Experimental Investigation Of Acid-Alkaline-Surfactant Optimization Using High Salinity Injection Water For Chemical EOR

by

SHAHRUL AZWAN BIN ZULKIFLI

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Shahrul Azwan B. Zulkifli

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Approved by,

Dr Khaled Abdalla Elraies
Lecturer
Geoscience & Petroleum Engineering Department
Universiti Teknologi PETRONAS
Bandar Seri Iskandar, 31750 Tronoh ,
Perak Darul Ridzuan, MALAYSIA

....

(Dr. Khaled Abdalla Elraies)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2011

CERTIFICATION OF ORIGINALITY

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

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SHAHRUL AZWAN BIN ZULKIFLI

ABSTRACT

In Chemical EOR, ASP flooding is proven to be cost-effective in recovering the remaining oil. However, ASP flooding is not compatible to be used in hard brine due to the reaction of alkali/surfactant with the divalent metal cations to produce insoluble precipitation. So, the aim of the research is to produce a new formulation that can be used together with hard brine without the occurrence of precipitations. A feasibility test was conducted to observe the compatibility of the new formulation with the hard brine. The acid was evaluated in this new formulation using alkalis (sodium carbonate and sodium hydroxide) and surfactant (Alpha Olefin Sulfonate). The precipitation is the key indicator to determine the compatibility of these chemicals in the hard brine that contain large quantity of metals cations. The aspects that need to be studied are including Acid – Alkali interaction in hard brine, Acid – Surfactant interaction in hard brine and Acid – Alkali – Surfactant interaction in hard brine. At the end in the experiment, it was found out that the acid to alkali ratio of 1.33:1 is the most optimum ratio as no precipitation was produced. So, this makes the new Acid – Alkali – Surfactant formulation an option for the CEOR process, particularly in the offshore operation.

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ABBREVIATIONS AND NOMENCLATURES

ASP	Alkali – Surfactant – Polymer
bpd	Barrel Per Day
CEOR	Chemical Enhanced Oil Recovery
EOR	Enhanced Oil Recovery
FYP	Final Year Project
GOR	Gas Oil Ratio
IFT	Interfacial Tension
mb/d	Million Barrel Per Day
OOIP	Oil Originally In Place
PI	Precipitation Inhibitor
ppm	Part Per Million

CHAPTER 1

INTRODUCTION

1.1 Background

Up to date, hydrocarbon still remains as the main source of energy. The demand for `hydrocarbon is increasing by an average of 2.2% (or 1.9 million bpd) per year and by 2012, it will reach 95.8 mb/d [1]. This uprising demand are drove by the developing nations whose require more energy as their economies are rapidly expand [2]. For the next five-, ten- or twenty-year frame, the supply for oil and gas will become a driving concern as we work to meet the demand [2].

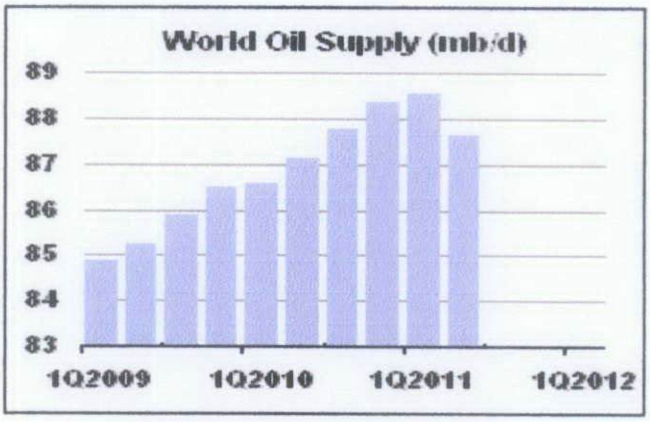


Figure 1: World Oil Supply [3]

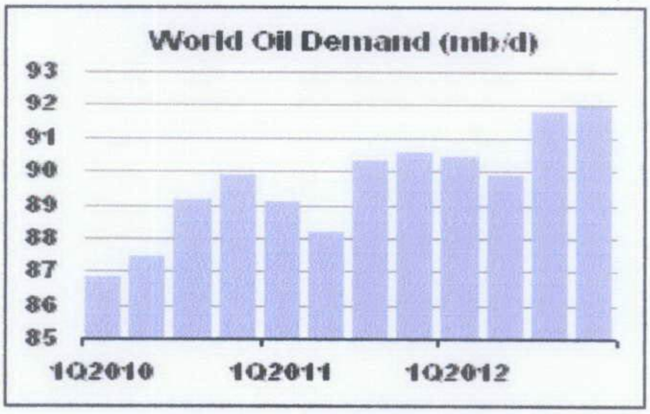


Figure 2: World Supply Demand [3]

With the recent studies, the demand of oil is growing faster than the supply [4]. Even though the supply is expanding with the discoveries of new sources, but the growth in demand outpace the supply [4]. Also, in several oil producing countries, they already past their maximum oil production [5]. Without sufficient exploration and development of new fields, any mean that can maintain the current oil production is greatly encouraged.

In any oil fields, the oil productions will initially being produced by the primary recovery [6]. In the primary recovery, the natural reservoir pressure displaced the oil and gas to production wells by (a) fluid expansion, (b) fluid displacement, (c) gravitational drainage, and/or (d) capillary expulsion [6]. Without a strong aquifer to support the pressure decline, the primary recovery will no longer able to displace oil to the production wells. So, the oil production will enter the second stage by using secondary recovery. In secondary recovery, a natural gas or a water injection method is used either to maintain the reservoir pressure or to displace oil to the production wells [6]. Later, when the secondary recovery processes have been ineffective, the tertiary recovery process will be implemented. The tertiary recovery process is commonly known as Enhance Oil Recovery (EOR).

In Malaysian fields, even with a good reservoir management, primary and secondary recovery only can recover up to 36.2% [7]. The remaining 63.2% of hydrocarbon will be the primary target for EOR techniques. Various techniques have been developed for EOR, namely miscible/immiscible displacement, chemical flooding (CEOR) and thermal recovery.

CEOR is a technique where various chemical combinations are injected into the reservoir to mobilize the residual oil after primary and secondary recovery process. CEOR processes are including surfactant (S) flooding, surfactant-polymer (SP) flooding, alkaline-surfactant (AS) flooding and alkaline-surfactant-polymer (ASP) flooding [8]. ASP flooding is considered as most promising and cost-effective chemical flooding process for light and medium oils [9].

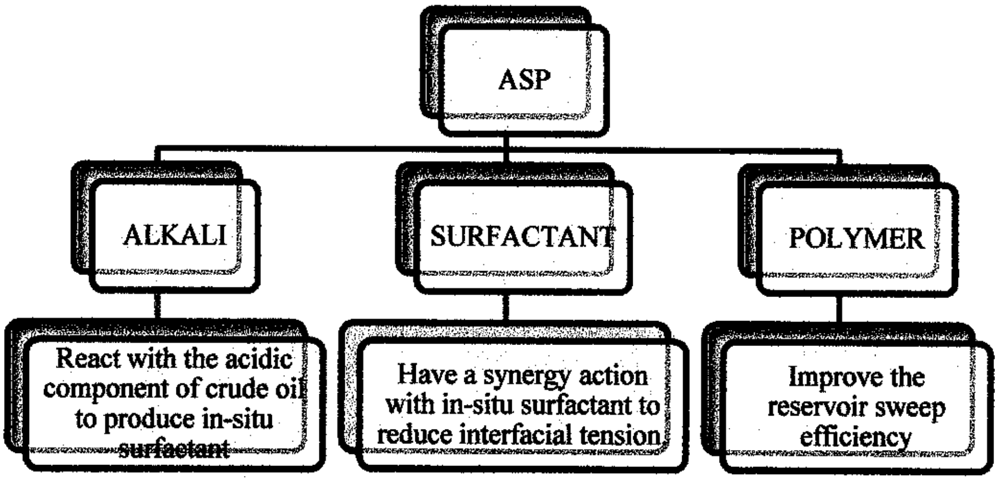


Table 1: ASP Components [8-11, 13-15]

ASP flooding can greatly enhanced oil recovery by increasing the capillary number, decreasing interfacial tension (IFT), and improving the mobility ratio [9]. Even with these advantages, the ASP flooding is not without disadvantages [10]. To have a better EOR performance, any problems associated with the ASP flooding must be eliminated and for this reason, this Final Year Project (FYP) research is proposed, such a process.

1.2 Problem Statement

One of the main problems associated with chemical flooding is precipitation problems [10]. ASP flooding requires softened water to prepare the chemical slug [11]. However, the sources for soft/fresh water are limited and for the offshore operation, the water treatment facilities must be installed to treat the seawater before it can be used to make the chemical slug. The installment will consume a large capital amount and space on the platform.

