from 1.5 to 2.5. Whereas the degree of polymerization (DP) is commercially at DP=10 (B. Bazin, et al, 2004).

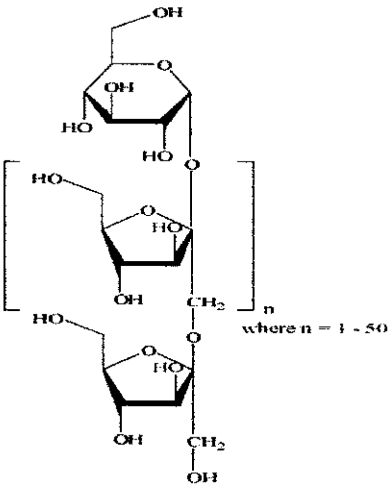

*Figure 3: Molecular structure of carboxy methyl inulins (CMI)*

### 2.2.3 Sodium of polyaspartic acid (PASP)

The sodium of polyaspartic acid (PASP) is also one of the green inhibitors that available in market and has promoted good performance against sulphate scale (N. Kohler, et al, 2002).

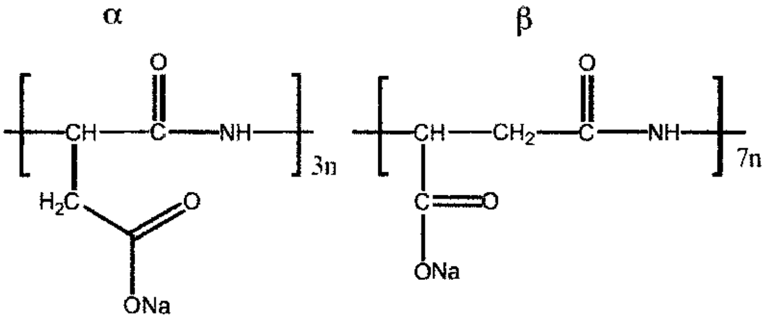

*Figure 4: Molecular structure of sodium polyaspartate (PASP)*

PASP is the polymeric inhibitor species which operate principally as nucleation inhibitors. This inhibitor is water soluble and green water treatment agent. It is non-phospor, non-nitrogen, non-pollution and fully biodegradable (Hgwaterchem, 2011). The reason why this type of inhibitor is biodegradable is because of the complex structure that has some degree of branching as shown in Figure 4.

The polyaspartate contains the α group and β group which the α group hold the pendant carboxylic acid groups one carbon atom further away from the peptide backbone than the β group (Taylor and Francis, 2009). The other factor that plays an important role to the polymer interaction with growth sites on the surface of growing mineral crystals is the molecular weight.

From the discussion of all the inhibitors above, it is decided that DTPMPA is used as the chosen conventional inhibitor and PASP as the green scale inhibitor for this study. The comparison of all the inhibitor is summarized in Table 2.

*Table 2: Comparisons of scale inhibitors conventional and green inhibitors*

| INHIBITORS | DESCRIPTION/ FUNCTIONS | LIMITATIONS | ADVANTAGES |
|---|---|---|---|
| **DTPMPA** | i. Scale inhibitor<br>ii. Deflocculant<br>iii. Sequestrant<br>iv. Water stabilizer in cooling water, boiler, oil-drilling | i. DTPMP works better at higher temperature<br>ii. Does not operate at lower pH values (< 4.5)<br>iii. Efficiency reduces in low $Ca^{2+}$<br>iv. Magnesium lowers inhibition efficiency<br>(B. Bazin, et al, 2004) | i. Very effective inhibitor for carbonate and sulphate based scales<br>ii. Commercially viable |
| **PPCA** | i. A type of phosphino polymer<br>ii. Able to inhibit sulphate scale | Phosphinate groups not bind well to rock compared to phosphonate group (Taylor and Francis, 2009) | i.Good for carbonate scale<br>ii. Presence of phosphorus atom gives better performance for barium sulphate (Taylor and Francis, 2009) |
| **CMI** | Green inhibitor that can be applied in various oilfield conditions | Lower adsorption lifetime compared to phosphonate in similar test conditions (B. Bazin, et al, 2004) | Excellent ecotoxicity profile for fresh and seawater species |
| **PASP** | i.Green inhibitor<br>ii. Inhibits both carbonate and sulphate scale.<br>iii. Corrosion inhibitor (R.J. Ross, et al, 1996) | Less efficient in high concentration | Squeeze lifetime of PASP is better than CMI and comparable with DTPMP |

### 2.3 Limestone

Limestone is one of the common formation types in the oil and gas well in the world. For investigating barium, the crushed limestone was used. Limestone is actually one of the carbonates sedimentology which is soluble in cold water. However, the solubility of carbonate decreases with increasing temperature and salinity. The sedimentary rock limestone usually contains two of the three minerals in carbonates which are aragonite and calcite. Aragonite is orthorhombic and usually brown to colorless in appearance. It reacts to acid (hydrochloric acid, HCl) and is chemically metastable. Whereas calcite is rhombodehral, colorless to white in appearance, also reacts with acid (HCl) and chemically stable.

Limestone is biogenic origins and habitually the fossils would be found as the organisms would live fossils in the rock. Nevertheless, the consolidated limestone contains the non-skeletal components of carbonates which typically are clasts. Clasts which are the reworked fragment of consolidated carbonate rocks or sediment are usually deposited either near their site of formation (intraclasts) or far from their original depositional environments (extraclasts). They are found in all environment types but are part of high-energy deposits (Bernerd Pierson, 2008). The limestone used in this study was taken from a field in Sarawak. Sarawak's fields are rich in carbonate formations.

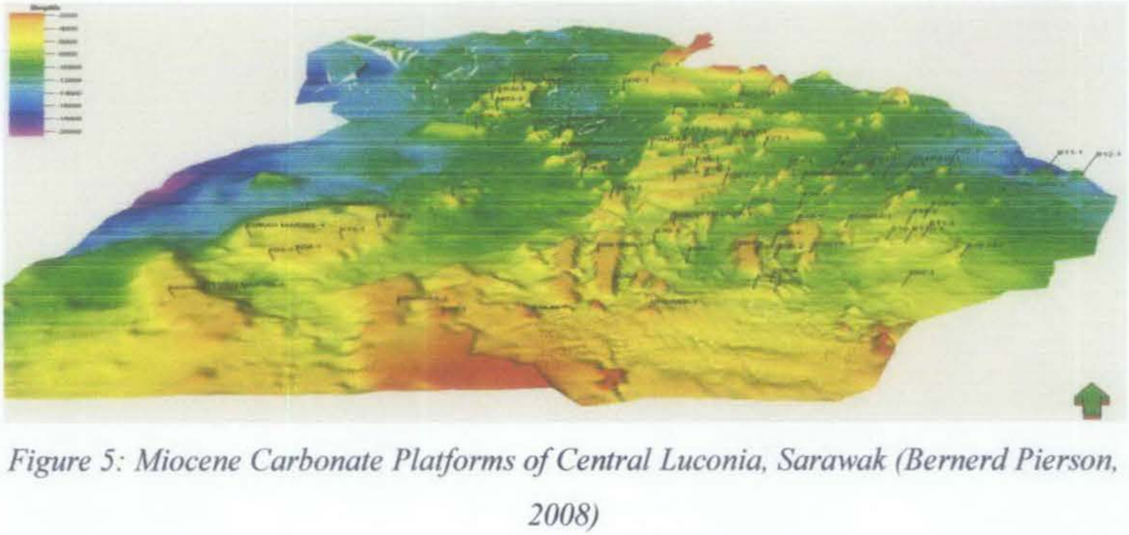

*Figure 5: Miocene Carbonate Platforms of Central Luconia, Sarawak (Bernerd Pierson, 2008)*

