EVALUATION OF NEW GENERATION OF VISCOELASTIC SURFACTANTS AS DIVERTING AGENTS FOR HIGH-TEMPERATURE FORMATIONS

A Thesis

by

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ABSTRACT

The viscoelastic surfactant (VES) is one of the newest chemicals that have been used as diverting agents to divert the acid to the desirable zones through directing the acid to the lowest permeability formations by building in-situ viscosity. This technique shows valuable properties in diverting and cleaning processes. However, the main problem associated with this technique is a temperature limitation; therefore, the research is continuing developing new chemicals that overcome the high-temperature short come.

This study aims to evaluate the rheological properties of five new types of the VES that are proposed to be used in oil industry through conducting the lab tests on this new generation of the VES. The spent acid system which contains 6 vol% VES was prepared and the PH was adjusted between 4 and 5 while the pressure was maintained at 400 psi.

The different types showed various performances in different conditions, VES001 showed high viscosity around 100 cp at a shear rate of 10 s\(^{-1}\) and temperature of 200\(^{\circ}\)F, while VES002 didn’t show any viscosity building in high temperatures (200 and 250\(^{\circ}\)F). VES003 and VES004 showed a high viscosity building around 120 cp in temperature of 250\(^{\circ}\)F at a shear rate of 10 s\(^{-1}\). Type 5 showed promising properties in high temperatures since it showed viscosity of 120 and 220 cp in 200 and 250\(^{\circ}\)F, respectively. Moreover, it’s viscosity didn’t peak even at 370\(^{\circ}\)F when it showed viscosity of 550 Cp at a shear rate of 87s\(^{-1}\).
Further tests were obtained on the VES005 to deeply evaluate both its capability as diverting agent and its compatibility with the other acid additives. The effects of several corrosion inhibitors on the performance of the VES were studied then the optimal inhibitor was used for the further studies. Core-flood tests were conducted to emulate the performance of the system inside the formations. Two types of Indiana limestone cores; 150 mD and 12 mD were used. The exciting diverting performance was observed through the low permeability core; however, some diverting performances were observed in the high permeability core. CT scan was used to reinforce these results.
DEDICATION

I dedicate my dissertation work to my beloved family: my father, Dr. Ali A. Ahmed; my mother, Wedad M. Youse; and my siblings, Omar, Osama, Abubakar, Ibtihal and Amar. My efforts and sweat notwithstanding, being far from you has been a tremendous suffering. Thank you for your forbearance.

Also, this work is dedicated to my friends and to my future soulmate even if I don’t know her yet

Finally, this work is dedicated to my future ME, the well-known professor Almostafa A. Alhadi
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All work for the thesis was completed independently by the student.

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CHAPTER I
INTRODUCTION

Introduction

The oil industry has been growing since the digging of the first wells in North America during the 17th century; this enormous growth has coincided with the augmenting energy demands supported by the innovative research in all manner of the industry aspects. This research focuses on the developing of new technologies that may help in both using the new resources that were difficult to be used in the past and simultaneously enhancing the usage of the current energy resources. Although the oil industry has been shocked as a result of the last rescission in the industry when the oil price has dramatically collapsed, the oil is still considered one of the cheapest and most efficient resources of the energy; therefore, the research on this precious energy resource has been continued after taking into consideration the price of the oil and gas.

Formation damage

One of the problems that associated with the oil production is the formation damage which can be characterized by the reduction in the reservoir permeability near the wellbore, on other words, impairment of oil transition of the reservoir to the wellbore (Civan 2000). This damage can be resultant of the drilling fluids during the drilling operations, completion fluid during the workover operations or the production processes (Civan 2000). During these operations, the fine solids may precipitate on the formation and then
Plug the rock pore space. The damage can be induced in the wellbore as a result of the formation nature, for instance, in the sandstone formation, the formations clay may swallow when be attached to the water (Gray et al).

In some cases, the formation conductivity is naturally low since the permeability of the reservoir is low such as the tight gas formation (Nasr-El-Din et al. 2003), therefore, the well stimulation can be referred to fracking this formation by injecting the acid with a pressure higher than the fracturing pressure which can result in opening more and wide channels between the wellbore and the formation.

The well stimulation by acid has been started in the last decades of the 18th century and has been profusely developing since that time (Thomas et al.); many new chemicals have been adding to the system in the aim of enhancing the treatments and minimize the formation damage. Many diverting techniques have been introduced to place the acid into the damage formation and to facilitate the cleaning up procedures. Also, many additives have been using simultaneously to overcome the problem that may happen during or after the treatment.

The Viscoelastic surfactant has been introduced to the industry almost in the beginning of the last century (Chang et al. 2001) and has been used widely in different formations and under various circumstances since it shows a tremendous effectiveness in achieving the treatment.
The surfactant

The surfactant is a chemical substance that can outstandingly alter the interfacial tension between two different liquids by adsorbing or concentrating at the interface between them (Green et al. 1998).

Surfactant types:

Ionic surfactant- holds a negative charge.

Cationic surfactant- holds a positive charge.

Zwitterionic surfactant- can be positive or negative depending on the value of the solution PH.

Amphoteric surfactant- contains two different components.

Non-ionic surfactant- has a polar but no charge.

These varieties and unique characteristics let the surfactant be used in multi-applications such as cleaning the pipelines and oil storages, treating waste water, enhancing oil recovery, wells stimulation, biological aspects and has been widely used in chemical industries.

The diverting agents

The reservoir formations are quite heterogeneous; thus, the formation properties such its permeability may vary markedly. Also, the damage- which often is resulted from the fluid-rock interaction- distributes unsteadily on the formation zones. By reason of this disparateness in the distribution of the damage and the properties of the formation zones,
the acid tends to invade the formation non-uniformly. Matrix stimulation tends to remove the damage or widen the channels that are easier to be treated; it means the zones that have higher permeability and low damage which in fact are least targeted. For the above reasons, the Fluid placement is an important factor that affects the success of the matrix stimulation treatment (Pye et al. 1970; Cooper et al. 1984). To overcome these problems either chemical or mechanical methods can be applied.

The mechanical methods

Many mechanical techniques have been used to place the fluid into the formation using different mechanical devices include bridge plugs, packers and perforation ball sealers, coiled tubing and others (Charles L. Smith et al.).

The demerits of these techniques include:

- They are expensive.
- Sometimes they are limited to the cased hole.
- They demand high pump rate.

The chemical methods

Many chemical diverters have been introduced to place the acid fluid in the desired zones and control the fluid leak-off. These techniques use different chemical materials to temporary form a low permeability cake or decrease the mobility of the acid by increasing the acid viscosity. The using materials include particulate diverters, foamed acid, gelled acid, viscoelastic surfactants and others. These various types and their advantages and drawbacks have been deeply discussed in chapter 2.
The diverting agents are evaluated in term of (Crowe et al.):

a- The ability of the diverter to place the fluid uniformly into all target zones.

b- Being effective under a wide range of the temperature.

c- Easiness of being broken down after the treatment and leave less or zero possible amount of the residual in the formation (less or zero formation damage and easy cleaning up procedures).

d- In the case of presence of gravel pack completion should be able to penetrate the gravel pack without plugging the formation.

The viscoelastic surfactant

The term viscoelastic refers to the materials that have both viscous components and elastic components (Nasr-El-DIN et al 2008).