The source of seawater is abundant for the offshore operations. By using the seawater, there is no need for the installment of the treatment facilities and save the operation cost for chemical flooding. The main reason is that the use of sea water will lead to the second problem, precipitation problems.

The sea water and reservoir brine contain high concentration of divalent metal cations such as Ca^{2+} and Mg^{2+}. So, alkali and surfactant in ASP flooding will react with these divalent metal cations to form precipitation. The chemical slug will not proceed effectively due to the extensive consumption of the chemicals. Therefore, softened water must be used to reduce the precipitation problems.

The problem can be eliminated by using a precipitation inhibitor (PI). This Final Year Project (FYP) will involve some researches to analyze to what degree the PI can reduce the precipitation problem and improve the recovery.

1.3 Objectives

This research is conducted to fulfill these objectives:

1. To reduce or eliminate the precipitation problems using precipitation inhibitor (PI).
2. To reduce the cost of the chemical EOR processes using seawater or reservoir water rather than softened water.
3. To conduct comprehensive fluid-fluid compatibility tests to select the optimum inhibitor concentrations.

1.4 Scope of Studies

The main focus on this research is to study fluid-fluid compatibility using high salinity injection water with the use of PI. The details studies are:

1. Acid – Alkali Interaction
    - To get the optimum acid to alkali ratio in brine
    -
2. Acid – Surfactant Interaction
    - To get the optimum acid to surfactant ratio.
    -
3. Acid – Alkali – Surfactant
    - To get the optimum acid to alkali ratio in the brine with the presence of surfactant.

CHAPTER 2

LITERATURE REVIEW

The demand for fossil fuels, especially oil will never stop increase. And with more oil fields already at the end of their primary and/or secondary recovery, some new techniques must be developed so that the remaining oil trap in the reservoir can be recovered. This technique, so-called Enhance Oil Recover (EOR) is proven to be able to extract the remaining oil left after primary and/or secondary recovery. EOR consists of several techniques, i.e. miscible/immiscible displacement, chemical flooding, thermal recovery and others.

2.1 Enhanced Oil Recovery in Malaysia: Possibility

In the oil recovery process, the first recovery method is known as primary recovery. It can be defined as the first stage of hydrocarbon production, in which the oil is displaced by natural reservoir energy from the reservoir to the production well. After producing for some times, the natural pressure is no longer sufficient enough to displace more oil. So, the secondary recovery will be implemented. By definition, secondary recovery is the second stage of hydrocarbon production during which an external fluid such as water or gas is injected into the reservoir. The objective of secondary recovery is either to maintain the reservoir pressure or to displace the oil to the production well.

Gradually, the secondary recovery with/without primary recovery will no longer be able to displace more oil. Even after primary and secondary recovery is implemented, a considerable amount of hydrocarbon resource is estimated to remain the ground [7]. With most of the fields are already entering maturing stage for primary and/or secondary depletion with declining oil rates and increasing water-cut and GOR trend, there is a need to implement the EOR processes [7]. This is clearly a proof state that the importance on Enhance Oil Recovery (EOR) technique to produce any remaining oil after the maturity of primary and secondary recovery.

The Enhance Oil Recovery (EOR) can be defined as an oil recovery enhancement method using means other than using the natural reservoir pressure that alter the original properties of oil.

The three major types of enhanced oil recovery methods are as follows:

1. Chemical Flooding
2. Miscible/immiscible displacement
3. Thermal Recovery.

Before implementing any EOR technique, field study should be conducted and the field's criteria will be screened to find the most suitable technique for a particular field. For Malaysia's fields, the screening studies have been conducted in 2000 involve 72 reservoirs [7] and from the studies, two (2) EOR techniques have been identified as the most suitable for Malaysia: gas injection and chemical injection [12].

For the gas injection, a good option to be used is CO_2 gas since Malaysia has abundance in many of its field [12]. But, the main problem here is that sources of CO_2 are quite far from the fields where gas injection EOR could be applied [12]. So, the second option is to use chemical flooding (CEOR). CEOR will enhance oil recovery by increasing the capillary number, decreasing interfacial tension (IFT) and improving the mobility ratio. One of the most proven techniques for CEOR is Alkali-Surfactant-Polymer (ASP) flooding.

Each technique has its own requirement and the chosen technique to be implemented is depending on the reservoir condition and crude oil properties. In this study, only Chemical Flooding will be discussed.

2.2 Chemical Flooding (CEOR) – ASP Flooding

Chemical Flooding (Chemical EOR) can be defined as a general term that uses special chemical solutions to reduce the capillary number to mobilize the remaining oil. Chemical EOR can be either surfactant, surfactant-polymer process, alkaline – surfactant, and alkaline-surfactant-polymer (ASP) process. From the laboratory experiments and field projects, it has been proven that the ASP flooding is effective in reducing the oil residual saturation through reduction of interfacial tension and mobility ratio between oil and water phases [13].

An ASP flood involves injecting predetermined pore volume of ASP into the reservoir. Often the ASP injection is followed by an additional injection of polymer. Upon completion of injection, a regular waterflooding behind ASP wall resumes again [12]. ASP flooding consists of alkali, surfactant and polymer that work synergistically to perform a good EOR. Together they are more effective than as components alone [12].

Each component in ASP flooding has its own function. Surfactant is added to reduce the capillary pressure by lowering the interfacial tension between water and oil [14]. This allows the residual oil to be mobilized and produced from the formation. The use of alkali gives many benefits to ASP flooding. The alkali reacts with acidic components in oil to form in-situ surfactants [14]. The use of polymer will increase water viscosity, thus increase the vertical and areal sweep efficiencies of the flood. The increased viscosity decreases the chance of fingering and allows more oil to be contacted on a macroscopic scale [14].

Even with varieties of advantages offered by ASP flooding, it is not without the problems. ASP flooding is commonly associated with the precipitation problems [9-11, 15].

There are some limitations to the application of ASP, especially the requirement of soft water to make the ASP slug. Surfactant and alkali used for the ASP process are not compatible in the hard brine or seawater. They react with the metals cations and form precipitation. Berger et al. [15] state that the implementing of ASP process must follow the general rule of thumb. For any ASP process, the divalent metal cations concentration needs to be less than 10 ppm in order to avoid the reaction of the alkali with divalent cations to form insoluble scales by the following reaction;

$$Na_2CO_3 + Ca^{+2} \longrightarrow 2Na^{+1} + CaCo_3$$

$$Na_2CO_3 + Mg^{+2} \longrightarrow 2Na^{+1} + MgCo_3$$

Thus, these precipitations will plug the wellbore and decrease the efficiency of the ASP. On the other hand, soft water is not always available, and softening hard brines may be very costly and not practical. So, a process that eliminates this problem is required so that the ASP flooding will have a better performance.

2.3 Improvising ASP – Organic Alkali

Researchers already conducted experiments to improve the performance of ASP flooding by eliminating problems associated with ASP flooding.

In their experiments, Berger et al. [15] used the organic alkali as the replacement for the inorganic alkali used in ASP flooding. As mention earlier, the ASP flooding will face the precipitation problem due to the reaction between the divalent metal cations and alkali [9-11, 15]. So, a new organic alkali was evaluated in ASP formulation containing commonly used surfactants and polymers [15]. To test the compatibility of the organic alkali, the effect of organic alkali on IFT, adsorption and viscosity was compared to that of a conventional inorganic alkali in the ASP formulations.

It is often desirable to use the produced fluid as the injection fluid in order to make the project economical [15]. Unfortunately, the metal divalent cations that exist in produced fluid and seawater source can react with the alkali to form precipitation, thus reduce the effectiveness of ASP flooding. To prevent the reaction, an organic alkali type is formulated into the ASP system to replace the inorganic alkali, such as sodium carbonate or sodium hydroxide. The most important parameter used to study the effectiveness of organic alkali is no precipitation occurrence when organic alkali is mixed together with the unsoftened brine [7]. Using organic alkali makes the injection process simpler since there is no need for a water treatment process for the injection water.

The organic alkali also must be able to provide the same advantages offered by the inorganic alkali. These are include raise the pH of injection brine, reduce the IFT, compatible with other components of ASP and also reduce the adsorption. From their experiments, Berger et al. [15] confirmed that organic alkali able to raise the pH of injection brine just as inorganic alkali. The IFT observed have no significant difference when the inorganic alkali is substituted by the organic alkali [15]. And the adsorption rate of surfactant using organic alkali is the same as that obtained using inorganic sodium carbonate alkali [15].

