

**FUNCTIONALIZED POLYMER-BASED MATERIALS**

**AS SCALE AND CORROSION INHIBITORS**

BY

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**MASTER OF SCIENCE**

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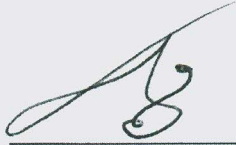
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This work is dedicated to my beloved parents.

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## LIST OF ABBREVIATIONS

<b>TGA</b>	:	Thermal Gravimetric Analysis
<b>FTIR</b>	:	Fourier Transform Infrared Spectroscopy
<b>XRD</b>	:	X-Ray Diffraction
<b>SEM</b>	:	Scanning Electron Microscopy
<b>TEM</b>	:	Transmission Electron Microscopy
<b>EDX</b>	:	Energy Dispersive X-Ray
<b>IE</b>	:	Inhibition Efficiency
<b>CR</b>	:	Corrosion Rate
<b>mpy</b>	:	Miles per Year
<b>NMR</b>	:	Nuclear Magnetic Resonance

## ABSTRACT

Full Name : [NADHEM ABDULHAMEED ABDO ISMAIL]  
Thesis Title : [FUNCTIONALIZED POLYMER-BASED MATERIALS AS SCALE AND CORROSION INHIBITORS]  
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The aim of this work is to introduce the synthesis and testing of functionalized chemical inhibitors for the inhibition of calcium carbonate, iron sulphide and carbon steel corrosion. Calcium carbonate is a scale which can form in the oil and gas industry tubulars. The scale is a mineral deposit that can occur in the tubing, pipelines and valves which hinders the flow of fluid leading to shut down and production loss. Calcium carbonate Scale usually happens in production and injection wells. Calcium carbonate scale precipitates when there is a pressure and temperature change, mixing of incompatible water and dehydration. The test method followed is static bottle test in which two incompatible cationic and anionic waters are mixed. It is important to know that the inhibitor used must be compatible with these waters (does not form a precipitate or cause phase separation).

In this work, different functionalized chemical inhibitors were prepared and tested for compatibility before inhibition screening test. After testing different chemicals for compatibility, the chemicals that are compatible with the brines were tested for inhibition at different inhibitor concentrations. The inhibition efficiency was calculated by the amount of calcium ions left in solution that is determined by chemical analysis (i.e.: ICP-OES).

The collected scale particles in the blank sample will be also characterized by different instrument including XRD, SEM and TEM. It is important to mention that a new polyacrylate based inhibitor was developed and tested towards calcium carbonate inhibition. This product showed a promising result at different temperatures and salts concentrations. The inhibitors were also tested at harsh environment. In addition, this study aimed in presenting more effective polymer material as inhibitor and dispersant of iron sulphide. L-glutamic acid grafted polyacrylamide has been synthesized and tested and found to be effective in preventing iron sulphide formation by hindering nucleation growth and preventing iron sulphide particles from settling. In order to evaluate the synthesized inhibitor performance a strictly anoxic experimental setup was successfully designed and implemented. Influence of temperature, pH and brine composition on inhibition was studied. The results show the potential ability of L-glutamic acid grafted acrylamide to inhibit iron sulphide formation and nucleation growth at various conditions. Moreover, the inhibitor was found to be effective in keeping iron sulphide particles apart at specific dosages thus lowering iron sulphide clustering. The results also show that the inhibitor is more effective at 60 C where maximum inhibition efficiency was recorded. At 60 C, the inhibition efficiency started at 60% at a relatively low concentration of inhibitor (i.e.50 ppm) after a reaction time of 16 hours. The inhibition efficiency was increased to 92% at 1% by volume inhibitor concentration. Based on these results, it is believed that this inhibitor will provide a novel chemistry for metal-sulphide scales. In the third part of this work, the effect of gallic acid-grafted polyacrylamide (GAGP) on carbon steel corrosion in 1 M hcl has been studied using weight loss, potentiodynamic and polarization resistance measurements. Both techniques showed an excellent agreement. Experimental results

showed that GAGP has worked effectively in the acidic environment. It was found that the inhibition efficiency increased with concentration. The process of inhibition is attributed to the adsorption of the inhibitor molecules and/or formation of complex at the electrode surface.