The viscosity

It is defined as the material resistance to the flow. The viscous material resists the shear rate and the strain when it is applied to the stress. Depending on the change in this resistance with the shear rate/stress these materials can be classified in many categories (SIJ University 2010):

1- Newtonian fluid:

In this kind of the fluids, the viscosity doesn’t change when the shear rate value is changed while the temperature is fixed and the shear stress changes linearly with the change in the shear rate.

2- Non-Newtonian fluid:
In this case, the relationship between the shear rate and shear stress is not constant. Due to the way that the apparent viscosity changes with the shear rate these fluids can be divided into many types.

![Shear stress/shear rate behavior in different types of fluids](image)

**Fig. 1: Shear stress/shear rate behavior in different types of fluids (Meyers et al. 2009).**

The elasticity

Elastic materials strain when the stress is applied to them and return to their original status when the stress is removed. When the materials stretched the energy is stored in their atoms and then this energy brings the materials back or can be dissipated in another kind of energy (Meyers et al. 2009).
Viscoelastic materials

Besides having the viscous and elastic characteristic the time is considered as an important variable in describing these materials. This kind of materials tends to lose energy when exposure to a load, however, they return to their original shape after the load is removed but they take some time to do so (at this period of time they have viscous components) (Meyers et al. 2009).

Fig. 2: The difference between a purely elastic material and viscoelastic materials when they lose energy (Meyers et al. 2009).
The viscoelastic surfactant

In general, all surfactant consists of two groups; the hydrophobic part which in usual a hydrocarbon chain that dissolves in oil and the hydrophilic part which an ion that dissolved in water. In the aqueous, the surfactant molecules self-associate in the contact surface between the different fluids (Green et al. 1998).

The surfactant that is used in preparing the VES-based acid is usually an amphoteric surfactant. The general formula of this surfactant contains Carboxylic acid that contains carboxyl group (COOH) and a Nitrogen atom, for example (Nasr-El-Din et al. 2008) used a carboxybetaine with a general formula:

\[
R-\text{CO-NH-}(\text{CH}_2)_nN^+-(\text{CH}_3)_2-(\text{CH}_2)_p\text{COO}^- \]

In the live acid, the group has a positive charge and the surfactant is cationic, in this case, there are repulsion forces between the positively charged head groups which lead to spherical micelles shape and therefore low viscosity fluids. When the acid reacts with the carbonate formation the PH increases and when it reaches the isoelectric point usually (2-3) PH the surfactant becomes zwitterionic (the carboxylic carries a negative charge and the nitrogen carries a positive one at the meantime). In the same time, the reaction of the acid with the formation leads to an increasing in the concentrations of the Ca\(^+\) and Mg\(^+\) ions which distribute themselves around the surfactant. The entanglements of these molecules result in 3d rod-like micelles shapes which enhance the acid viscosity.
The reactions of HCl with the limestone and the Dolomite were given by the following equation (R. L. Thomas at el.):

\[
\text{CaCO}_3 + 2\text{HCl} \rightleftharpoons \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2
\]

\[
\text{CaMg(CO}_3\text{)}_2 + 4\text{HCl} \rightleftharpoons \text{CaCl}_2 + \text{MgCl}_2 + 2\text{H}_2\text{O} + 2\text{CO}_2
\]

Fig. 3: Surfactant gel and breaking mechanism (Nasr-El-Din et al. 2008)
How to break the viscoelastic surfactant gel

1- In water injector wells the water can be injected to reduce the salt/surfactant concentrations (Nasr-El-Din et al. 2008)

2- The hydrocarbon (oil or gas) is found to break the rod-like micelles completely (Samuel et al. 1997)

3- Mutual solvent entirely breaks the viscosity of the surfactant close to water viscosity (Nasr-El-Din 2008, L. Li et al. 2010).
CHAPTER II
LITERATURE REVIEW

History of the well stimulation

The very first stimulation job was recorded in 1895 when Ohio oil company acidized two wells. Although the productivity of the wells increased significantly, however, the casing tubes were ultimately corroded by the acid. One year later the patent of using the HCL acid to treat the damage in the limestone formation was issued to Dr. Herman Frasch of Standard Oil Company. The patent hasn’t noticed the corrosion resulting damage but the usage of the acid in the well stimulation (Thomas et al. 1998).

The second attempt for using the acid in well stimulation was conducted in 1928. Dr. Herbert Dow injected many acids into brine wells through many treatments which were projected to increase the productivity of the natural brine and solve the problem of brine disposal as well. But the outcome of these projects was not pleasant enough due to both the corrosion problem and the high cost of the materials that were used to protect the metal equipment. This inspired the Dow Chemical Company to inaugurate many projects in the aim of overcoming the corrosion problems by developing corrosion inhibitors.

These projects were crowned by Dr. John Grebe when he noticed that the arsenic acid acts like acid inhibitor. In 1932 Dow Chemical company in cooperation with Pure oil company Have successfully boosted the productivity of a “dead” well in the Greendale Pool, Michigan to 16 BOPD by injecting 500 gallons of the acid using arsenic acid as inhibitor into the well. In 1935 the Halliburton Oil Well Cementing Co. started applying the acidizing services commercially beside the Dow Well Services Group.
In that period around 6000 oil and gas wells were treated by Dowell Incorporated, leading to increasing the productivity of the well by an average of 412 % as Drs. Grebe and Stoesser of Dowell published in WORLD PETROLEUM.

Although the attempts of using the acidizing in the sandstone formations started by 1933 in Texas followed by giving the patent to Standard Oil Company, however, the breakthrough was recognized in 1946 when Dowell introduced the mud acid to overcome the formation plug. HCL and HF have been used to treat the sandstone formation since HCL has been noticed to reduce the PH and minimize the formation damage.

The humongous applications of acidizing addressed a lot of problems related to the using of the acid systems such as acid sludge, acid-induced emulsions, spent acid clean up and others. Therefore, between 1950 -1960 the research focused on developing many acid additives to solve the previous issues. Numerous acid additives have been used such as anti-sludge acid and clay control agents.

**Evaluation of the different diverting agents**

In 1969 (Smith et al) introduced the oil soluble water soluble granular organic as a new diverting agent that has limited solubility and temperature constraints. Both solubility and filtration tests were conducted to evaluate the diverter. Then the laboratory tests were followed by field applications. the results indicated that the new system can be used in different well’s completion types, moreover, the successful field applications included a wide range of the temperature up to 250 F and the rapid clean can be achieved in low temperature (90 F).³
In 1971 (Crowe et al) evaluated the wide range of the diverting agents that have been used in the acidizing treatments. The evaluation compared viscous gel, gums, emulsion, polymer acid solid organic acid and a new introducing system that depends on the oil soluble resin mixture to divert the acid into the formation. He compared the capability of the different diverters to flow into different permeability formations and the formation damage that the treatment causes. The test was conducted on the sandstone cores, which firstly were saturated with HCL acid until the acid has no more effects on the permeability of the cores (constant permeability was reached to be used as a reference to measure the formation damage). Then the diverting agent introduced to the cores. The author concluded the fact that the oil soluble resin mixture had a peace impact of the formation because it can be easily cleaned up after the formation and in order to increase its efficiency as a diverter Agent only a small amount of the substance should be used to control the diversion. He also summed up that the viscous fluid and the emulsion were ineffective diverters.4