As the conclusion, the organic acid can be used in ASP formulations to replace the inorganic alkali so that no or less precipitation problem will occur. The organic alkali also can be used to provide alkalinity and reduce adsorption compare to similar formulations using conventional inorganic alkalis [15].

2.4 Improvising ASP – Novel Alkali

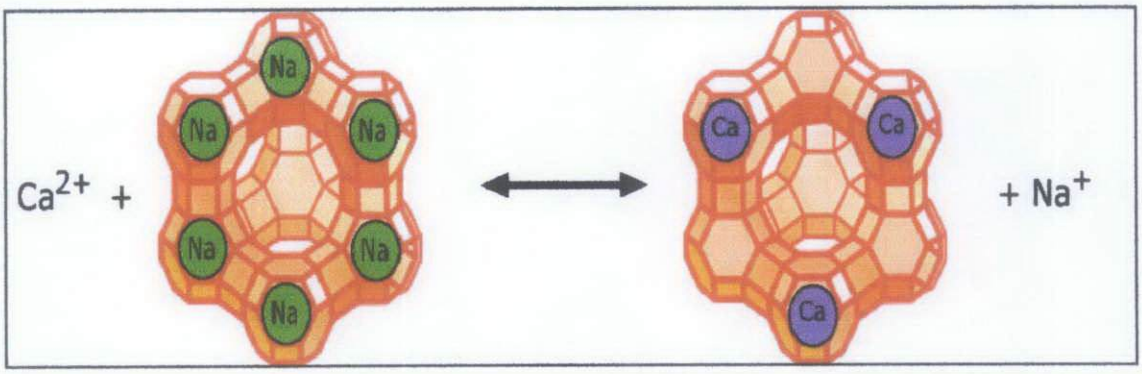
ASP flooding using conventional alkali requires soft water [9]. However, the source of fresh water is limited and softened water will require much cost. Without softened water, the conventional alkali will react with the divalent metal cations in the hard brine and seawater to form precipitation. A form of borax known as metaborate has been identified having the ability to provide tolerance to high divalent metals cations concentration and prevent precipitation [9]. In some cases like in enhanced imbibitions experiments in silica and carbonate rocks, the use of sodium metaborate can outperform sodium carbonate [9].

The experiments are conducted using hard salinity brine based on actual reservoir formation brine composition. This is to observe to compatibility of the sodium metaborate with divalent metal cations. From the test, the sodium metaborate is proved able to provide the benefits of alkali in hard brine and was shown to tolerate to Ca^{2+} and Mg^{2+} up to 6600 ppm divalent cations, thus prevent precipitation [9]. The use of sodium metaborate in the ASP formulation will allow the ASP flooding to have a good oil recovery even when be used in hard brine.

2.5 Improvising ASP – Water Softening

One of the major problems associated with the ASP flooding is precipitation [9], [10], [11], [15]. When alkali reacts with the Ca^{2+} and Mg^{2+} in the hard brine, it will form insoluble scale and finally precipitate. This will reduce the efficiency of ASP flooding. To prevent any reaction between alkali and the divalent cations, the general rule of thumb state that the divalent metal cations concentration should be less than 10ppm [15].

So, to prevent the precipitation, softened water must be used to mix the chemical slug. Water softening is a process that reduces calcium and magnesium ions concentration in hard water [14], [15]. This can be done through the process known as ion-exchange. In this process, the Ca^{2+} and Mg^{2+} ions trade place with the sodium ions [14-20].



This occurs in three steps:

1. Hard water runs through a resin bed of small plastic beads or zeolite. The beads are covered with sodium ions. As hard water flows past the ions, the hardness ions swap places with the sodium ions. Eventually, the beads contain only calcium and magnesium and softening stops. It is then time to regenerate the beads.
2. To regenerate, the bead is being flooded with brine solution that rich in sodium ions. This is to help the bead to regain its original sodium concentration.
3. Once completed, the same process is repeated and in the end, the calcium and magnesium are flush from the beads.

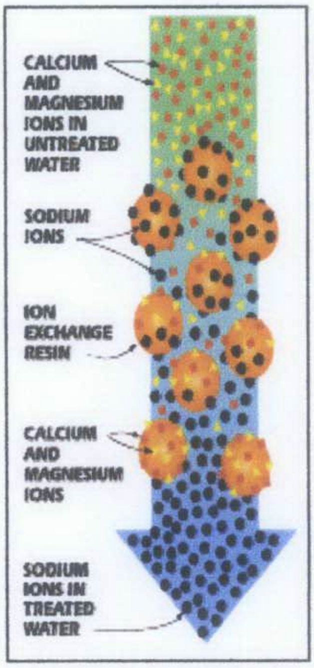


Figure 4: Ion Exchange Process [20]

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

Research	Plan	Experiment	Discussion
• ASP Flooding – benefit and weakness • New formulation – improvement of ASP • Introduction of acid into the ASP	• Design experiment procedure and condition • Determine materials, tools and equipment for experiment	• Preparation of the chemicals • Conduct the fluid-fluid compatibility tests	• Record data and present graphical form • Discussion base on result and conclusion

Table 2: Research Methodology

3.2 Project Activities

The research was conducted in three (3) main parts. First part is the brine preparation. The brine was used in all the tests to study the compatibility of the chemicals with the presence of divalent metal cations. The second part is to conduct the laboratory experiment to study the compatibility of fluid-fluid interaction using different acid to alkali ratio. All the tests were conducted to study the effect of the sodium salt precipitation inhibitor (PI) in eliminating or reducing the precipitation problems. The third part of the research is to analyze all the data gathered.

3.2.1 Brine Preparation

Brine Preparation (for 1 Liter)

1. To prepare 35000ppm of brine, pour 1000 ml of distilled water in a beaker.
2. Place 86.6802 grams of sodium chloride, 4.184 grams of magnesium chloride hydrate and 1.467 grams calcium chloride hydrate inside the beaker filled with 1000ml of distilled water.
3. Stirred the beaker slowly and gradually heat up the mixture to accelerate salts dissolves in the distilled water. Ensure during heating, the temperature does not exceed or reach boiling temperature to avoid evaporation.
4. After all salts have been dissolves, allow the brine to cool down.

3.2.2 Acid – Alkali Compatibility Test

Different acid to alkali weight ratios are used to investigate the performance of the precipitation inhibitor (PI) in preventing the Ca^{2+} and Mg^{2+} precipitations. In this test, the alkali concentration was maintained at 0.6% and the concentrations of acid were varied.

Procedure:

1. Five (5) test tubes are used in the test and each test tube is filled with 10ml brine.
2. For each test tube, use acid acrylic concentration of 0, 0.4, 0.6, 0.8 and 1.0% respectively. The alkali (sodium carbonate) concentration is maintained at 0.6%.
3. Conduct the test at 80°C
4. Record the data for daily basis, if possible.
5. Repeat Step 1 until Step 4 but replace the sodium carbonate with sodium hydroxide.
6. Analyze the data and observe for precipitation in any sample.

3.2.3 Acid – Surfactant Compatibility Test

Different acid to surfactant weight ratios were used to investigate the performance of the precipitation inhibitor (PI) in preventing the Ca^{2+} and Mg^{2+} precipitations. In this test, the surfactant concentration was maintained at 0.6% and the concentrations of acid were varied.

Procedure:

1. Five (5) test tubes are used in the test and each test tube is filled with 10ml brine.
2. For each test tube, use acid acrylic concentration of 0, 0.4, 0.6, 0.8 and 1.0% respectively. The surfactant (alpha olefin sulfonate) concentration is maintained at 0.6%.
3. Conduct the test at 80°C
4. Record the data for daily basis, if possible.
5. Analyze the data and observe for precipitation in any sample.

3.2.4 Acid – Alkali – Surfactant Compatibility Test

For this test, all of the chemicals were combined together to test their compatibility in the brine. The test was conducted to find the optimum concentration of alkali and acid to produce enough PI concentration to prevent any precipitation in the presence of surfactant.

Conduct the test:

1. Five (5) test tubes are used in the test and each test tube is filled with 10ml brine.
2. The first acid to alkali ratio to be tested is at 0.66:0.1.
3. For each test tube, use alkali concentration of 0.4, 0.6, 0.8, 1.0 and 1.2% respectively. The surfactant concentration is maintained at 0.6%.
4. Conduct the test at ambient temperature and also at 80°C.

5. Record the data for daily basis, if possible.
6. Repeat Step 1 until Step 5 but use acid to alkali ratio of 1:1 and 1.33:1, respectively.
7. Repeat Step 1 until 6 but use another type of alkali.
8. Analyze the data and observe for precipitation in any sample.

