ABSTRACT

This project entitled evaluation of polyaspartate for mitigating $BaSO_4$ was to evaluate and test the efficiency of polyaspartate the green scale inhibitors to replace the conventional scale inhibitors in mitigating Barium Sulphate scale. Scale deposition is one of the most serious oil field problems that mainly come from water injection systems. The precipitation of these mineral scales can create a major cause of formation damage either in injection or producing wells, block production tubing, reduce the porosity and permeability of the reservoir and many more. Scale inhibitor was invented to overcome the problems. However, conventional scale inhibitor does not have biodegradable ability and the chemical may harm the marine environment if the discharge of the chemicals was being thrown into the sea. With respect to the oil industry, international environmental statutes and guidelines have decided to restrict the use and discharge of potentially toxic chemicals into the sea and by this requirement, it is important and urgent to replace the conventional scale inhibitor with more environmental friendly green inhibitor. Scope of study included in the detailed analysis on polyaspartate in mitigating $BaSO_4$ scale, the green scale inhibitors in order to achieve the objectives stated above. The proposed methods for this project are by conducting Tube Blocking Test and Static Jar Test for both dynamic and static condition. Its objective is to evaluate the efficiency of chemical inhibitors to prevent the formation and deposition of sulphate scales. It was proven that from both of the test that were conducted, Polyaspartate can exhibit a competitive inhibiting efficiencies in sulphate scale formation.

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CHAPTER 1

1. INTRODUCTION

1.1 Background of the study

Scale deposition is one of the most serious oil field problems that mainly come from water injection systems. The process is done when the well is injected with seawater into the oilfield reservoir. This is to maintain the reservoir pressure as well as improving the secondary recovery for offshore oil-bearing during oil recovery. However, a common problem with this technique is the formation water in the reservoir often contains high concentrations of alkaline-earth metal ions such as Ba^{2+}, Ca^{2+}, and Sr^{2+} and the injected seawater contains sulfate ions (SO_4^{2-}). When these two types of water come into contact and mixed together, the result would be highly insoluble mineral scales that usually consist of calcium carbonate (calcite), barium sulfate (barite), and sometimes a small amount of radioactive strontium sulfate. The precipitation of these mineral scales can create a major cause of formation damage either in injection or producing wells, block production tubing, reduce the porosity and permeability of the reservoir and many more. This problem had been overcome by engineers by inventing the scale inhibitors but over recent years, there has been an increasing demand in oilfield scale prevention to replace the conventional mineral scale inhibitors with more environmentally friendly "green" scale inhibitors.

Barium sulfate scale is one of the most difficult scaling problems because of the low solubility of barium sulfate in most fluids and also the low reactivity of most acids with barium sulfate scale. For this project, it is required to do extensive evaluation specifically on mitigating Barium Sulphate scaling using polyaspartate as the green scale inhibitors replacing the conventional scale inhibitors. This is due to the current discovery on polyaspartate as green scale inhibitors that not only have biodegradable abilities but also can act both scale and corrosion inhibitor.

1.2 Problem statement

1.2.1 Problem identification

Precipitation of mineral scales had caused many problems in oil and gas production operations. The build-up of scale inside well bores causes millions of dollars in damage every year if the scale was not been treated. Engineers overcome the problem by using scale inhibitors to reduce the scale precipitation.

However, the conventional scale inhibitors had negative impact on environment. In the field of the mineral scale inhibition, chemicals are usually discharge directly into the reservoir section surrounding the production well and produced back with the formation fluids. The oil industries currently face severe restrictions regarding the discharge of chemicals into the environment. In the area of water treatment, polyacrylate and phosphonates scale inhibitors and dispersants are often used to mitigate the scale precipitation because of the low toxicity of the inhibitors. However, both of the scale inhibitors are non-biodegradable. Biodegradability is the ability of the chemicals to break down into simple, non-toxic materials by the aid of fungi and microorganisms. This is important mechanism for reducing and limiting the build-up of chemicals in the environment.

In order to satisfy the current environmental legislation for produced water disposal, engineers has led the search for biodegradable alternatives to conventional scale inhibitors. Polyaspartates, that was origin from polyaspartic acid, offer a promising alternative to conventional scale inhibitors. In addition to their activity as scale inhibitors and dispersants, polyaspartates have also been shown to have corrosion inhibition, particularly for CO_2 corrosion environments often found in oil field applications.

1.2.2 Significant of the project

Currently, the international environmental statutes and guidelines had made a requirement to restrict the use and discharges of potentially toxic chemicals into the sea as it will effects on marine environments. Due to this concern and discharge limitations into the sea, the search for green scale inhibitors that have biodegradable abilities that will give no harm to the marine environment to replace the conventional scale inhibitors are increasingly urgent and demanded.

In the mid 1990s, a North Sea Conference in Esbjerg, Denmark (1995) and a White Paper from Norwegian Ministry of Environment: Environmental Policy for a Sustainable Development (1996-97) proposed the idea of a "zero discharge" policy. Selle, O.M., Paltiel and et al. agreed that the zero discharge policy can be achieved by the systematic and continuous reduction of harmful discharges into the sea, it will create less risk of environmental impact. The regulations had been applied since the policy is being proposed and it is a requirement now to create environmentally friendly, biodegradable, low toxic green scale inhibitors to replace the current conventional scale inhibitors. However, the green scale inhibitor must maintain the original function of the conventional scale inhibitor and the green inhibitor must at least equal and expected to have greater effectiveness than the conventional scale inhibitor.

1.3 Objective(s)

To evaluate and test the efficiency of polyaspartate the green scale inhibitors in mitigating Barium Sulphate scale to replace the conventional scale inhibitors.

To compare the inhibitor efficiency between polyaspartate, as the green scale inhibitor with the conventional scale inhibitor in both static and dynamic condition.

1.4 Scope of study

Scope of study included on the detailed analysis on polyaspartate, the green scale inhibitors. The main objective of the study was to test the effectiveness of replacing the conventional scale inhibitors with polyaspartate, the green scale inhibitors. The experiments that need to be conducted must show that polyaspartate may act as competitive inhibiting efficiencies in their ability to reduce barium sulfate scale formation. In order to achieve the objective of this project, there are two experiments that were conducted, which are Static Jar Test and Tube Blocking Tests. The procedure and methods in conducting both of the experiments was analyzed and finalized and the result will be compared for both of the static and dynamic condition as well as in order to test the efficiency of Polyaspartate in replacing the conventional scale inhibitor.

1.5 Relevancy of the project

As stated above, scale formation in surface and subsurface oil and gas production equipment has been recognized to be a major operational problem as it causes major formation damage either in injection or producing wells. It also costs lots of additional problems to the well such as equipment wear and corrosion and flow restriction. Due to this factor, a major decrease in oil and gas production will occurred plus there will decrease in oil or gas productivity.

Many of oil wells in oil industry had experience and suffered flow restriction due to scale deposition within the oil producing formation matrix and the downhole equipment which is generally in primary, secondary and tertiary oil recovery operation as well as in the surface production equipment. Scale inhibitor was invented to overcome the problems. However, conventional scale inhibitor does not have biodegradable ability and the chemical may harm the marine environment if the discharge of the chemicals was being thrown into the sea.

With respect to the oil industry, international environmental statutes and guidelines have decided to restrict the use and discharge of potentially toxic chemicals into the sea and by this requirement, it is important and urgent to replace the conventional scale inhibitor with more environmental friendly green inhibitor.

1.6 Feasibility of the project within the scope and time frame

For Tube Blocking Test (TBT), the main equipment is available at Block 15 meanwhile all the chemicals that are needed for the test are also available. The details of the chemicals that were used will be discussed in Chapter 3. For this test, one run can take around 3 hours. The total tests that were needed for the tested parameters (concentration, temperature, flow rate) are 10 runs for each inhibitor. So the total runs for both of the inhibitors are 20 runs. However, the equipment must be tested with several runs in other to get the accurate results. If possible, each test was being repeated for three times thus making the total runs was 60 runs for both of green and conventional inhibitors. It was estimated that one day can run up to three runs maximum. The preparation of the brines is also taking into account. So the estimated time that was used to finish the TBT is 2 months maximum. Several tests was started at the end of FYP 1 and conducted until FYP 2.

For Static Jar Test, the main equipments are available at Block 5. The other chemicals that are needed are also available and the details of the chemicals used in the test are also discussed in Chapter 3. The test was varied with three temperatures. For one temperature, there are 5 concentration of inhibitor that was used. It was estimated for one day to complete the test for one temperature. So each inhibitor had 3 tests according to the temperature making two inhibitors had 6 tests in total. The preparation of the brines is also taking into account. This is for taking the samples. Then, the samples will be analyzed by the spectrometer to obtain the barium concentration. For this test, 17 samples maximum can be analyzed in one day. There are 102 samples that were taken for both of the green and conventional inhibitors. So in total, the maximum time that was needed to finish static jar test 1 and half months. The test was conducted in FYP 2. In total, both of the tests can be conducted within the time provided.

CHAPTER 2

2. LITERATURE REVIEW

2.1 Water flooding

Water injection is a method that is used to improve oil recovery in the oil industry as well as maintaining the reservoir pressure. The main objective of water-flooding is to put water into a rock formation at certain rate and pressure with low cost and risk. In order to achieve the objective of the method, therefore the water must be treated before injection. Besides improving the oil recovery and maintaining the reservoir pressure of the well, this treatment can also solve problems such as suspended matter, corrosivity of water scale deposition, and microbiological fouling and corrosion that usually occurred with the individual injection waters.

According to Bagci *et al.* (2000), formation damage is a well-known phenomenon in many waterflooding operations. This damage depends on many factors, such as the quality of the injected water and rock mineralogical composition. Movement of particles in reservoirs has long been recognized to cause formation damage.
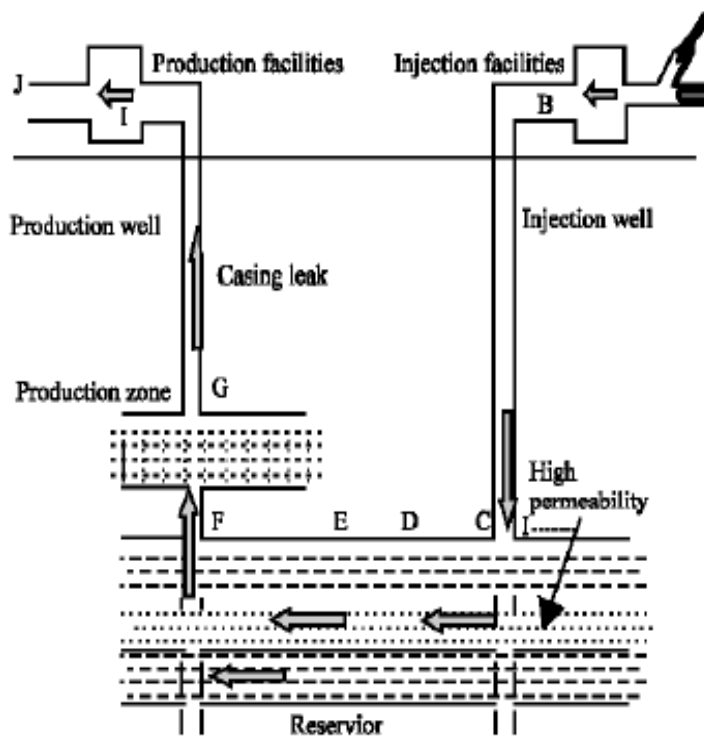
Location	Change which could produce scale formation
A to B	Mixing of brines for injection
B to C	Pressure and temperature increase
C to D	Pressure decline and continued temperature increase solution composition may be adjusted by cation
C to F	Exchange, mineral dissolution or other reactions with the rock
D to F	Mixing of brines in the reservoir
E to J	Pressure and temperature decline. Release of carbon dioxide and evaporation of water due to the pressure decline if a gas phase is present or formed between these locations.
F	Mixing of formation water and injection water which has "broken through" at the base of the production well
G	Mixing of brines produced from different zones.

Figure 1: Diagram indicating changes which could produce scale at different locations. (Merdhah *et al., 2008*)
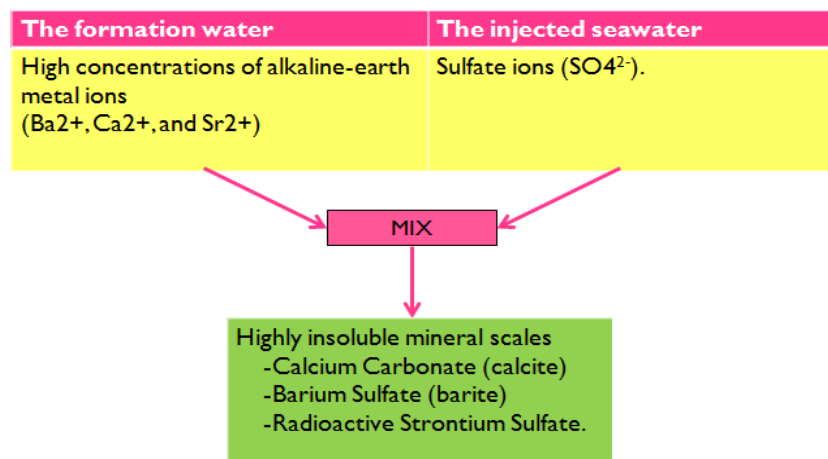
According to the Figure 1 above which is in the surface equipment, pressure and temperature will decrease from the flow string until the surface in the production well plus changes in thermodynamic conditions will occur. This will again create scale precipitation. Usually, these scales can create damage in the well-bore when there are large drop in pressure but there were usually no changes in temperature.

2.2 Scale deposition

Scale deposition is one of the serious oil field problems. The build-up of scale inside well bores causes millions of dollars in damage every year. Scale precipitation formed as the result of changes in the ionic composition, pH, pressure and temperature of the brine. Common scales that usually formed are calcium carbonate ($CaCO_3$) and barium sulphate ($BaSO_4$).