In 1978 (Scherubel et al.) discussed the foamed acid as a new concept in fracturing acidizing to harness the fluid leak off during the treatment. They conducted the test on the limestone cores and reached out that this technique is effective on 100 permeability which was considered as a breakthrough in that time. Also, they noticed the relative improvement in the acid stability in the high temperatures when using the gel. Many field attempts were done to prove the laboratory tests. First well was treated using 10500 gallons of 20% HCL foamed with nitrogen resulting in increasing the well productivity from (5-6) BOPD to 12 BOPD. The other well treated by water-based gel followed by the foamed acid resulting in boosting the well productivity from zero to 46 BOPD which reached 76 BOPD 30 days
later. they summed up that using the water–based gel then following by the foamed acid can minimize the fluid loss while the temperature still limits the acidizing efficiency.\textsuperscript{5} In 1978(Norman) discussed the advantages and the drawbacks of the gel agents that had been using in acidizing. He addressed both the instability of the polymers that have been using in a strong acid system and the necessity of the high concentrations of the polymers to create the sufficient gel. He developed new cationic gelling materials to skip these issues. the new system had been examined giving a stable acid in all strengths of HCL. the field tests showed a good result since the first well production increased from 2-5 BOPD to more than 200 BOPD on the first day of the treatment to fluctuated between 20-23 BOPD 4 months later while in the second well the productivity only increased from 3 BOPD to 8 BOPD. The author concluded that the laboratory tests showed a good result while the field tests proved the success of this agent in some formations rather than the other formations.

In 1979 (Pabley) introduced a new stimulation technique that uses High strength cross-linked acid and in 1980 (Pabley et al.) discussed this new system associated with field treatment. The laboratory test showed that the new system has much better retardation effects on the formation testing up to 350 F. the new system gives a deep penetration of the live acid which results in a higher formation conductivity. The acid concentrations and the temperature control the system breaking which eliminates the need of the breaker. the new system had been applied to the oil well in Greater Aneth, San Juan county, Utah. The well production increased to 20 BOPD and 6 BWPD which presents 6 times greater than initial well productivity.\textsuperscript{7}
In 1982 (Pabley et al.) underpinned their previous study by applied the cross-linker system in the wide ambit of the wells in various limestone and dolomite formations. More than 45 jobs had been conducted using HCL cross-linked acid in more than 12 various formation types with conditions that varied from 70 bottom hole temperatures up to 275 F BHT. The acid concentration was differed from 3 up to 28% HCL while the volume that had been pumped ranged from 500 gals to 36,000 gals. In the wells that have BHT, more than 200 F the formation was first cooled down by pumping viscous fluid which was either Oil based or water based cross-linked system/gelled system. The result showed a tremendous increasing in the wells productivities after the treatments. The figure below compared the productivity of the wells before and after the treatment in Phosphoria formation, Mission Canyon Formation, and Green River Formation:

Fig. 4: Production increases in Phosphoria formation (Pabley et al. 1982)
Fig. 5: Production increases in Mission Canyon formation (Pabley et al. 1982)

Fig. 6: Production increases in Green River formation (Pabley et al. 1982).
The study concluded that the cross-linker acid resulted in successful treatments which increased the oil productivity, showed deep penetrations of the live acid and more efficiency in cleaning up procedures.8

In 1989 (Crowe et al) discussed the Fluid loss control as an important factor in achieving a successful acidizing treatment. The acid treatment aims to either reform the current formation damage or open a new channel to increase the reservoir conductivity to the wellbore. This improvement is measured by the length of the penetration which inversely proportional to the acid spending or fluid loss. They mentioned the problem that happens when the pumping pressure falls below the fracturing pressure as a result of the expansion of the fluid in a matrix near the wellbore. The other problem that related to the acid fracturing treatment is the tendency of the acid to enter the zones that have a high permeability resulting in wormholes. This study addressed many types of the acid control agents that have been developed to overcome this problem. The oil soluble acid system was found to be the most effective system in high-pressure treatment conditions which limited by the necessity of a high concentration of the additives which may lead to a high-cost treatment. To overcome this high cost another technique has been used which relays on injecting a viscous nonreactive pad before the acid. These techniques have two goals; firstly to cool down the formation and the tube and secondly to form a filter cake that is difficult to be penetrated by the acid. This technique was widely used; however, the studies showed that it is ineffective in preventing the acid from penetrating the filter cake. In order to enhance this technique, many stages of it were developed and had been used.
They studied the factors that affect the fluid loss and came up with that the higher injection rate increases the wormhole depth while the depth decreased when the temperature increased. Also, the acid concentration affects the penetration depth when increasing the acid concentration from 15 to 28% resulted in doubling the penetration depth. The study summed up that the new system that used acid gelled in many stages gave a good result in blocking the wormholes which show promise for enhancing the acid treatment.

In 1998 (Thomas et al) conducted a laboratory and computer simulation study to evaluate the acidizing treatment performance when bullhead and using the coiled tubing technique in horizontal, deviated and vertical wells. The author addressed that the usage of the CT in placing the treating fluid is better than using the conventional tubing or casing since they are inefficient and due to the time-consuming. The foam and temporary cross-linker gelled acid was used as a divergent agent since the studies at that time showed they were best-diverting agents especially the TCGT. The computer simulation and many fields studies were run to evaluate the different techniques that can be used in acidizing the carbonate formation. The result of the wells study was summarized in the chart10 below:
Fig. 7: Pre & post treatment into 4 vertical wells using different placement and diverting techniques (Thomas et al. 1998).

The study summed up that both the computer simulations and the field studies show that using the CT as a placement technique with the foam or cross-linked acid gave a good result in covering the damage zones uniformly and increasing the productivity.¹⁰
The viscoelastic surfactant-based acid

In 2001 (Chang et al.) have developed a new self-diverting agent that causes in situ Gelling of the acid in the carbonate reservoir. The new system uses a special type of the surfactant that has both viscous and elastic properties. The new acid system uses a single component that forms rod-like micelles when the Ca+ ions and the PH increase as a result of acid spending, therefore, the viscosity will increase to form in situ gelled. The second advantage of the new system is the greatly decreasing in the formed gelled acid when its exposure to the hydrocarbons which mean a rapid and easy cleaning up efforts. Multi-cores flow experiments and rheology measurements have been conducted to study the diversion of the new system in different permeability cores. The viscosity as a function of the spent acid gelled, the acid PH and temperatures have been measured. After conducting the core flood tests the cores were scanned with the Computed Tomographic every cm of the cores. The results of the rheology tests show that the viscosity of the spent acid increases when the acid PH increases above 2, at the same time they show that the new system can work until 200 F and if the cooling technique is using it can work until 220-230 F. The core flood tests compared the usage of different types of diverting agents with the new system. The tremendous stimulation effectiveness has been noticed when the new system was used in both high permeability and low permeability formations. The figures below has been used by the authors to summarize their studies result:
Fig. 8: VES based spent acid viscosity profile as a function of the PH (Chang et al. 2001).
The study summed up that the new system has a good capability in stimulation and diversion since the viscosity will be build up in the target zones, moreover, the built-up viscosity will be sustained when the spent acid PH goes up to 2 comparing to the polymer gelled when it will be broken down when the PH becomes 3.5-4. Furthermore, the new system has less damage potential to the formation and can be easily cleaned up when the VES in situ gelled be attached by the hydrocarbon.