3.3 Supplementary Test

To confirm experiments that have been conducted earlier and also to have a better view on the fluid-fluid compatibility, a series of experiments have been conducted. These experiments have been conducted after the result for the earlier experiments were observed.

3.3.1 Acid – Alkali Compatibility Test

As discussed earlier, the metaborate has been found to be compatible to be used with the hard brine. So, an experiment has been conducted to study the compatibility of metaborate with acid in the hard brine. In this experiment, I mixed acid acrylic with sodium metaborate in the hard brine to observe the any interaction between these two chemicals.

Procedure:

1. Five (5) test tubes are used in the test and each test tube is filled with 10ml brine.
2. For each test tube, use acid acrylic concentration of 0, 0.4, 0.6, 0.8 and 1.0% respectively. The alkali (sodium metaborate) concentration is maintained at 0.6%.
3. Conduct the test at 80°C
4. Record the data for daily basis, if possible.
5. Analyze the data and observe for precipitation in any sample.

3.3.2 Acid – Alkali Compatibility Test

From the observation of earlier experiments, the mixture of acid acrylic with sodium hydroxide precipitated in any acid to alkali ratios. But, as the acid to alkali ratios is increased, the mixture is taking some times before it started to precipitate. So, this test is conducted to find the acid – alkali ratio that can prevent the precipitation. In other word, more acid concentration is used compare to alkali concentration to prevent the precipitation, if possible.

Procedure:

1. Three e) test tubes are used in the test and each test tube is filled with 10ml brine.
2. For each test tube, use acid acrylic concentration of 2.4, 3.0 and 3.6% respectively. The alkali (sodium metaborate) concentration is maintained at 0.6%.
3. Conduct the test at 80°C.
4. Record the data for daily basis, if possible.
5. Analyze the data and observe for precipitation in any sample.

3.3.3 Acid – Surfactant Compatibility Test

Similar with the earlier acid – surfactant compatibility test, this test use acid acrylic together with surfactant (Alpha Olefin Sulfonate) to study the interaction between these chemical. But, in this experiment, we will mix acid and surfactant in distilled water. In the earlier experiment, the combination of acid and surfactant with hard brine produced precipitation. It is because the presence of divalent metal cations in the hard brine. So, this supplementary test is conducted in the distilled water to prove that the precipitation occur only because the presence of metal cations, not because the nature of the surfactant itself.

Procedure:

1. Three (3) test tubes are used in the test and each test tube is filled with 10ml brine.
2. For each test tube, use acid acrylic concentration of 0, 0.6, and 1.0% respectively. The surfactant (alpha olefin sulfonate) concentration is maintained at 0.6%.
3. Conduct the test at 80°C.
4. Record the data for daily basis, if possible.
5. Analyze the data and observe for precipitation in any sample.

3.4 Gantt Chart

	Month								
Activities	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**
Research on Chemical EOR		▨							
Detail Studies on ASP Flooding		▨							
Design experiment procedure and condition			▨						
Determine material, tools and equipment for experiment			▨						
Conduct the Tests					▨	▨	▨		
Daily Observation of the Tests						▨	▨		
Record data and present in graphical form						▨	▨		
Evaluation and discussion based on result							▨	▨	
Research documentation				▨			▨	▨	

Table 3: Gantt Chart

3.5 Key Milestone

Key milestone	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**
Completion of paper research on Chemical EOR and ASP Flooding		▨							
Completion of experiment design and selection of tools			▨						
Completion of conducting the tests							▨		
Completion of data record and evaluation							▨		
Completion of project								▨	

Table 4: Key Milestone

3.6 Tools

Materials

1. Acid Acrylic
2. Sodium Carbonate
3. Sodium Hydroxide
4. Sodium Metaborate
5. Alpha Olefin Sulfonate (AOS)

Equipments

1. Test Tubes
2. Oven
3. pH Meter

CHAPTER 4

RESULTS AND DISCUSSION

A new chemical EOR formulation is developed to overcome the precipitation problem associated with Alkaline-Surfactant-Polymer (ASP) flooding. In this research, several compatibility tests had been conducted to observe the performance of acid, alkali and surfactant in brine. The interaction of acid-alkali-surfactant was monitored as the main objective of the research is to come out with the most optimum acid to alkali ratio. The key indicator for this research is the precipitation.

4.1 FLUID-FLUID COMPATIBILITY TEST

4.1.1 Acid-Alkali Interaction Test

The earlier researches have confirmed that the conventional alkali used in the ASP Flooding is not compatibility with water containing some amount of divalent metal cations [9 - 11, 15]. The reaction between alkali/surfactant and Ca^{2+}/Mg^{2+} will produce some insoluble salt that will precipitate and reduce the efficiency of the chemicals. So, it is important to remove the divalent metal cations from water before implementing any chemical EOR. In this study, the acid acrylic is used together with alkali and surfactant. Acid acrylic will react with Na^+ to form precipitation inhibitor (sodium acrylate) and prevent the reaction between alkali/surfactant with metal cations.

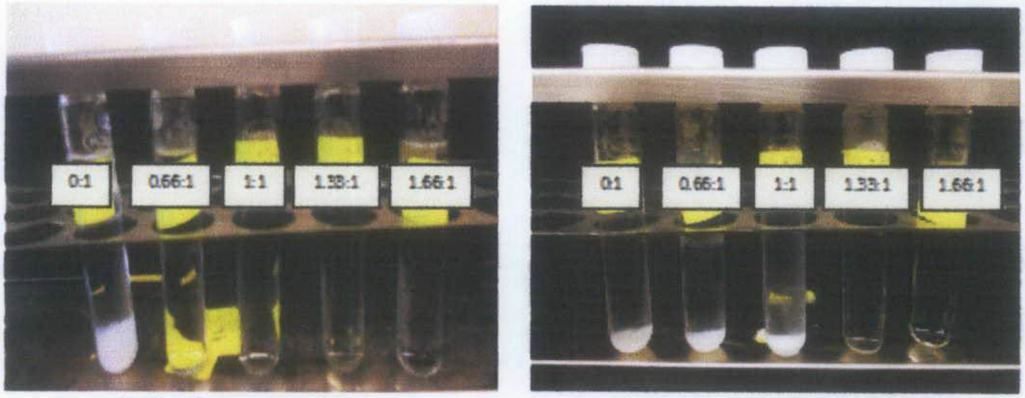
With enough precipitation inhibitor (PI), there should be no precipitation can be observed in any sample. So, in this first test, there were five (5) acid to alkali ratios to be tested to find the most optimum ratio. The concentration of alkali was maintained at 0.6%. The table below presented the result of the experiments. As the acid to alkali ratio was increased, the performance of PI was also increase as the precipitation will form later or no precipitation at all. With small acid to alkali ratio, the generated PI was not sufficient enough to prevent the precipitation. All the acid concentration was neutralized by the alkali. And as the acid to alkali ratio was increased, sufficient concentration of PI was generated and was able to prevent the precipitation.

Table 5: Summary of the acid to alkali compatibility test

Acid Acrylic + Alkali (Sodium Carbonate) **80 °C** **Alkali: Sodium Carbonate = 0.6%**					
Days	0% pH: 10.2	(0.66:1) pH: 7.19	(1:1) pH: 6.32	(1.33:1) pH: 5.89	(1.66:1) pH: 5.63
0	ppt	-	-	-	-
3	ppt	ppt	-	-	-
17	ppt	ppt	c	-	-
21	ppt	ppt	ppt	-	-
50	ppt	ppt	ppt	-	-
Acid Acrylic + Alkali (Sodium Hydroxide) **80 °C** **Alkali: Sodium Hydroxide = 0.6%**					
Days	0% pH: 12.47	(0.66:1) pH: 12.09	(1:1) pH: 11.63	(1.33:1) pH: 11.25	(1.66:1) pH: 10.52
0	ppt	c	c	-	-
1	ppt	ppt	ppt	ppt	ppt
29	ppt	ppt	ppt	ppt	ppt