## ملخص الرسالة

الاسم الكامل: ناظم عبد الحميد عبده اسماعيل.

عنوان الرسالة: بوليمرات وظيفية لتثبيت تآكل الحديد الصلب وتثبيت ترسب الجير الحي وكبريتات الحديد في أنابيب التنقيب عن النفط والغاز.

التخصص: هندسة كيميائية.

ديسمبر 2020:

الهدف من هذا العمل هو صناعة واختبار المثبطات الكيميائية الوظيفية لتثبيت كربونات الكالسيوم وكبريتيد الحديد وتآكل الصلب الكربوني. كربونات الكالسيوم عبارة عن ترسبات يمكن أن يتشكل في أنابيب التنقيب عن النفط والغاز. المواد التي من الممكن أن تتشكل هي عبارة عن رواسب معدنية يمكن أن تحدث في الأنابيب وخطوط الأنابيب والصمامات مما يعيق تدفق النفط أو الغاز مما يؤدي إلى الإغلاق وفقدان الإنتاج. تتكون كربونات الكالسيوم عادة في آبار الإنتاج والحقن. ترسب كربونات الكالسيوم عندما يكون هناك تغير في الضغط ودرجة الحرارة ، وخط الماء غير المتوافق في التركيب. طريقة الاختبار المتبعة هي اختبار التثبيت الثابتة حيث يتم خلط اثنين من المياه الكاتيونية والأنيونية غير المتوافقة. من المهم معرفة أن المانع المستخدم يجب أن يكون متوافقاً مع هذه المياه (لا يشكل راسباً أو يسبب فصلاً في الطبقات) .في هذا العمل ، تم تحضير مثبطات كيميائية وظيفية مختلفة واختبار توافقها قبل اختبار فحص التثبيت. بعد اختبار مواد كيميائية مختلفة من أجل التوافق ، تم اختبار المواد الكيميائية المتوافقة مع المحاليل الملحية للتثبيت عند تراكيز مختلفة من المثبطات. تم حساب كفاءة التثبيت من خلال كمية أيونات الكالسيوم المتبقية في المحلول والتي يتم تحديدها بواسطة التحليل الكيميائي (أي . ICP-OES : سيتم أيضاً تمييز جسيمات الحجم المجمعة في العينة الفارغة بأداة مختلفة بما في ذلك XRD و SEM و TEM. من المهم أن نذكر أنه تم تطوير واختبار مثبط جديد قائم على البولي أكريلات لتثبيت كربونات الكالسيوم. أظهر هذا المنتج نتيجة واحدة عند درجات حرارة مختلفة وتركيزات أملاح مختلفة. تم اختبار المثبطات أيضاً في بيئة قاسية. بالإضافة إلى ذلك ، هدفت هذه الدراسة إلى تقديم مادة بوليمر أكثر فعالية كمثبط ومشتت لكبريتيد الحديد. تم تصنيع بولي أكريلاميد المطعمة بحمض L- الجلوتاميك واختباره ووجد أنه فعال في منع تكوين كبريتيد الحديد عن طريق إعاقة نمو النواة ومنع جزيئات كبريتيد الحديد من الاستقرار. من أجل تقييم أداء المثبط

المصنع ، تم تصميم وتنفيذ هيكل التجربه ليكون خالٍ من الأوكسجين بدقة. تمت دراسة تأثير درجة الحرارة ودرجة الحموضة وتركيب المحلول الملحي على التثبيط.

علاوة على ذلك ، وجد أن المثبط فعال في إبقاء جزيئات كبريتيد الحديد متباعدة عند جرعات محددة وبالتالي تقليل تكتل كبريتيد الحديد. أظهرت النتائج أيضًا أن المثبط يكون أكثر فعالية عند 60 درجة مئوية حيث تم تسجيل أقصى كفاءة تثبيط. عند 60 درجة مئوية ، بدأت كفاءة التثبيط عند 60% بتركيز منخفض نسبيًا للمثبط (أي 50 جزء في المليون) بعد زمن تفاعل مدته 16 ساعة. تمت زيادة كفاءة التثبيط إلى 92% عند تركيز 10000 جزء في المليون. بناءً على هذه النتائج ، يُعتقد أن هذا المانع سيوفر كيمياء جديدة لترسبات كبريتيد المعادن.