## 2.4 Static Adsorption

The static adsorption test is one of the experimental procedures used in laboratory to evaluate the application of new scale inhibitors. The purpose of this test is to evaluate the adsorption for scale inhibitors from seawater onto the crushed minerals; limestone will be used in this case. The procedure of the experiment is briefly as follows:

Firstly the solution of synthetic formation water will be prepared. Then crushed mineral which is the limestone will be added to the formation water and left for some time to allow reaction with the formation water. Scale inhibitors will then be prepared using synthetic seawater composition. The solution of seawater and scale inhibitor will then be added to the solution of formation water and limestone. This sample is then shaken and left to sit overnight at desired temperature. The solution then will be filtered and the sample will be analyzed. The concentration of scale inhibitor and the pH of the solution are certainly is subject to the decided test parameters.

The test that will be conducted, static adsorption test is based on the measurement of the nucleation stimulation period for barium sulphate in the presence of various scale inhibitors at the same concentration, evaluated by the ranking of scale inhibitors according to their efficiency in nucleation development impediment. This test is conducted in the no flowing condition which suggested by the name itself, static adsorption.

The static adsorption occurs due the anion-cation interaction between the scale inhibitors molecules and the scale which in this case is the barium sulphate. As explained earlier, the alkaline earth metal is the cation while the sulphate in the seawater is the anion, the interaction then will cause the formation of barium sulphate, in the presence of scale inhibitors. The scale inhibitor which is an anion will then interact with barium and retarding the formation of barium sulphate crystal.

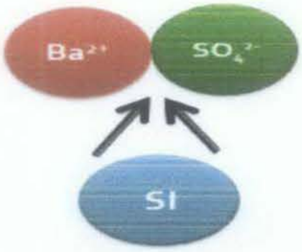

*Figure 6: The anion scale inhibitor (SI) molecules interact with the cation barium retarding the crystallization of barium sulphate*

## 2.5 Test parameters

The static adsorption test will be conducted at different temperature, pH and concentration. This is to compare the performance of each condition and decide for the best one to be use in industrial application. Those parameters are as follows:

### 2.5.1 Temperature

The temperatures chosen for testing this inhibitor using static adsorption technique are at 50°C and 90°C. This is to consider the optimum heat condition for the DTPMPA and PASP to work effectively. DTPMPA works better at high temperature and polymer such as PASP usually works better at lower temperature (K.S. Sorbie, N. Laing, 2004).

### 2.5.2 pH

The pH of the brine is very important for performing the static adsorption test using the scale inhibitors. This is because, the inhibitory function of the scale inhibitors are very much dependent and sensitive to the pH. Most of the scale inhibitors are very effective at pH >5.5 but relatively ineffective at more acidic pH.

The pH chosen for testing the DTPMPA and PASP are 7 and 8.6. It is important to observe the behavior and performance of the inhibitor at neutral condition. Nevertheless it is rather important to observe the performance at pH 8.6 to make a comparison and decide for the best pH that the scale inhibitor could work on. The pH 8.6 was chosen since DTPMPA operates better in alkaline condition while PASP has the original value of 9-10 and both work suitably and comparably at pH 8.6.

### 2.5.3 Concentration

The concentrations that the scale inhibitors will be tested are at 1000 ppm and 5000 ppm. It is a pertinent range to determine whether the inhibitor; DTPMPA and PASP works better at higher concentration or lower concentration. It is suggested by other research that polymer such as aspartate operates better at lower concentration (C.E. Inches, et al, 2006).

# CHAPTER 3

# METHODOLOGY

## 3.1 Experimental Details

Static adsorption experiment has been conducted with various parameters as below to obtained different condition of the samples.

*Table 3: Test parameters for static adsorption experiment*

| Inhibitors concentration (ppm) | Temperature (°C) | pH |
|---|---|---|
| **1000** | 50-90 | 7-8.6 |
| **5000** | 50-90 | 7-8.6 |

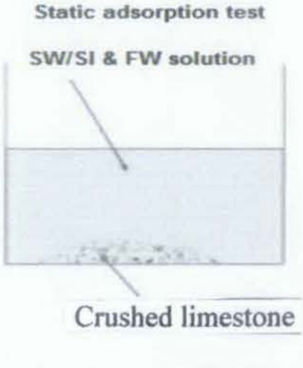

*Figure 7: Static adsorption test (M. Kahrwad, et al, 2008)*

As shown by the table above, the scale inhibitors are actually sensitive to the temperature, pH and the concentrations of itself. The inhibitors has been tested in the different condition of the parameters. Some modification had been made to the basic procedure of traditional static adsorption test. Usually, the test is conducted by using only seawater, scale inhibitor and crushed rock. However in this study, formation water had been introduced into the solution which contained the crushed mineral. This is to allow the reaction of barium and sulphate to observe the adsorption of scale inhibitor and the concentration of barium.

To prepare a sample, firstly synthetic formation water according to particular concentration of barium was prepared using barium chloride. It was set to desired pH. Then 50 mL of the formation water was added with 10 g of crushed limestone. The solution was left for 12 hours to allow the reaction of formation water and crushed mineral.

Meanwhile, the stock solution of scale inhibitor was prepared by adding 50 mL of the synthetic seawater which had been prepared earlier with preferred pH to a specified concentration of scale inhibitor. This solution was then added to the synthetic formation water solutions which contained the crushed mineral and were left to sit at desired temperature for 24 hours.After 24 hours, the samples were observed for any physical changes. They were then being filtered with 22µm filter paper and the sample solutions were measured for pH and barium concentration. The procedure of the experiment is summarized in the Figure 8.

