The Effect of Precipitation Inhibitor on Surfactant/Alkali/Acid/Crude Oil System

By

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CERTIFICATION OF APPROVAL

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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.

(NUZUL NADHIRAH HASHIM)
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As this project completed, I would like to express my biggest gratitude to the God Almighty for His willingness to let this project went smoothly without any major problems.

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ABSTRACT

This project is to observe the IFT behavior when precipitation inhibitor is created in the solution. It is also aimed to identify the optimum concentration of surfactant, alkali and acid. As the conventional ASP is always limited to fresh water, new approach need to be applied as brine hardness becomes the biggest limitation in ASP. In this project, it is suggested that by adding acid, precipitation inhibitor will be accumulated from the related reaction and enable the conventional ASP to be used with hard brine. The scope of study related to this project will be interfacial tension itself, as well as the optimum concentration for the related chemical for the best IFT retention. Different solutions with brine hardness at 35 000 ppm is prepared, and IFT measurement is done by using Spinning Drop Interfacial Tensionmeter. All readings are taken at 30^{0}C. The result showed that below optimum concentration, the chemicals work successfully but failed when is in excess.

CHAPTER 1 BACKGROUND STUDY

1.1 INTRODUCTION

The conventional Alkali-Surfactant-Polymer (ASP) is one of the chemical flooding used to enhanced oil recovery.Briefly explained, alkali is used to formed in-situ surfactant and to increase the pH of the surface rock as to decrease the surfactant adsorption by the rock. Surfactant is used to reduce the interfacial tension between oil and water. Polymer is used to increase the sweep efficiency by increasing the slug viscosity. The function of each chemical can be summarized as below;

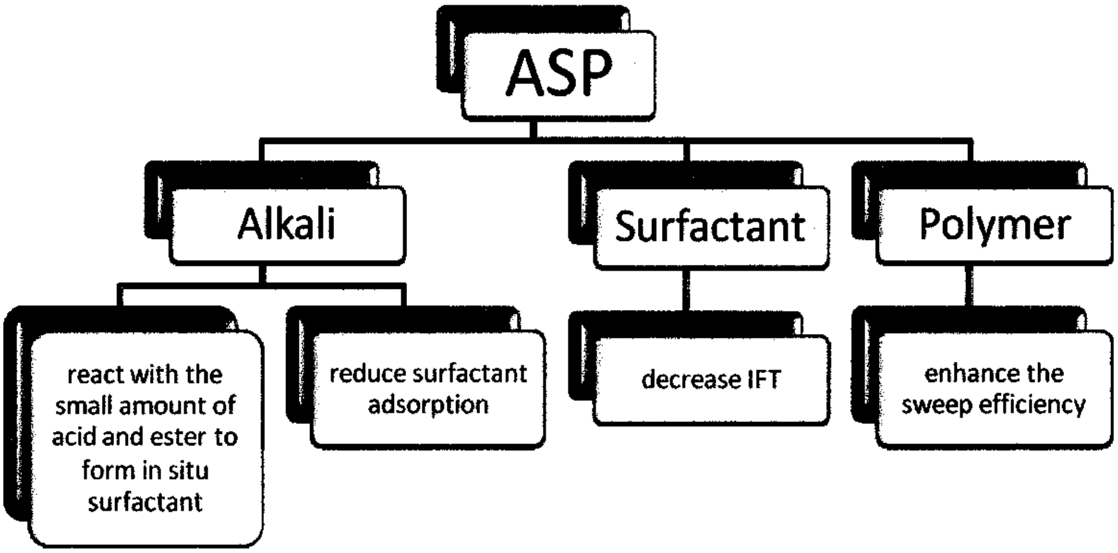

Figure 1: ASP; Chemical function.

With each chemical has its own function, it is limited to fresh water. This is due to the fact that in hard water or hard brine, the chemical reaction will lead to solid precipitation and thus reducing the efficiency of the chemical injection.

This project suggest to use acid as the precipitation inhibitor together with the chemical slug as to widen its compatibility in hard brine. As the result, the surfactants will successfully decreasing the IFT and increase the oil recovery.

IFT, or interfacial tension derived from surface tension, where the molecules of the liquid are trying to minimize the surface area as small as possible. Interfacial tension is the surface tension between two different liquid. The residual oil in the reservoir is due to high IFT between oil and water, causing the oil to trap in the rock and immobile.

Surfactant which acts like soap will help to create oil micelle and increase the mobility of oil in water, reducing the IFT between the oil and water. Polymer helps to drive the slug, providing a better control of the slug.

This project will analyze the effect of adding the acid in the system on IFT with different concentration of acid and alkali (together with surfactant) will be tested for the best oil recovery.

1.2 PROBLEM STATEMENT

The attainment of a low interfacial tension (IFT) is crucial in the immiscible displacement process in the porous media. Total hardness ions of the injection water have a significant impact on IFT behavior. It increases the IFT between the injected chemical slug and residual oil. This reduces the efficiency of the chemical slug where most of the residual oil will be trapped in the reservoir.

This project suggest to use the acid as precipitation inhibitor as to at least reduce the solid accumulation in the solution. However, as we introduce the PI, the increasing of salt itself will increase the salinity.

1.3 OBJECTIVES

PI will prevent the reaction between divalent metal cations and alkali or surfactant and thus helps to reduce IFT. The objectives of this project are stated as below;

1. To investigate the effect of precipitation inhibitor on IFT performance.
2. To identify the optimum alkali, surfactant and acid concentration.

1.4 SCOPE OF STUDY

To achieve the objectives for this project, few scope of study is identified;

1. Effect of Precipitation Inhibitor on IFT.
2. Optimum Concentration of Alkali.
3. Optimum Concentration of Surfactant.
4. Optimum Concentration of Acid.