Fig. 9: VES based spent acid viscosity profile as a function of the Temperature in different shear rate (Chang et al. 2001).
Application of the VES in offshore horizontal wells

In 2003 (Nasr-El-Din et al.) studied the using of the VES-based acid in the horizontal wells, since, the treatment into the horizontal wells more challenging that the vertical wells as a result of its long leg, huge formation heterogeneity and the difficulties in the cleaning up processes due to the low drawdown which demand long time in cleaning up. These difficulties exacerbate when treating the tight formation. The treatments were conducted on different formations in two different fields; one of them is a totally offshore field and the second one is an only partial offshore field. The treatments involved 100 offshore horizontal wells using the viscoelastic surfactant-based acid. While 90 wells were treated in the first field 6 of them which located on the same platform were used to compare the VES-based acid with the polymer-based acid. 5 of them were treated with the VES while the sixth one was treated with the polymer-based acid. The following table summarizes the result of this evaluation:
Another well had been chosen to evaluate the using of the VES-based acid, the productivity of this well increased from 1,830 BOPD to 10,900 BOPD. This well sustained high productivity for more than two years and water cut remained approximately constant. The study addressed many other cases that the well productivity increased after had been treated by the VES-based acid.

The study addressed the notice successes in treating the offshore horizontal wells in spite of the difficulties that can face the operation in these conditions. These challenges can be illustrated by the limitation of the capacity of both the crane of the offshore rig and the rig deck which constrains the volume of acid that can be used, moreover, the limitations of the CT length and the high length of the opened hole section. Furthermore, the cleaning

<table>
<thead>
<tr>
<th>Well #</th>
<th>Pre-job status</th>
<th>After-job Water cut (vol%)</th>
<th>After-job Oil rate (BOPD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, polymer acid</td>
<td>flowing</td>
<td>9</td>
<td>4123</td>
</tr>
<tr>
<td>2</td>
<td>dead</td>
<td>0</td>
<td>5,624</td>
</tr>
<tr>
<td>3</td>
<td>flowing</td>
<td>0</td>
<td>5,680</td>
</tr>
<tr>
<td>4</td>
<td>flowing</td>
<td>0</td>
<td>6,150</td>
</tr>
<tr>
<td>5</td>
<td>flowing</td>
<td>0</td>
<td>5,850</td>
</tr>
<tr>
<td>6</td>
<td>flowing</td>
<td>0</td>
<td>5,358</td>
</tr>
</tbody>
</table>
Up of the spent acid is really a big issue in the offshore wells which decreases the quantity of the using acid, moreover, those fields that have been treated considered as sour oil reservoirs which demanded special treatment to the H2S.

This study concluded that using the Viscoelastic surfactant based acid overcomes all the previous problems and resulted in increasing the productivity of more than 100 wells that were treated. Also, long production sustainability and lower water cut were noticed after the treatment.\textsuperscript{12}

Application of the VES in gas wells

In 2003 (Nasr-El-Din et al.) addressed applying the new VES system for first time in a gas formation in Saudi Arabia. One of the hardships that might limit the treatment was the temperature of the formation which ranges between 250 to 280 F which can result in accelerating the acid spending and also demand high corrosion inhibitor volume since the acid is more corrosive in high temperature. The second obstacle represented by the properties of the reservoir (tight gas reservoir in presence of many fractures) which make a leak-off problem is a real issue. The other problem is the H2S content (10 mol\%) which limits the selectivity of the fluids to avoid future productions probable problems. These formations had been treated by gelled acid and in situ gelled acid which both have many disadvantages that have been enumerated by the authors. In the formation that contains a high level of H2S using any metallic iron as cross-linker may result in a huge formation damage which demands using an iron control agent, moreover, the polymer based systems are difficult to be mixed beside the necessity of using many additives and require long blending time. Finally, the residue will remain in the formation after the treatments which
Will result in formation damage. To overcome all these drawbacks, the authors introduced using the VES-based acid for the first time to fracture the high-temperature tight gas wells. Five wells have been treated by injecting first borate-gel to frack the formation followed by alternating stages of emulsified acid and borate gel pad and in the last step, the VES was used. The treatment results in three wells are shown in the table below:

<table>
<thead>
<tr>
<th>wells</th>
<th>Pre-job productivity</th>
<th>BHST</th>
<th>After job productivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.1 MMscfd</td>
<td>259</td>
<td>43 MMscfd</td>
</tr>
<tr>
<td>2</td>
<td>11.61 MMscfd</td>
<td>259</td>
<td>53.27 MMscfd</td>
</tr>
<tr>
<td>3</td>
<td>16 MMscfd</td>
<td>-</td>
<td>58.9 MMscfd</td>
</tr>
</tbody>
</table>

This summarization of this study was the noticing of the significant increasing in the high-temperature sour gas wells productivities after they were treated with the VES acid. The rapid cleaning up operations and blending and pumping the acid without problems were indicated.
Application of the VES in water injectors

In 2003 (Al-Muhareb et al.) studied using the new VES system to enhance the injecting wells injectivity and overcome the problems that associated with the polymer based acid systems. These vertical wells were used to maintain the reservoir pressure in a carbonate reservoir. The VES used to prepare non-reactive viscous pad, emulsified acid, and VES leak-off control Acid. The experimental tests had been done before the well was treated. The treatment indicated the simplicity when using the VES in operations, leak-off control was acceptable and an enormous stimulation was achieved. The pre-test results in the vertical well was compared to a horizontal well and the comparison showed many promises of using this technique in the horizontal wells.

The conclusion of using VES in different wells and under various conditions

In 2007 (Nasr-el-Din et al.) summed up many lessons and evaluations of using VES in Saudi Arabia under different circumstances range from vertical, horizontal, tight gas to sour formations among temperatures that vary from (100-250 F).

1- Matrix acidizing of seawater injectors

The sea water injectors were treated by VES to overcome the formation damage that resulted from using the polymer-based acid, the wells that were treated by the VES showed less formation damage and long sustainable pre-treatment productivity without noticing of any operational problems. The figure below was used to show the injectivity index of two wells stimulated with polymer-based acid and well that stimulated by VES-based acid:
Fig. 10: Comparison of injectivity index (after treatment injectivity/pretreatment injectivity) of 3 seawater injectors that were treated by different acids (Nasr-El-Din et al. 2007).

Many notices have been concluded from this treatment by the authors such as the destroying of the gelled surfactants by the mutual solvents which demand using a spacer before and after using the VES fluid. Secondly, the ferric iron will negatively affect the viscosity of the VES, therefore, it should not be mixed with high concentrations of the ferric iron (<100 mg/l) and clean tank and equipment should be used.

2- Treatment of horizontal wells with open hole completion

More than 100 wells have been treated and the authors pointed out that usage of the VES-based acid demands fewer stages than the other diverters, can save approximately
Two days of rig time, decreases the friction losses in the coiled tubing and required less acid volume which makes using the VES-based acid operationally preferable.

3- **Stimulation of extended-reach wells**

The treatments of horizontal wells by using coiled tubes and VES-based acid were conducted and several lessons were extracted from them. Firstly, the acid additives and their effects on/by the rubber seals of the tractor should be examined. Secondly, the length of the tractor can help in avoiding the CT’s stuck in the washouts process and finally using the mechanical diversion with the chemical one was very effective in getting rid of the drilling mud filter cake in horizontal wells.