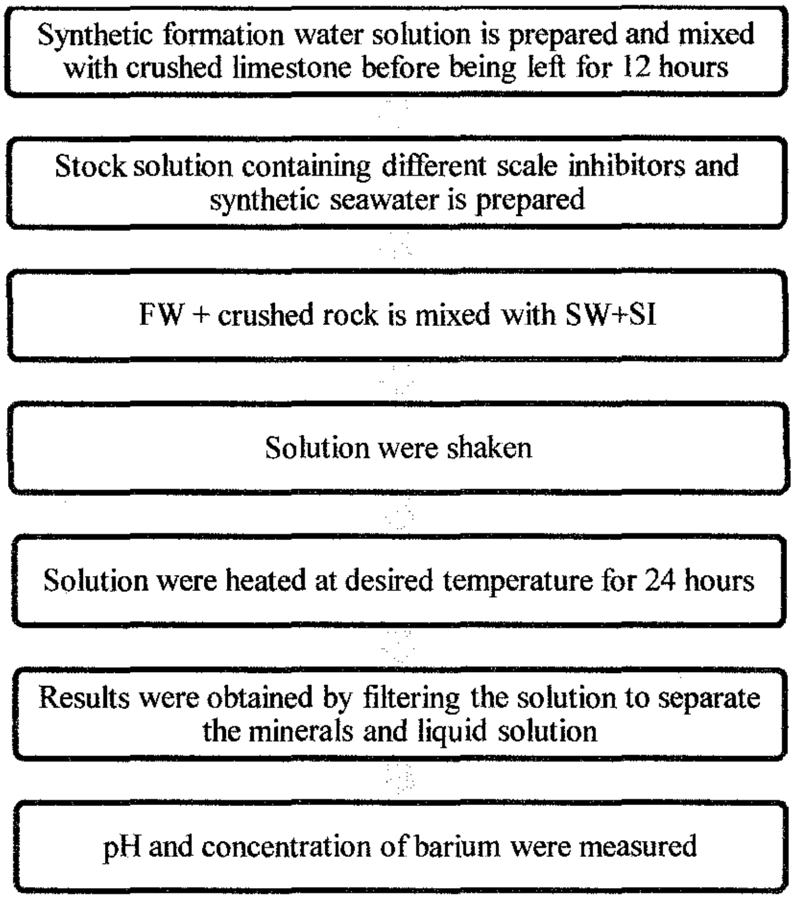

*Figure 8: Experiment procedure*

In conducting the experiment, the synthetic formation water and synthetic seawater is prepared with various ions composition of where the calculations of each mineral contained in the seawater is shown in the appendices. The composition of the synthetic seawater is shown below.

*Table 4: Synthetic formation water composition*

| Ions | Formation water, (ppm) | Concentration (g/L) | Mass for 8L |
|---|---|---|---|
| **Barium** | 250 | 0.44857 | 3.58856 |

*Table 5: Seawater composition*

| **Ions** | Seawater water, (ppm) | Concentration (g/L) | Mass for 8L |
|---|---|---|---|
| **Sodium** | 10200 | 22.79 | 182.32 |
| **Potassium** | 384 | 0.732 | 5.856 |
| **Magnesium** | 1300 | 10.8719 | 86.9752 |
| **Calcium** | 400 | 1.4671 | 11.7368 |
| **Chloride** | 18520 | 30.5305 | 244.244 |
| **Sulphate** | 2582 | 3.8175 | 30.54 |

### 3.2 Materials, Equipment and Tools

In this study several materials and equipment had been used to conduct the static adsorption test. Those materials and equipment are as follows:

Materials:

- Limestone
- Scale inhibitors (DTPMPA & PASP)
- Synthetic seawater ions: sodium chloride, potassium chloride, magnesium chloride, calcium chloride, sodium sulphate
- Synthetic formation water ions: barium chloride

*Figure 9: DTPMPA*

*Figure 10: From left: the limestone from formation, limestone been crushed to smaller cube, smaller size of crushed limestone*

Equipment and tools:

- Glass ware: Conical flasks, measuring cylinders, beakers, glass rod
- Filter paper
- Pump
- Water bath
- pH meter
- Spectrophometer

*Figure 11: Spechtrophometer*

## 3.3 Key Mile Stone and Planning

*Table 6: Gantt chart for the Second Semester Project Implementation*

| Activities | Week | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| Attain required materials and equipment | ▨ | ▨ | | | | | | | | | | | | | |
| Preparing the stock solution and crushed minerals | | | ▨ | | | | | | | | | | | | |
| Conduct static adsorption experiment | | | ▨ | ▨ | ▨ | | | | | | | | | | |
| Evaluate first stage result | | | | | ▨ | ▨ | | | | | | | | | |
| Submission of progress report | | | | | | ▨ | | | | | | | | | |
| Improve and continue experimental work | | | | | | | ▨ | ▨ | ▨ | | | | | | |
| Acquire and interpret results of second stage | | | | | | | | ▨ | ▨ | ▨ | | | | | |
| Pre-EDX | | | | | | | | | | | ▨ | | | | |
| Submission of Draft Report | | | | | | | | | | | | ▨ | | | |
| Submission of Dissertation (soft bound) | | | | | | | | | | | | | ▨ | | |
| Submission of Technical Paper | | | | | | | | | | | | | ▨ | | |
| Oral Presentation | | | | | | | | | | | | | | ▨ | |
| Submission of Project Dissertation (Hard Bound) | | | | | | | | | | | | | | | ▨ |

# CHAPTER 4

# RESULTS & DISCUSSION

## 4.1 Results & Discussion

The static adsorption experiment conducted using the synthetic seawater, synthetic formation water and crushed limestone results are as follows:

*Table 7: Results from scale inhibitor DTPMPA*

| SI concentration (ppm) | Temperature (°C) | pH (initial) | Average pH (final) | Observation |
|---|---|---|---|---|
| **1000** | 50 | 7 | 1.29 | Clear solution |
| **5000** | 50 | 7 | 0.66 | Yellowish solution without precipitation |
| **1000** | 90 | 7 | 1.47 | Clear solution |
| **5000** | 90 | 7 | 0.66 | Yellowish solution without precipitation |
| **1000** | 50 | 8.6 | 1.45 | Clear solution |
| **5000** | 50 | 8.6 | 0.71 | Yellowish solution without precipitation |
| **1000** | 90 | 8.6 | 0.33 | Clear solution |
| **5000** | 90 | 8.6 | 0.65 | Yellowish solution without precipitation |

*Table 8: Results from scale inhibitor PASP*

| SI concentration (ppm) | Temperature (°C) | pH (initial) | Average pH (final) | Observation |
|---|---|---|---|---|
| **1000** | 50 | 7 | 8.77 | Clear solution with white precipitation |
| **5000** | 50 | 7 | 8.79 | Yellowish solution with cloudy precipitation |
| **1000** | 90 | 7 | 8.45 | Clear solution |
| **5000** | 90 | 7 | 8.46 | Yellowish solution with precipitation |
| **1000** | 50 | 8.6 | 8.48 | Clear solution with white precipitation |
| **5000** | 50 | 8.6 | 8.58 | Yellowish solution with cloudy precipitation |
| **1000** | 90 | 8.6 | 8.88 | Clear solution with white precipitation |
| **5000** | 90 | 8.6 | 8.85 | Yellowish solution with bulky white precipitation |

From the results that have been obtained, it is observed that the pH of the stock solution changed drastically on DTPMPA while the PASP did not give much effect on the final pH measurement. Nevertheless the final pH of PASP stock solution with initial pH of 7 is a bit alkaline. It ranges from 8.45 to 8.49.