CHAPTER 2 LITERATURE REVIEW

2.1 ALKALI-SURFACTANT-POLYMER FLOODING

Alkali-Surfactant-Polimer has been used as one of the chemical injection to enhance oil recovery after primary and secondary drive have achieve it best performance. It is theorized that the alkali reacts with small amounts of acids and esters present in the crude oil to form surfactants in-situ that combine with the injected surfactant to produce synergistic mixtures at the oil/brine interface. The alkali is also claimed to reduce the amount of surfactant adsorption onto the formation, especially in limestone reservoirs. By increasing the pH the iso-electric point of limestone is exceeded the surface becomes negatively charged. This increases the electrostatic repulsion between the rock surface and the negatively charged anionic surfactants and thus reduces adsorption[2].

The surfactant reduces the interfacial tension between the brine and residual oil and therefore increases the capillary number[2].

Polymer is used to increase the viscosity of the injection fluid for better profile control. The combination of surfactant, alkali and polymer results in a process where residual oil can be economically removed from the reservoir[2].

Conventionally, the ASP slug contains[9]:

- A surfactant (or more that one) that will mobilize the remaining oil by enhancing the microscopic sweep efficiency though favorable alteration of rock/fluids interaction such as: oil-water interfacial tension, reservoir wettability, oil-water relative permeabilities.
- An alkali to reduce the adsorption of the (expensive) surfactant on the reservoir rock. If the oil has moderate or high Total Acid Number (TAN) then the alkali will also react with the oil to generate in situ petroleum soaps, which also act as surfactants.
- Possibly a solvent such as Butanol or Ethylene Glycol Butyl Ether (EGBE) to enhace surfactant solubility.
- Polymer to increase the slug viscosity to about that of oil, which reduces the mobility ratio and improves the sweep efficiency.

2.2 ASP IN HARD BRINE

ASP works excellently in recovering the oil left after primary drive or water flood technique. However, ASP is limited to be used with fresh water. This is due to the existence of divalent metal cations in hard water. It will lead to reaction between the divalent metal cations and alkali which in the end will result to scales formation. The scales or solid precipitations from the reaction can plug the pores and prevent the oil from being produced. Instead of increasing the oil recovery, it will reduce the oil recovery.

A general rule of thumb for applying the ASP process is that the divalent cations concentration needs to be less than 10ppm in order to avoid the reaction of alkali with the divalent cations to form insoluble scales[2].

Thus, if ASP project is selected, water treatment equipments should be included in the field development plan as one of the surface facilities. Because of this limitations[2], Berger et. all. (2006) said that this will lead to bigger lost as stated below;

1. The up-front equipment cost, the operation cost and the sludge disposal often become the "stopper" for ASP project.
2. If water treatment equipment is built and pilot test prove unsuccessful or the project be cancelled prematurely, the expense for the water treatment cannot be recovered.
3. The space required and the water source is generally limited for off-shore operations.

2.3 SOLUTIONS FOR ASP IN HARD BRINE

By eliminating the water treatment process and the use of salt tolerant surfactants will help to create more feasible and economical EOR technique for off-shore application.

A few methods has been tested in labotary as to solve this problem. Berger et. all. (2006) describes the use of organic alkali to tolerate the hard brine. The experiment conducted gave good result, as he mentioned that the studies have found that brine tolerant, low adsorbing formulations for ASP can be formulated by including certain salts of weak acids, hereafter reffered to as organic alkalis. The organic alkali is used to provide alkalinity, reduce adsorption, complex multivalent cations, minimize the surface equipment and minimize the formation damaged compared to similar formulations using conventional inorganic alkalis[2].

He replaced the inorganic alkali (which is used sonventionally in ASP such as sodium hydroxide and sodium carbonate) with the organic alkali. In his experimental works, the organic alkali used is derived from the sodium salts of certain weak polymer acids.

On the other hand, Flaaten et. all. (2008) has introduced borax, white compound which occurs as minerals in some alkali salt deposit and found out that it also helps ASP to tolerate with hard water.

A form of borax kown as metaborate has been found to sequester divalent cations such as Ca^{2+} up to 6600ppm divalent cations and thus prevent precipitations. Thus this novel alkali can be used with hard brines at a pH of about 11 whereas sodium carbonate will precipitate in the presence of divalent cations. A surfactant formulation in hard brine with metaborate included showed good oil recovery in a core flood[6].

In the experiment he conducted, he used metaborax, a form of borax which was discovered to sequester divalent cations such as Ca^{2+} and prevent precipitation. In his paper, he described laboratory and modeling approach to ASP flooding in reservoirs containing very hard saline brines without the need for soft brine.

However, their study is limited to the reservoir properties they are studying. Each reservoir has different properties, which explain why sometimes the same EOR technique will not work on two different reservoirs. Thus, we need to discover new method as to give wider options that will favor the reservoirs located in Malaysia.

2.4 INTERFACIAL TENSION

Interfacial Tension (IFT) is a measurement of the cohesive (excess) energy present at an interface arising from the imbalance of forces between molecules at an interface (gas/liquid, liquid/liquid, gas/solid, liquid/solid). As two different liquid are in contact with each other, the molecules at the interface will experience imbalance forces, resulting to the accumulation of free energy at the interface[1].

The energy accumulated will give arise to excess energy called surface energy, which is the measurement of energy needed to increase the surface area of the interface by a unit amount. Mathematically expressed by[1];

$$\text{Surface Energy} = \frac{E}{A}$$

With E = energy and A = area. The common unit used are $\frac{dynes}{cm}$ or $\frac{mN}{m}$, which is equivalent to each other. However, IFT can also be expressed by $\frac{Force}{length}$, in which the force is describe as having a line tension. This force tends to minimize the surface area of the liquid, thus explaining why liquid drops are in sphere shape.

This excess energy exists at any interface. If the surface investigated is tested for one type of liquid, it is referred as surface tension. On the other case, if the surface investigated is the interface of two immiscible liquids it is referred as interfacial tension, IFT. In either case the more dense fluid is referred to as the "heavy phase" and the less dense fluid is referred to as the "light phase"[1]. Solid surfaces also may be described to have an interfacial tension normally referred to as Surface Free Energy (SFE), but direct measurement of its value is not possible through techniques used for liquids.