Solid scale formation mainly results from changes in physical-chemical properties of fluids (i.e., pH, partial pressure of CO^2, temperature, and pressure) during production or from chemical incompatibility between injected and formation waters (Collins *et al., 2005).*

The main source of scale precipitation is when mixing two incompatible waters. Two waters are incompatible when they interact chemically and precipitate minerals when mixed. A common example of incompatible waters are involving the sea water with high concentration of SO_4^{-2} and low concentrations of Ca^{+2}, Ba^{+2}/Sr^{+2}, and formation waters with very low concentrations of SO_4^{-2} but high concentrations of Ca^{+2}, Ba^{+2} and Sr^{+2}. Mixing of these waters will cause precipitation of $CaSO_4$, $BaSO_4$, and/or $SrSO_4$. Other type of water that is incompatible when mixed with seawater is the field produced water or disposal water. Scale usually formed in down-hole pumps, tubing, casing flow-lines, heater treaters, tanks and other production equipment and facilities.

The formation water	The injected seawater
High concentrations of alkaline-earth metal ions (Ba2+, Ca2+, and Sr2+)	Sulfate ions ($SO4^{2-}$).

MIX

Highly insoluble mineral scales
-Calcium Carbonate (calcite)
-Barium Sulfate (barite)
-Radioactive Strontium Sulfate.

Figure 2: Formation of mineral scale by mixing two incompatible waters

Figure 2 above shows that when these two types of water come into contact and mixed together, the result would be highly insoluble mineral scales. A scale will also occur when a high water cut part of the water is act as free water. The rate of scale deposition will be proportional to the rate of free water production. Scale may be formed in the flow line only, in both flow line and tubing, and sometimes in the perforations and in the formation near the wellbore depending upon where the formation water becomes supersaturated.

Scale deposition can also involved with one type of water due to super-saturation with scale-forming salts related to changes in the physical conditions where the water exists.

As the water enters the reservoir, three main phenomena occur (Bertero *et al., 1988):*

1. Along the water flow path, temperature increases due to heat exchange with the reservoir rock and fluids.

2. Pressure decreases along the flow path.

3. Injection water mixes with reservoir brine

The most common oilfield scales are listed in Table 1 below as well as the primary variables that affect their solubility. The scales that been listed are sulfates such as calcium sulfate (anhydrite, gypsum), barium sulfate (barite), and strontium sulfate (celestite) and calcium carbonate including the less common scales have also been reported such as iron oxides, iron sulfides and iron carbonate.

Table 1: Most common oilfield scales (Merdhah *et al., 2008*)

Name	Chemical Formula	Primary Variables
Calcium Carbonate	$CaCO_3$	Partial pressure of CO_2, temperature, total dissolved salts, pH
Calcium Sulfate: Gypsum Hemihydrate Anhydrite	$CaSO_4.2H_2O$ $CaSO_4.H_2O$ $CaSO_4$	Temperature, total dissolved salts, pressure
Barium Sulfate	$BaSO_4$	Temperature, pressure
Strontium Sulfate	$SrSO_4$	Temperature, pressure, total dissolved salts
Iron Compounds: Ferrous Carbonate Ferrous Sulfide Ferrous Hydroxide Ferrous Hydroxide	$FeCO_3$ FeS $Fe(OH)_2$ $Fe(OH)_3$	Corrosion, dissolved gases, pH

Barium sulfate is the inorganic compound with the chemical formula $BaSO_4$. It is a white crystalline solid and it is odourless plus insoluble in water. In general barium sulphate scale results from water incompatibility, primarily from either seawater injection or seawater breakthrough, co mingling with produced water rich in barium. The highly insoluble of Barium sulphate will deposit at temperature drops across the production processing plant. At higher temperatures, the deposition of $BaSO_4$ decreases and vice versa.

The principal mechanisms of Barium sulphate in both offshore and onshore oil field system is when mixing the two incompatible brines most commonly formation water rich in barium cations with sulfate rich seawater resulting to the precipitation of sulfate scales, such as $BaSO_4$.

$$Ba^{2+} + SO_4^{2-} \longleftrightarrow BaSO_4$$
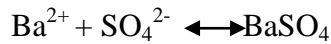
Among the most onerous of all scaling species is that of sulfates, particularly barium and strontium sulfates (Oddo and Tomson, 1994).

Barium sulfate solubility increased with temperature increase, with increase ionic strength of brine, and with pressure. Barium sulfate precipitation was affected most strongly by temperature (Moghadasi *et al., 2003a).*

2.2.1 Scaling problem with oilfield scale

Oil field scales costs are high and expensive as the scale precipitation can create problems such as:

- Decline in oil and gas production
- Frequently pulling of downhole equipment for replacement
- Re-perforation of the producing intervals
- Re-drilling of plugged oil wells
- Stimulation of plugged oil-bearing formations
- Other remedial workovers through production and injection wells.
- The porous media of formation becomes plugged and may be rendered impermeable to any fluids.

2.3 Squeeze treatment

When the formation of sulphate or carbonate scale is a problem in producer wells, the most common remedy is to treat the formation with a scale inhibitor in a "squeeze" treatment (Vetter, 1973).

It is a common practice in the oil industry to perform squeeze treatment to overcome scale inhibition that creates formation damage in the reservoir by using scale inhibitors. The objective of squeeze treatment is to maintain the maximum amount of inhibitor in the formation itself by:

- Adsorption of the inhibitor on the rock substrate by a physico chemical process
- Precipitation or phase separation of the inhibitor away from the near wellbore area in an organized form.

The procedure of squeeze treatments is by changing the solution chemistry, for example Ca^{2+}, pH, temperature and many more. However, the reactions that controlled the inhibitor adsorption and release are very complex. The squeeze treatment is consisting of three solutions that will be injected into the well. The three solutions are:

1) The preflush solution
2) The pill solution
3) The overflush solution

After the injection, the well will be shut-in for around 24 hours to 48 hours. Regardless the mechanism for inhibitor appointment is adsorption or precipitation, the squeeze treatment still can be applied.

Several factors, such as pH, $[Ca^{2+}]$, $[Mg^{2+}]$, temperature, rock mineralogy etc, affect the adsorption level and the shape of the adsorption isotherm (Baraka-Lokmane and Sorbie, 2006).

To overcome the scale precipitation problems, engineers had two alternatives which are to do re-injection on site of the produced water or the use scale inhibitors. Due to low biodegradability of conventional scale inhibitors that did not satisfy the current environmental legislation, it is important for engineers to replace the conventional scale inhibitors with environmental safe green scale inhibitors. For this project, it was to replace the conventional scale inhibitors with biodegradable chemicals by using polyaspartate as the scale inhibitors.

2.4 Polyaspartate as the green scale inhibitors

Aspartic acid is an α-amino acid with the chemical formula $HOOCCH(NH_2)CH_2COOH$. (Wikipedia., 2012). The carboxylate anion, salt, or ester of aspartic acid is known as aspartate. Aspartic acid is found in:

- Animal sources: luncheon meats, sausage meat, wild game
- Vegetable sources: sprouting seeds, oat flakes, avocado, asparagus, young sugarcane, and molasses from sugar beets.
- Dietary supplements, either as aspartic acid itself or salts (such as magnesium aspartate)
- The sweetener aspartame (NutraSweet, Equal, Canderel, etc.)

Polyaspartic acid (PASP) was developed in the early 1990s and found to have a great biodegradable capability (Hasson *et al., 2011*). PASP is easy to purchase and has lots of applications and advantages. The main purposes of PASP are as below:

- A scale and corrosion inhibitor in water treatment plants
- low-temperature cooling towers
- a biodegradable scale control chemical for oil field and other mining operations
- green chemical for detergent formulations
- As a fertilizer synergistic agent promoting nutrients absorption by crops.

Polyaspartate are condensation polymers based on aspartic acid and they are synthetic polyamides that are structural and functional analogues of biomineralization controlling proteins (Hasson *et al., 2011*). The structural formula of PASP is as Figure 3 below:
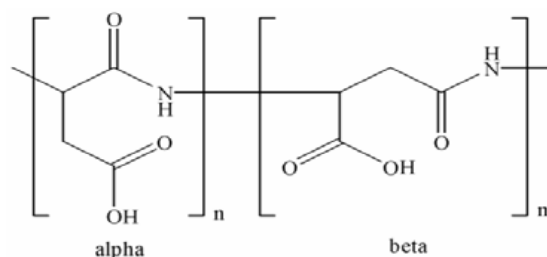

Figure 3: Structure of polyaspartate (PASP) (Inches *et al., 2006*)

Polyaspartates are prepared through 3 different syntheses that are based on intermolecular dehydration: thermal polycondensations with or without an acid catalyst and bulk polycondensations with catalyst. (Hasson *et al., 2011*)
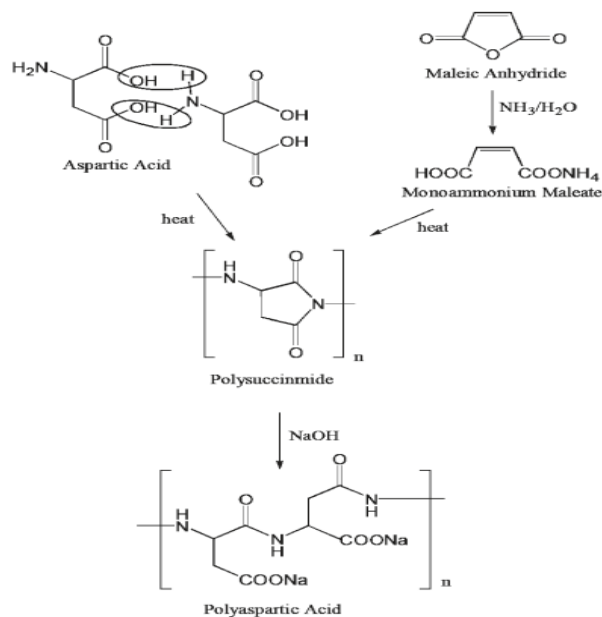

Figure 4: Polyaspartate synthesis (Hasson *et al., 2011*)

In the thermal condensation process showed in Figure 4 above, the aspartic acid is first converted to a linear thermal polycondensation polymer known as polysuccinimide by heating the acid to a temperature above 180°C. The polysuccinimide is then transformed into polyaspartic acid by alkaline hydrolysis with aqueous base such as sodium hydroxide. The yield is high almost nearing complete conversion. Catalyst is used in this process to lowers the condensation temperature and also to enable less time needed for the reaction to take place. Molecular weights from 2000-30000 Mw are readily obtained from this process depending upon the catalysts and conditions used. (Inches *et al., 2006*)

An alternative way to produce polysuccinimide is by thermal polymerization of maleic acid and ammonium hydroxide at temperatures above 160°C. The polyaspartates obtained from maleic derived polysuccinimide are generally less than 2500 Mw. The polyaspartate made via thermal polycondensation of aspartic acid has a higher Mw and has a more linear morphology. It performs better in some applications compared to the polyaspartate made via a maleic acid plus ammonia

which has lower Mw and the synthetic route leads to branching. This limits the effectiveness of this polyaspartate in a number of applications. (Aquero Company, 2012)

Plenty and lots of polyaspartate formulations are synthesized for different applications. Polyaspartic acid can be different in molecular weight, molecular weight distribution, degree of branching, and purity. All of these characteristics and its properties are depend on its synthesis. The structure and chemical characteristics of polyaspartate will be different from each other as there were different approaches that were used to obtain it.

Polyaspartates are dispersants, same with the conventional scale inhibitor, polyacrylates. It can absorb onto the suspended matter. Dispersants do not stop the formation of scale and the mechanism of dispersants is that it keeps the scale particles suspended in the bulk fluid by transferring a negative charge to the particles. These negatively charged will push with each other and will prevent aggregation and precipitation into larger scale particles.

Low-molecularweight PASPs usually used as general-purpose antiscalants, meanwhile the high-molecular-weight PASPs usually used as general purpose dispersants. The optimum molecular weight for the inhibition of calcium carbonate, calcium sulfate and barium sulfate mineral scales was studied to be between 1000 and 4000 Mw. The weight average molecular weight is calculated by Size Exclusion Chromatography. The optimum molecular weight of polyaspartates for inhibition of calcium carbonate and barium sulfate are in the range of 3000-4000 Mw meanwhile for calcium sulphate inhibition, the optimum molecular weight lies in 1000-2000 Mw. (Ross *et al., 1996*).

It is recommended to use polyaspartate that have the optimum weight for barium sulphate inhibiton which in the range of 3000-4000 Mw. This molecular weight of the polyaspartate can be obtained by the polyaspartate made via thermal polycondensation of aspartic acid.

CHAPTER 3

3. RESEARCH METHODOLOGY

3.1 Project activities

3.1.1 The Dynamic Tube Blocking Test (TBT)

The Dynamic Tube Blocking Test (TBT) method is used to evaluate the efficiency of chemical inhibitors to prevent the formation and deposition of mineral scales such as calcium carbonate, calcium sulfate, barium sulfate and strontium sulfate. The TBT method aims to:

1. Determine the Minimum Inhibitor Concentration (MIC) required in preventing the formation of scale.
2. Perform comparative tests with different inhibitors in the same conditions.

The scale inhibitor efficiency is measured and determined by the ratio of the time needed to block the tube in the presence of inhibitor divided by the time needed to block the tube without inhibitor, the blank time.

The scale inhibitor performance is then evaluated in terms of Minimum Inhibitor Concentration (MIC).

Overview of PMAC Systems

The tube blocking test experiments was being conducted by using PMAC Automated Scale Rig. It is a tool that are responsible for the design, operation and efficiency of water handling systems in which thermal, pressure or chemical changes influence the deposition of scales. It provides an accurate method for selecting the most effective ways to control scale deposition under dynamic conditions.

All of the systems have the option to include automatic sampling and testing of inhibitors as well as real time data logging and data manipulation through the spreadsheets.

Technical specification

Table 2: Function of parts of TBT equipments

Equipment	Function
Back pressure valve	The backpressure valve controls the system pressure and is a constant flow valve. It is advised not to over-tightening the valve as this could cause irreparable damage.
Oven	The unit contains three brine preheat coils and the test coil. The oven has fan assisted to 300°C and is controlled via software at the PC.
Pumps	Three Knauer HPLC pumps are supplied to fit with 10 ml/minute heads. The pump is operated by dual piston to allow a smoother fluid supply to the system.
Pump heads	The heads are supplied at rate 10 mls/minute maximum. It is fitted with back flushing facility which will avoid salting behind the valve seals.
Solvent organizer	The solvent organizer is a low pressure gradient mixing device that can deliver up to four different fluids to the HPLC Pump. The software controls all electrical functions of the solvent organizer.
Transducers	Two pressure transducer used in PMAC unit. A system transducer measures the system pressure meanwhile a differential transducer measures the change in differential pressure across the test coil caused by scaling.
Backpressure heat exchangers	The backpressure heat exchangers are used to reduce the outlet fluid temperature to allow safe operation of the Back Pressure Valve.