# CHAPTER 1

## INTRODUCTION

### 1.1 Scale Definition and Types

A scale is a solid mineral precipitate that forms from produced salt water in the oil and gas industry. Scale is persistent problem in the oil and gas industry because of the ability of water to dissolve salts which will precipitate when conditions such as temperatures and PH are altered [1]. There is a potential of scale to form wherever water production occurs[2]. Figures 1 and 2 show a scale in tubulars and pipes taken from SAUDI ARAMCO JOURNAL OF TECHNOLOGY

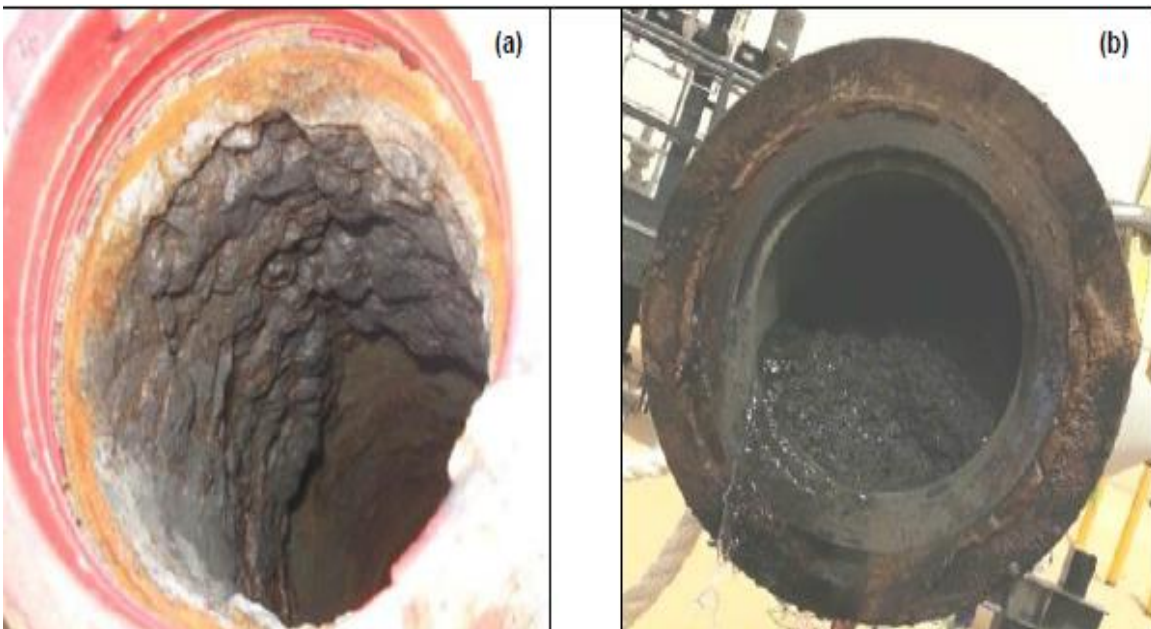
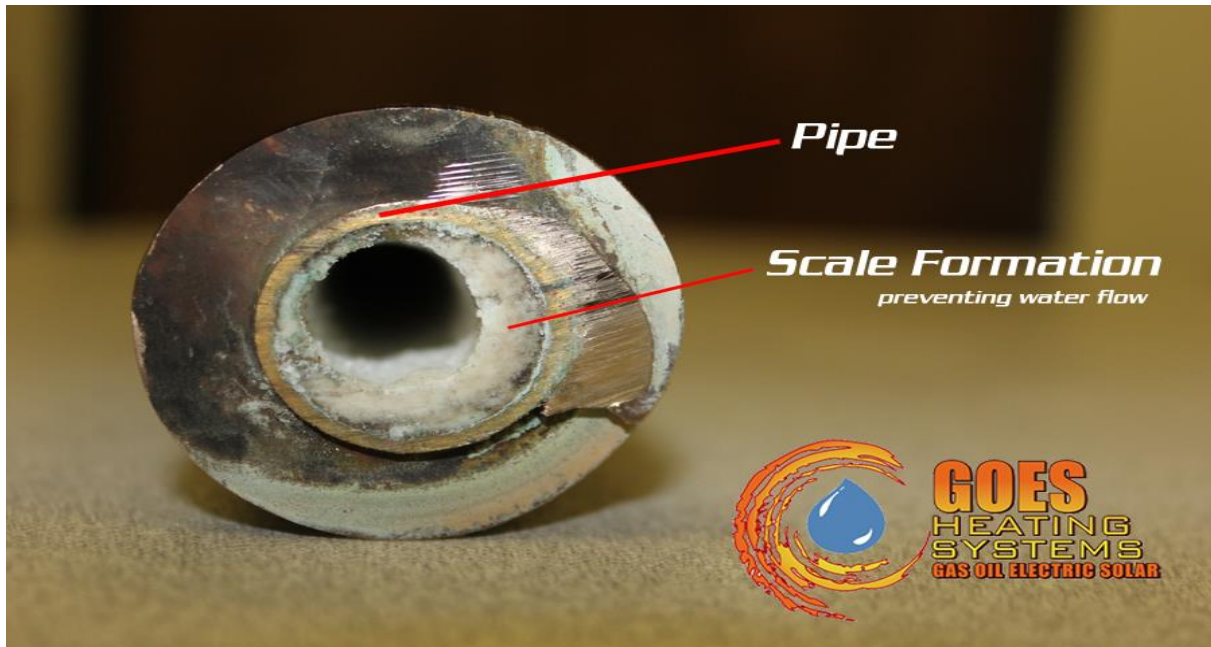