2.5 FACTORS AFFECTING IFT

There are lots of factors that contributing to IFT reduction or increment, it is largely depends on the substance contained in the liquid. Among the factors are the surfactant properties and concentration, crude oil composition and types of chemical used. From Chen et. all. (2007), he has listed the factors[3] as below;

1. **SALINITY** (Hardness of brine)

   The salinity value is related to inorganic ion composition in the solution. Through the experimental works done, he found that the lower the salinity, the lower the IFT will be. This is due to the inorganic composition. As the salinity is low, the inorganic composition increases, aiding in surfactant adsorption at the interface resulting to lower IFT. However, when the salinity is high, the high inorganic composition will result to decreasing in surfactant solubility and thus, raising the IFT

2. **CALCIUM AND MAGNESIUM ION CONCENTRATION**

   For calcium ion, the increasing in its concentration will result to decreasing and then increasing IFT. At low concentration of calcium ion, the divalent cations neutralize electric charge of the anionic surfactant and thus compress the interfacial double layer. This will decrease the repelling force between surfactant with some charge in micelle, so more surfactant can enter the micelle.

   With the increasing of calcium ion concentration, the precipitation cannot occur easily due to the dispersive action of surfactant on calcium ion. Although the surfactant can still entered the interface array, the degree of freedom decrease significantly to some extend but still in order of 10^{-3} mN/m.

   Further increase of calcium ion will causes the precipitation to occur, which a number of surfactant starts to deposit with calcium ion. This will cause the surfactant concentration to decrease, resulting to increase in IFT adruptly.

When concentration of magnesium is taken into account and being compared to calcium ion, the alkaline condition of the solution affects IFT significantly. This is due to the difference solubility of the ion, for example under strong alkaline conditions where pH=11, the solubility of magnesium ion is very low, compared to calcium ion at 0.432 mg/L and 2.2 x 10^5 mg/L respectively.

3. ORGANIC COMPOUND

A few types of organic compound are tested to observe its effect on IFT. Below are the conclusion obtained from the experimental work done;

- **Mixed Aromatic Hydrocarbon.** Ultra low IFT can be obtained within the concentration of 5-100 mg/L of mixed aromatic hydrocarbon, 0.2% wt of surfactant 1% wt of sodium hydroxide. No abrupt changes comes with increasing concentration of mixed aromatic hydrocarbon.
- **Fatty Acid.** The lower carbon number has no effect while the higher carbon number causes the interfacial activity of the system deteriorate and increase the IFT.
- **Aliphatic Hydrocarbon.** The long chain aliphatic hydrocarbon has slightly better affect on IFT compared to the short chain. However, this organic group has little effect on IFT.
- **Hydroxybenzene.** The IFT is high even with the low concentration of hydroxybenzene.
- **Different Alcohol.** IFT increase with only very low content (5 mg/L) of higher carbon number alcohol. Higher carbon number will cause higher IFT.

Chen et. all. (2007) conclude that the main types of inorganic compound that would increase IFT significantly are hydroxybenzene, higher carbon number fatty acids and higher carbon number alcohol[3].

Okasha et. all. (2009) also studied few factors[7] that contributing in changes of IFT. He focused on one of the carbonate reservoirs located in Saudi Arabia conclude that;

5. **Decrease of IFT with increasing oil temperature.** This due to the weakening of intermolecular forces at oil/brine interface as the temperature increase. Increasing in temperature also causes the density of the liquid, which in the end will result to decreasing IFT.
6. **Presence of divalent calcium and magnesium cations.** He mentioned that the presence of these ions may have specific interactions with ionizable species at oil/brine interface. However, no further explanations are included.
7. **Little increase in IFT with pressure at constant temperature.**
8. **Decrease in IFT as brine salinity increase.**

2.6 ULTRALOW IFT

According to capillary theory, under the conditions of the pressure gradient that can be reached through present technology, in order to activate the residual oil left by waterflooding, IFT of ASP/crude oil should be decreased to a 10^{-3}mn/m level[3].

According to Berger et. all. (2006), a capillary number of about 10^{-6} is found after completion of the typical water flood and this number must be increased by at least 2 or 3 orders of magnitude in order to efficiently displace the oil. The IFT between the oil and water during and following water flooding is in range of 10^{1} to 10^{0}mN/m. By using the proper surfactant in the chemical slug, IFT can easily decreased to 10^{-2}mN/m or less, which in the end result to increasing capillary pressure by at least 2 to 3 orders of magnitude[2].

Rosen (2004) in his book, Surfactant and Interfacial Phenomena also mentioned that to displace the oil in the pores and capillaries of the reservoir rock, an aqueous solution-oil interfacial tension of 10-3 mN/m is generally required. This means that the interface energy across the interface must be large. To achieve this, the nature of the materials on both sides of interface must be similar. Oil and water however, have a very different nature which the similarities between both can only be achieved when both sides have similar concentration of surfactant, oil and water[8].

CHAPTER 3 METHODOLOGY

3.1 RESEARCH AREA

3.1.1 NEUTRALIZATION PROCESS

This project will first observe the effect of using pure salt on the IFT performance as it will directly function as the precipitation inhibitor. Neutralization process is crucial as to understand and extract the pure sodium salt through experimental work to ensure that the substances is free from other component; 100% pure. The sodium salt will be extracted through titration process by mixing the acid and alkali solution in titration process.

3.1.2 EFFECT OF PRECIPITATION INHIBITOR ON IFT

IFT is one of the most important aspect that in the end will determine the appropriate ASP injection solution, thus the objective of injecting a conventional ASP is to decrease IFT between oil and water. The formula introduced in this project is a new formula; theoretically by introducing a precipitation inhibitor in this formula will help to prevent the unwanted reactions and reduces the IFT. This project is to observe how the precipitation inhibitor affects IFT.

3.1.3 OPTIMUM CONCENTRATION OF ALKALI

Alkali will react with acid before it increases the pH of the surface charge in the reservoir or react with small amount acidic component in crude oil. Low alkali concentration will not be adequate to complete its functions in the reservoir but too much alkali will be a waste as the additional alkali does not help to further decrease IFT.