The set up for the four different channels are:

1) Channel A is to supply the seawater without inhibitor (anion)

2) Channel B is to supply the seawater with inhibitor (anion + inhibitor)

3) Channel C is to supply the acetic acid (de-scaling solution)

4) Channel D is to supply deionised water

Figure 5: TBT equipments as a whole set

General principal for the evalution of scale inhibitors

The Tube Blocking Test method in general using PMAC Automated Scale rig

Two incompatible brine which are the seawater and the formation water will be pumped through a capillary coil and maintained at the pressure and temperature conditions that had been set according to the production system. Scale would build up on the capillary as both of the water mix together and this will create differential pressure across the capillary. The differential pressure is used to measure the severity of the scaling. Then the inhibitor will be introduced into the system and the effect of the inhibitor will be monitored.

Procedure on conducting The Dynamic Tube Blocking Test (TBT)

Before conducting the experiment, we need to identify and prepare the solutions that will be used in the tests. The solutions that will be involved for this experiment are:

1) Sea water (SW)
2) Formation water (FW)
3) 15% Acetic acid solution
4) Polyasparate with different concentration in sea water

Brine preparation

The brines were prepared through calculations from the molecular weight. The brines are prepared for 50:50 mixture of sea water and formation water to achieve a "severe" scaling system. We need to calculate the concentrations of salt required to give the desired concentration of each ion in the brine.

Sea water can be formed by mixing Sodium sulphate and sodium chloride with distilled water and the formation water can be formed by mixing Barium chloride and sodium chloride with distilled water. There were specific calculations to calculate the exact amount of the chemicals involved to be put into the distilled water.

The detailed calculations are displayed at the Appendices. Distilled water is pure and free of salts making it a very poor conductor of electricity. By adding NaCl to the distilled water, it will become an electrolyte solution, able to conduct electricity.
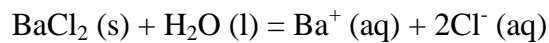
- Chemical formula for seawater:

$$NaCl(s) + H_2O(l) = Na^+(aq) + Cl^-(aq)$$
$$NaSO_4^{2-}(s) + H_2O(l) = Na^+(aq) + SO_4^{2-}(aq)$$
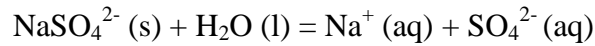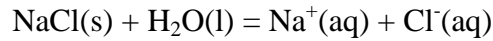
- Chemical formula for formation water:

$$BaCl_2(s) + H_2O(l) = Ba^+(aq) + 2Cl^-(aq)$$

Table 3 shows that the ions of synthetic formation and injected waters.

Table 3: Ions of synthetic formation and injection waters (Merdhah *et al., 2008*)

Ionic	Normal salinity formation water (ppm)	High salinity formation water (ppm)	Normal barium formation water (ppm)	High barium formation water (ppm)	Angsi seawater (ppm)
Sodium	52,132	52,132	42,707	42,707	10,804
potassium	1,967	1,967	1,972	1,972	375
Magnesium	4,260	4,260	102	102	1,295
Calcium	7,000	30,000	780	780	429
Strontium	500	1,100	370	370	6.60
Barium	10	10	250	2,200	-
Chloride	99,653	146,385	66,706	67,713	19,307
Sulfate	108	108	5	5	2,750
Bicarbonate	350	350	2,140	2,140	159

Usually for Malaysia's case, the concentration of ion in the reservoir for FW and SW are as table 4 below:

Table 4: Ionic compositions of the different waters for moderate sulfate scaling conditions (ppm)

Ions	Formation water	Sea water	50:50 mixtures
Ba^{2+}	250 mg/L	0 mg/L	125 mg/L
SO_4^{2-}	0 mg/L	2582 mg/L	1291 mg/L
Na^{2+}	5200 mg/L	10200 mg/L	7700 mg/L

From table 5 below, we can see that the summary of the amount of salts that are needed to make formation water and sea water.

Table 5: Amount of salts required to make FW and SW in certain amount of distilled water

Formation water			Sea water		
Volume of distilled water (litre)	NaCl (g) (5200 ppm Na)	BaCl$_2$ (g) (250 ppm Ba)	Volume of distilled water (litre)	NaCl (g) (10200 ppm Na)	Na$_2$SO$_4$ (g) (2582 ppm SO$_4$
1	13.2183	0.4447	1	25.9825	3.8178
2	26.4366	0.8894	2	51.965	7.6356
3	39.6549	1.3341	3	77.9475	11.4534
4	52.8732	1.7788	4	103.93	15.2712
5	66.0915	2.2235	5	129.9125	19.089
6	79.3098	2.6682	6	155.895	22.9068

Meanwhile, to prepare the 15% acetic acid, the acid must be diluted in 99.8% distilled water. The formula below was used:

$M_1V_1 = M_2V_2$

99.8% V_1 = 15% (1000 ml)

V_1 = 150.30 ml

 So in 1 litre of distilled water, 150.30 ml of acetic acid must be inserted to achieve 15% acetic acid.

To prepare the polyaspartate in the seawater:

1ml of polyasparate = 1000 ppm in 1 litre of seawater.

It can be concluded in the table 6 below:

Table 6: Volume of scale inhibitor to create certain concentration in 1 litre of seawater

	Polyaspartate or phosphonate	
	0.5 ml	500 ppm
1 litre of sea water	1 ml	1000 ppm
	3 ml	3000 ppm
	5 ml	5000 ppm

Detailed procedures of the experiment by using the software are as below:

This test was conducted by using PMAC software. After setting up the parameters that we need to observe during the test according to the manual of the software given, enter the start button. After enter the button, water will be pumped through the system at the desired flow rate, ml per minutes using both pump 1 and pump 3. Pump 1 is the formation water, pump 3 that have four different channels as stated earlier. When all temperatures are stable at the desired values, the formation water and the sea waters will be introduced into the system in 50:50 ratios. This is step 1 which is the prescale section.

Then, the capillary is allowed to scale up to 10 psig pressure differential, at which the time for the injection water pump is switched to the inhibited brine. It means that after mixing the seawater and formation water at desired flow rate at prescale section, the program will move to step 2, which is the scaling test section when either the set time had elapsed or the differential pressure had reached 10 psi. In step 2, the scaling test, pump 1 will flow at desired rate and also pump 3 would flow an inhibited ion for a set time or until the differential pressure reach the set point to start the cleaning cycle. In this experiment, it was set to be 500 psi.

After the set time for step 2 had elapsed, the cleaning program will starts. Solvent from channel C (descaling solution), which is the 15% acetic acid, would be pumped at 3ml/minutes for 20 minutes followed by the deionised water at 5ml/minutes. If the tube is severely blocked and the differential reaches a second set point, an internal solenoid valve will open to prevent damage to the transducer. In this test it was set to 20 psi.

There were three parameters that had been applied throughout the experiments to investigate the effect of the parameters to the tests. The parameters are the flow rate, concentration and temperature. Below in figure 6 and figure 7 are the test screen before and hitting the start button meanwhile figure 8 are the test screen after hitting the start button.
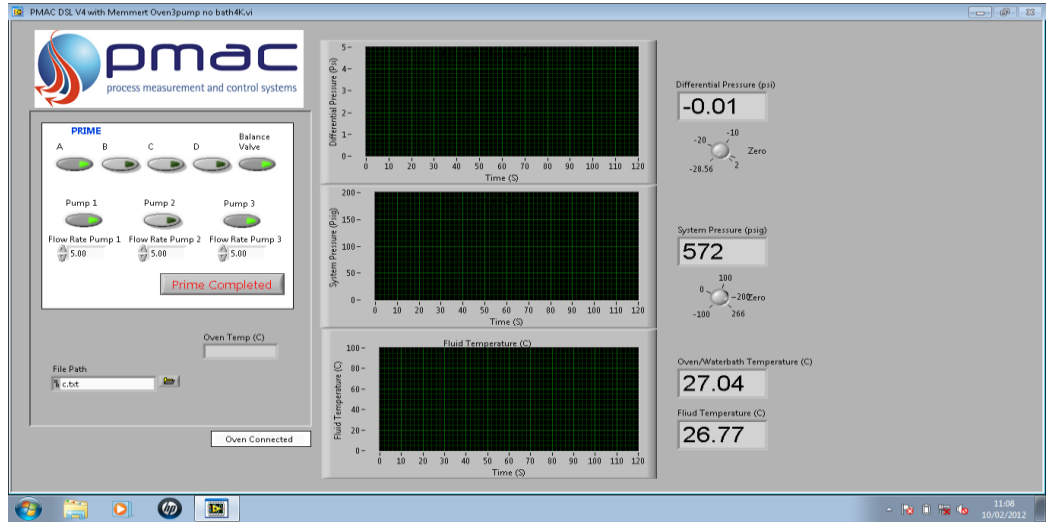
Figure 6: The program screen after system pressure had been set and differential pressure = 0
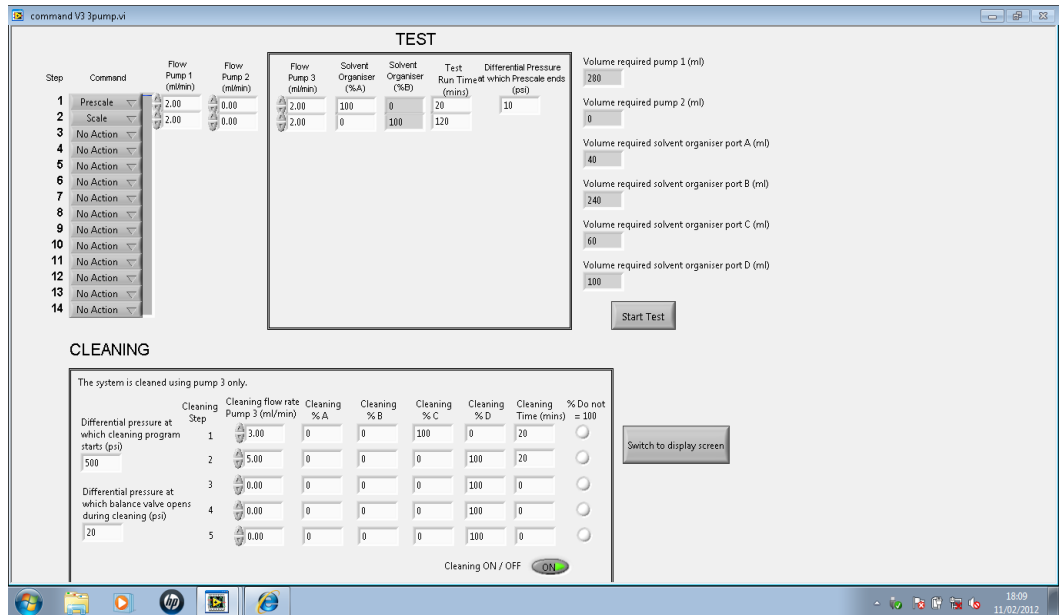

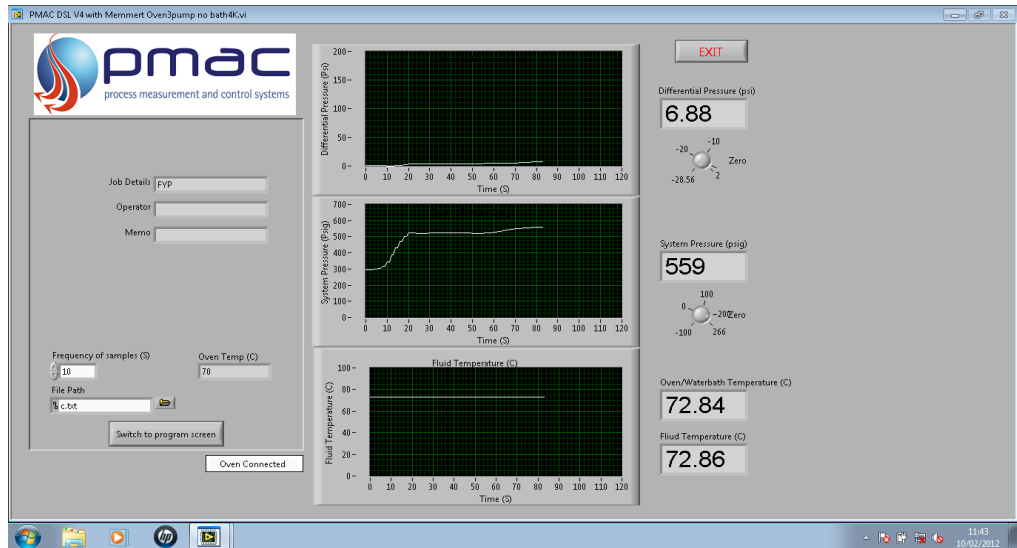**Figure 7: The test screen to insert the desired parameters**

Figure 8: The program screen in the early test

There were three parameters that were used and vary for this experiment. The parameters are the flow rate, concentration of the inhibitor and temperature. In this experiment, only pump 1 and pump 3 were used. In table 7 below are the details of the mentioned parameters:

Table 7: List of detailed parameters that were used in the tests

Flow rate (ml/minutes)	Concentration of inhibitor (ppm)	Temperature (°C)
Temperature = 50°C Concentration = 5000 ppm	Temperature = 50°C Flow rate = 2ml/min	Concentration = 5000 ppm Flow rate = 2ml/min
1.0	500	50
3.0	1000	70
5.0	3000	90
	5000	

3.1.2 Jar test

Inhibitors were initially evaluated by using the static jar test. In jar testing, two incompatible brine are mixed in the presence of inhibitor. The inhibitor efficiency will then be calculated by the amount of soluble metal cations that remains in solution with time. The conventional Jar Test is performed routinely in the industry according to the tests procedures in the NACE standards N° TM 0197-97 and TM0374-2001. Jar test aims at ranking the various products in static conditions and is generally completed with TBT which is more suitable and appropriate for inhibitor evaluation in dynamic conditions. However, there is no standard method for the TBT.