4- **Using VES in deep sour gas well**

Treating deep and sour gas wells showed that using VES-based acid was so effective in stimulating these types of wells, moreover, the cleaning up processes were so fast and short when compared to other diverting agents. Furthermore, The VES had fewer friction losses thus significantly decreased the hydraulic HP that required to frack the formations.
Effects of the additives on the rheology properties of the VES-based acid

1- Effect of the shear rate on the apparent viscosity

Nasr-EL-Din et al. (2007) reported that the apparent viscosity of the live acid and spent acid is independent of the shear rate history in the room temperature, same result was concluded by L. Li et al. (2010), however, the apparent viscosity values showed different values when obtaining during the increasing shear sweep than decreasing sweep at 100 c (Nasr-EL-Din et al. (2007)) which indicates that the surfactant micelles didn’t go back to their original status when the shear rate was decreased.

2- Effect of the surfactant concentration

The acid was found to behave as Newtonian fluid when the surfactant concentration was below 3 vol%, although the viscosity of the acid when the surfactant concentration was 1 vol%, was less than 2 vol% (Nasr-EL-Din et al. (2007)). Thus, the surfactant concentration is an important factor that gives the acid the shear-thinning behavior because in high concentration there are enough micelles to entangle.

3- Effect of the pressure

Al-Sadat et al. (2014) investigated the effect of the pressure on the rheological properties of the viscoelastic surfactant and the noticed that there were slightly increase in these properties in high pressures (500 & 1000 psig) which reinforce the fact that the pressure has a little effect on the fluids viscosities.
4- Effect of the corrosion inhibitors

The effects of two types of the inhibitors on life and spent viscoelastic surfactant–based acid was tested by Nasr-El-Din et al. (2008). The result showed the effects of the acid inhibitors depend on of both the inhibitor type and the temperature.

5- Effect of the different additives

Nasr-EL-Din et al. (2008) studied the effect of various additives on the spent and live VES acid. In live acid, the mutual solvent and Fe (III) reduced the apparent viscosity under all temperature range while the Citric acid increased the viscosity and non-ionic surfactant increased the viscosity at 100 c. The demulsifiers and an anionic surfactant greatly reduced the apparent viscosity of the spent acid while the Citric acid and iron control agents slightly reduced it. The mutual solvent found to break the surfactant micelles almost entirely, therefore, the apparent viscosity of the spent acid found to be equal to the water viscosity (approximately) after adding the mutual solvent.

6- Effect of the methanol

Low concentration of methanol increased the spent acid’s viscosity at a temperature more than 150 F while the high concentration reduced the viscosity and caused phase separation (Nasr-EL-Din et al. 2008). This result was sustained by Al-Sadat et al. (2014) when they found that increasing the methanol concentration to 20.0 wt% in salt-free environment reduced the acid viscosity by more than 70% even they studied different VES system.
7-Effect of the temperature

The effect of the temperature on the VES acid system has been widely studied since the high temperature presents a limitation of the matrix acidizing in general. Li et al. (2010) reported an increasing in the VES system viscosity when the temperature is increasing to reach its peak at 135 F then decreased dramatically to reach the viscosity of the water at 194 F at a constant shear rate 10 S-1. Nasr-EL-Din et al. (2008) examined a different VES system type; however, they noticed a slightly similar result when the apparent viscosity of the spent and live surfactant system increased and reach its peak at around 160-170 F then decreased and in some case formed the second peak.

In 2005 (Kalur et al.) attributed the increasing in the viscosity of the viscoelastic surfactant and binding salt solution to the growth of the length of cylindrical micelles after studying the rheological properties of the solution and the length of the growth micelles that associated with the viscosity, Nasr-El-Din et al. 2008 referred this to the restructure of the surfactant micelles and/or distribution of the ions around the micelles.

In 2016 (Wei et al.) studied the rheological properties of the solution of different chain length of cationic Gemini surfactant, 2-hydroxypropyl-1, 3-bis (alkyldimethylammonium chloride) (n-3(OH)-n (2Cl) with the organic salt. The study has been conducted to n= 12, 14 and 16 and interpreted the presence of the second peak. For the system with n= 12, the viscosity decreased when the temperature increased. The system with n=14 is transparent under different concentrations, isotropic under a polarizing microscope and is shows
Birefringent phenomena. The system of \( n = 16 \) appeared as an opalescent gel in low temperature and showed viscoelastic properties.

The authors used the figure below to show the apparent viscosity change with temperature for these systems at zero shear rates:

![Graph showing zero-shear rate viscosity of different systems under different temperatures](image)

**Fig. 11: Zero-shear rate viscosity of different systems under different temperatures**

(Wei at al.2016).

From the rheological test, the studied shows that the viscosity of the \( n=14 \) system decreased with temperature until it reached 27 C then increased with the increasing in temperature and then started decreasing after reaching its summit. Same trends were observed on the \( n=16 \) system although the viscosity wasn’t measured below 30 C temperature. These trends were attributed by the authors to the changes in the structure of
The system based on Cryo-TEM and conductivity tests results and these changes can be summarized in many stages:

1- In low temperature, the chloride ion and hydroxyl groups in the system and crystallized water molecules formed herringbone-like micelles to cylindrical worm-like micelles.

2- The increasing temperature disrupts the hydrogen bond and releases some counterions which let to dissociated micelles structure.

3- When the viscosity is reduced to its peak the increasing in temperature lead to disordering of the micelles and maximize the end cap energy then those micelles formed a network structure which increases the apparent viscosity of the system in the narrow temperature range.

4- When temperature increases the network, structure returns to spherical or rod-like micelles.

The authors used the figure below to explain these stages:

![Mechanism of micelles formation](image)

**Fig. 12: Mechanism of micelles formation (Wei at al.2016).**
CHAPTER III

THE PROJECT OBJECTIVE

This project aims to evaluate the ability of five new types of viscoelastic surfactants to divert the acid inside the high-temperature formations. These Chemicals are R&D chemicals which were produced by OXITENO company who sponsored the project to be used in matrix acidizing treatments.

The Evaluation will be through studying the change in the Rheological properties of these various viscoelastic surfactants types due to the change in the shear rate at high temperatures (more than 2000F).

Secondly, the effect of various corrosion inhibitors on the rheological behaviors of the promising VES is to be studied.

Thirdly, after evaluating the Rheological properties, the behavior of the promising Viscoelastic surfactants is to be studied and examined inside the different formations through core-flood tests.
CHAPTER IV
EXPERIMENTAL SECTION

Materials
The new types of the viscoelastic surfactants, HCL acid, CaCO3, CaCl2, corrosion inhibitors, ROOT Blender, HT/HP Viscometer, Zeta potential, and core-flood system.

Methodology

Spent acid preparation study

a- The viscoelastic surfactant based acid. The mixture was prepared by adding 6% vol corrosion inhibitor, other additives, and 6% volume of the surfactant to the 15% wt. HCl acid.

b- Spent surfactant based Acid: Three methods were used to prepare the spent surfactant based acid (Nasr-El-Din2008). The Three methods were evaluated first by using control viscoelastic surfactant to select the optimal method to prepare the VES samples:

Method 1:

The VES-based live acid was prepared by adding 5% volume of the viscoelastic surfactant to 15% wt HCL, then the CaCO3 was added to the solution slowly while the system was being mixed by laboratory blender. The CaCO3 was being added until the PH of the solution reached 4.5.
Method 2:

The required quantity of CaCl$_2$ was calculated then added to the deionized water to simulate the spent acid.