3.1.4 OPTIMUM CONCENTRATION OF SURFACTANT

The optimum concentration of surfactant is important as to prepare the minimum limit of the surfactant concentration in order to achieve the desired IFT value. If the concentration is too little the chemical slug will not work, and often the engineers will used more as a safety measurement.

3.1.5 OPTIMUM CONCENTRATION OF ACID

Acid will react wil alkali to produce in-situ precipitation inhibitor which will prevent the unwanted reaction that will result to solid precipitation. Thus, by identifying the minimum concentration of acid in given condition, it will enable the engineers to set a minimum limit as to benefit the cost.

3.2 LABOTORARY WORK

3.2.1 METHODOLOGY

The experimental work will be divided into few sections;

3.2.1.1 BRINE PREPARATION

1. 1000ml distilled water is poured in a beaker to prepare 35000 ppm brine.
2. 86.6802 grams of sodium chloride salts is placed, 4.184 grams of magnesium chloride and 1.467 grams calcium chloride inside the beaker filled with 1000ml of distilled water.
3. The mixture is stirred slowly and gradually being heated up to assist the salts dissolving in the distilled water. The temperature should not exceed or reach boiling temperature to avoid evaporation.
4. After all salts have been dissolves, allow the brine to cool down.

Refer Appendix A for salt calculations example.

3.2.1.2 ALKALI AND SURFACTANT PREPARATION

1. The solution is prepared by referring to the table below;

SAMPLE NO.	AOS WEIGHT PERCENTAGE (%)	WEIGHT (g)
1	0	0
2	0.2	0.0515
3	0.4	0.1031
4	0.6	0.1546
5	0.8	0.2062
6	1	0.2577

Table 1; Surfactant weight for respective weight percentage.

SAMPLE NO.	Na_2CO_3 WEIGHT PERCENTAGE (%)	WEIGHT (g)
1	0	0
7	0.2	0.0515
8	0.4	0.1031
9	0.6	0.1546
10	0.8	0.2062
11	1	0.2577

Table 2; Alkali weight for respective weight percentage.

2. Alkali and surfactant are weighted accordingly and is mixed with 25ml of brine.
3. The sample is labeled accordingly.

Refer to Appendix B for weight percentage calculation example.

NOTED that all solutions are made with 35 000 ppm brine.

3.2.1.2 OPTIMUM CONCENTRATION FOR ALKALI AND SURFACTANT

1. Set the temperature at 30^0C.
2. 2ml of Sample 1 is injected into the tube. Ensure no bubble in the solution before closing it.
3. The tube is dried, then inserted into the equipment.
4. Starting from 100 rpm, the tube is run to rotate and the speed is increased gradually until 1000 rpm.
5. About 2ml of Angsi crude oil is measured using 5ml syringe. Carefully, the oil is injected into the tube containing solution Sample 1.
6. As soon as the oil forms a droplet, the syringe is pulled instantaneously.
7. The speed is increased until the droplet is stable. Tilting angle can be adjusted to help stabilize the oil droplet.
8. The equipment is calibrated and the measurement is records. Ten readings are taken.
9. Step 1-7 is repeated with Sample 2, Sample 3, Sample 4, Sample 5 and proceeded with alkali solutions (Sample 6, Sample 7, Sample 8, Sample 9, Sample 10 and Sample 11. Alkali concentration at 0 wt% is the same solution at 0 wt% surfactant.)

NOTED that before IFT measurement is performed, RI index and density is measured, both at 30^0C.

3.2.1.3 ALKALI-SURFACTANT-ACID SYSTEM PREPARATION

1. The solution is prepared by referring to the table below;

SAMPLE NO.	ACRYLIC ACID WEIGHT PERCENTAGE (%)	WEIGHT (g)
12	0	0.00
13	0.2	0.05
14	0.4	0.10
15	0.6	0.15
16	0.8	0.20
17	1	0.25

Table 3; Acrylic acid weight for respective weight percentage.

2. Acid is weighted accordingly and is mixed with 25ml of distilled water.
3. Alkali and surfactant are weighted referring to table below and mixed into the mixture.

	WEIGHT PERCENTAGE (%)	WEIGHT (g)
NA2CO3	0.6	0.15
AOS	0.6	0.15

Table 4; Weight for alkali and acid for Set A.

4. The sample is labeled accordingly.
5. Set B is prepare by using 1.0 wt% of alkali. Step 1 to 4 is repeated by changing weight of alkali to 0.25 g. The sample is labeled Sample 18, Sample 19, Sample 20, Sample 21, Sample 22, and Sample 23 accordingly.

Refer to Appendix B for weight percentage calculation example.

3.2.1.4 IFT BEHAVIOR IN ALKALI-SURFACTANT-ACID SYSTEM

1. Refer to the steps taken for Optimum Concentration for Alkali and Surfactant.
2. The experiment is done using solution from Set A and Set B.

3.2.2 APPARATUS

IFT measurement will be conducted by using Spinning Drop Interfacial Tensionmeter. This equipment is used due to the accuracy provided by this equipment, compared to Pendant Drop instrument. Other apparatus needed are the basic laboratory apparatus such as test tube, thermometer and measuring cylinder.

Figure 2; On the left, oil droplets in the tube of spinning drop interfacial tensionmeter machine. On the right, example of IFT measurement by IFT machine.

3.4 GANTT CHART

NO.	ACTIVITIES /WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Lab Work	■	■	■	■	■	■	■							
2	Progress Report Submission								■						
3	Data Analysis									■	■				
4	Pre EDX											■			
6	Dissertation Submission												■		
7	Technical Paper Submission													■	
8	Oral Presentation														■
9	Project Dissertation Submission														■

Table 5; Activities done and expected activities to be done in future.

CHAPTER 4 RESULTS & DISCUSSIONS

4.1 RESULT

4.1.1 OPTIMUM CONCENTRATION FOR SURFACTANT

SAMPLE NO.	AOS WEIGHT PERCENTAGE (%)	IFT (mN/m)
1	0	9.2936
2	0.2	1.4553
3	0.4	0.7948
4	0.6	0.731
5	0.8	0.7479
6	1	0.6374

Table 6; IFT for different surfactant concentration.