Procedure of the jar test

The formation water and the seawater were prepared by the same calculations as in TBT experiments. The calculations are shown at the appendices. Both of the formation water and the seawater will be mixed in a 50:50 mixing ratio to create a 'severe' scaling system. The amount for each of the brine is 100 ml. The concentration of the scale inhibitor was chosen in 5 different values which are 10 ppm, 25 ppm, 50 ppm, 100 ppm and 250 ppm.

First, brines will be prepared. Then, separate the formation water and the seawater in 5 beakers for each type of water as the concentration of the scale inhibitor has 5 values. Add another set of formation water and sea water to prepare the blank solution (no inhibitor). The set of FW and SW are as shown in figure 9 and 10 below
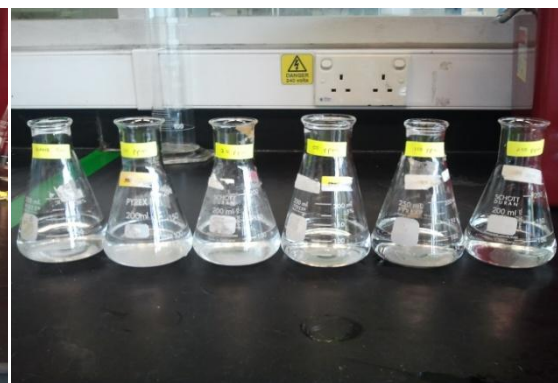

Figure 9: Formation water   Figure 10: Seawater

The scale inhibitor will then be diluted in the seawater for each beaker and buffered to pH 5-6 by using buffer solution as shown in figure 11 below. For blank solution, no inhibitor required, only put the buffer to change the pH.
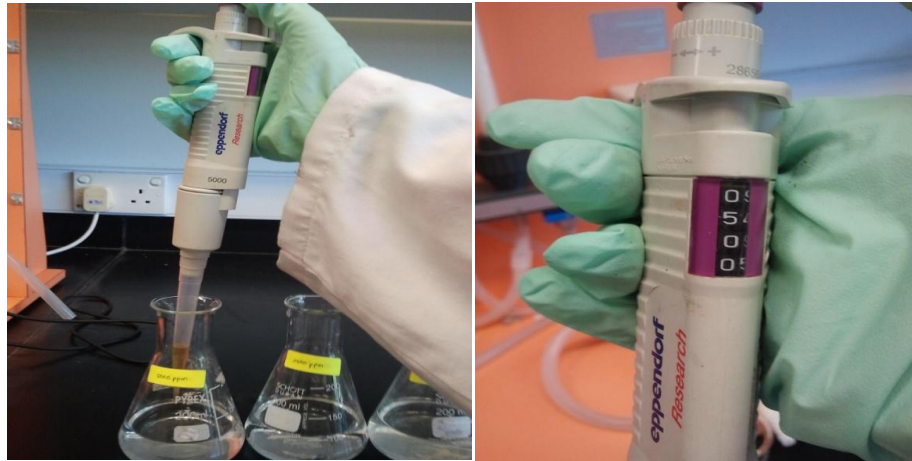

Figure 11: Scale inhibitor was diluted in the seawater (e.g 500 ppm)

Table 8: Volume of scale inhibitor to create certain concentration

Volume of PASP (ml)	Volume of distilled water (ml)	Concentration (ppm)
0.25	1000	250
0.05	500	100
	1000	50
	2000	25
	5000	10

The buffer solution can be prepared by the procedure below and shown in figure 12: 13.60 g of sodium acetate tri-hydrate and 0.5 g of acetic acid was dissolved in distilled water making up to the mark in a 100 ml beaker.

Figure 12: Buffer solution was diluted in SI/SW and measured by pH meter

Continue put the buffer solution in the seawater/scale inhibitor (SW/SI) until the solution reach to pH 5-6. Measure the pH by using the pH meter. Shake the beaker. Then, put all the beakers involved in the waterbath for the solutions to be heated to the desired test temperature for one hour. In this experiment, 95°C, 55°C and 25°C of temperatures are chosen. For waterbath shaker, the rotation of the waterbath was set to 70 rpm. This is done so that the solution is more or less the same condition in the reservoir. Below is the figure of waterbath shaker.
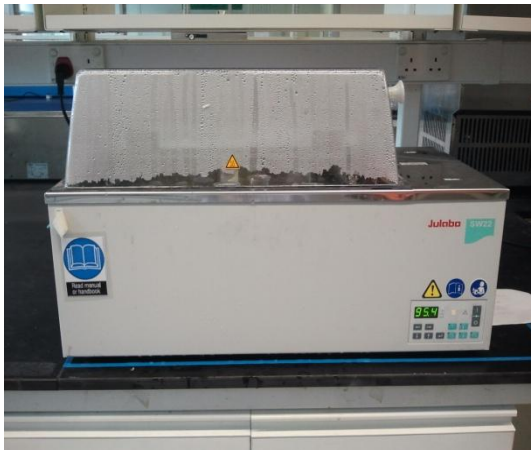
Figure 13: Waterbath shaker at 95 degree Celcius   **Figure 14: Beakers of SW and FW**
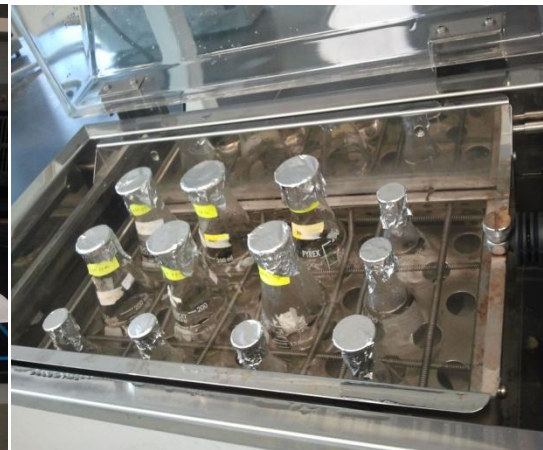
After one hour, the formation water will be mixed with the seawater as in figure below:

Figure 15: FW mixed with SW

After mixing the FW with SW, take a sample from each bottle at t = 0. Then, samples of the mix solution will be taken at 2 hours and 22 hours respectively including the blank solution. All of the samples will then be diluted in a

KCI/DETPMP quenching solution. In order to prepare the quenching solution, below procedure was being followed:

In 1 litre distilled water, 3000 ppm of KCI and 1000 ppm of DETPMP will be added. Then, the solution will adjust to a pH value of pH 8-8.5 by adding NaOH solution into the quenching solution. Add 9 ml of quenching solution into test tube and take 1 ml of the sample and mix it with the quenching solution. The sample will then be analyzed by ICP (Inductively Coupled Plasma spectroscopy.

Figure 16: The test tubes samples for analyzing the barium concentration

After getting the result of the concentration of barium, the percentage efficiency of the inhibitor for barium sulphate inhibition can be calculated by using the formula below:

$$\% \text{ efficiency} = 100 \times \frac{(C_l - C_B)}{(C_O - C_B)}$$

C_l = concentration of barium at sampling time, 2 hours or 22 hours

C_B = concentration of barium in blank solution (no inhibitor)

C_O = concentration of barium in originally solution, at t = 0

After calculating the efficiency, the values will be plotted with the concentration of scale inhibitors. The performance from both conventional and green scale inhibitors can be analyzed.

Procedure on determining the Barium concentration

First, select the test provided by the DR 5000 Spectrometer. Choose 20 Barium. Then fill a square sample cell with 10 ml of the sample. Then, add the contents of one BariVer® 4 Barium Reagent Powder Pillow to the cell. Shake the cell until the reagent dilute into the solution. If barium is present, a white turbidity will develop.

Then, start the timer in 5 minutes. A five minute reaction will begin. Then, do the blank preparation by filling another square sample cell with 10 ml sample same as before. When the timer expires, wipe the blank and put into the cell holder. Press ZERO to zero the instrument. We can see that the value shown at the screen is 0 mg/L Ba^{2+}.

Then, take and wipe the prepared sample before and put it into the cell holder. Press read. The screen will show the value of barium concentration for example 30 mg/L of Ba^{2+}. Proceed with other samples and record the reading of barium concentration.

3.1.3 Comparison between static jar tests with tube blocking test

The differences between the static conditions tests with dynamic conditions test are explained in terms of residence times. The static jar test method are much longer to be complete, usually for a few hours compared to the in the dynamic method which usually only take a few minutes to be complete. Plus, some inhibitors are efficient to prevent crystal growth while others are more efficient to prevent nucleation due to their chemistry. A test in static condition is more efficient in preventing the crystal growth while nucleation inhibitors are more efficient when tested in dynamic conditions.

Even there are lots of attempts to make use of TBT; there is still a lack of methodology for selecting the best inhibitor treatment by this technique. The main experimental parameters in this method are the temperature, concentration of the inhibitor and the flow rate.

3.2 Key milestone

Submission of Progress Report

16th March 2012

Submission of Poster

6th April 2012

Submission of Final Report (CD Softcopy & Softbound)

16th April 2012

SEDEX

17th and 18th April 2012

Submission of Technical paper

20th April 2012

Final Oral Presentation

30th April 2012

Submission of hardbound copies

4th June 2012
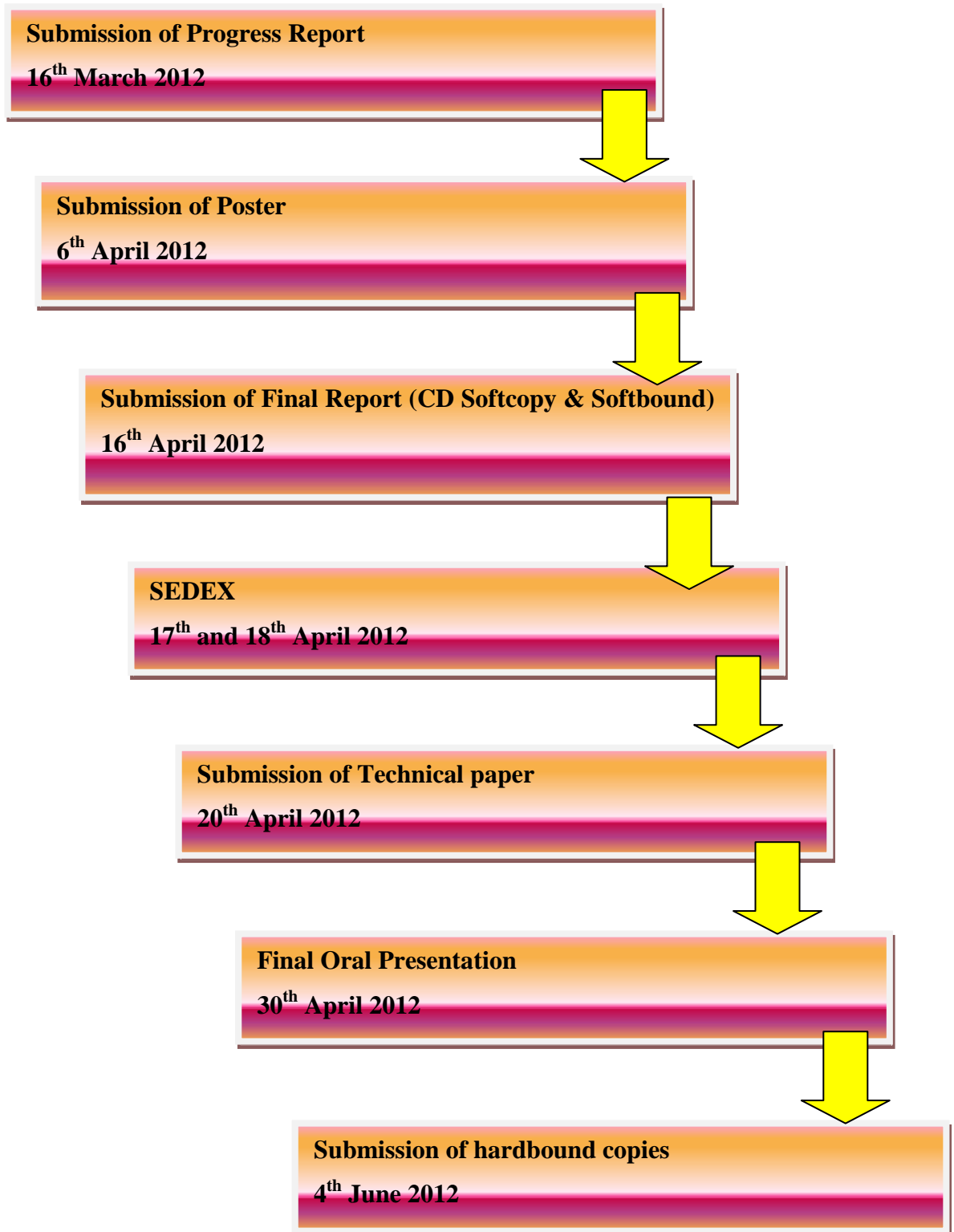
3.3 Gantt chart for FYP II

No.	Detail/week	1	2	3	4	5	6	7	Mid semester break	8	9	10	11	12	13	14	15	16
1	Project work continues	███	███	███	███	███	███	███		██								
2	Submission of Progress Report																	
3	Project Work Continues										███	███						
4	PRE-EDX Poster Submission													▣				
5	SEDEX														██			
6	Submission of Final Report (CD Softcopy & Softbound)														██			
7	Submission of Technical paper																	
8	Final Oral Presentation (Viva)															▣		
9	Submission of hardbound copies																	▣

3.4 Tools required

Table 9: Tools required in TBT and Static Jar Test

Tube blocking test (TBT)	Static Jar Test
Scale Inhibitors • Phosphonates (DETPMP) • Polyaspartates (PASP)	Scale Inhibitors • Phosphonates (DETPMP) • Polyaspartates (PASP)
Chemicals • Barium Chloride • Sodium Chloride • Sodium Sulphate • Acetic acid	Chemicals • Barium Chloride (BaCl) • Sodium Chloride (NaCl) • Sodium Sulphate (Na_2SO_4) • Sodium Acetate Tri-hydrate • Sodium hydroxide • BariVer® 4 Barium Reagent Powder Pillow • Potassium (KCl) • Sulphuric acid • Acetic acid
Tools • Beakers • Measuring cylinder • Syringe • Weighing scale • Spatula	Tools • Beakers • Measuring cylinder • Conical flasks • Pipette • Aluminum foil • Gloves • Test tubes • Syringe • Weighing scale • Spatula
Equipments • TBT equipments • Weighing scale	Equipments • Waterbath shaker • pH meter • Weighing scale • DR Spectrometer 5000