The reaction of the HCL with CaCO$_3$ is shown by the following equation (Nasr-El-Din et al. 2008):

\[
2 \text{HCl} + \text{CaCO}_3 \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}
\]

The density of 36.5\% HCL acid is given as 1.18 gm/ml, therefore, to calculate the density of the 15\% wt. HCL; the density of the water assumed to be 1 gm/ml, then 15/36.5 percent of 36.5 HCL was added to the water.

The density of 15\% wt. HCL = \( .411 \times 1.18 + .589 \times 1 = 1.074 \) gm/ml which approximately equal the value that has been written in the literature.

To calculate the amount of CaCl$_2$ that is required to simulate 100 ml of the acid the following steps were conducted:

- The mass of 15\% wt. HCL that was used = 1.074 gm/ml \times 95 ml = 102.032 g (15.3 g of HCL and 86.727 g of H2O)
- The number of moles of HCL = 15.3 g/36.5 g/mole = 0.41918 moles.
- The number of moles of CaCl$_2$ = 0.41918/2 = 0.20959 moles.
- The mass of CaCl$_2$ = 0.20959 \times 111 = 23.26 g.
- The percentage of CaCl$_2$ = 23.26/(86.727 + 3.77262 + 23.26) = 20\%.

Method 3:

200 ml of the acid system was prepared by adding CaCO$_3$ to the live acid in the warring blender until the PH reached 4.5 then the viscoelastic surfactant was added.
Quickly to the solution then the PH was measured again to ensure that it's between 4 and 5. Then the sample was left for 20 minutes to allow the gas to come out of the sample before putting the sample in the centrifugal device for 5 minutes and 3000 rpm.

After preparing the spent acid all the samples were put in the viscometer and exposed to three different temperatures: 100, 200 and 300. In each temperature, the shear rate was measured at a low value as 10 s$^{-1}$ and then increased stepwise to reach 800 s$^{-1}$ and then down-sending to 10 s$^{-1}$.

After preparing the spent VES based acid and life VES based acid, the Rheological properties of both of them were measured using Grace M5600 Viscometer.

The methods of measuring were conducted by adjusting the viscometer to different temperatures and different shear rates before running the viscometer.

The data were analyzed and interpreted and the results of the comparison were summed up.

Rheological experiments

A commercial calcium Chloride CaCl$_2$.2H$_2$O (MW 147.01 g/mole) was used to prepare 15% wt spent acid. 5 types of VES were used to prepare the samples. The VES was added to the spent acid quickly to avoid the generation of the unwanted foam. The pressure was maintained at 400 psi since the pressure has an insignificant effect on the VES (Al-Sadat et al.2014). Many droplets of HCL were added to the solution to adjust the PH to be ranged from 4 to 5 in order to simulate the conditions where the rod-micelles are formed (Nasr-
El-Din et al. 2008). The PH of the solution before the surfactant was added was 5.7 to 6. After adding the viscoelastic surfactant, the PH changed insignificantly except in one type where the PH dropped to be 4.35 as shown in the table below:

<table>
<thead>
<tr>
<th>VES type</th>
<th>PH before adding the VES</th>
<th>PH after adding VES</th>
<th>PH after adding drops of HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>VES001</td>
<td>5.7</td>
<td>5.6</td>
<td>4.84</td>
</tr>
<tr>
<td>VES002</td>
<td>5.7</td>
<td>5.74</td>
<td>4.79</td>
</tr>
<tr>
<td>VES003</td>
<td>5.84</td>
<td>4.35</td>
<td>4.35</td>
</tr>
<tr>
<td>VES004</td>
<td>6</td>
<td>5.9</td>
<td>4.3</td>
</tr>
<tr>
<td>VES005</td>
<td>5.75</td>
<td>8</td>
<td>4.6</td>
</tr>
</tbody>
</table>

A centrifuge device was used after the samples had been prepared at 5000 rpm for 10 minutes to make sure that all the gas bubbles and foam have been removed from the sample.
An HP/HT rheology viscometer was used to measure the rheological properties of these samples at temperatures of 200 and 250°F. To measure the viscosity as a function of the shear rate; in each temperature, the shear rate was increased in step-wise to peak at 900 s⁻¹. Once the maximum shear rate was reached the shear rate was gradually decreased and the viscosity was constantly measured.

The experiments on the first type were conducted several times in order to understand the real properties of this type since it showed promising results at 200°F and to eliminate the generated foam. In the first time, the rheological properties were measured directly after preparing the methods while in the second time and the third time was measured after 1 and 2 days respectively.

![Rheological properties measurements steps and setup](image)

*Fig. 13: Rheological properties measurements steps and setup*
Effect of various inhibitors on the VES

- 15% wt. HCl VES-based spent acid was prepared as had been described above, then 6% volume of various inhibitors (CI-25, CI-35, and IEA600) were added to the spent acid system.

- With each inhibitor, the viscosity as a function of the temperature was measured between 75 and 310 °F.

- The pressure was kept constant at 400 psi, while the share rate was kept stagnant at 87 s⁻¹.

Core-flood Test

Different Indiana limestone cores were used to simulate the performance of the VES inside the formation.
Fig. 14: Core-flood setup.

The core-flood test steps:

- Firstly, the weight of the cores was measured and recorded.
- The cores were put in an oven with 212°F for 24 hours.
- The weight was measured again and the cores were put back at same conditions.
- The core samples were weighted again to make sure they are completely dry.
- The core samples were saturated with water for 24 hours and weighted again.
- Core-flood test was conducted on each core using deionized water at constant flow rate 1 cm³/min, 2 cm³/min then 3 cm³/min.
- The overburden pressure was kept at 800 psi while the backpressure was kept at 400 psi.
- The core samples were weighted again and the permeability and porosity of each core were calculated.
- CT scan was conducted on each core.
- The acid system was prepared and the acid components are shown in the table below.
- The DI-water overburden pressure was kept constant at 1600 psi while the backpressure was kept stagnant at 800 psi.
- DI-water was injected until the pressure drop stabilized then the acid was injected, when the acid had broken through the injection was altered to the DI-water immediately.
- The tests were conducted at 200°F and Flow rate of 2 ml/min.
- CT-scan was conducted again to indicate the wormhole formation.
<table>
<thead>
<tr>
<th>Table. 4: Live acid system components</th>
</tr>
</thead>
<tbody>
<tr>
<td>6% vol viscoelastic surfactant.</td>
</tr>
<tr>
<td>.6% vol CI-25 corrosion inhibitor.</td>
</tr>
<tr>
<td>15% wt. hydraulic acid.</td>
</tr>
</tbody>
</table>
CHAPTER V
RESULTS AND DISCUSSION

Spent acid preparation methods experiments results

The result at 100°F can be seen through the figures below:

Fig. 15: Comparison of the apparent viscosity of VES control type using the three preparation methods at 100°F temperature.
Fig. 16: Apparent viscosity of VES control type using the First Method of preparation at 100°F temperature.
Fig. 17: Apparent viscosity of VES control type using method 3 of preparation at 100°F temperature.
Fig. 18: Apparent viscosity of VES control type using the method 2 of preparation at 100°F temperature.
The figures below illustrate the result at 200°F:

**Fig. 19:** Comparison of the apparent viscosity of VES control type using the three preparation methods at 200°F temperature.
Fig. 20: Comparison of the apparent viscosity of VES control type using Method 2 at 200°F temperature.
Fig. 21: Comparison of the apparent viscosity of VES control type using Method 1 at 200°F temperature.
Fig. 22: Comparison of the apparent viscosity of VES control type using Method 3 at 200°F temperature.
The figures below show the results at a temperature of 300°F:

![Viscosity vs Shear Rate](image)

**Fig. 23:** Comparison of the apparent viscosity of VES control type using the three preparation methods at 300°F temperature.
Fig. 24: Comparison of the apparent viscosity of VES control type using the method 1 at 300°F temperature.
Fig. 25: Comparison of the apparent viscosity of VES control type using the method 2 at 300°F temperature.
Fig. 26: Comparison of the apparent viscosity of VES control type using method 2 at 300°F temperature.
Spent acid preparation methods results discussions

Advantages and disadvantages of each method

<table>
<thead>
<tr>
<th>Table. 5: The advantages and disadvantages of preparation methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>method</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>Method 1</td>
</tr>
<tr>
<td>Method 2</td>
</tr>
<tr>
<td>Method 3</td>
</tr>
</tbody>
</table>
The conclusions of the experiments

1- The three methods showed the same results approximately, and the measurements differences can be attributed to the slight differences in the PH or the preparation methods.