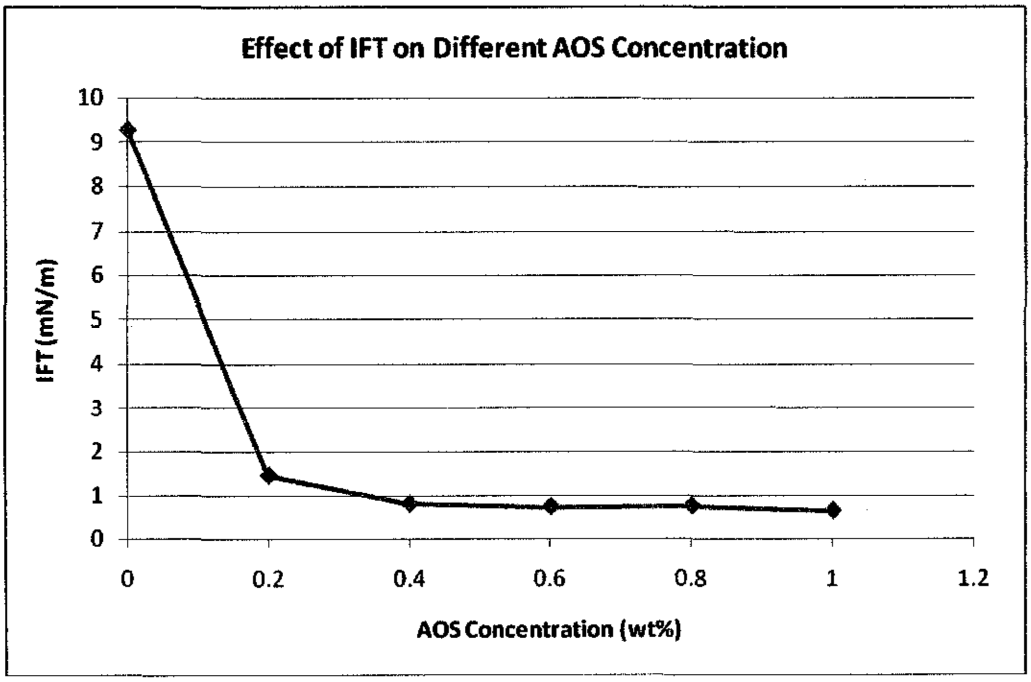

Figure 3; Graph effect of different AOS concentration on IFT. (1 mN/m = 1 dynes/cm)

4.1.2 OPTIMUM CONCENTRATION FOR ALKALI

SAMPLE NO.	NA2CO3 WEIGHT PERCENTAGE (%)	IFT (mN/m)
1	0	9.2936
7	0.2	5.8576
8	0.4	5.8394
9	0.6	4.1552
10	0.8	3.919
11	1	3.3366

Table 7; IFT for different alkali concentration.

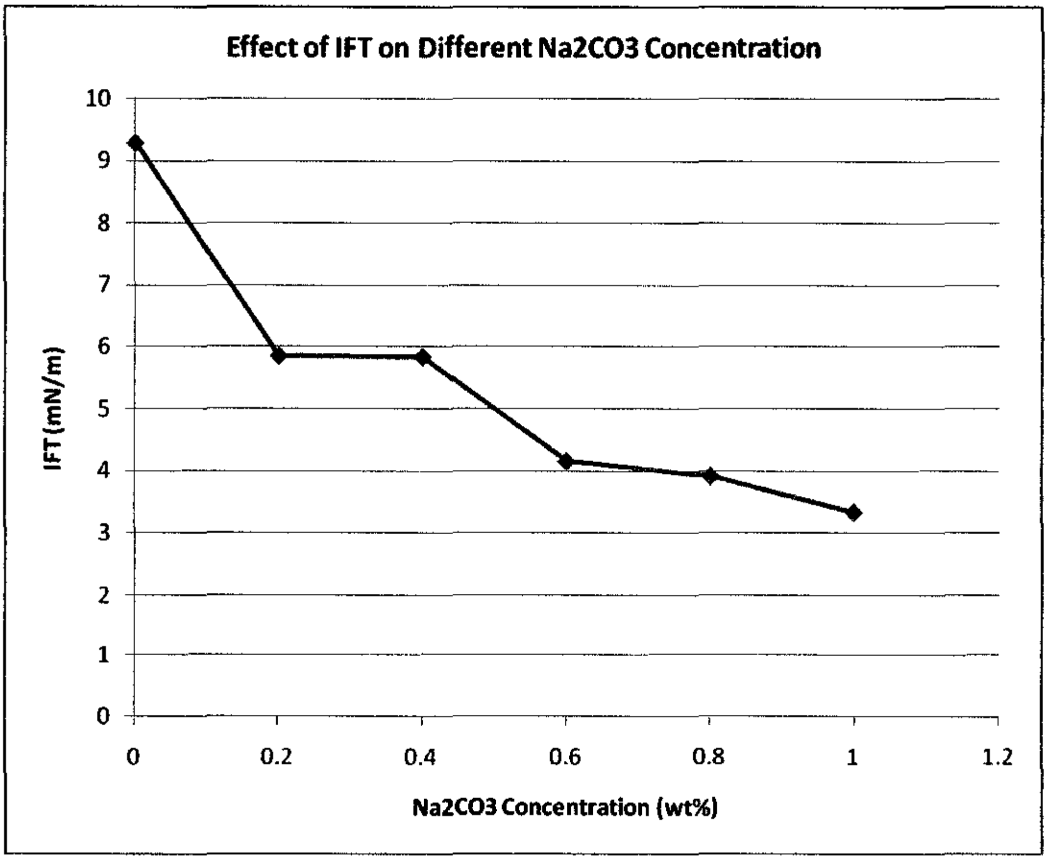

Figure 4; (1 mN/m = 1 dynes/cm)

4.1.3 IFT BEHAVIOR IN ALKALI-SURFACTANT-ACID SYSTEM

4.1.3.1 SET A

(0.6 wt% Alkali – 0.6 wt% Surfactant – Acrylic Acid)

SAMPLE NO.	ACRYLIC ACID WEIGHT PERCENTAGE (%)	IFT (mN/m)
12	0	1.7197
13	0.2	0.0849
14	0.4	0.0422
15	0.6	0.3402
16	0.8	0.5932
17	1	1.4956

Table 8; Effect of different acid concentration in 0.6 wt% alkali and 0.6 wt% surfactant.