Below is the picture of the Tube Blocking Tests apparatus taken from Block 15:

Figure 17: The equipment for dynamic tube blocking testing of scale inhibitors

Static Jar tests (In block 5)

- Water bath shaker
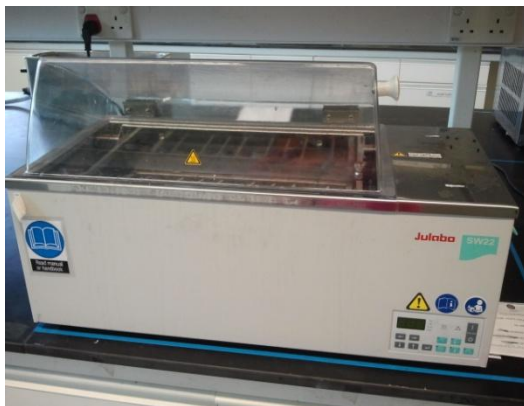
Figure 18: Water bath shaker

Figure 19: Water bath shaker from inside

- pH meter

Figure 20: pH meter

- beaker, test tubes

Figure 21: Conical flask   **Figure 22: Test tubes**

- Spectrometer to determine barium concentration (Block 5)

Figure 23: Spectrometer DR 5000

CHAPTER 4

4.0 Result and discussion

4.1 Tube Blocking Test (TBT) Experiments (Dynamic conditions)

4.1.5 Results and discussion of the TBT experiments

PASP Performance at various concentrations – BaSO$_4$ scale
(Q = 2ml/min, Temperature = 50°C)
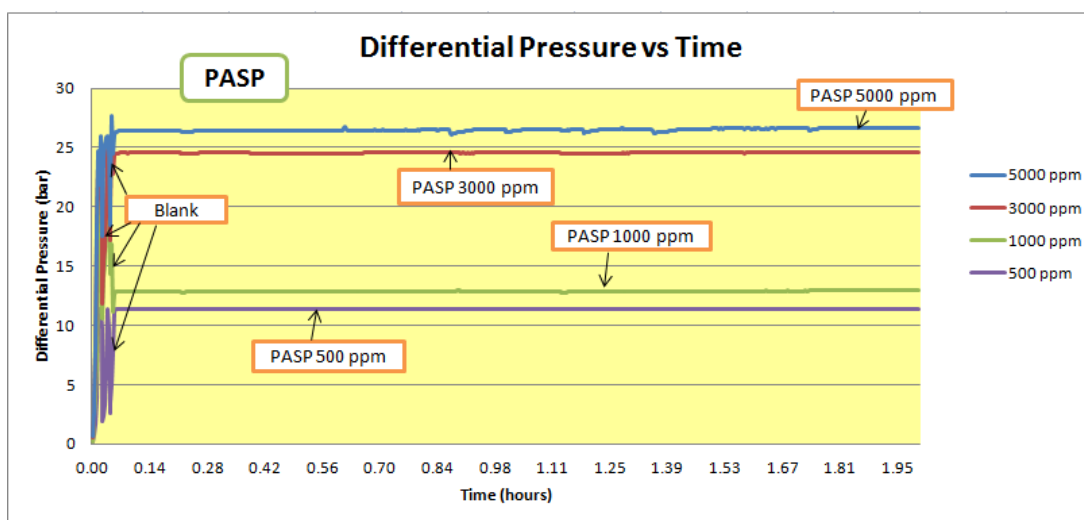
<div align="center">Figure 24: Concentration effect (PASP)</div>

From the figure 24 above, it was shown that the differential pressure versus time for different concentration of Polyaspartate in a range of 500 ppm until 5000 ppm. It shows the effect of the scale inhibitor concentration in time (hours) compared to the blank time. The temperature and the flow rates are constant for all the concentrations tested. From 0 hours to around 0.1 hours for the four concentrations, the scale had built up as the differential pressure increase. Then the program introduced the inhibitor to reduce the scale. The constant pattern after the prescale section (blank time) indicates that the inhibitors is mitigating the barium sulphate. At the end of two hours, all of the concentration of inhibitors tested can still mitigate the Barium Sulphate as there are no increases in the differential pressure. We can also see that the higher the concentration of the inhibitor, the higher the differential pressure.

PASP Performance at various temperature – BaSO4 scale
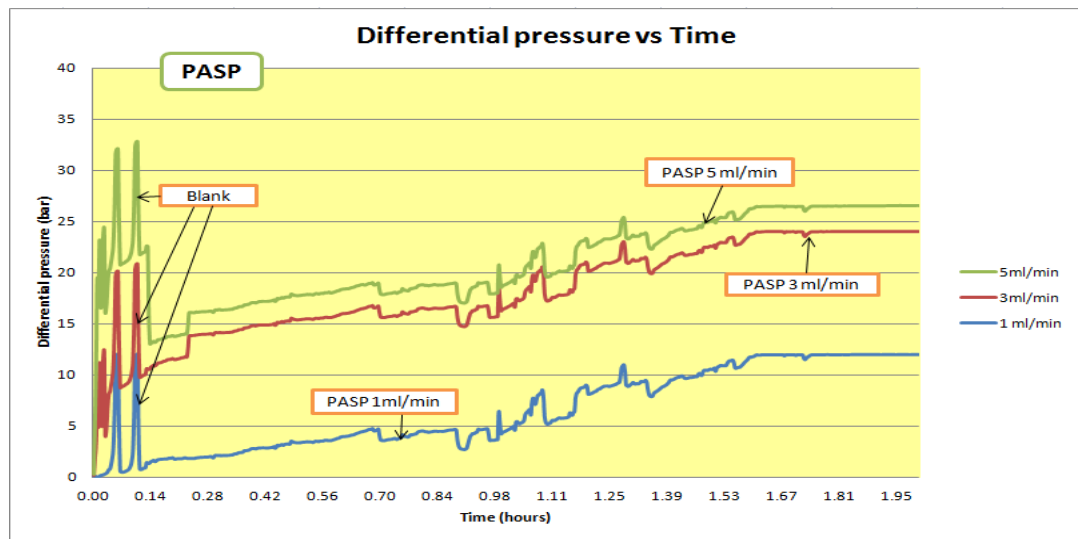
(Q = 2ml/min, Concentration = 5000 ppm)
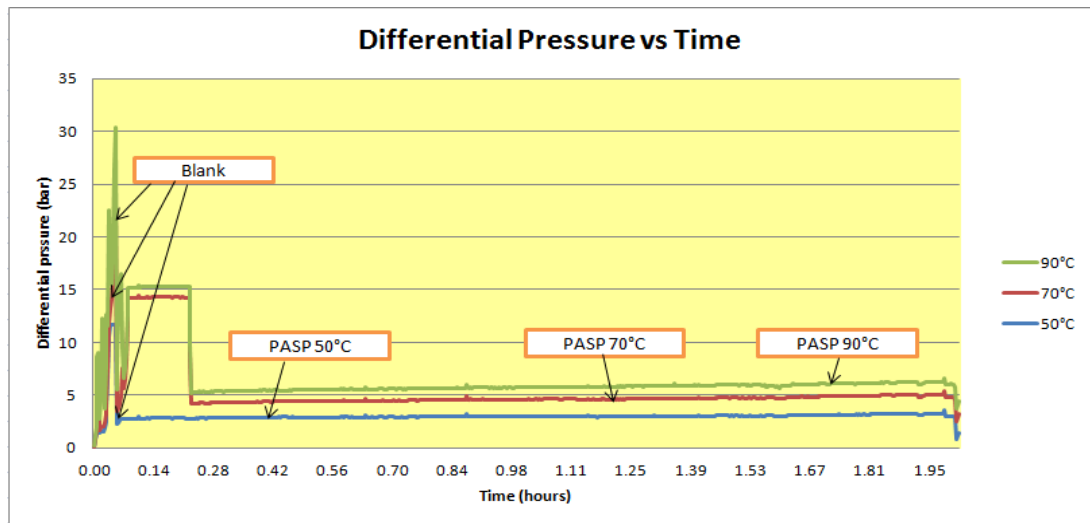
Figure 25: Temperature effect (PASP)

From the figure 25 above, it was shown that the differential pressure versus time for different temperature of Polyaspartate in 50°C, 70°C and 90°C. It shows the effect of temperature of the inhibitor in time (hours) compared to the blank time. The concentration and the flow rates are constant for all the concentrations tested. From 0 hours to around 0.1 hours for the three temperatures, the scale had built up as the differential pressure increase. Then the program introduced the inhibitor to reduce the scale. The constant pattern after the prescale section (blank time) indicates that the inhibitors is mitigating the barium sulphate. At the end of two hours, all of the temperature of inhibitors tested can still mitigate the Barium Sulphate as there are no increases in the differential pressure. We can also see that the higher the temperature of the inhibitor, the higher the differential pressure.

PASP Performance at various flow rate – BaSO₄ scale
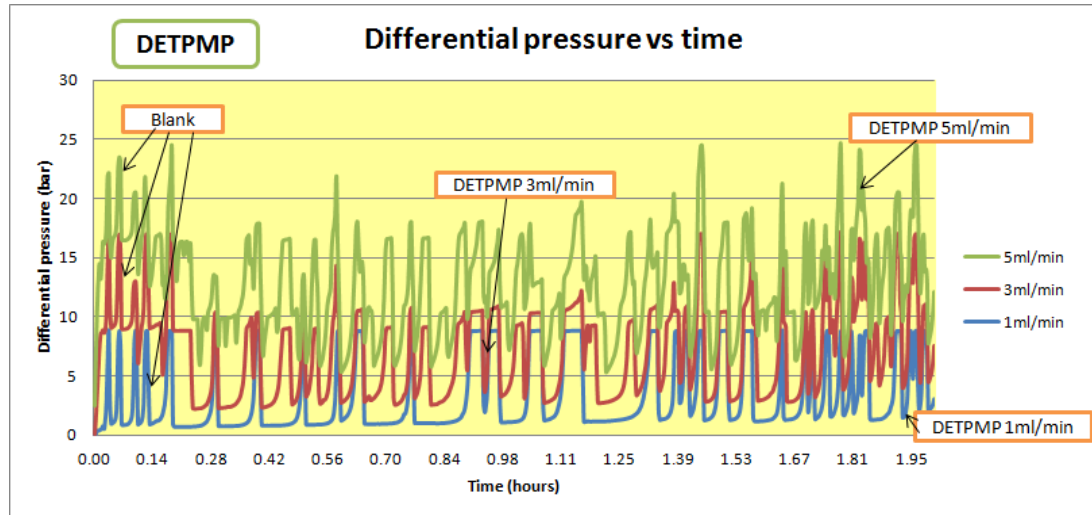**(Concentration = 5000 ppm, Temperature = 50°C)**

Figure 26: Flow rate effect (PASP)

From the figure 26 above, it was shown that the differential pressure versus time for different flow rates of Polyaspartate in 1 ml/min, 3 ml/min and 5 ml/min. It shows the effect of flow rates of the inhibitor in time (hours) compared to the blank time. The concentration and the temperature are constant for all the concentrations tested. From 0 hours to around 0.14 hours for the three flow rates, the scale had built up as the differential pressure increase. Then the program introduced the inhibitor to reduce the scale. The pattern after the prescale section (blank time) shows that the differential pressure is increasing slowly then became constant at the end of the two hours. The pattern still indicates that the inhibitor is mitigating the barium sulphate as there was no sudden increase in the differential pressure. At the end of two hours, all of the temperature of inhibitors tested can still mitigate the Barium Sulphate. We can also see that the higher the temperature of the inhibitor, the higher the differential pressure.

DETPMP Performance at various flow rate – BaSO4 scale

(Conncentration = 5000 ppm, Temperature = 50°C)

Figure 27: Flow rate effect (PASP)

From the figure 27 above, it was shown that the differential pressure versus time for different flow rates of conventional scale inhibitor, DETPMP in 1 ml/min, 3 ml/min and 5 ml/min. It shows the effect of flow rates of the inhibitor in time (hours) compared to the blank time. The concentration and the temperature are constant for all the concentrations tested. From 0 hours to around 0.14 hours for the three flow rates, the scale had built up as the differential pressure increase. Then the program introduced the inhibitor to reduce the scale. However, The pattern after the prescale section (blank time) was abruptly goes up and down for the whole 2 hours. It shows that the differential pressure had some disturbance along the way. It was assumed that the pattern should be constant as well same with the green inhibitors that shows the conventional scale inhibitor mitigate the barium sulphate. After analyzing the problems, according to (B. Bazin *et al*. 2005), some of the scale inhibitor efficiency is known to be very sensitive to pH variations. It is recommended to perform inhibitor testing in pH conditions as close as possible to the reservoir conditions. In this test, to set the pH, buffer solutions must be used. It was tested that DETPMP efficiency was found to be very pH sensitive. In this case, DETPMP should be tested with pH 6 in order to get the accurate results.

There are no data for the other two parameters, concentration and temperature for the conventional scale inhibitors due to the leaking problems that occurred to the TBT equipments. There was a huge leakage when the test is running after testing the flow rates effects on conventional scale inhibitor at the relieve valves behind the equipment. Several attempts had been done to overcome the problem but the machine is still not in a good condition. By the results that was obtained before the equipment encounter the problem, it is clearly shown that Polyaspartate, the green scale inhibitors can mitigate the barium sulphate scale and exhibit a competitive inhibiting efficiencies with the conventional scale inhibitor in sulphate scale formation. Inhibitor efficiency was determined by the ratio of the time needed to block the tube in the presence of the inhibitor divided by the time needed to block the tube without inhibitor (blank). However, the inhibitor efficiency cannot be measured as the inhibitor still can mitigate the barium sulphate within the time set and there are no tube blocking time in the presence of inhibitor recorded.