Figure 1:Scale precipitation in tubulars [3]



**Figure 2: Scale precipitation in pipes [4]**

There are different types of scales that can happen in the oil and gas industry. Table 1 shows the most encountered types of scales. This work will focus on the first type of scale which is calcium carbonate scale or calcite.

**Table 1: common oilfield scales[5]**

Category	Chemical formula	Mineral name
Carbonates	$CaCO_3$	Calcite
Carbonates	$FeCO_3$	Siderite
Chlorides	$NaCl$	Halite
Hydroxides	$Mg(OH)_2$	Brucite
Sulfates	$CaSO_4 \cdot 2H_2O$	Gypsum
Sulfates	$CaSO_4$	Anhydrite
Sulfates	$BaSO_4$	Barite
Oxides	$Fe_2O_3$	Hematite
Sulfides	$FeS$	Troilite

Scale forms due to the change of different conditions and factors such as pressure changes, temperature changes, PH changes, impurities, additives, changes in flowrates and mixing of compatible waters[6]. The former has the highest percentage among others especially in primary

production wells and injection wells. It causes the minerals in solution to form an insoluble precipitate. The precipitate deposits in the wellbore or the well pump. Scale can develop almost immediately, or it can build up over several months before becoming noticeable[7]. Calcium carbonates develops quickly and needs to be treated quickly as well to avoid shutdown and loss of production equipment. The effect of scale depends on location of deposition and the amount deposited. Scale can restrict and completely block fluid flow in tubing and flowlines[6], [8], [9].

Deposition of scale is a very costly problem. Stuck downhole pumps, plugged perforations and tubing strings, choked flowlines, frozen valves, equipment damage, and downtime during maintenance all contribute to cost. Scale restricts production and causes inefficiency and failure of production equipment[10]. As fields mature and require waterflood operations, the scale problems have an increased effect on well economics. Scale disposal can be quite costly. The most economical way to manage wells that tend to scale is to use an inhibitor to prevent the scale from forming [11].

Scales can be categorized into three different types water soluble, acid soluble and acid insoluble[2], [12]. This classification is rough since scale is rarely formed in its pure form. This classification is not accurate, but it is sufficient for lab analysis and experimental testing.

The scale deposit usually contains a mixture of scale categories in different percentages depending on conditions under which scale forms[13]. The most widely used method to identify types of scale in the lab is XRD instrumental method[14]. This method is fast and requires little amount of sample.