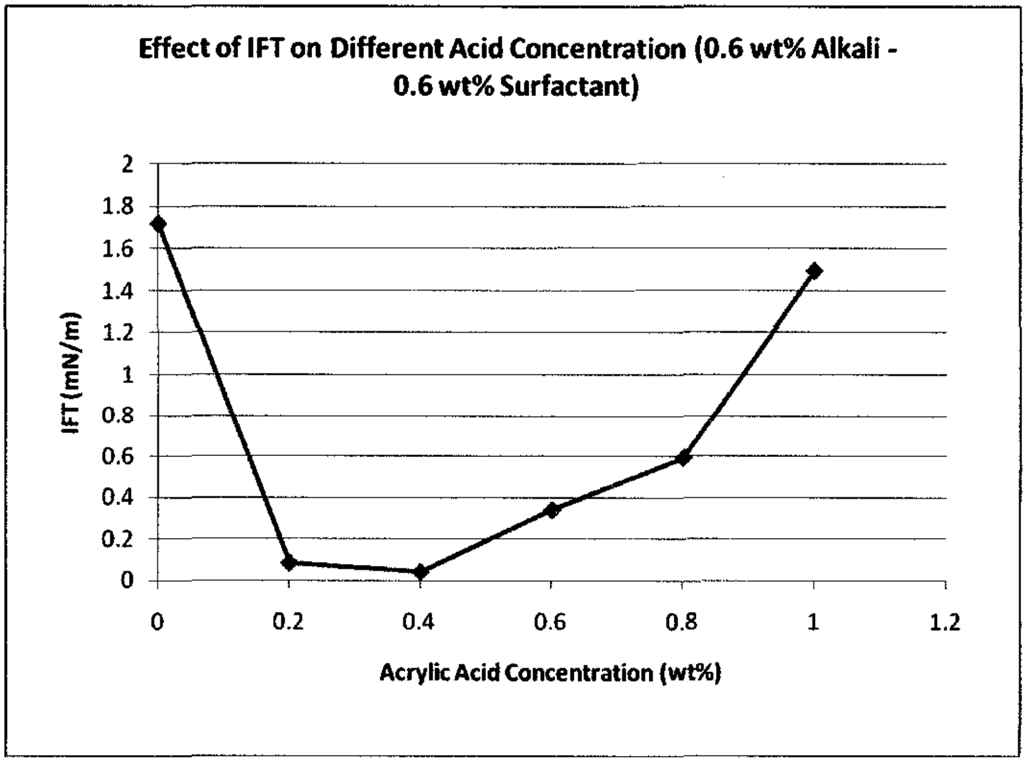

Figure 5; Graph effect of different acid concentration in 0.6 wt% alkali and 0.6 wt% surfactant.(1 mN/m = 1 dynes/cm)

4.1.3.2 SET B

(1.0 wt% Alkali – 0.6 wt% Surfactant – Acrylic Acid)

SAMPLE NO.	ACRYLIC ACID WEIGHT PERCENTAGE (%)	IFT (mN/m)
18	0	0.1654
19	0.2	0.24435
20	0.4	0.1026
21	0.6	0.2479
22	0.8	0.4014
23	1	0.1634

Table 9; Effect of different acid concentration in 1.0 wt% alkali and 0.6 wt% surfactant.

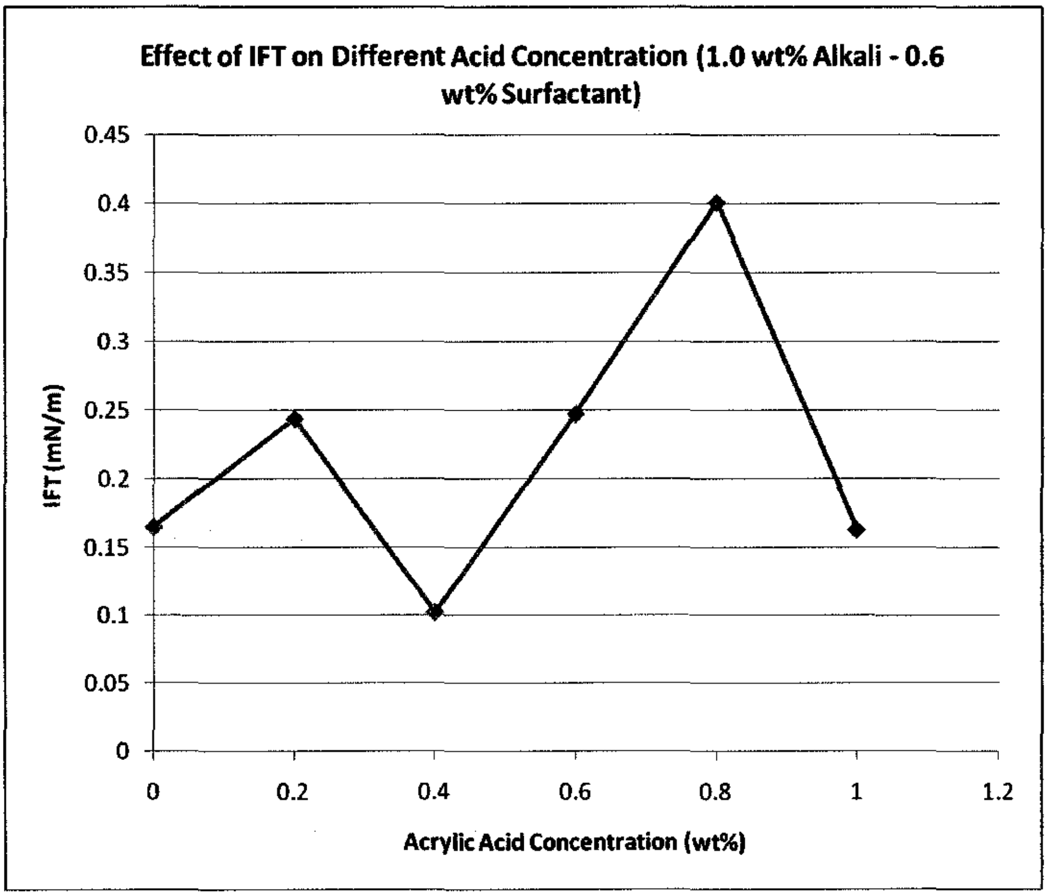

Figure 6; Graph effect of different acid concentration in 1.0 wt% alkali and 0.6 wt% surfactant.(1 mN/m = 1 dynes/cm)