4.2 Static Barium Sulphate inhibition efficiency tests (Jar tests)

4.2.1 Results and discussion of the Static Jar test experiments

From (C.E Inches, 2006) conclude that for 50:50 ratio of seawater and formation water, the sample must be diluted 10 times dilution. From (G.M. Graham, 2001) conclude that 1 ml of the sample must be diluted in 19 ml quenching solution but it was for 10:90 ratio of SW:FW. Another journal from (G.M. Graham, 1997) conclude that for a ratio of 50:50 SW:FW, 4 ml of the sample must be diluted 6 ml quenching solution. However, this is for low scaling brine efficiency test. From this experiment, it is to create a severe or medium scaling system. So 1 ml of the sample must be diluted in 9 ml of the quenching solution to create the medium scaling brine efficiency the ratio of SW:FW 50:50.

Table 10 and 11 below is the results that obtained from the test conducted for both green and conventional scale inhibitors. The detailed calculations on the efficiency of inhibitors are shown in the Appendices.

Table 10: Results of barium concentration and efficiency of PASP

PASP, 95°C			
Concentration of inhibitor (ppm)	Time (hours)	Barium concentration (ppm)	Efficiency of inhibitor (%)
BLANK	2	10	-
	22	11	-
10	0	1	-
	2	2	88.9
	22	9	20
25	0	3	-
	2	4	85.7
	22	8	37.5
50	0	3	-
	2	4	85.7
	22	7	50
100	0	2	-
	2	3	87.5
	22	6	55.5
250	0	3	-
	2	4	85.7
	22	6	62.5

Table 11: Results of barium concentration and efficiency of DETPMP

Concentration of inhibitor (ppm)	Time (hours)	Barium concentration (ppm)	Efficiency of inhibitor (%)
DETPMP, 95°C			
BLANK	2	8	-
	22	10	-
10	0	3	-
	2	4	60
	22	7	42.86
25	0	3	-
	2	4	80
	22	6	57.14
50	0	3	-
	2	4	80
	22	6	57.14
100	0	2	-
	2	3	83.33
	22	5	71.4
250	0	2	-
	2	3	83.33
	22	4	75

The quenching solution that was used in most journals is using KCI/PVS or KCI/PPCA. Due to unavailability of PVS and PPCA, the inhibitor was replaced with DETPMP. All PVS, PPCA and DETPMP are the conventional scale inhibitors.

As explained before, the percentage of efficiency of the inhibitor was calculated by the formula below:

$$\% \text{ efficiency} = 100 \times \frac{(C_1 - C_B)}{(C_O - C_B)}$$

C_1 = concentration of barium at sampling time, 2 hours or 22 hours

C_B = concentration of barium in blank solution (no inhibitor)

C_O = concentration of barium in originally solution, at t = 0

Figure 28 below is the inhibition efficiency profile at 95°C at 2 hour sampling.
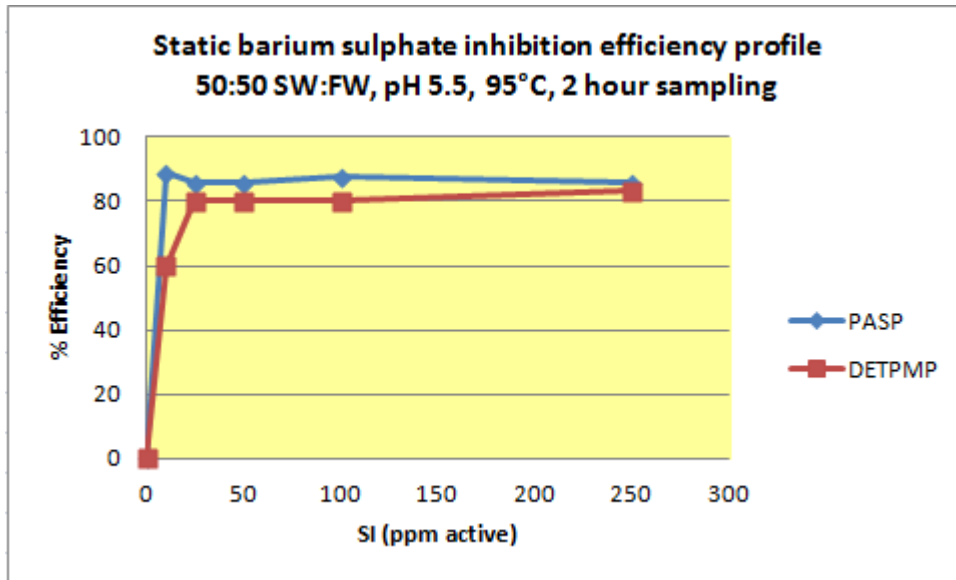
Figure 28: Inhibition efficiency profile, 95°C, 2 hour sampling

From figure 28 above, it was shown that the inhibition efficiency of the PASP and DETPMP at 95°C at 2 hour sampling time. The concentrations of the inhibitors were varied from 10 ppm to 250 ppm for both of the inhibitors. The patterns of the graph are more or less the same and both can mitigate almost 100 % of the barium sulphate scale within 2 hours. For DETPMP, the efficiency of the inhibitor was increased from 60% to 84% as the concentration of the inhibitor increase meanwhile for PASP, the efficiency of the inhibitor was maintained around 85% as the concentration of the inhibitor increase. It shows that PASP performance is better that DETPMP for 2 hours sampling time.

Figure 29 below is the inhibition efficiency profile at 95°C at 22 hour sampling.
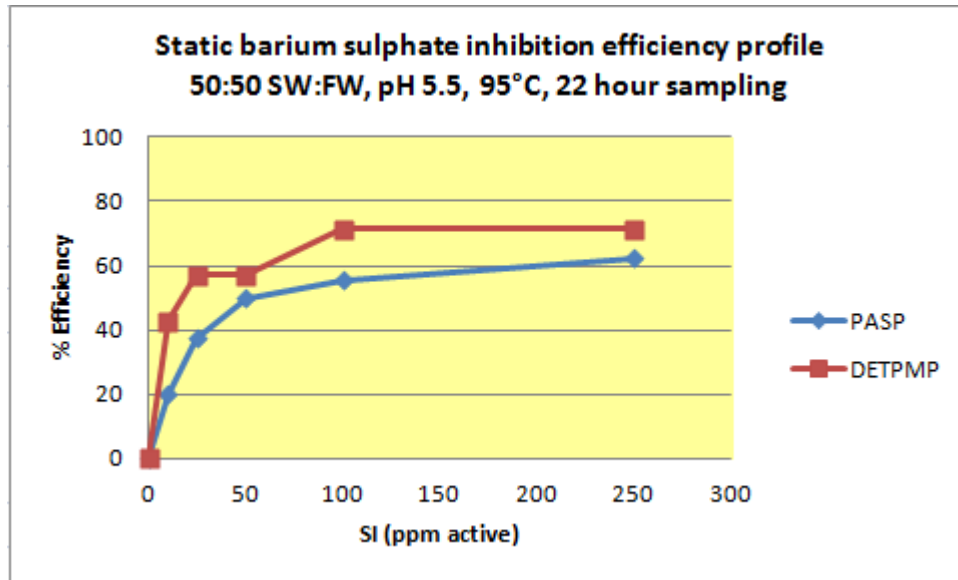
Figure 29: Inhibition efficiency profile, 95°C, 22 hour sampling

From figure 29 above, it was shown that the inhibition efficiency of the PASP and DETPMP at 95°C at 22 hour sampling time. The concentrations of the inhibitors were varied from 10 ppm to 250 ppm for both of the inhibitors. The patterns of the graph are more or less the same and both can mitigate from 40% - 70% of the barium sulphate scale within 22 hours. For DETPMP, the efficiency of the inhibitor was increased from 40% to 70% as the concentration of the inhibitor increase meanwhile for PASP, the efficiency of the inhibitor was increased from 20% to 60% as the concentration of the inhibitor increase. It shows that DETPMP performance is better that PASP for 22 hours sampling time. PASP only can inhibit 50 % of the scale so in 22 hours in 95°C conditions, PASP cannot mitigate the scale.

For this Static Jar Tests, all of the 6 tests to take the samples for 95°C, 55°C and 25°C had been conducted. To determine the barium concentration in the samples taken, barium reagent pillow powder must be dilute in the sample before put in the spectrometer to calculate the barium concentration. However, there are shortage of the barium reagent and the test that was fully completed are as discussed above. For 55°C and 25°C, the inhibitor efficiency cannot be calculated. Due to short time, the test cannot be continued as the reagent takes 4-6 weeks to arrive.

CHAPTER 5

5.0 CONCLUSION AND RECOMMENDATION

Both of static jar tests and tube blocking tests are conducted to evaluate the efficiency of the green scale inhibitor, polyaspartate compared to the conventional scale inhibitor, phosphonate. It is to prove that the green inhibitor can act the same and provide more advantages than the conventional scale inhibitors. For static jar test, two incompatible brine are mixed in the presence of inhibitor. In the TBT method, the differential pressure across a thin steel tube is observed as a function of time while the two components of the scaling brine are injected at the inlet of the tube. Based on the results above, in Tube blocking test, it is proven that PASP can mitigate the barium sulphate scale as well as the conventional scale inhibitor. For the Static Jar Test, PASP succeed in mitigate the scale for 2 hours but not in 22 hours compared to DETPMP which succeed in mitigate the scale for both of the sampling time. There are lots of improvements that need to be done in future in order to achieve accurate results from both of the experiments. Lots of readings and analyzing of the journals must be done so that technical error can be avoided when conducting the experiments. Some of the recommendations for each of the test will be discussed below.

5.1 Recommendations for TBT test

1. Use a smaller concentration of scale inhibitor or longer the test runs time to observe a full overview of the inhibitors properties and detect the time that were needed to block the tube in the presence of the inhibitor.

2. To maintain the efficiency of the apparatus, for every inhibitor concentration, the tube must be clean up with EDTA, pH 11.5-12 for sulphates before performing the next test with another concentration.

3. Temperature variations during the test can changes the water viscosity and this will affect the differential pressure in the tube. It is recommended to use

long preheating tubes upstream capillary entrance for a suitable temperature control.

4. Some of the scale inhibitor is known to be sensitive to pH variations, so it is recommended to perform the test as close as possible as those encountered in the field. This can be done by using buffer solutions to change the pH.

5. The test can proceed by determining the Minimum Inhibitor Efficiency (MIC) that was required to prevent the formation of the scale. This can be done by decreasing the inhibited brine concentration until the tube block and the differential pressure increases.

5.2 Improvements of Static Jar Test

1. For a better result, the concentration of the inhibitor must be observed in a wide range of value from 10 to 5000 ppm for example to obtain a full overview of the scale inhibitors parameters.

2. Use different ratios of SW:FW to further investigate the efficiency of the scale inhibitors.

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2. Inches, C.E., Sorbie, K.S. and Doueiri, K.El.: "Green Inhibitors: Mechanisms In The Control Of Barium Sulphate Scale", Paper No. 06485, presented at NACE Int. CORROSION 2006 Conference and Exhibition, San Diego, Ca, 12 – 16 March 2006.

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APPENDICES

Appendix 1: Detailed calculation for brine preparation

<u>To make the formation water:</u>

For Ba ion:

First find the molecular weight of $BaCl_2, 2H_2O$ salt.

MW of $BaCl_2, 2H_2O$ = 244.18 g/mol

Then find the molecular weight of Ba.

MW of Ba = 137.28 g/mol

Then calculate the percentage, % of Ba in $BaCl_2, 2H_2O$ salt.

$$\frac{137.28}{244.18} \times 100 = 56.2208\%$$

Then find the concentration of $BaCl_2, 2H_2O$ to give 250 ppm of Ba.

$$\frac{100\%}{56.2208\%} \times 250 \ mg/L = 444.7 \ mg/L$$

444.7 mg/L = 0.4447 g/L

So 0.4447 gram of $BaCl_2, 2H_2O$ in 1 litre of distilled water is needed.

For Na ion:

MW of NaCl = 58.44 g/mol

MW of Na = 22.99 g/mol

The percentage, % of Na in NaCl

$$\frac{22.99}{58.44} \times 100 = 39.339\%$$

The concentration of NaCl to give 5200 ppm of Na:

$\dfrac{100\%}{39.339\%}$ x 5200 mg/L = 13218.3 mg/L

13218.27 mg/L = 13.2183 g/L

So 13.2183 gram of NaCl in 1 litre of distilled water is needed.

So in 1 litre of distilled water, 0.4447 g of $BaCl_2$, $2H_2O$ and 13.2183 g of NaCl will be added to make the formation water.

To make the sea water:

For SO_4^{2-} ion:

MW of NaSO4 = 142.05 g/mol

MW of SO4 = 96.07 g/mol

The percentage, % of SO_4 in $NaSO_4$ salt.

$\dfrac{96.07}{142.05}$ x 100 = 67.63%

The concentration of $NaSO_4$ to give 2582 ppm of SO_4.

$\dfrac{100\%}{67.63\%}$ x 2582 mg/L = 3817.8 mg/L

3817.8 mg/L = 3.8178 g/L

So 3.8178 gram of Na_2SO_4 in 1 litre of distilled water is needed.

For Na ion:

MW of NaCl = 58.44 g/mol

MW of Na = 22.99 g/mol

The percentage, % of Na in NaCl

$\dfrac{22.99}{58.44}$ x 100 = 39.339%

The concentration of NaCl to give 10200 ppm of Na:

<u>100%</u>   x 10200 mg/L = 25928.468 mg/L

39.339%

25928.468 mg/L = 25.9285 g/L

So 25.9285 gram of NaCl in 1 litre of distilled water is needed.

So in 1 litre of distilled water, 3.8178 g of Na_2SO_4 and 25.9285 g of NaCl will be added to make the formation water.