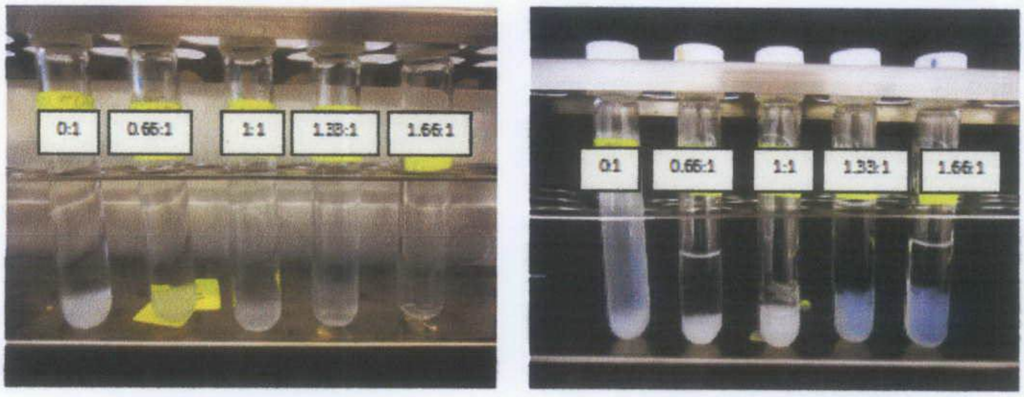
ppt denotes precipitation, - denotes clear solution, c denotes cloudy

For the sodium carbonate, the optimum ratio for PI to prevent the precipitation is 1.33:1 while for sodium hydroxide, there is no optimum ratio as all the ratios resulted in precipitation occurrence. As discuss earlier, higher ratios resulting in higher concentration of PI. So, for strong alkali like sodium hydroxide, higher ratio was required so that sufficient PI could be generated to prevent any precipitation. When the alkali was changed to sodium carbonate, lower ratio should be anticipated as sodium carbonate is a weaker alkali compare to sodium hydroxide. So, less concentration of PI was needed to sufficiently absorbed at active growth site of divalent metal cations and prevent any reaction that can produce precipitation. And as seen from the result, there was no precipitation observed when the acid to alkali ratio is 1.33:1. So, it could be concluded that the acid to alkali ratio of 1.33:1 is the optimum ratio that could prevent the precipitation when sodium carbonate is used.



Sodium Carbonate at 0 day

Sodium Carbonate after 50 days



Sodium Hydroxide at 0 day

Sodium Hydroxide after 50 days

Figure 5: Performance of precipitation inhibitor on preventing precipitation over time

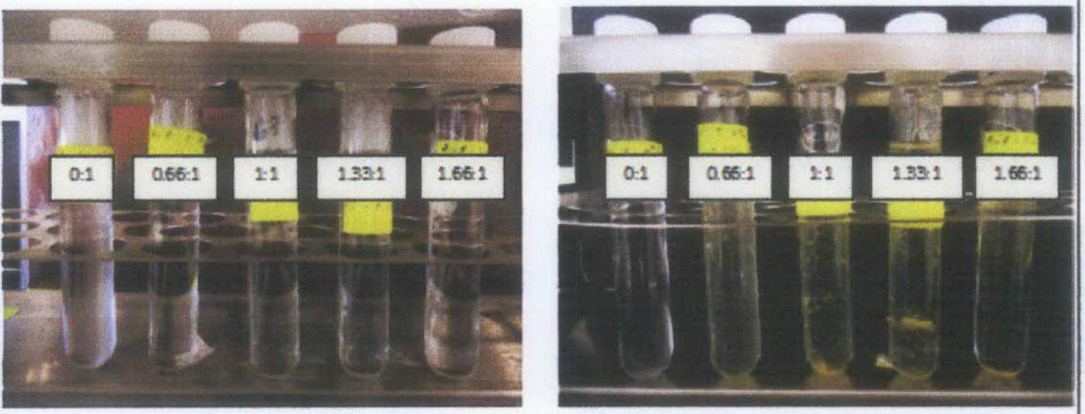
4.1.2 Acid – Surfactant Interaction Test

Similar to acid-alkali interaction test, this test was also conducted to find the optimum ratio that gave no precipitation. The compatibility test was conducted in the 35000 ppm of brine where different acid to surfactant ratios were tested. The concentration of surfactant was maintained at 0.6%. As shown in the result below, even without acid, the first sample remained clear up until the fifth day. There possible reason is that, the surfactant that is used in the tests, Alpha Olefin Sulfonate (AOS) is an anionic-type that has excellent hard water resistance [21]. So, it could resist the reaction with the metal cations. Also, the acid acrylic used in the test reacted with the Na^+ in the brine and form PI that help to prevent the precipitation.

Table 6: Acid-Surfactant Interaction Test

<table>
<tr><th colspan="6">Acid Acrylic + Surfactant (AOS)
80 °C
Surfactant: AOS = 0.6%</th></tr>
<tr><td>Days</td><td>0%
pH: 8.43</td><td>(0.66:1)
pH: 3.01</td><td>(1:1)
pH: 2.72</td><td>(1.33:1)
pH: 2.59</td><td>(1.66:1)
pH: 2.55</td></tr>
<tr><td>0</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>6</td><td>p</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>9</td><td>p</td><td>p</td><td>p</td><td>-</td><td>-</td></tr>
<tr><td>15</td><td>p</td><td>p</td><td>p</td><td>p</td><td>-</td></tr>
<tr><td>22</td><td>p</td><td>p</td><td>p</td><td>p</td><td>p</td></tr>
</table>

p denotes precipitation, - denotes clear solution



Surfactant at 0 day

Surfactant after 29 days

Figure 6: The effect of different acid concentration on surfactant compatibility over time

After several days, the clear solutions change into yellow solutions. The possible explanation is that when the solutions were kept under 80 °C, the surfactant degrades over time. When acid acrylic was added into the hard brine, the sodium ions in the brine were not enough to react with all the acid concentration. So, the generated precipitation inhibitors were not enough to prevent the reaction between divalent metal cations and surfactants that were added later into the solution. Consequently, surfactant loss its weigh in degradation form.

4.1.3 Acid – Alkali – Surfactant Interaction Test

The compatibility of acid-alkalis-surfactant with 35000ppm brine was investigated for different ratios at 80 °C. For these tests, acid to alkali ratios of 0.66:1, 1:1 and 1.33:1 were used to study the fluid-fluid compatibility in hard brine. The concentration of surfactant was maintained at 0.6%. Different samples would have different concentration of acid and alkalis but it still be maintained at the selected acid to alkali ratios. The tables below summarize the result of the compatibility tests.

Table 7: Acid - Alkali - Surfactant (0.66:1)

Acid Acrylic + Alkali (Sodium Carbonate) + Surfactant (AOS)					
Acid:Alkali = 0.66:1					
Surfactant: AOS = 0.6%					
Days	Alkali Concentration				
	0.40%	0.60%	0.80%	1%	1.20%
	Acid Concentration				
	0.26%	0.40%	0.53%	0.6%	0.80%
	pH: 8.32	pH: 8.34	pH: 8.41	pH: 8.47	pH:8.49
0	-	c	c	c	-
1	c	c	c	c	c
4	p	p	p	p	p
Acid Acrylic + Alkali (Sodium Hydroxide) + Surfactant (AOS)					
Acid:Alkali = 0.66:1					
Surfactant: AOS = 0.6%					
Days	Alkali Concentration				
	0.40%	0.60%	0.80%	1%	1.20%
	Acid Concentration				
	0.26%	0.40%	0.53%	0.6%	0.80%
	pH: 11.55	pH: 11.86	pH: 12.06	pH: 12.16	pH: 12.22
0	p	p	p	p	p

ppt denotes precipitation, - denotes clear solution, c denotes cloudy

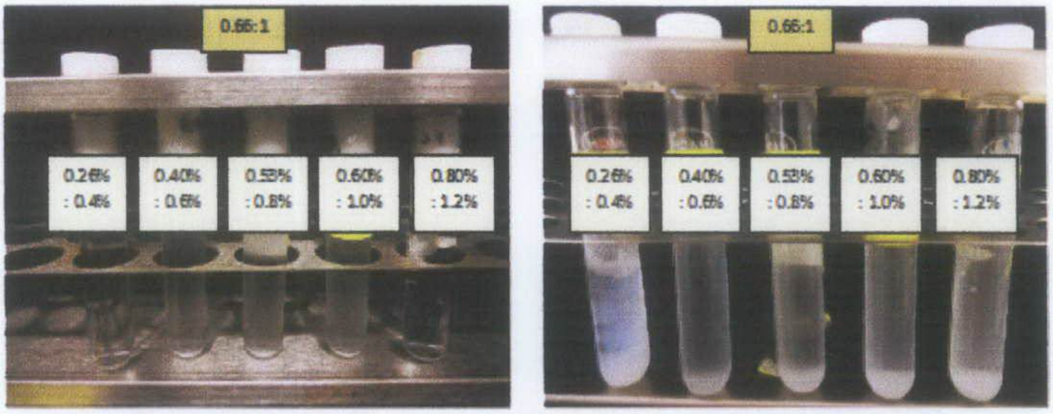
Table 8: Acid - Alkali - Surfactant (1:1)