8.2 OBSERVATIONS

	Observation
OPTIMUM CONCENTRATION FOR SURFACTANT	
During solution preparations	▪ The solutions are cloudy at all concentration. ▪ White foam, identified as soap scum formed when the solutions are mixed, the quantity is increase as the concentration increase.
During IFT measurement	▪ Easy to form oil droplet in the tube for IFT measurement.
OPTIMUM CONCENTRATION FOR ALKALI	
During solution preparations	▪ The solutions are cloudy at all concentration.
During IFT measurement	▪ Easy to form oil droplet in the tube for IFT measurement.
IFT BEHAVIOR IN ALKALI-SURFACTANT-ACID SYSTEM (SET A)	
During solution preparations	▪ The solutions are cloudy at all concentration. The intensity of the cloudiness decrease with increasing acid. ▪ White foam, identified as soap scum formed when the solutions are mixed, the quantity is almost the same at all concentration.
During IFT measurement	▪ Hard to form oil droplet in the tube for IFT measurement.
IFT BEHAVIOR IN ALKALI-SURFACTANT-ACID SYSTEM (SET B)	
During solution preparations	▪ The solutions are cloudy at all concentration. The intensity of the cloudiness decrease with increasing acid. ▪ White foam, identified as soap scum formed when the solutions are mixed. At 0.6 wt% and 0.8 wt% acid concentration, more soap scum accumulated compared to the others.
During IFT measurement	▪ Hard to form oil droplet in the tube for IFT measurement.

Table 10; The physical observation observed while experiments were performed.

Figure 7; The solutions for varying concentration of surfactant in 35 000 ppm brine, increasing from left to right (0 wt% - 1.0 wt%).

Figure 8; The solutions for varying concentration of alkali in 35 000 ppm brine, increasing from left to right (0 wt% - 1.0 wt%).

Figure 9; The solutions for varying concentration of acid in 35 000 ppm brine, 0.6 wt% of alkali and 0.6 wt% of surfactant, increasing from left to right (0.2 wt% - 1.0 wt%).

Figure 10; The solutions for varying concentration of acid in 35 000 ppm brine, 1.0 wt% of alkali and 0.6 wt% of surfactant, increasing from left to right (0.2 wt% - 1.0 wt%).

Figure 11; On the left, 0.6 wt% of alkali and 0.6 wt% of surfactant. On the right, 1.0 wt% of alkali and 0.6 wt% of surfactant. Both contain 0.0 wt% acid, 35 000 ppm of brine is used.

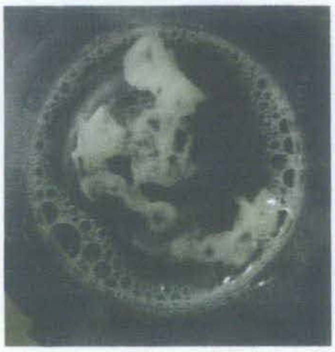

Figure 12; Soap scum accumulated in the solutions resulted from the reaction between surfactant and divalent metal cations.

8.3 DISCUSSIONS

In general, through the observation made, the soap scum accumulated due to the surfactant reaction towards the excess cations. The cloudy solutions are also due to brine hardness. As the easiness to form the oil droplets in the tube during IFT measurement are the early indication for IFT. Oil droplet is easier to form in high IFT environment compare to lower IFT.

8.3.1 OPTIMUM CONCENTRATION FOR SURFACTANT

This experiment is done as to identify the optimum concentration of surfactant to be used in the chemical injection. The optimum concentration will theoretically give the lowest IFT value between oil and water. From the experimental data done, the lowest point is at 1 wt% and the highest point is at 0 wt%, yielded IFT value of 0.6374 dyne/cm and 9.2936 dyne/cm respectively.

Theatrically, we are supposed to choose 1 wt% of surfactant as the optimum concentration for surfactant. However, when the result is observed closely, the behavior of IFT with different surfactant concentration is not directly proportion. At weight percentage of 0% to 0.6%, the trend is declining, from 9.2936 dyne/cm to 0.7310 dyne/cm. It increases at 0.8 wt% to 0.7479 dyne/cm before decreases at 1wt% to a value of 0.6374 dyne/cm.

This shows that IFT starts to stabilize after the surfactant reaches 0.4 wt%. As to decide the optimum concentration for surfactant, the IFT value taken at weight percentage higher than 0.6% can be ignored, as there are no significant changes in IFT readings. Thus, the lowest point valid for interpretation is at 0.6 wt%, making this value is as the optimum concentration for surfactant.

4.3.2 OPTIMUM CONCENTRATION FOR ALKALI

The objective of this experiment is to identify the optimum concentration for alkali. The theory behind to choose the best concentration is just the same as optimum concentration for surfactant; the concentration at which yields the lowest IFT value. For alkali, the highest value is 9.2936 dyne/cm at 0 wt% and the lowest is 3.3366 dyne/cm at 1 wt%.

The IFT behavior does not shows any anomalies; IFT value keeps on decreasing with increasing of weight percentage. At 0.2 wt% - 0.4 wt%, the IFT barely changes as the alkali is suspected to react with the cations in the solution, preventing the accumulation of in-situ surfactant. As the alkali concentration increase to 0.6 wt%, IFT decreases significantly, from 5.8394 dyne/cm to 4.1552 dyne/cm. At this concentration, active cations have reacted with alkali to the ideal concentration at which the excess alkali is allowed to react with the acidic component in the oil to accumulate surfactant. The exact point where this reaction occurred lies between 0.4 wt% and 0.6 wt%.