Appendix 2: Graphs that was obtained from TBT before combined

Polyaspartate evaluation

Flow rate, ml/minutes (constant temperature and concentration of PASP)

For 1ml/minutes:
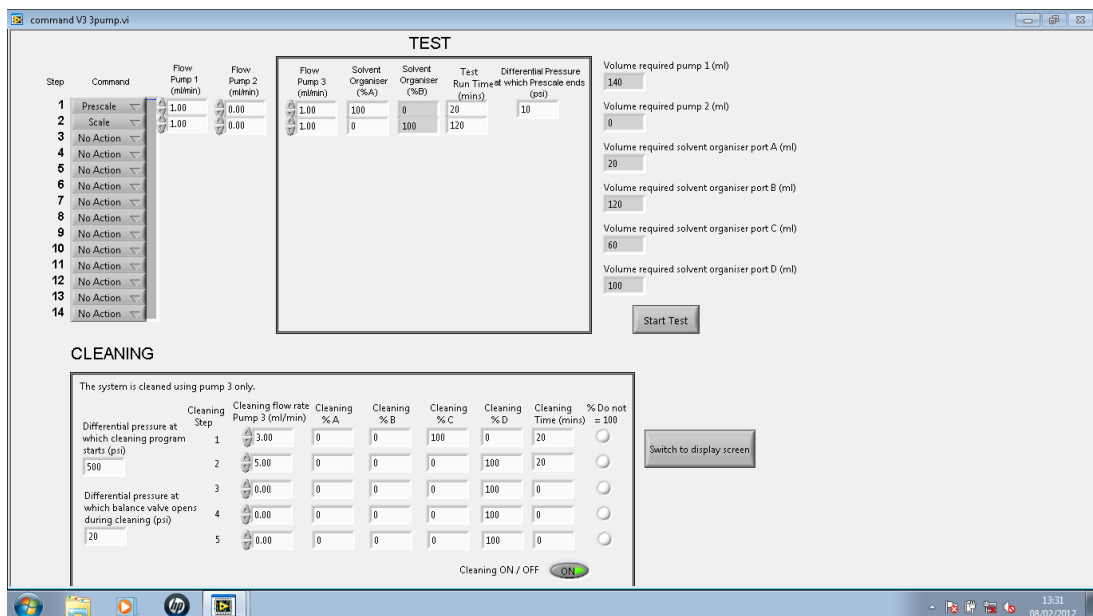
Figure 30: The test screen for 1ml/minutes flow rate
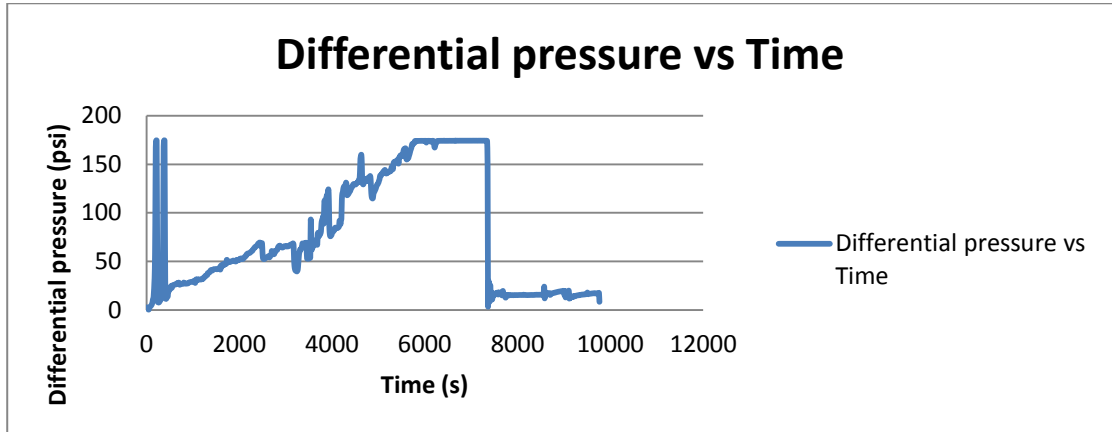
Figure 31: PASP performance at 1ml/minutes flow rate

For 3ml/minutes:

Figure 32: The test screen for 3ml/minutes flow rate
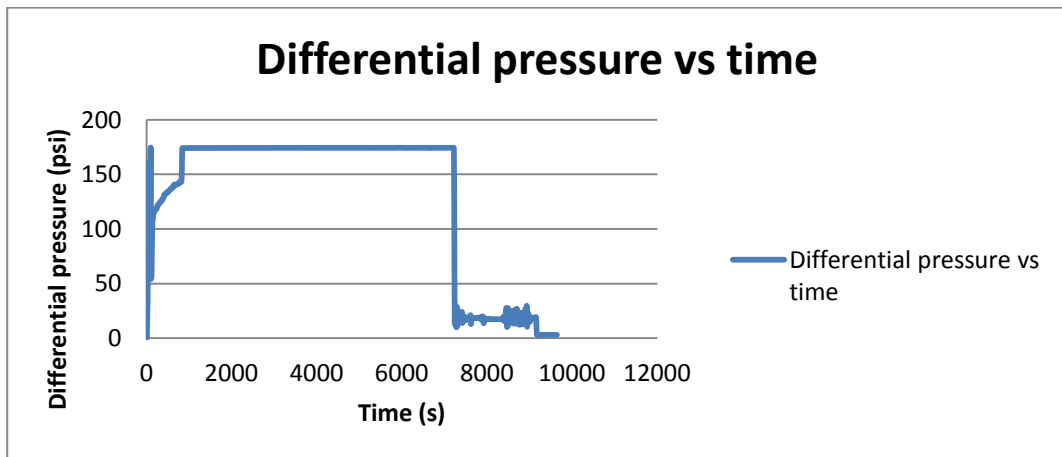
Figure 33: PASP performance at 3ml/minutes flow rate

For 5ml/minutes
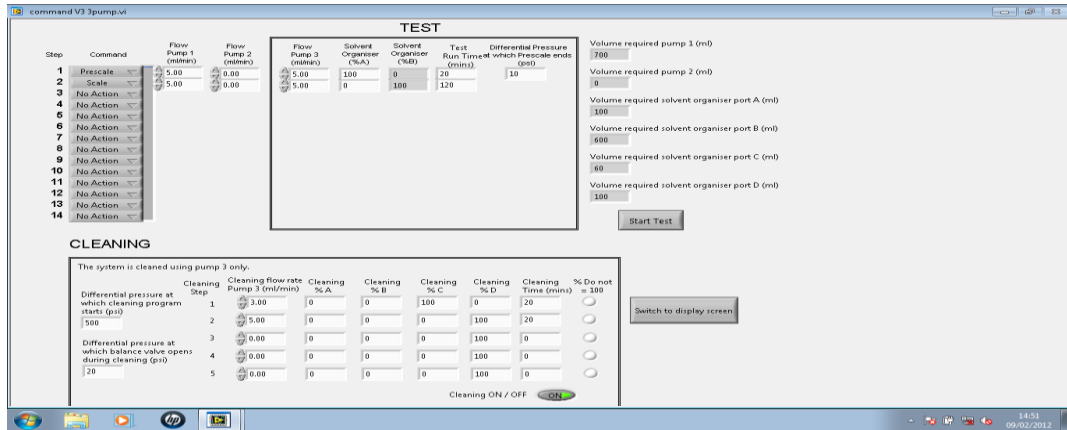
Figure 34: The test screen for 5ml/minutes flow rate
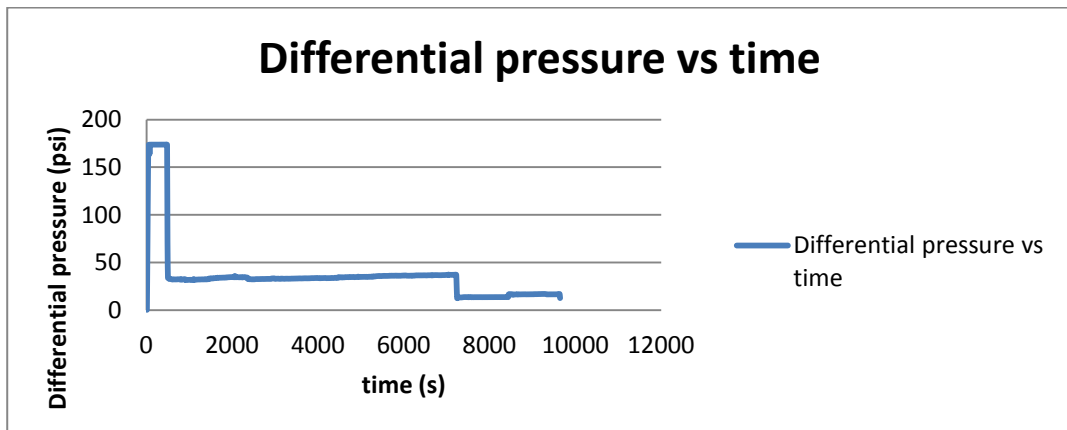
Figure 35: PASP performance at 5ml/minutes flow rate

Concentration, ppm (constant temperature and flow rate of PASP)
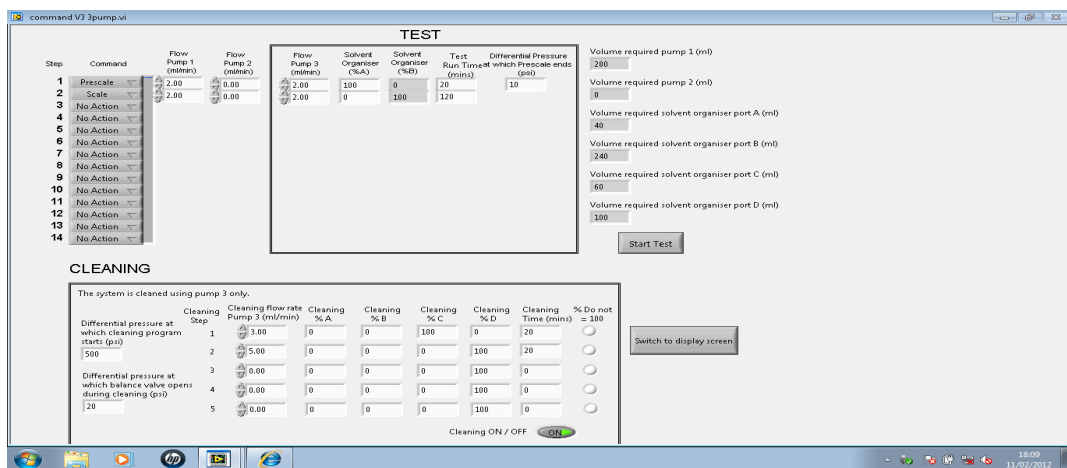
Figure 36: The test screen for different concentration of PASP (500 ppm, 1000 ppm, 3000 ppm, 5000 ppm)

For 500 ppm:
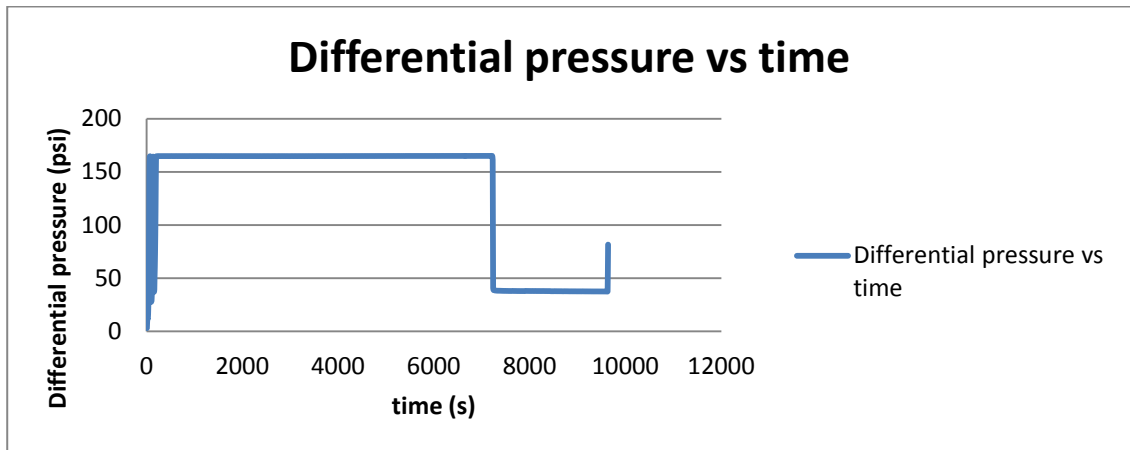
Figure 37: PASP performance at 500 ppm

For 1000 ppm:
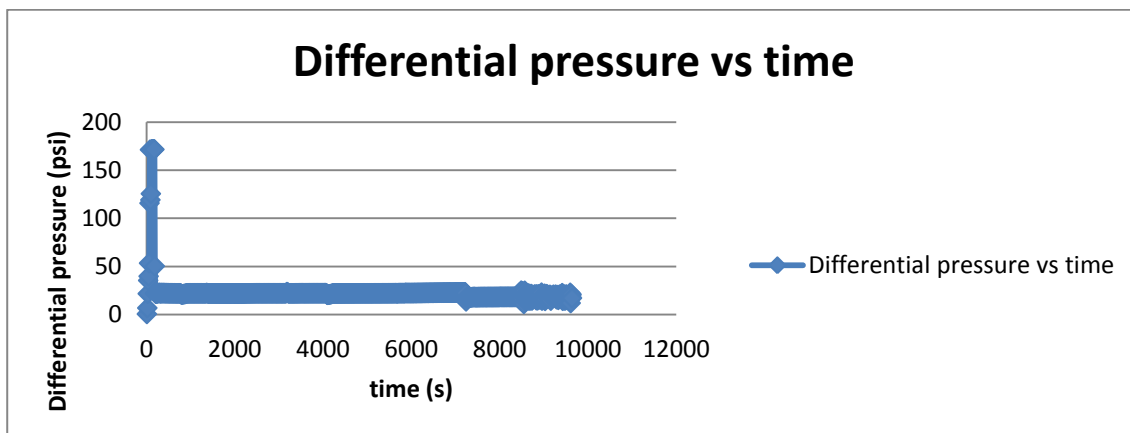
Figure 38: PASP performance at 1000 ppm