The solution of DTPMPA samples had featured an acidic condition in the final result. This may be due to the characteristic of the DTPMPA itself which is acidic in nature. The pH of DTPMPA is 2 at 25°C, thus when it being mixed with the seawater, the initial pH of the seawater (7 or 8.6) will be reduced. Whereas for PASP, its pH is around 9 to 10 at room temperature which tend to give alkaline effect when being mixed with the samples solution.

The samples which contained DTPMPA and PASP exhibited different appearances in the end of the experiment. The color of the samples had changed from clear to yellowish and cloudy with respect to different inhibitors as shown in the figures below.

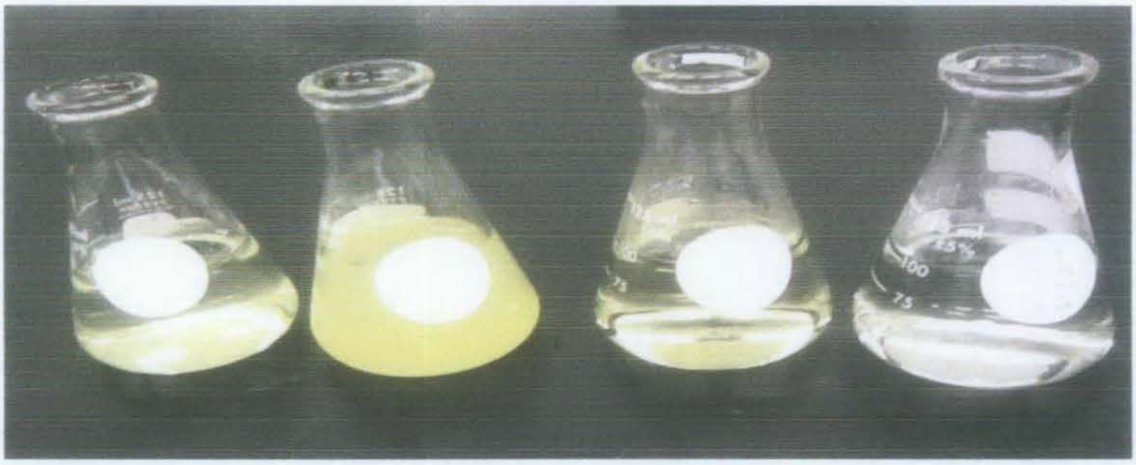

*Figure 12: Stock solution before being added to formation water with crushed mineral. From the left: DTPMPA 1000ppm, DTPMPA 5000ppm, PASP 5000ppm and PASP 1000ppm*

*Figure 13: Sample after being heated 24 hours. From the left: without scale inhibitor, PASP 1000ppm, PASP 5000ppm, DTPMPA 5000ppm, DTPMPA 1000ppm all at pH 7 and 90°C*

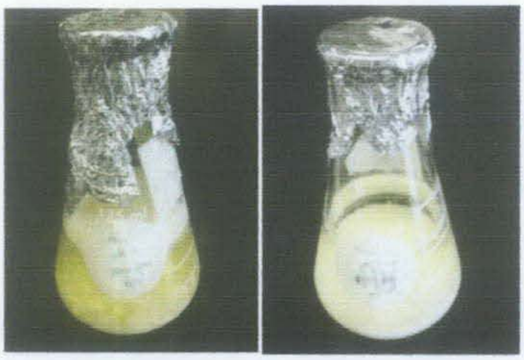

*Figure 14: Sample after being heated for 24 hours PASP 5000ppm. From left: PASP 1000ppm both at pH 7, 50°C*

*Figure 15: Sample after being heated for 24 hours. From left: DTPMPA 1000ppm, DTPMPA 5000ppm and without scale inhibitors all at pH 7, 50°C*

*Figure 16: Sample after being heated for 24 hours PASP 1000ppm. From left: PASP 5000ppm both at pH 8.6, 50°C*

*Figure 17: Sample after being heated for 24 hours. From left: DTPMPA 1000ppm, DTPMPA 5000ppm and without scale inhibitors all at pH 8.6, 50°C*

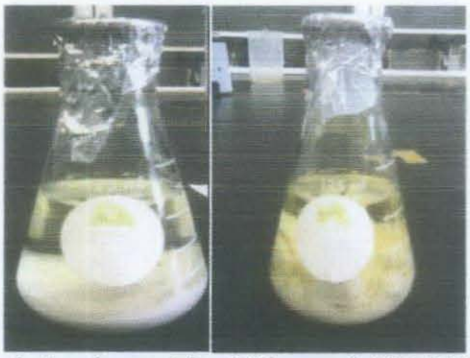

*Figure 18: Sample after being heated for 24 hours PASP 1000ppm. From left: PASP 5000ppm both at pH 8.6, 90°C*

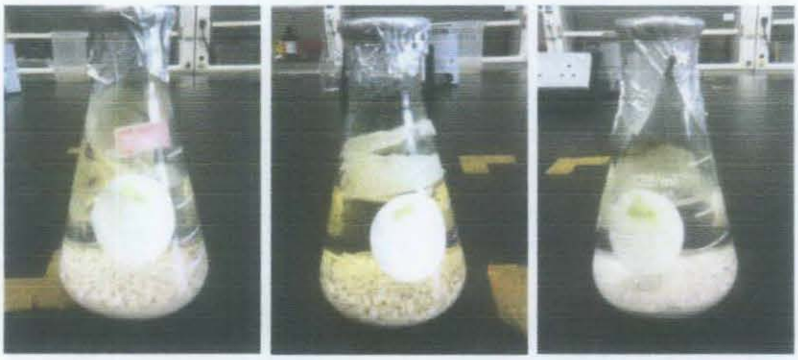

*Figure 19: Sample after being heated for 24 hours. From left: DTPMPA 1000ppm, DTPMPA 5000ppm and without scale inhibitors all at pH 8.6, 90°C*

To evaluate the performance of scale inhibitor, the final concentration of barium in the solution were measured after being heated. The concentration varies according to the temperatures, pH and concentration nonetheless it does not vary in wide range.

*Table 9: Barium concentration at the end of experiment*

| SI type | SI concentration (ppm) | Initial pH | Temperature (°C) | Final Ba concentration (mg/L) | Adsorption level, Γ (mg/g of rock) | % of Barium inhibited |
|---|---|---|---|---|---|---|
| **PASP** | 1000 | 7 | 50 | 9 | 1.36 | 93.88 |
| **PASP** | 5000 | 7 | 50 | 14 | 1.31 | 90.48 |
| **PASP** | 1000 | 7 | 90 | 40 | 1.05 | 72.79 |
| **PASP** | 5000 | 7 | 90 | 84 | 0.61 | 42.86 |
| **PASP** | 1000 | 8.6 | 50 | 9 | 1.36 | 93.88 |
| **PASP** | 5000 | 8.6 | 50 | 19 | 1.26 | 87.07 |
| **PASP** | 1000 | 8.6 | 90 | 35 | 1.1 | 76.19 |
| **PASP** | 5000 | 8.6 | 90 | 20 | 1.25 | 86.39 |
| **DTPMPA** | 1000 | 7 | 50 | 6 | 1.39 | 95.92 |
| **DTPMPA** | 5000 | 7 | 50 | 12 | 1.33 | 91.82 |
| **DTPMPA** | 1000 | 7 | 90 | 8 | 1.37 | 94.56 |
| **DTPMPA** | 5000 | 7 | 90 | 12 | 1.33 | 91.84 |
| **DTPMPA** | 1000 | 8.6 | 50 | 5 | 1.4 | 96.60 |
| **DTPMPA** | 5000 | 8.6 | 50 | 9 | 1.36 | 93.88 |
| **DTPMPA** | 1000 | 8.6 | 90 | 4 | 1.41 | 97.28 |
| **DTPMPA** | 5000 | 8.6 | 90 | 17 | 1.28 | 88.44 |