2- In 100°F temperature, the sample 1 and 2 showed low viscosity in low high rate in the beginning which can be attributed to the insufficient time that was taken by the viscometer to reach the wanted temperature.

3- In 300°F temperatures, the third method showed approximately fewer viscosities than the other two methods which may indicate that not all amount of the CO2 has escaped from the fluid.

4- In the case of comparison between different types of the fluids, any method can be used if it is conducted to all fluids.

5- Method number 1 takes a lot of time; therefore, method 2 or 3 is suggested to be used.
Part 2: Evaluations of the new VES generation

The evaluation of the rheological properties of the new generations of VES

The first type VES001 generated a lot of foam when it was added to the spent acid. Although the fluid mixing was 200 cm$^3$ which it was way below the 500 cm$^3$ that were reported to be a maximum amount mixing to avoid the foam generation (Nasr-EL-Din et al. 2008). The result showed a high viscosity (120 cp) at a temperature of 200°F and shear rate of 10 s$^{-1}$. To fully evaluate this type, many techniques were used to get rid of the generated foam or/and to prevent foam generation. At the first time, the only amount of 50 cm$^3$ Fluid mixing was prepared then the test was conducted again. At the second time, the sample was heated while mixing using a stirring device. At the third test, the sample was left for 2 days before it was tested. In all tests, the PH was maintained at 4.8 to have an excellent comparison. Roughly, the VES showed similar results and the average results are shown in figure 1 below:
Fig. 27: Apparent viscosity of type 1 at 2000°F as a function of the shear rate, this is average since the test was repeated several times using various techniques to get rid of the generated Foam. All the results showed the quite same result.

At 250°F, the VES001 didn’t show any viscosity building. Also in this temperature, the apparent viscosity profile when in decreasing shear sweep was totally different than the increasing shear sweep viscosity profile. This means that when the micelles are destroyed by the high shear rates, they could not return to the first structure when the shear rate is reduced (Nasr-El-Din et al.2008) as shown in figure2.
Fig. 28: Apparent viscosity of type 1 at 250°F as a function of the shear rate, the high apparent viscosity was 5 cp which shows a weak viscosity building.

Figure 3 and 4 show the result of type 2 (VES002) at 200 and 250°F, respectively. At both temperatures, this type didn’t show any viscosity Building. Furthermore, at both temperatures, there was a hysteresis (fig.3, fig.4), and the viscosity through the decreasing sweep was totally different than increasing sweep similar to VES001 at 250°F. This performance questions the ability of these types to divert the acid into the targeted formation.
Fig. 29: Apparent viscosity of type 2 at 200°F as a function of the shear rate, low viscosity is shown.
Both Type 3 and 4 showed similar performances; they were dependent on the history of the shear rates at both temperatures. In 200°F they didn’t show any viscosity building and their apparent viscosity equaled the viscosity of the water approximately (Fig.5, Fig.7). However, in 250°F they showed a high viscosity building (more than 120 cp) at a shear rate of 10 s^{-1}. But the viscosity was dropped significantly in the next shear rate steps (more than 100 s^{-1}). Fig.6 and Fig.8 illustrate the performances of these types at 250°F.

**Fig. 30: Apparent viscosity of type 2 at 250°F as a function of the shear rate, low viscosity is shown.**
Fig. 31: Apparent viscosity of type 3 at 200°F as a function of the shear rate, almost shows the viscosity of the water; no viscosity building was observed.
Fig. 32: Apparent viscosity of type 3 at 250°F as a function of the shear rate, this type shows a high viscosity building in a shear rate of 10 s\(^{-1}\); however, it shows very low viscosity in the other rates and approximately viscosity of the water in the decreasing shear rate sweep.
Fig. 33: Apparent viscosity of type 4 at 200°F as a function of the shear rate, it shows no viscosity building in all shear rates.
Fig. 34: Apparent viscosity of type 4 at 2500°F as a function of the shear rate, this type shows a high viscosity building in a shear rate of 10 s⁻¹, however, it shows roughly the water viscosity in the other rates.
Type 5 results

Low acid stability was observed during the preparation of the spent acid since the acid was separated into 2 phases; mechanical mixture had been used to mix the acid before the rheological test was conducted. However, this type showed a unique result comparing to the other types, firstly at 200°F temperatures, the viscosity was independent of the shear rate history, in other words, the micelles returned to the previous structure when the shear rate was decreasing. However, at a temperature of 250°F, there was a hysteresis and the viscosity during the increasing sweep was notably different than the decreasing shear rate sweep.

Secondly, this type showed a high viscosity at low shear rates like 10 s⁻¹ and a moderate viscosity at higher shear rates (more than 100 s⁻¹). This gradually dropping is different than the other types where the shear rate dropped significantly even if it showed a high viscosity at low shear rates. Fig.9 and Fig.10 below show the viscosity profile of this type in 200 and 250°F temperatures, respectively:
Fig. 35: Apparent viscosity of type 4 at 2000F as a function of the shear rate, this type shows a high viscosity in 2000F temperature, also the viscosity was being building back when the shear rate was decreased.
Fig. 36: Apparent viscosity of type 5 at 250°F as a function of the shear rate, this type shows a higher viscosity in 2500°F temperature than 2000°F, however, there is hysteresis; the viscosity wasn't being built back when the shear rate was decreased.

To fully understand the rheological behaviors of this type, an apparent viscosity profile as a function of temperature was examined, the shear rate was chosen to be 10 s⁻¹ since this type showed a high viscosity in this shear rate. However, the sample that was used had been prepared 3 days before the test was generated, therefore, the result was higher than
The previous test when the test was conducted right after the sample had been prepared. Fig. 11 illustrates the result of the test which indicates that the first peak was reached at a temperature of 178°F, yet there is more than one peak which is compatible with one of the unique properties of the viscoelastic surfactant (multiple peaks in the viscosity-temperature profile).

**Fig. 37: Viscosity of Type 5 VES005 as a function of temperature, the first peak was reached at 178°F.**
The effect of the inhibitors on VES005 result and discussions

Since only VES005 showed promising results, more experiments including core-flood tests were suggested to be conducted on it. Therefore, using corrosion inhibitors became a necessity since metal equipment was going to be used in the further studying.

Three types of commercial corrosion inhibitors (CI-25, CI-35, and IEA600) on VES005 were selected based on the literature reviews and previous works in our lab.