For 3000 ppm:
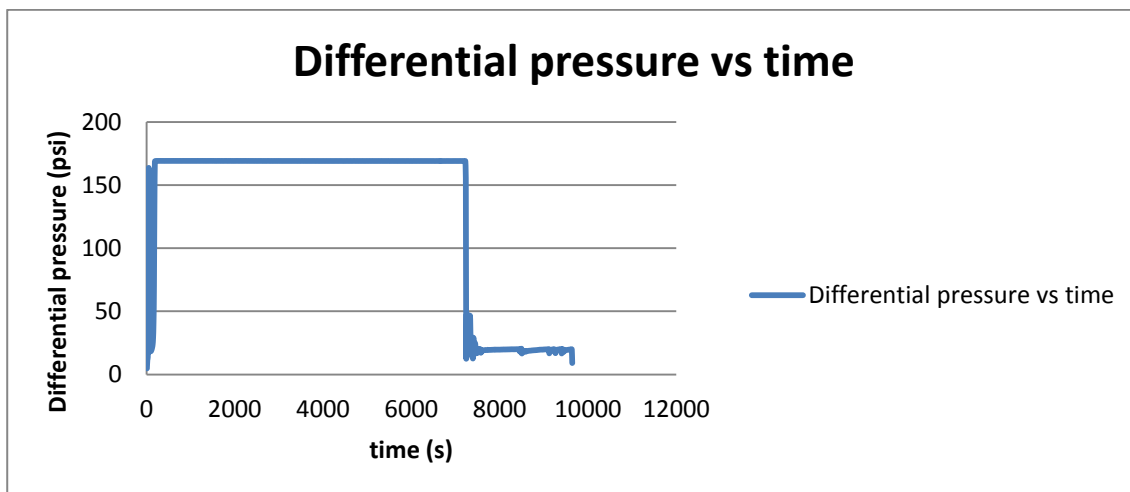
Figure 39: PASP performance at 3000 ppm

For 5000 ppm:
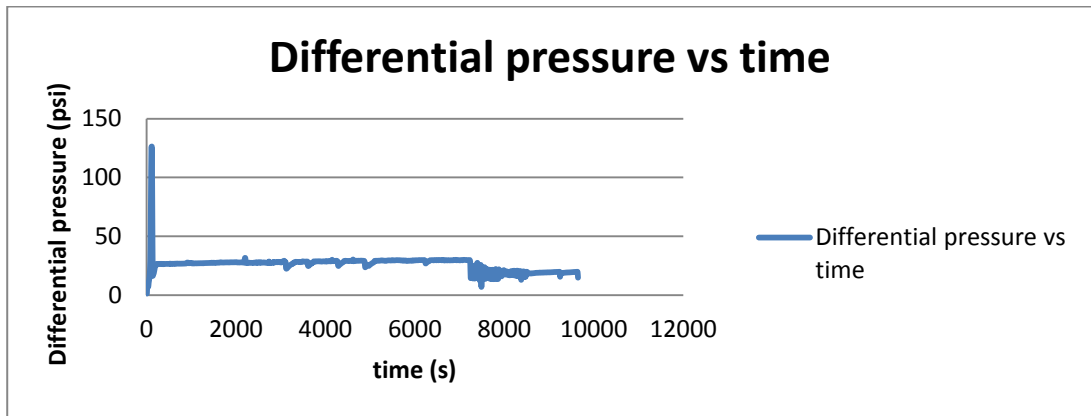
Figure 40: PASP performance at 5000 ppm

Temperature, °C (constant flow rate and concentration of PASP)

For temperature 50°C:
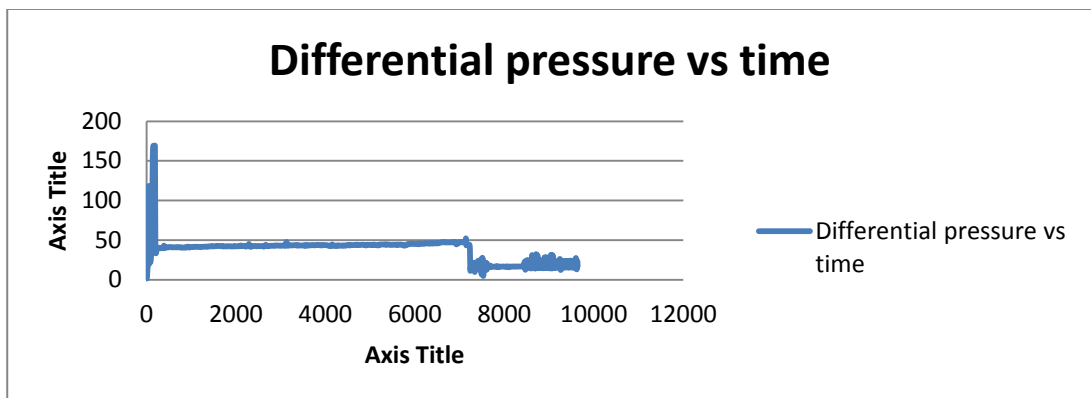
Figure 41: PASP performance at 50 degree Celsius

For temperature 70°C:
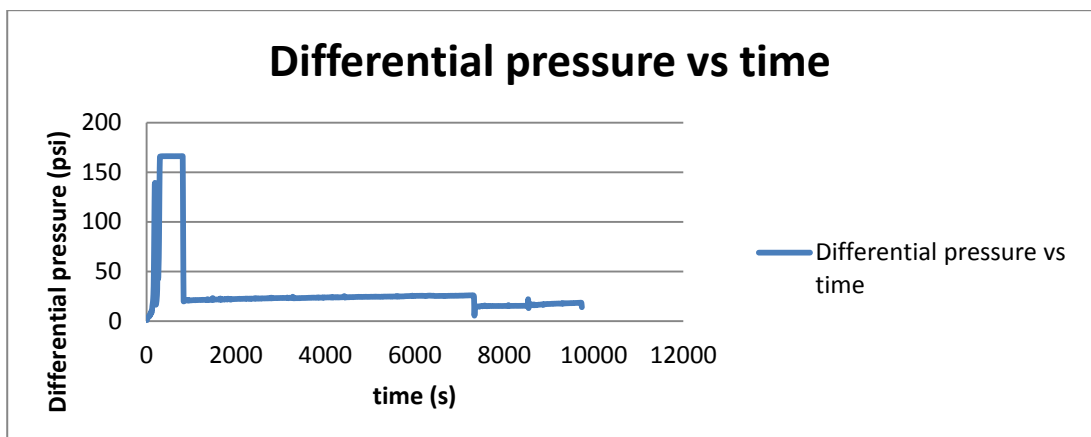
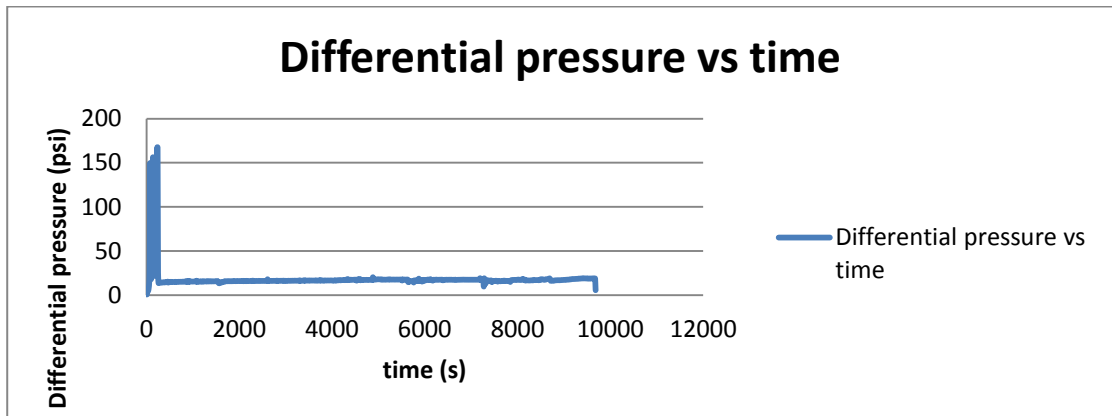**Figure 42: PASP performance at 70 degree Celsius**

For temperature 90°C:

Figure 43: PASP performance at 90 degree Celsius

Phosphonate evaluation

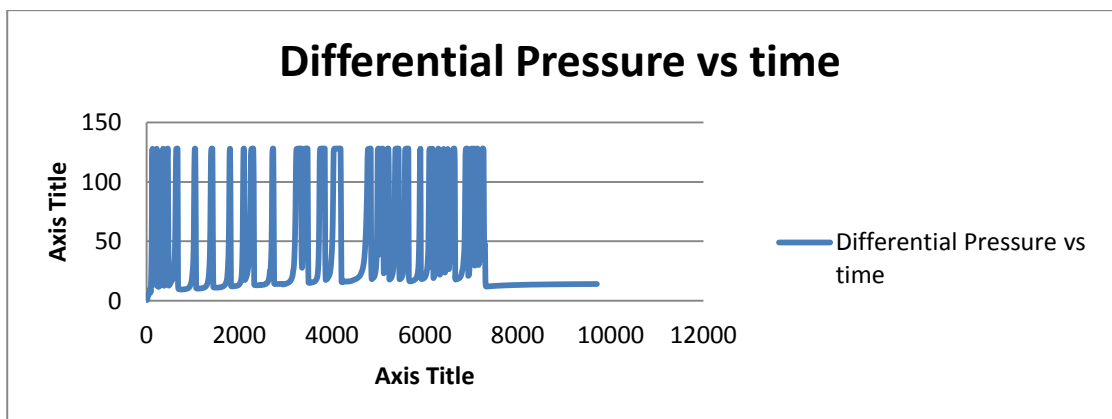**Flow rate (constant temperature and concentration of DETPMP)**

For flow rate 1ml/min:

Figure 44: DETPMP performance at 1ml/minutes flow rate
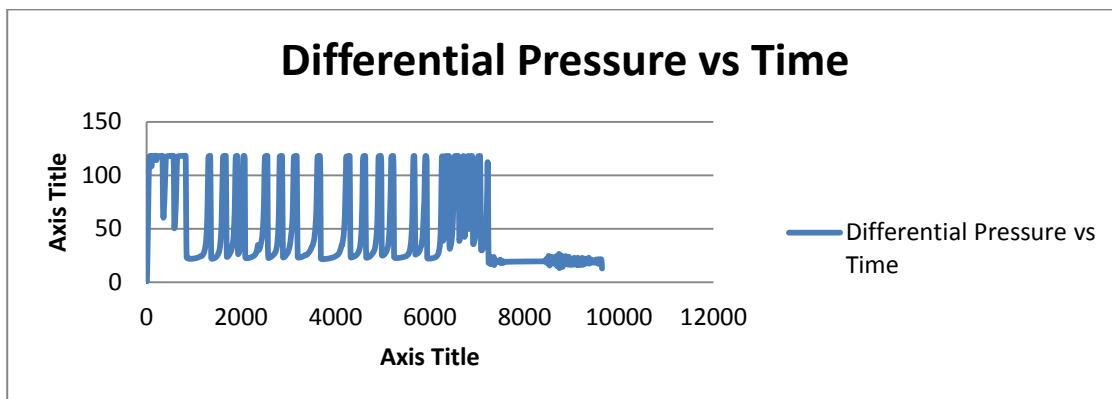
For flow rate 3ml/min:

Figure 45: DETPMP performance at 3ml/minutes flow rate
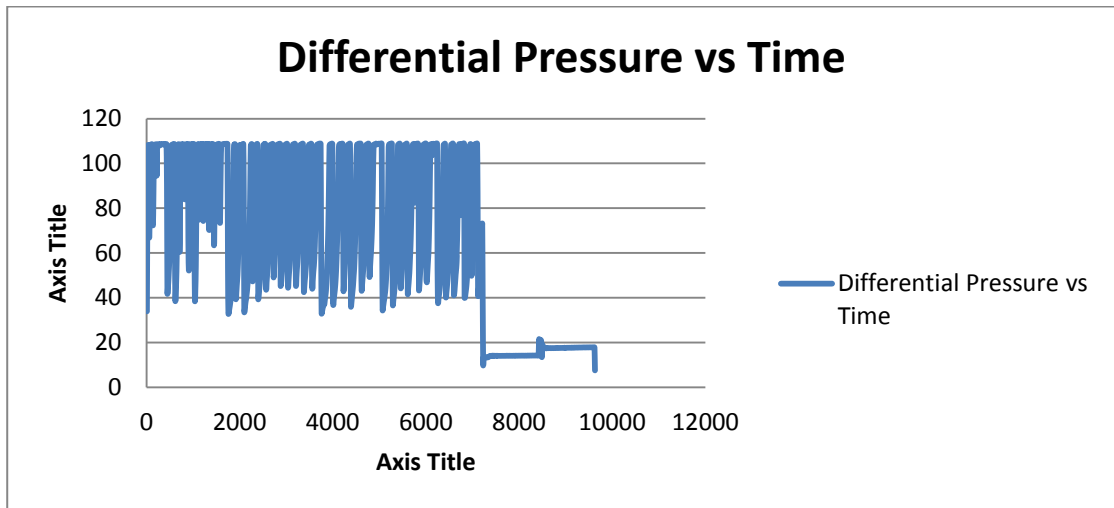
For flow rate 5ml/min:

Figure 46: DETPMP performance at 5ml/minutes flow rate

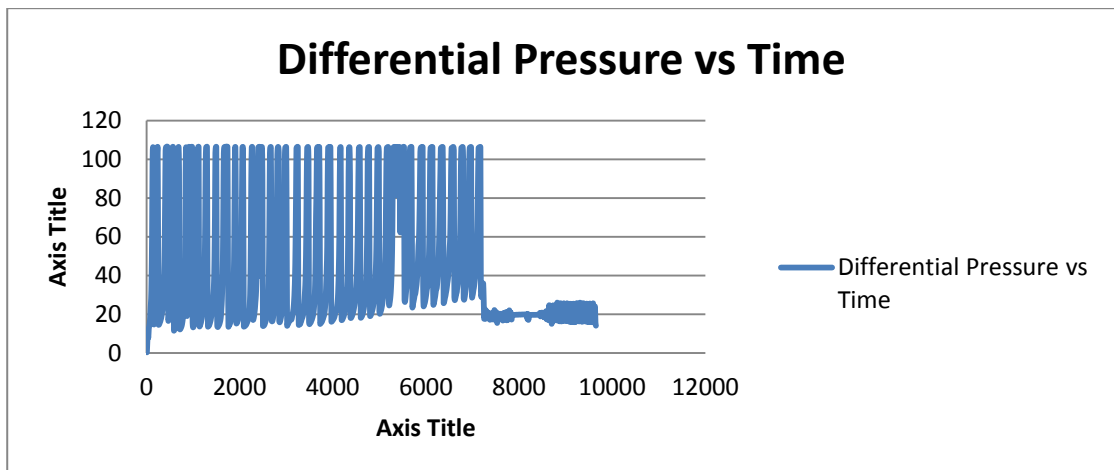**Temperature (°C) (constant flow rate and concentration of DETPMP)**

For temperature 50°C:

Figure 47: DETPMP performance at 50 degree Celsius