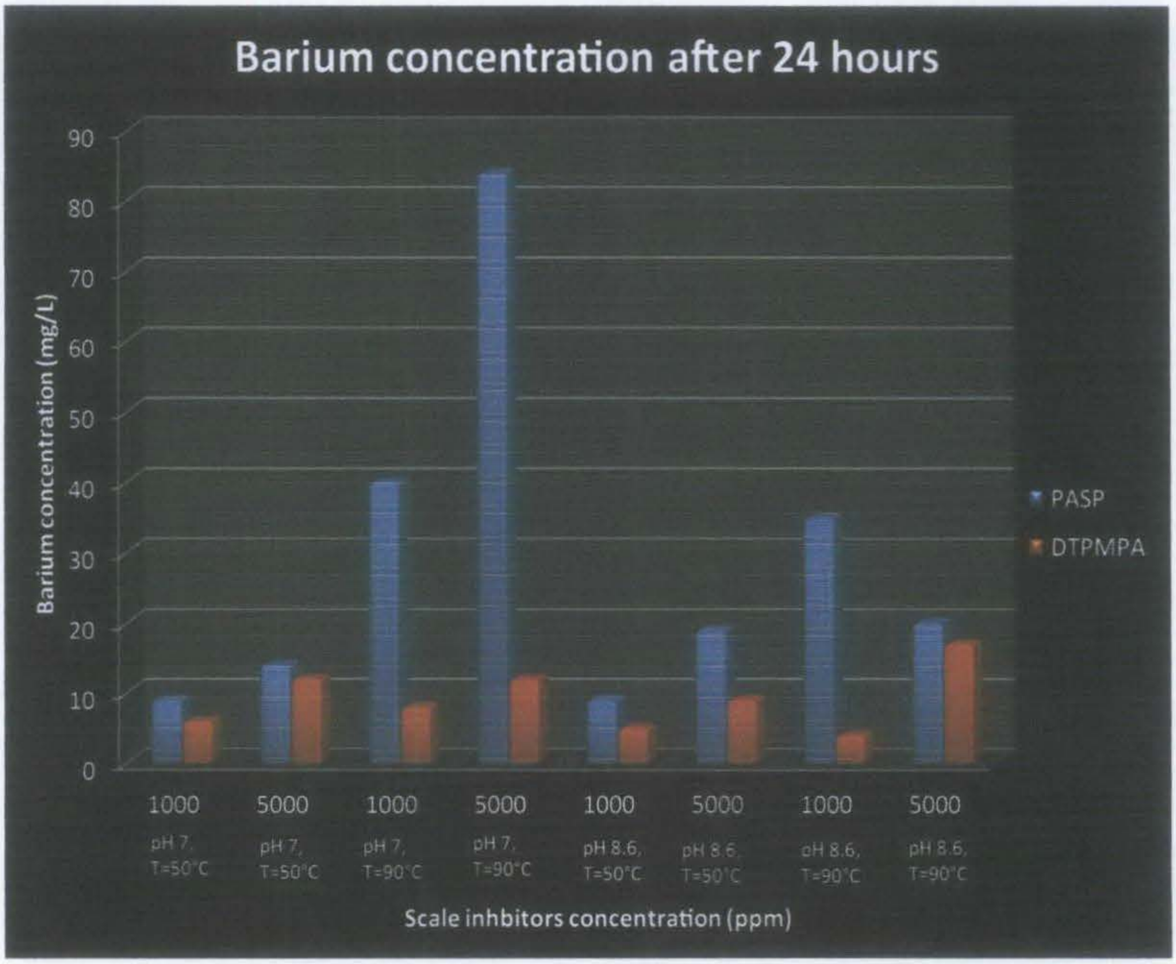

*Figure 20: Barium concentration after 24 hours*

The figure shows the concentration of barium at the end of the experiment. The concentration of barium from the sample solution was measured using the Hach Spectrophometer. The results of the experiment had shown that the samples concentrations of barium using DTPMPA are actually a bit lower compared to the samples concentration of using PASP. Nevertheless, the average percentage of difference between concentrations of barium using DTPMPA and PASP is ±10%.

DTPMPA has been proved worked in the static adsorption experiment conducted. The measurements of the final concentrations of barium are much lower than the initial concentration. Initially, the concentration of barium in every sample was 147 ppm. However, DTPMPA results shown that it inhibited more barium at lower concentration compared to higher concentration at both temperature 50°C and 90°C.

PASP also exhibited final concentrations of barium much lower than initial concentration in every sample. However, the overall results are a bit higher compared to DTPMPA. At temperature 90°C, PASP exhibited poor performance in inhibiting barium sulphate precipitation. It can be seen clearly from the graph above that in the pH 7 sample solution at 90°C, 1000 ppm PASP had left 40 mg/L barium uninhibited. While for pH 7 sample solution at 90°C, 5000 ppm of PASP had been unable to inhibit 84 mg/L of barium. From this observation, it showed that PASP actually has better inhibition tendencies at lower temperature. Furthermore, PASP exhibited that it has better inhibition tendencies at lower concentration rather than high concentration at both temperatures tested.