As to choose the optimum concentration for alkali, the objective is changed. Instead of looking for the lowest IFT, the objective now is to identify the concentration at which all cations have reacted with alkali. This is due to the fact that we are dealing with hard brine, in which alkali can only be functioning well when the excess cations are absence. Thus, 0.6 wt% is chose as the optimum point.

4.3.3 IFT BEHAVIOR IN ALKALI-SURFACTANT-ACID SYSTEM

As the optimum concentration for surfactant and alkali has been determined (0.6 wt% for both chemicals) the final steps is to analyze the resulting IFT from the combination of these 3 chemicals, acid, alkali and surfactant. There are 2 sets of solution prepared, both has specific objectives.

4.3.3.1 SET A

Set A is prepared at 0.6 wt% of alkali and 0.6 wt% of surfactant with varying concentration of acid. This set is to observe the optimum concentration for acid with the present of alkali and surfactant.

It is observed that increasing acid concentration cause the IFT to decrease only until 0.4 wt% acid. Higher concentration of acid causes the IFT to increase instead of decreasing. It seems that up only at this concentration, the chemicals work ideally according to the theory stated before.

At concentration higher than 0.4 wt%, the acid reacts with alkali to produce more precipitation inhibitor. The precipitation inhibitor will attract the active site of cations, eventually decreasing the free divalent metal cation in the water. Due to the increase of substances in the solution, the IFT is observed to increase instead of decreasing. Other than precipitation inhibitor, the excess acid concentration also causes IFT to increase.

Thus, 0.4 wt% is identified as the optimum concentration for acid at 0.6 wt% of alkali and 0.6 wt% of surfactant.

4.3.3.2 SET B

This set is to confirm back the experimental data done on set A. It is to observe the behavior of IFT when the concentration used is in excess. As alkali is paired with acid to produce precipitation inhibitor, only alkali concentration is kept higher that the optimum concentration identified before. For this set, the concentration used is 1 wt% of alkali and 0.6% of surfactant with varying acid concentration.

As the concentration exceeds the CMC, the effect on IFT is not uniform. It increases and decreases without any specific trend. This confirms the theory that the solution work best at optimum condition but would not give any satisfying result if higher concentration is used.

CHAPTER 5 CONCLUSION

All objectives aimed at the beginning of the project are achieved;

1. To investigate the effect of precipitation inhibitor on IFT performance.
2. To identify the optimum alkali, surfactant and sodium salt concentration.

As been identified before, the optimum alkali is at 0.6 wt%, and 0.6 wt% for surfactant. At weight percentage lower than this concentration, the IFT follows a trending; increase trending or decrease trending. However as the concentration increases, the IFT behave randomly. The optimum acid concentration is identified at 0.4% acid in 0.6 wt% of alkali and 0.6 wt% of surfactant.

In future, the chemicals combination should be tested further. As IFT is very much dependant on the types of substances used, different types of surfactant, alkali, acid and different combination of each could result to different behavior. The objective to find chemicals combination at lower cost should be at higher interest as the theory is proven to succeed.

CHAPTER 6 REFERENCES

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Appendix A

SALT MASS CALCULATION FOR BRINE PREPARATION

The brine is prepared based on the Na^+, Mg^{2+} and Ca^{2+} ions. Since the salt is in formed of chloride and chloride hydrate, molecular weight fraction is needed to calculate the amount of salt needed to prepare such brine. In this example, calculation for brine with hardness salinity of 5000 ppm will be shown:

Molecular Weight for $NaCl$ = 58.44 g/mol

Molecular Weight for $MgCl_2.H_2O$ = 203.31 g/mol

Molecular Weight for $CaCl_2.H_2O$ = 147.02 g/mol

Molecular Weight for Na = 22.98977 g/mol

Molecular Weight for Mg = 24.3050 g/mol

Molecular Weight for Ca = 40.078 g/mol

<u>Amount of ions weight needed for 5000 ppm brine:</u>

5000 ppm = 5 g (ions) / 1 L (distilled water)

Hardness of Mg^{2+} and Ca^{2+} are chosen at 500 and 400 ppm respectively.

500 ppm (Mg^{2+}) + 400 ppm (Ca^{2+}) +4100 ppm (Na^+) = 5000 ppm

Also equivalent to

[0.5g (Mg^{2+}) + 0.4g (Ca^{2+}) + 4.1g (Na^+)]/ 1 L = 5g (ions) / 1 L = 5000 ppm

To calculate $NaCl$ needed for above mass:

Mass Na = (MW Na / MW NaCl) * mass NaCl

Mass NaCl required = Mass Na * 1/(MW Na / MW NaCl)

= 4.1g * 1 / (22.98977/58.44)

= 10.422 g

To Calculate $MgCl_2.H_2O$ needed fo above mass:

Mass Mg = (MW Mg / MW $MgCl_2.H_2O$) * mass $MgCl_2.H_2O$

Mass $MgCl_2.H_2O$ required = Mass Mg * 1/(MW Mg / MW $MgCl_2.H_2O$)

= 0.5g * 1/ (24.3050/203.31)

= 4.18 g

To Calculate $CaCl_2.H_2O$ needed fo above mass:

Mass Ca = (MW Ca / MW $CaCl_2.H_2O$) * mass $CaCl_2.H_2O$

Mass $CaCl_2.H_2O$ required = Mass Ca * 1/(MW Ca / MW $CaCl_2.H_2O$)

= 0.4 g * 1/ (40.078/147.02)

= 1.467 g

-End of calculation-

Appendix B

WEIGHT CALCULATION FOR SURFACTANT/ALKALI/ACID CONCENTRATION

All solutions made are in 25 ml. The brine used is 35 000 ppm brine, assumed to have density at value of 25 g/ml.

At 0.2 wt%, mass needed is calculated as follows;

0.2/100 * 25 = 0.05g

For other value of weight percentage, replace the value respectively to calculate the weight needed.

-End of calculation-