Acid Acrylic + Alkali (Sodium Carbonate) + Surfactant (AOS)					
Acid : Alkali = 1:1					
Surfactant: AOS = 0.6%					
Days	Alkali Concentration				
	0.40%	0.60%	0.80%	1%	1.20%
	Acid Concentration				
	0.40%	0.60%	0.80%	1%	1.20%
	pH: 8.00	pH: 7.94	pH: 7.58	pH: 7.38	pH:7.30
0	-	-	-	-	-
7	p	p	p	c	c
22	p	p	p	p	p
Acid Acrylic + Alkali (Sodium Hydroxide) + Surfactant (AOS)					
Acid : Alkali = 1:1					
Surfactant: AOS = 0.6%					
Days	Alkali Concentration				
	0.40%	0.60%	0.80%	1%	1.20%
	Acid Concentration				
	0.40%	0.60%	0.80%	1%	1.20%
	pH: 11.57	pH: 11.72	pH: 11.96	pH: 12.05	pH: 12.13
0	p	p	p	p	p

Table 9: Acid - Alkali - Surfactant (1.33:1)

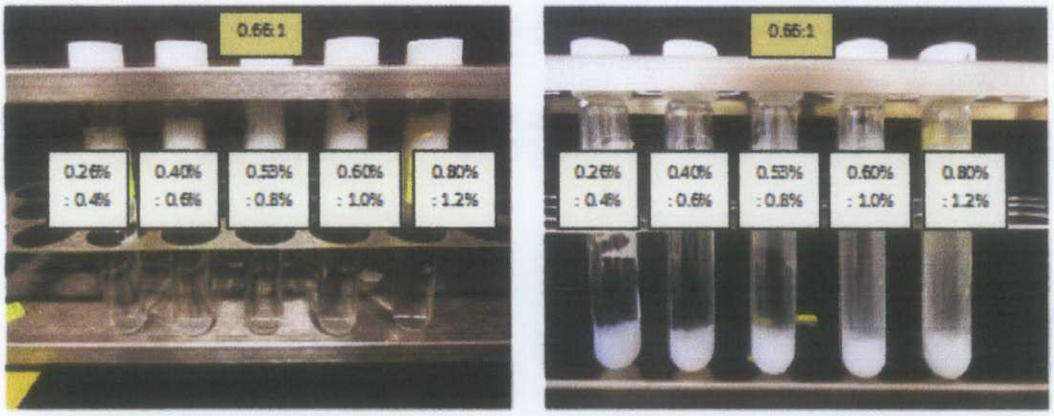
Acid Acrylic + Alkali (Sodium Carbonate) + Surfactant (AOS)					
Acid : Alkali = 1.33:1					
Surfactant: AOS = 0.6%					
Days	Alkali Concentration				
	0.40%	0.60%	0.80%	1%	1.20%
	Acid Concentration				
	0.53%	0.80%	1.06%	1.33%	1.59%
	pH: 6.71	pH: 6.65	pH: 6.64	pH: 6.61	pH:6.57
0	-	-	-	-	-
7	-	-	-	-	-
45	-	-	-	-	-
Acid Acrylic + Alkali (Sodium Hydroxide) + Surfactant (AOS)					
Acid : Alkali = 1.33:1					
Surfactant: AOS = 0.6%					
Days	Alkali Concentration				
	0.40%	0.60%	0.80%	1%	1.20%
	Acid Concentration				
	0.53%	0.80%	1.06%	1.33%	1.59%
	pH: 11.51	pH: 11.65	pH: 11.86	pH: 11.98	pH: 12.03
0	p	p	p	p	p
20	p	p	p	p	p

ppt denotes precipitation, - denotes clear solution, c denotes cloudy



Effect of different sodium carbonate concentration on inhibitor performance at day 0

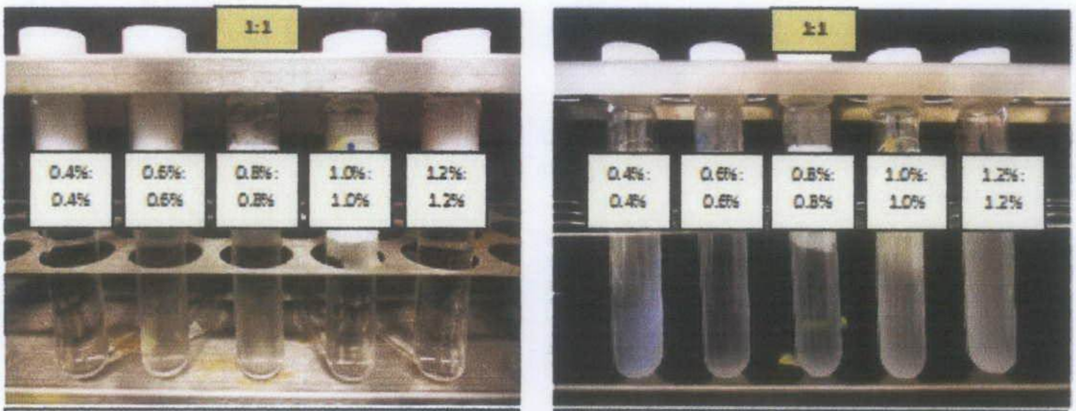
Effect of different sodium carbonate concentration on inhibitor performance after 22 days



Effect of different sodium hydroxide concentration on inhibitor performance at day 0

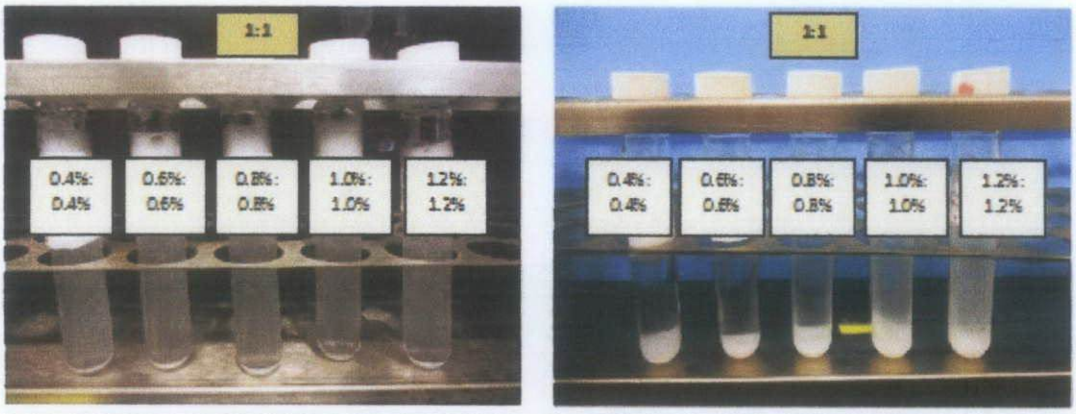
Effect of different sodium hydroxide concentration on inhibitor performance after 22 days

Figure 7: Performance of inhibitor for different type of alkalis



Effect of different sodium carbonate concentration on inhibitor performance at day 0

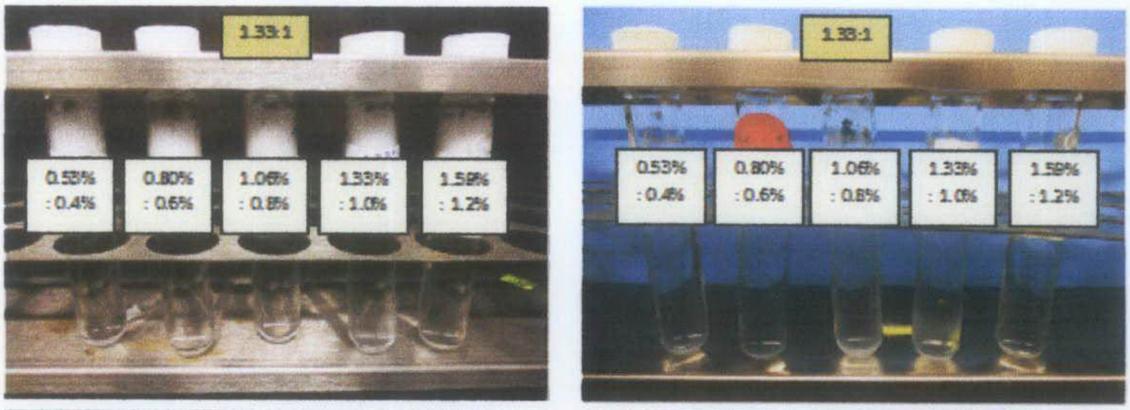
Effect of different sodium carbonate concentration on inhibitor performance after 22 days