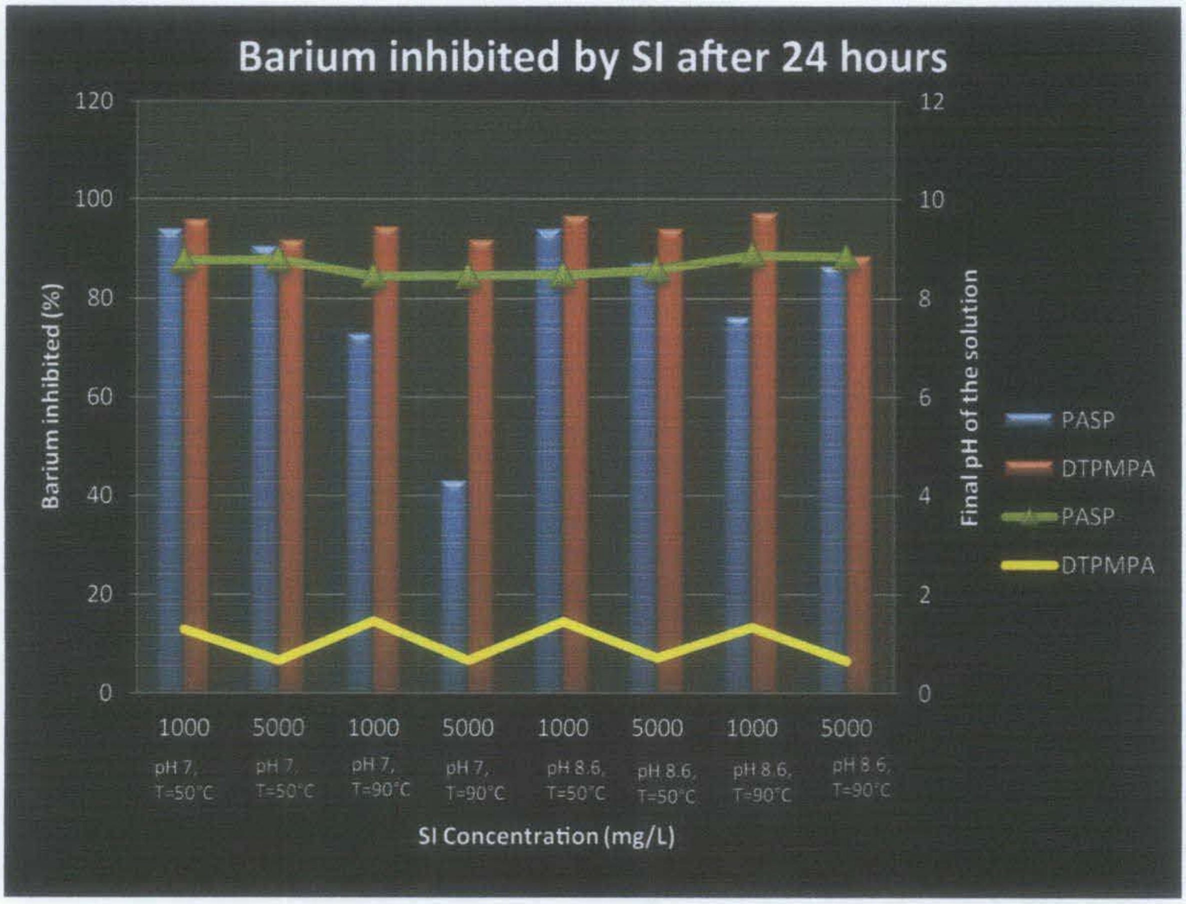

*Figure 21: Percentage of barium inhibition*

Figure 21 shows the inhibition of barium by both inhibitors and the effect of inhibitors concentrations to the final pH of the samples solution. DTPMA results had given very acidic pH value to the samples solution at the end of the experiment. This behavior has indicated that the DTPMPA which is acidic in standard condition has affected the initial pH of the samples solution.

Whereas for PASP, even it is acidic in nature, somehow the acidity does not have much effect on the final pH of the sample solution after being heated at 50°C and 90°C. The level of pH decrement for PASP samples at all tested pH, temperatures and concentrations did not drop drastically. It can be clearly seen from the graph above.

From the figure above, the observations also shown that the PASP works better at lower temperature, 50°C for both pH 7 and 8.6 rather than at higher temperature, 90°C. Even so for DTPMPA, the percentages of barium inhibition are much higher at higher temperature, 90°C for both pH 7 and 8 compared to at lower temperature, 50°C. The percentage of each sample can be seen in Table 9.

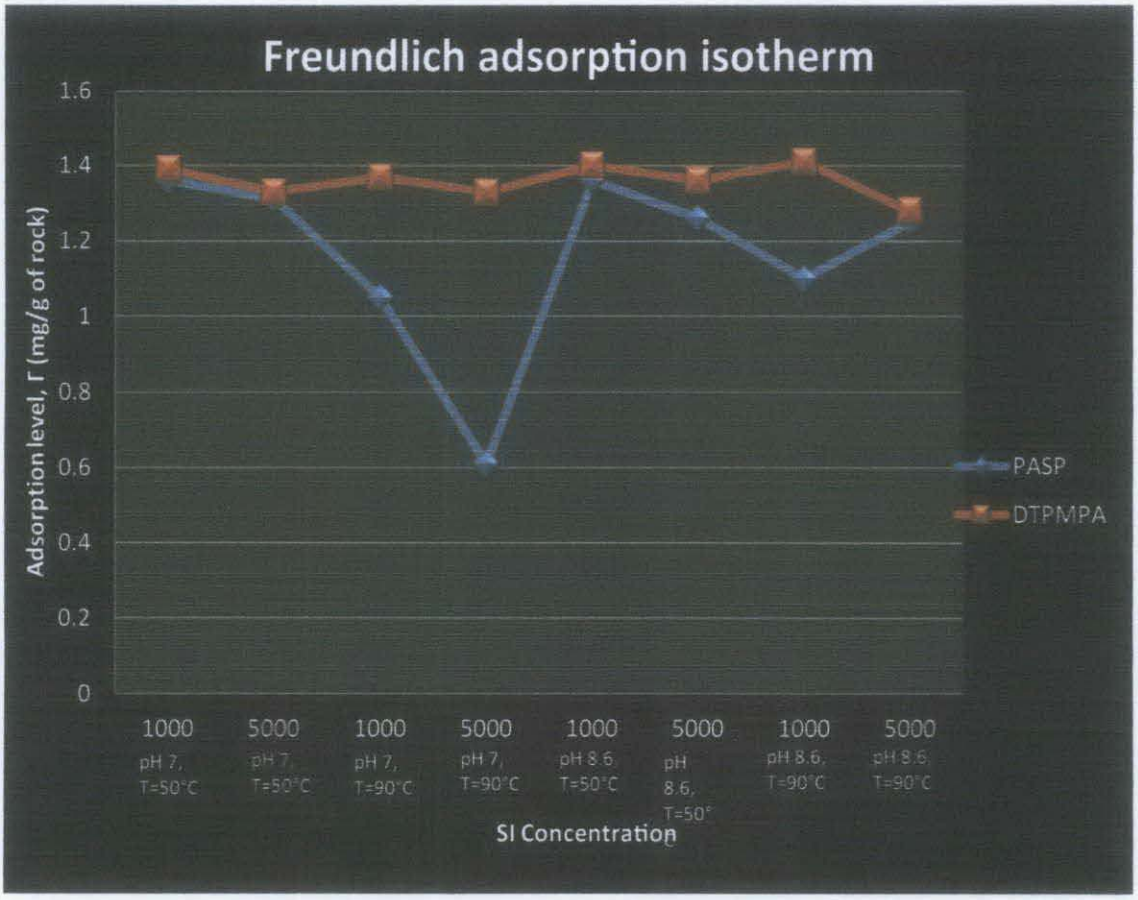

*Figure 22: Adsorption level of barium on rock based on Freundlich adsorption isotherm*

In this study, instead of measuring the concentration of inhibitor at the end of the experiment, the some modification has been done by measuring the final concentration of each sample solution. From the concentration measured, the performance of both scale inhibitors DTPMPA and PASP are analyzed by calculating the adsorption level, Γ (in mg/g) as below:

$$\Gamma = V\ (C_o\text{-}C_{eq})\ /\ \mathrm{m}$$

Where $C_o$ is the initial concentration of barium in the solution (mg/L or ppm), volume, V (L) of bulk solution, $C_{eq}$ the equilibrium concentration, and m (g) is the mass of the crushed minerals. The mathematical form of adsorption isotherm can be derived from Freundlich form (M. Kahrwad, et al, 2009).