## 1.2 Characteristics of Calcium Carbonate

The most important characteristics of calcium carbonate scale that should be studied is solubility rates and precipitation tendencies. Oilfield problems with calcium carbonate ( $\text{CaCO}_3$ ) often center around its inverse solubility behavior [13], [15]. Calcium carbonate becomes less soluble at higher temperatures[16], . This behavior is depicted in Figure 1. The effect becomes more complicated when other precipitation factors are encountered [17]. In general, the following physical changes cause calcium carbonate scale to form [18]:

Pressure decreases, temperature increase, pH increase (such as the loss of  $\text{CO}_2$ ), Calcium concentration increase and Carbonate increase. Small changes in temperature can result in large quantities of calcium carbonate precipitation [20].

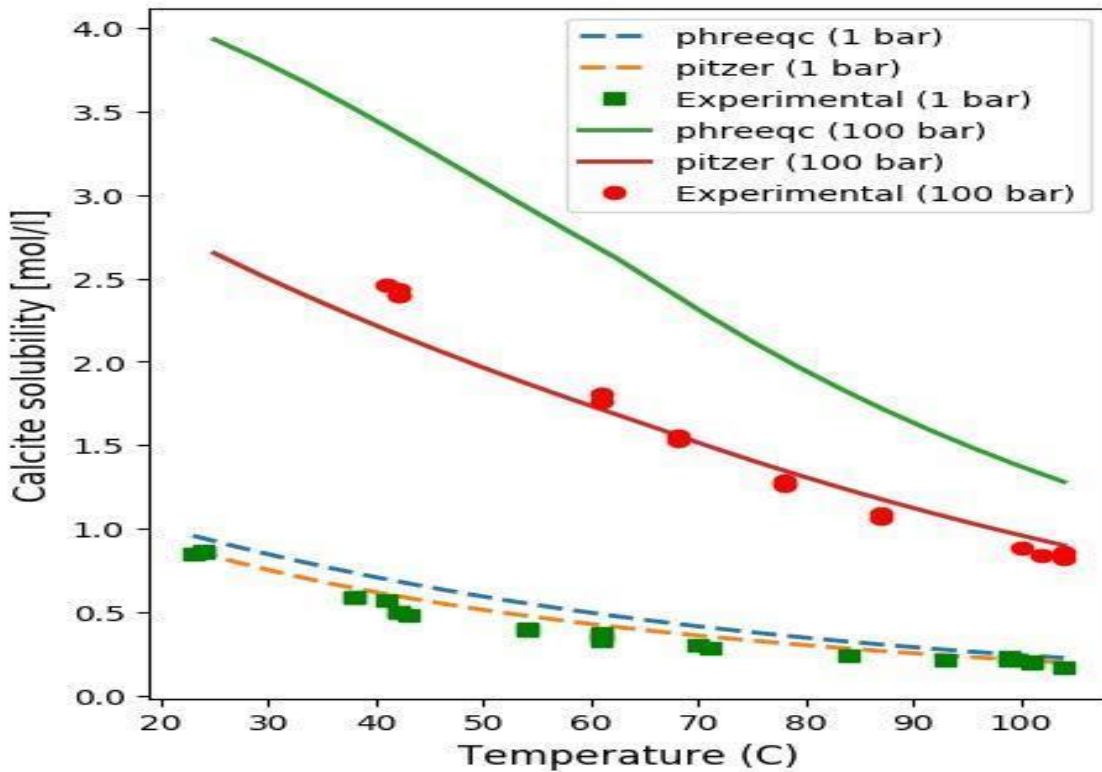


Figure 3: Calcite solubility vs Temperature [19]

Changes in the concentration of calcium or carbonates occur when waters from different zones mix at the wellbore, in surface collecting equipment[22].

### **1.3 Objectives**

This work aimed in formulating effective materials as scale and corrosion inhibitors such as calcium carbonate, iron sulfide scales, etc. The inhibition efficiency will be investigated. The specific objectives of this work are to:

- 1) Synthesize different polymer-based inhibitors including polyacrylate based polymers that have potential inhibition in different scales and corrosion media.
- 2) Characterize and evaluate the performance of the synthesized inhibitors towards scales such as calcium carbonate scale using the static bottle test method.
- 3) Evaluate the inhibitors at different environment conditions
- 4) collect the scale samples and do XRD, SEM and TEM characterization.
- 5) Evaluate the performance of the synthesized inhibitors towards CO<sub>2</sub> and H<sub>2</sub>S corrosion.