Effect of different sodium hydroxide concentration on inhibitor performance at day 0

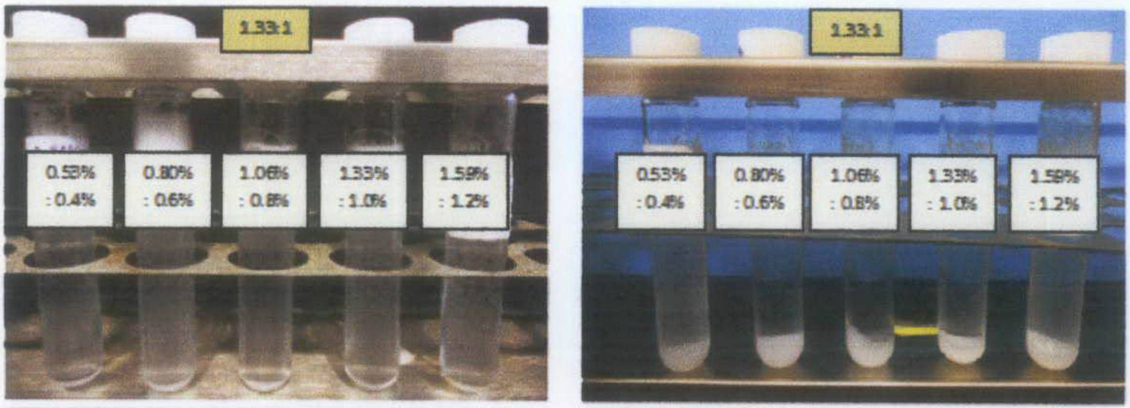
Effect of different sodium hydroxide concentration on inhibitor performance after 22 days

Figure 8: Performance of inhibitor for different type of alkalis



Effect of different sodium carbonate concentration on inhibitor performance at day 0

Effect of different sodium carbonate concentration on inhibitor performance after 45 days



Effect of different sodium hydroxide concentration on inhibitor performance at day 0

Effect of different sodium hydroxide concentration on inhibitor performance after 45 days

Figure 9: Performance of inhibitor for different type of alkalis

As shown in the table above, precipitations were formed for all the acid to alkali ratios that used sodium hydroxide. As for sodium carbonate, the acid to alkali ratios of 0.66:1 and 1:1 were not the optimum ratios as precipitation could be observed in the samples that used those ratios. On the other hand, the ratio of 1.33:1 could possibly be the most optimum ratios as the solutions remain clear up to 45 days. As the conclusion, the sodium hydroxide is a strong alkali that all the selected acid to alkali ratios are not able to generate sufficient PI to prevent precipitation. And as for sodium carbonate, only the ratio of 1.33:1 is able to generate sufficient PI to prevent any precipitation. For lower ratios, acid concentration is fully neutralized by the Na^+ and the generated PI is not able to prevent all the precipitation.

4.2 SUPPLEMENTARY TESTS

4.2.1 Acid Acrylic – Sodium Metaborate Interaction Test

The earlier researchers had found that the metaborate can sequester the divalent metal cations. Thus, no precipitation could be observed when metaborate is used in the Alkali – Surfactant – Polymer formulations. So, for this research, sodium metaborate was used to investigate the compatibility of sodium metaborate with acid acrylic in the hard brine.

The earlier results prove that the acid to alkali ratio of 1.33:1 could prevent precipitation when using sodium carbonate. For sodium metaborate, several ratios had been selected to see at which ratio the precipitation could be prevented.

Table 10: Acid Acrylic - Sodium Metaborate Compatibility Test

Acid Acrylic + Alkali (Sodium Metaborate) **80 °C** **Alkali: Sodium Metaborate = 0.6%**					
Days	0% pH: 9.94	(0.66:1) pH: 6.45	(1:1) pH: 4.80	(1.33:1) pH: 4.39	(1.66:1) pH: 3.97
0	-	-	-	-	-
1	ppt	-	-	-	-
7	ppt	-	-	-	-

ppt denotes precipitation, - denotes clear solution

Up to 7th day, sodium metaborate give a better performance compare to sodium carbonate and sodium hydroxide. For sodium hydroxide, all the ratios precipitated after one day. And for sodium carbonate, the solution with 0% acid precipitated instantly and the solution with the ratio of 0.66:1 precipitated after 3rd day. For sodium metaborate, the solution without acid would precipitate after the first day. But, when the acid acrylic was added to the solutions, the precipitation could be prevented. So, for the sodium metaborate, a better result could be anticipated. Unfortunately, the experiments could not be continued due to some technical errors.

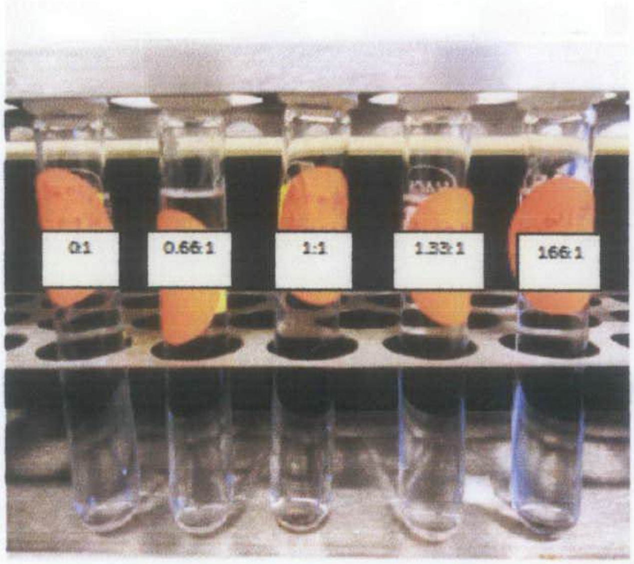


Figure 10: Acid Acrylic - Sodium Metaborate Compatibility Test

Remark: After the 7th day, there was some technical error where the temperature was increased to more than 100°C. The mixture vaporized, and the experiment could not be continued.

4.2.2 Acid Acrylic – Sodium Hydroxide Interaction Test

From the experiment that had been conducted, it was found that up to 1.66:1 of acid – alkali ratio, the precipitation would still occur. The possible reason is that even the acid concentration was increase up to 1.66 for 1 concentration of alkali, the generated precipitation inhibitor (PI) is still not enough to fully prevent the reaction between alkali/surfactant with divalent metal cations. So, the precipitation still could be observed in all the ratios.

So, this supplementary test was conducted to find any possible acid to alkali ratio that could fully prevented the precipitation form occur. The acid acrylic – sodium hydroxide interaction test was repeated by using higher acid concentration. The selected ratios were 4:1, 5:1 and 6:1.

Table 11: Acid - Alkali Interaction

Acid Acrylic + Alkali (Sodium Hydroxide) **80 °C** **Alkali: Sodium Hydroxide = 0.6%**			
Days	(4:1) pH: 4.58	(5:1) pH: 4.10	(6:1) pH: 4.06
0	-	-	-
7	-	-	-

- denotes clear solution

As the acid to alkali ratios were increased, more precipitation inhibitor (PI) would be generated. So, even using sodium hydroxide which is stronger than sodium carbonate and sodium metaborate, the higher acid to alkali ratios could prevented the precipitation. All the solutions remain clear after 7th day.

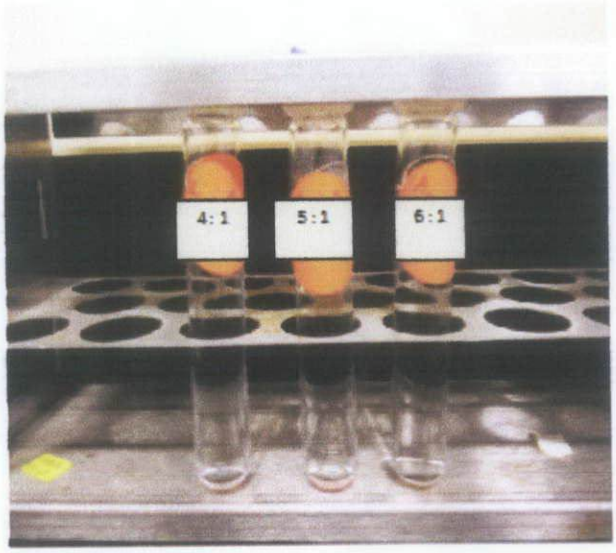


Figure 11: Acid Acrylic – Sodium Hydroxide Compatibility Test in Higher Ratio

Remark: After the 7th day, there was some technical error where the temperature was increased to more than 100°C. The mixture vaporized, and the experiment could not be continued.