The figure above shows that the performance trend is a bit different between DTPMPA and PASP. The trend of DTPMPA shows that the adsorption level of barium on the rock is more or less the same at range 1.3 to 1.4. However the PASP gives adsorption level of barium on the rock lower than DTPMPA. This shows that the percentage of barium adsorb by the rock is low. It could be resulted from the activities of the inhibitors which adsorbing on the rock surface and prevent the barium from contacting with sulphate to form precipitation. This explains why the level of adsorption of barium on the rock is very low. The results for each sample are shown in Table 9.

## 4.2 Comparison with Previous Study

This study is focusing on the evaluation of the two different inhibitors which are the conventional one and the green inhibitors. Both of the inhibitors were tested with the same variables and parameters.

The results that will be obtained from this experiment are expected to support the usage of the green inhibitor. As shown from previous study of other scholars, the results that they have obtained had shown positive observation for the usage of the green inhibitors.

The comparison had been made from the test temperature point of view. In previous studies, it shows that temperature factor also influence the activity of the inhibitors both green and commercial. DTPMPA performing better at high temperature compare to lower temperature. This has been proven in this study and it is parallel to study of K. S. Sorbie and N. Laing, 2004 entitled "How Scale Inhibitors Work: Mechanisms of Selected Barium Sulphate Scale Inhibitors Across a Wide Temperature Range".

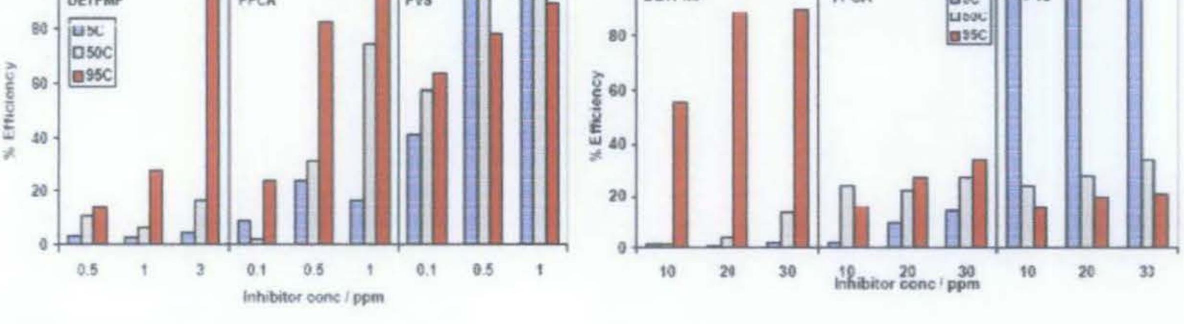

*Figure 23: $BaSO_4$ inhibition efficiency of DETPMP, PVS and PPCA on different formation water/seawater mixture after 22 hours( K.S Sorbie et al, 2004)*

The study of K.S Sorbie et al on working mechanism scale inhibitor for barium sulphate shows as figure above where it is observed that DETPMP which is the polymeric type of inhibitor works better at higher temperature, PPCS follows a similar trend to DETPMP but the inhibition efficiency drops off much less radically than DETPMP at temperature drops and PVS works much better at lower temperature (K.S Sorbie et al, 2004). Similar to the results obtained from the experiment, it is observed that DTPMPA which is also the polymeric type of inhibitor gave better inhibition at high temperature.

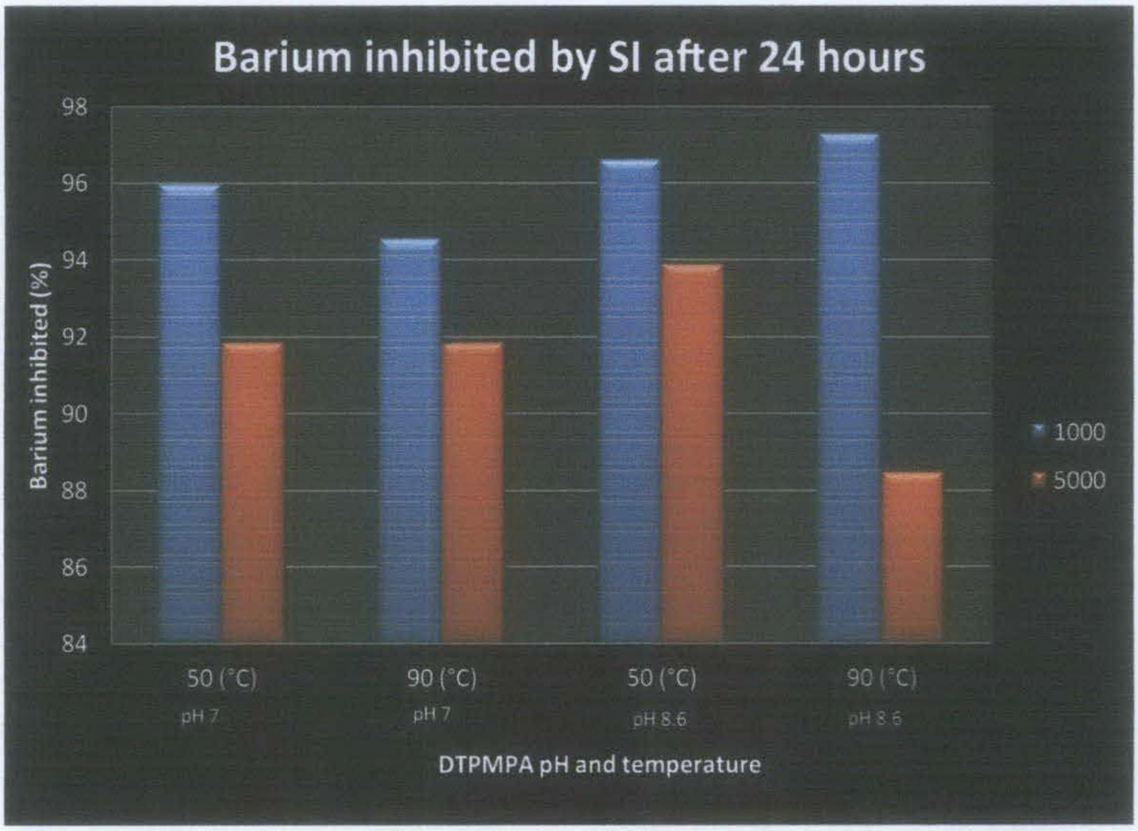

*Figure 24: Percentage of barium inhibited using DTPMPA at temperature 50°C and 90°C*

The graph above shows that the DTPMPA works better at higher temperature as compared to lower temperature at the pH of 8.6 and concentration of 1000 ppm. However for pH 7, the concentration 5000 ppm at 90°C gives slightly better performance compared to 50°C.