The effects of these inhibitors were studied by adding 6% volume of the inhibitors to the spent acid system, then the impact of these types on the spent acid system was evaluated at wide range of temperature (75 to 310 °F), shear rate of 87 s⁻¹ while the pressure was kept constant at 400 psi.

The results of the experiments are illustrated in the figure below:
As it can be seen from the figure, the IEA-600 inhibitor resulted in a high decrease in the performance of the spent acid. The CI-35 showed a positive impact on the viscosity building of the spent acid in low temperatures (until 200°F) then start to impact negatively on the performance of the spent acid system. While CI-25 showed no effect approximately on the spent acid system in all temperatures which make it a good candidate to be used with the acid system.
Core-flood tests result and experiments

The dry and saturated weights were used to determine the porosity of the cores, while the injection of the water with different flow rates was used to calculate the average permeability.

Porosity measurements

<table>
<thead>
<tr>
<th>Time of weighing</th>
<th>Core A</th>
<th>Core B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before drying</td>
<td>380.42</td>
<td>380.24</td>
</tr>
<tr>
<td>After 1st drying</td>
<td>380.21</td>
<td>380.00</td>
</tr>
<tr>
<td>After 2nd drying</td>
<td>380.18</td>
<td>379.97</td>
</tr>
<tr>
<td>After Di-water 24 hrs saturation</td>
<td>406.57</td>
<td>407.2</td>
</tr>
<tr>
<td>Porosity</td>
<td>.2639</td>
<td>.2723</td>
</tr>
</tbody>
</table>
Permeability measurements

Fig. 39: The pressure drop at different flow rates when the DI-water was injecting through Core A.
Fig. 40: The pressure drop at different flow rates when the DI-water was injecting through Core B.
The measurement details are shown in the table below:

<table>
<thead>
<tr>
<th>core</th>
<th>flow rate cm$^3$/s</th>
<th>Area cm$^2$</th>
<th>Length cm</th>
<th>pressure atm</th>
<th>Permeability Darcy</th>
<th>Permeability mD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core B</td>
<td>0.0167</td>
<td>11.395</td>
<td>15.24</td>
<td>1.79</td>
<td>0.012</td>
<td>12.389</td>
</tr>
<tr>
<td></td>
<td>0.033</td>
<td>11.395</td>
<td>15.24</td>
<td>3.57</td>
<td>0.0125</td>
<td>12.486</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>11.395</td>
<td>15.24</td>
<td>5.371</td>
<td>0.0125</td>
<td>12.451</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average permeability, $K_i$ 12.44</td>
</tr>
<tr>
<td>Core A</td>
<td>0.0167</td>
<td>11.395</td>
<td>15.24</td>
<td>0.176</td>
<td>0.126</td>
<td>126.36</td>
</tr>
<tr>
<td></td>
<td>0.033</td>
<td>11.395</td>
<td>15.24</td>
<td>0.281991</td>
<td>0.15809171</td>
<td>158.09</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>11.395</td>
<td>15.24</td>
<td>0.3958</td>
<td>0.16896</td>
<td>168.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average permeability, $K_i$ 151.137</td>
</tr>
</tbody>
</table>

**Shear rate calculations**

The shear rate is calculated by the following equation (Rojas et al. 2008 & Yu et al. 2010):

$$\dot{\gamma} = \frac{u}{\phi L}$$
Where \( u \) is Darcy velocity (m/s), \( L \) is characteristic length (0.05 \( K^{0.5} \))

<table>
<thead>
<tr>
<th>Core sample</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity, Volume fraction</td>
<td>0.2639</td>
<td>0.2723</td>
</tr>
<tr>
<td>Injection rate, ( \text{Cm}^3/\text{min} )</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Permeability, ( \text{mD} )</td>
<td>151.14</td>
<td>12.44</td>
</tr>
<tr>
<td>Shear rate, ( S^{-1} )</td>
<td>180.41</td>
<td>609.1</td>
</tr>
</tbody>
</table>

### Table. 8: Properties of the core samples/ shear rate measurements

**The core-flood test results and discussions**

The VES showed an excellent diverting performance through the low permeability core (Core B), that can be indicated by the enormous tortuosity of the pressure drop (Fig. 40). At the beginning of the acid injection, the pressure drop increased as a result of the acid viscosity which is higher than the water viscosity. Once the wormhole was created the pressure drops started decreasing. However, when the acid and formation reaction moved on the calcium cations \( \text{Ca}^+ \) and the PH increased, therefore, the VES formed rod-wormlike micelles which increased the viscosity expressively. This resulted in an observed pressure drop increases. Then the acid
created another wormhole and the processes were repeated again until the acid broke through the core. A similar result was shown by the Core A; however, less pressure drop zigzag was observed (Fig. 39) which means less in-situ viscosity building.

Fig. 41: Pressure drop across Core A during core-flood test.
Scanning

The CT-scan has reinforced the observations that were known from the pressure drop profile through the core-flood tests. When the core A was scanned one dominant wormhole was observed through the core. The wormhole kept changing its direction slightly, however, multiple small wormholes were created through the core. Additionally, the diameter of the wormhole decreased significantly from the inlet to the outlet of the core. At the outlet, multiple wormholes were clearly observed (Fig. 41).

Fig. 42: Pressure drop across Core B during core-flood test.
The propagation of the wormhole through low permeability core B was much excited when it's seen through CT-Scan. The dramatic tortuosity of the wormhole was clearly observed (Fig. 42) since the acid deviated its direction multiple times and took quite different paths. Multiple small wormholes were observed through the cores.

Fig. 43: CT scan images of Core A after treatment.
Fig. 44: CT scan images of Core A after treatment.
Fig. 45: Outlet and Inlet of Core A after the test with 6% Vol% VES-based 15% HCl.
Fig. 46: Outlet and Inlet of Core A after the test with 6% Vol% VES-based 15% HCl.
Conclusions

1- Type 4 and 3 (VES004 and VES003) showed similar performance approximately; they built a high viscosity (120 cp) at a temperature of 2500F and shear rate of 10 s⁻¹. However, no viscosity building was observed at 2000F.

2- Type two (VES002) didn’t show any viscosity building in 200 and 2500F temperature.

3- Type 5 (VES005) showed promising rheological properties in 200 and 2500F, however, it is independent of the shear history just in 2000F.

4- The viscosity building of VES005 increases with temperature, the peach wasn’t reached although the test was conducted at 3600F.

5- The inhibitor CI-25 showed the non-negative effect on VES005 viscosity at a shear rate of 87s⁻¹ up to 3100F.

6- The core flood tests showed a limited diverting performance of VES005 in high permeability core (150 mD) and High diverting performance in low permeability core (12 mD) when the acid changed its directions several times and wormholes were observed through CT scan.

7- Based on the lab test, VES005 is highly recommended to be used as a diverting agent for high-temperature formations. While VES004 and VES003 performance are limited to low shear rate.
**Future work**

1- The lab test should be continued through studying the effects of the other additives on VES005.

2- The dual core-test can be conducted to examine the performance of the VES in different permeability zones in the same formations.

3- The evaluations through the core-tests can be done at higher temperatures.

4- The pilot test and field experiments can be done to reinforce the lab tests studies.
REFERENCES


https://doi.org/10.2118/56533-MS.

https://doi.org/10.2523/95006-MS.


https://doi.org/10.2118/89418-PA.


SPE-38622-MS.pdf. (n.d.).