4.2.3 Acid Acrylic – Surfactant (AOS) Interaction Test

Acid acrylic – surfactant (Alpha Olefin Sulfonate, AOS) interaction test has been conducted in the hard brine and it was found out that the AOS is not compatible to be used in hard brine. The AOS reacted with the divalent metals cations and formed precipitation. And to confirm that the AOS was precipitated because of it reacted with metal cations, not because of its nature; the interaction test was repeated in the distilled water that contained no or less metal cations.

Table 12: Acid - Surfactant Interaction

Acid Acrylic + Surfactant (AOS) **80 °C** **Surfactant: AOS = 0.6%**					
Days	0%	(0.66:1)	(1:1)	(1.33:1)	(1.66:1)
0	-	-	-	-	-
7	-	-	-	-	-

- denotes clear solution

From the result, it was clear that in distilled water, the acid – surfactant solutions did not precipitate. With no divalent metals cations in the distilled water, there should be no reaction that could produce precipitate. So, the solutions should remain clear.

Remark: After the 7th day, there was some technical error where the temperature was increased to more than 100°C. The mixture vaporized, and the experiment could not be continued.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 CONCLUSION

This research is conducted to investigate the fluid-fluid compatibility using hard brine for chemical EOR. A new chemical formulation is developed and its effectiveness in preventing any precipitation problems associated with the Alkali-Surfactant-Polymer flooding is studied. The main objective of this research is to use sea water rather than softened water to make the chemical slugs. In the process, the original properties of chemical EOR is maintained so that this new formulation still can give same performance with the conventional chemical EOR, if not better.

The key indicator in the test is the formation of precipitation. So, to prevent the precipitation, the precipitation inhibitor is generated by the neutralization reaction between acid and alkali. The first part of the test is to study the compatibility of acid-alkali in the hard brine. The compatibility of acid-surfactant in the hard brine is also need to be tested to observe the tolerance of surfactant with hard brine. The following are the major finding of the research.

1. The sodium hydroxide cannot be used in this new formulation for any selected acid to alkali ratios as the precipitation can be observed in all the samples. Sodium hydroxide is a strong alkali and a higher acid to alkali ratio may be required to generate sufficient PI to prevent the precipitation.

2. With an optimum acid to alkali (sodium carbonate) ratio, a sufficient concentration of PI is generated to prevent the precipitation. With a lower ratio, the PI is not sufficient to prevent the precipitation. As the result, the precipitation is formed instantly. As the acid to alkali ratio is increased, more PI is generated and longer time is required to get the precipitation in the samples.

And when the optimum acid to alkali ratio is used, 1.33:1, the solution remains clear up to the date. So, the chosen optimum ratio chose is 1.33:1.

3. For the acid-surfactant compatibility test, the sample without acid started to precipitate in the sixth day. The surfactant used in this test, Alpha Olefin Sulfonate has high resistance to hard water. And with PI generated from the reaction of acid and Na^+, the solution can remain clear up to the fifth days before the first precipitation start to be observed .

4. For sodium metaborate, with addition of acid acrylic into the solutions, all the solutions remain clear up to 7th day. The sodium metaborate is weaker than sodium carbonate, so a lower acid to alkali ratios is anticipated to prevent any precipitation. From the result, the lowest ratio, 0.66:1 could generate enough precipitation inhibitor (PI), thus prevent any precipitation form occur.

5. As discussed earlier, sodium hydroxide is a strong alkali that reacts aggressively with the metal cations to form precipitation. So, more acid concentration is needed to react with sodium ions to generate sufficient amount of PI to prevent the precipitation. So, the test is repeated with higher ratios of acid – alkali. From the result, the solutions remain clear because the generated PI is enough to prevent any precipitation.

6. In the hard brine, acid – surfactant solutions form precipitation after several days due to reaction between surfactant and metal cations. However, the precipitation is also possible because the sulfonate group of the surfactant. So, acid – surfactant test in repeated using distilled water. No precipitation is observed for this test. This prove that the precipitation occur because of the reaction between surfactant and metal cations.

5.2 RECOMMENDATION FOR FUTURE WORK

There are several recommendations that can be implemented to improve the project:

1. In this research, acid to alkali ratio of 1.33:1 was selected as the optimum ratio in preventing the precipitation. So, for the future work, try to use other ratios between 1:1 and 1.33:1 and find any possible ratio that also can eliminate the precipitation. A lower ratio means reduce the need from using a higher concentration of acid, thus reduce the operational cost.

2. Using the acid to alkali ratio of 1.33:1, the formulation need to be mixed together with polymer and observe the compatibility of the Acid – Alkali – Surfactant (AAS) with Polymer in hard brine. Polymer should be expected to improve the total effectiveness of the AAS.

3. The new formulation should be tested using different brine hardness so that the overall performance of AAS in preventing the precipitation in other brine hardness can be investigated.

REFERENCES

1. Seeking Alpha. 13 July 2007 <http://seekingalpha.com/article/40982-international-energy-agency-oil-supply-demand-trends-for-2007-2012>
2. Ralph Glass. 31 December 2010 <http://www.ajmpc.com/priceforecast/13/249/AJM-s-Canadian-price forecast.html?
3. Highlights of the latest OMR 13 July 2011 <http://omrpublic.iea.org/>
4. Aaron Smith @CNNMoney. 16 June 2011 < http://money.cnn.com/2011/06/16/news/international/iea_oil_gas/index.htm>
5. Total <http://www.planete-energies.com/content/oil-gas/companies/world/consumption-oil-production-statistics.html>
6. B.C. Craft, M.F. Hawkins and R.E. Terry, *Applied Petroleum Reservoir Engineering*. Second Edition, Englewood, Cliffs NJ: Prentice Hall PTR. pp. 5, 1991.
7. M.K. Hamdan, N. Dorman, D. Hussain, and Z. Ibrahim, "Enhance Oil Recovery in Malaysia: Making it a Reality," presented at Asia Pacific oil and gas conference and exhibition, Jakarta, April 5-7, 2005, SPE 93329.
8. Z. Ibrahim, A.A Abdul Manap, P. Abdul Hamid, H. Vai Yee, L. Pen Hong, and K. Wyatt, "Laboratory Aspect of Chemical EOR Process Evaluation for Malaysian Oilfields," presented at Asia Pacific oil and gas conference and exhibition, Adelaide, September 11-13, 2006, SPE 100943.
9. K.A. Elraies, I.M. Tan, M. Awang, and M.T. Fathaddin, "A new Approach to Low-Cost, High Performance Chemical Flooding System," presented at SPE Production and Operations Conference and Exhibition, Tunis, June 8-10, 2010, SPE 133004
10. Y. Wang, J. Liu, B. Liu, Y. Liu, Hongxing, Wang and G.Chen, "Why Does Scale Form in ASP Flood? How to prevent from it?--A Case Study of the Technology and Application of Scaling Mechanism and Inhibitor in ASP Flood Pilot Area of N-1DX Block in Daqing," presented at the 6th International Symposium on Oilfield Scale, Aberdeen, UK, May 26-27, 2004, SPE 87469.

11. A. K. Flaaten, Q.P. Nguyen, J. Zhang, M. Hourshad and G. A. Pope, "ASP Chemical Flooding without the Need for Soft Water," presented at SPE Annual Technical Conference and Exhibition, Denver, Colorado, September 21-24, 2008. SPE 116754
12. Terry Knott. 20 April 2009 <http://www.oilonline.com/default.asp>
13. E. Carrero, V. Q. Nestor, S. Pintos, L.E. Zerpa, "Global sensitivity analysis of Alkali – Surfactant – Polymer enhanced oil recovery process," Journal of Petroleum Science and Engineering, vol. 58, pp. 30-31, 2006.
14. N. Mohr, "Alkaline – Surfactant – Polymer Flooding: Maximizing Existing Reserves with Chemical Enhanced Recovery," vol. 4, pp. 1, 2009.
15. P.B. Berger and C. H. Lee, "Improved ASP process using organic alkali," presented at SPE/DOE symposium on improved oil recovery, Tulsa, April 22 – 26, SPE 99581.
16. Ryan Day.
< http://www.ehow.com/way_5268177_water-softening-methods.html>
17. 9 April 2010. < http://water.ygoy.com/what-are-water-softening-methods/>
18. AquaScams. < http://www.chem1.com/CQ/hardwater.html>
19. CMHC-SCHL.
< http://www.cmhc-schl.gc.ca/en/co/maho/wawa/wawa_005.cfm>
20. Thomas Klenck. 1 August 1998.
<http://www.popularmechanics.com/home/improvement/interior/1275126>
21. http://www.ultramarinepigments.net/aos.htm