# CHAPTER 5

# CONCLUSION & RECOMMENDATION

## 5.1 Conclusion

From the experiment conducted, it is concluded that the performance and reaction of both DTPMPA and PASP have effect on three categories. There are namely the pH, temperature, and concentration.

### pH

DTPMPA results gave very acidic pH value of the solutions at the end of the experiment. This indicates that the natural behavior of DTPMPA which is acidic affected the initial pH of the solution. Whereas for PASP, even it is acidic in nature, it does not affect the pH of the solution at significant level. The use of DTPMPA affects the acidicity of the solution at the end of the experiment. If used in industry the acidity of the environment will be affected.

### Temperature

The performance of PASP is quite good at 50°C, but reducing at 90°C. DTMPA exhibit excellent performance at temperature 90°C compared to temperature 50°C. Nonetheless, at 50°C, it showed good inhibition effect too. As for PASP, it may not be suitable to use in higher temperature condition however, it projected more or less the same performance with DTPMPA.

### Concentration

DTPMPA exhibited final concentration of barium much lower than the initial barium concentration. This proves that it worked in inhibiting the barium from contacting with sulphate to react. However, the reactions gave better results at the lower concentration of scale inhibitor. This is the same for PASP which exhibit better results of inhibition at lower concentration of scale inhibitor at both temperatures and pH. They actually showed better inhibition tendencies at lower concentration tested.

The study of static adsorption test for investigating barium sulphate inorganic scaling is parallel to needs of the industry. This study is not only focusing on how to prevent this problem, but also recommending an alternative that promote the green effect to the environment. From this study, it can be observe whether or not the green inhibitor is compatible and efficient enough to treat barium sulphate scaling.

## 5.2 Recommendation

Generally, it is proven that PASP can operate at the same condition as the polymeric type of inhibitors except within the extreme temperatures. It prevents the accruement of barium ion in the solution, thus avoiding the reaction of barium and sulphate. Compared to PASP, DTPMPA works better in higher temperature, however it is toxic (R. J. Ross, et al, 1996). PASP also has other advantages as compared to DTPMPA, it is not only a good inhibitor but it also has corrosion inhibition activity (R. J. Ross, et al, 1996).

To obtain accurate results, the experiment should be conducted in several runs. As a comparison to the other researches by other scholars, it shows that PASP could still work in high temperature (C.E. Inches, et al, 2006). The slightly different result from this experiment may be due to some errors that might be occurring in the procedures.

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# APPENDICES

## 1. Example of calculation for ions composition:

i. Sodium sulphate, $Na_2SO_4$

Amount of $Na_2SO_4$ needed for seawater:

Atomic weight:

Na = 22.99

S = 32.07

O = 16

Molecular weight of $Na_2SO_4$ = 142.05 g/mol

% $SO_4$ in $Na_2SO_4$ = 96.07/142.05 x 100

= 67.4175%

Concentration of $Na_2SO_4$ to give 2582ppm of $SO_4$:

(100/67.4175) x 2582 = 3829.86 mg/L

= 3.82986 g/L

For 10L of distilled water, amount of $Na_2SO_4$ needed is:

10L x 3.82986 g/L = 38.2986 g

## 2. Adsorption Level, Γ Expression (M. Kahrwad, et al, 2008)

Assume Freundlich form as follows:

$$\Gamma_{eq}\left(C_{eq}\right) = \alpha\,(\,C_{eq})^{\beta} \text{ ------------------------------------------------------------ } (1)$$

Where $C_{eq}$ is in ppm and Γ is in mg of barium / g of rock. By definition, initially the mass of barium in the system is$V.C_o$. At equilibrium, the mass of barium is partly in the solution that contains inhibitor $V.C_{eq}$ and crushed minerals$[m\,\Gamma_{eq}(C_{eq})]$, however, since the original mass is conserved then the equation would give

$$V.C_o = m\,\Gamma_{eq}\left(C_{eq}\right) + V.C_{eq} \text{ ------------------------------------------------- } (2)$$

Solving equation 2 would give:

$$C_o = m\,\Gamma_{eq}\left(C_{eq}\right) + V.C_{eq} \text{ ----------------------------------------------------}(3)$$
$$C_o = \frac{m}{v}\,\Gamma_{eq}\left(C_{eq}\right) + C_{eq} \text{ --------------------------------------------------------}(4)$$

Define $F(C_{eq})$ as follows:

$$F(C_{eq}) = \frac{m}{v}\,\Gamma_{eq}\left(C_{eq}\right) + C_{eq} - C_o \text{ ---------------------------------------------}(5)$$

Where the correct equilibrium concentration, $C_{eq}$ is given by the root of equation 5 [i.e., where $F(C_{eq}) = 0$].

$$C_o = \frac{m}{v}\,\alpha\left(C_{eq}\right)^{\beta} + C_{eq} \text{ ---------------------------------------------------------}(6)$$

Using Freundlich parameters below, equation 6 can be solved for $C_{eq}$ (C in ppm, α = 0.021, β = 0.73).

## 3. Example of calculation for inhibitor adsorption using Freundlich adsorption isotherm (M. Kahrwad, et al, 2008)

Adsorption level, $\Gamma = V\,(C_o - C_{eq})/m$ (mg SI/ g rock)

Where V is volume, $C_o$ is the initial concentration and $C_{eq}$ is the final concentration

Volume of stock solution (seawater + SI) = 100mL
Mass of crushed minerals = 10g
Initial inhibitor concentration = 1000ppm

$$\Gamma = V\,(C_o - C_{eq})\,/\,\mathrm{m}$$

$$\Gamma_{eq}\left(C_{eq}\right) = \alpha\,(C_{eq})^{\beta}$$

$$V.C_o = m\,\Gamma_{eq}\left(C_{eq}\right) + V.C_{eq}$$

$$C_o = m\,\Gamma_{eq}\left(C_{eq}\right) + V.C_{eq}$$

$$C_o = \frac{m}{v}\,\Gamma_{eq}\left(C_{eq}\right) + C_{eq}$$

$$C_o = \frac{m}{v}\,\alpha\left(C_{eq}\right)^{\beta} + C_{eq}$$

Substitute the equation with the value below with both $\alpha$ and $\beta$ are constant:

$\alpha = 0.021$
$\beta = 0.73$

Given:

m = 10g
V = 0.1L
Co = 1000 and 5000 (ppm)
Known that: $C_o = \frac{m}{v}\,\alpha\left(C_{eq}\right)^{\beta} + C_{eq}$

$$1000 = \frac{10}{0.1}\,(0.021)\left(C_{eq}\right)^{0.73} + C_{eq}$$

Thus:

$C_{eq} = 739.1485$

Substitute $C_{eq}$ to the initial adsorption level equation;

$$\Gamma = V\,(C_o\text{-}C_{eq})\,/\,\mathrm{m}$$

The $\Gamma$ value calculated is 2.6085 (mg SI / g rock)