### **1.4 Methodology**

This section is subdivided into four parts. Each part will include an explanation of the preparation method and test method used

#### **1.4.1 Brines preparation**

There are two types of brines or synthetic waters, scaling and non-scaling brines used in this study. Scaling brine is a supersaturated brine in which at least one pair of scaling ions is present in an amount above its saturation concentration; the high concentration is to promote the

formation of scale crystals. Scaling brines are typically prepared for use in scale inhibitor selection projects via the Dynamic Scale loop or scale bottle test. Non-scaling brine is a non-saturated brine is a solution where all pairs of scaling ions are present in an amount below their saturation concentration. Non-scaling brines are used for compatibility test. The reagents used in the brine's preparation procedure are in table 3.

**Table 2: Reagents used for brine preparation**

<b>Cation chloride salts</b>	<b>Sodium anion salts</b>	<b>PH Adjustment Reagents</b>
NaCl	NaHCO <sub>3</sub>	1 M acetic acid solution
KCl	Na <sub>2</sub> CO <sub>3</sub>	0.1 M Sodium hydroxide
MgCl <sub>2</sub> .6H <sub>2</sub> O	Na <sub>2</sub> SO <sub>4</sub>	-
CaCl <sub>2</sub> .2H <sub>2</sub> O	Na <sub>2</sub> S.9H <sub>2</sub> O	-
SrCl <sub>2</sub> .6H <sub>2</sub> O	NaF	-
BaCl <sub>2</sub> .2H <sub>2</sub> O	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> anhyd	-
(FeCl <sub>2</sub> .4H <sub>2</sub> O)	CH <sub>3</sub> COONa.3H <sub>2</sub> O	-
(ZnCl <sub>2</sub> )	-	-
PbCl <sub>2</sub>	-	-
MnCl <sub>2</sub> .4H <sub>2</sub> O	-	-
LiCl	-	-

Not all the reagents in table 3 are used. The usage of the reagents depends on the targeted brines composition. Different scale tests need the use of suitable reagents. Sometimes the targeted environment is a mix between two or more scales.

### 1.4.2 Non-Scaling Brines

Non-scaling brine is used for compatibility test throughout this research work. Since the targeted scale is calcium carbonate, the reagents used are sodium chloride, potassium chloride, magnesium chloride hexahydrate, sodium bicarbonate and sodium sulphate. The amounts of reagents used depends on the interrelated ions concentrations. The ion concentrations and respective reagents amounts are listed in table 4.

**Table 3: Ion concentrations for compatibility test [49]**

Ion	Conc.(ppm)	Source(salt)	g-Salt(for 500 ml)
Na <sup>+</sup>	19047	Nacl	24.56
K <sup>+</sup>	703	Kcl	0.67
Mg <sup>2+</sup>	1286	Mgcl <sub>2</sub> .6H <sub>2</sub> O	5.38
Ca <sup>2+</sup>	3942	Cacl <sub>2</sub> .2H <sub>2</sub> O	7.23
Sr <sup>2+</sup>	62	Srcl <sub>2</sub> .6H <sub>2</sub> O	0.09
cl <sup>-</sup>	39119	-	-
SO <sub>4</sub>	1847	Na <sub>2</sub> SO <sub>4</sub>	1.37
HCO <sub>3</sub>	500	NaHCO <sub>3</sub>	0.34
TDS	66530		39.64

To prepare 500 ml of non-scaling brine for compatibility test, 500 ml beaker is filled up to 400 ml with DI water. A stirrer bar is added then the beaker is placed on the magnetic stirrer and the stirring speed is adjusted to get good homogeneity. Salts are weighed in a plastic weighting boat according to the amounts calculated in table 4. The weighting plastic boat is rinsed with DI water after each addition of salts to ensure that all salts are added to the brine. Once all salts are added, the beaker is filled up to 500 ml with DI water. The brine is filtered using 0.45 mm filter paper. After filtration, the PH is adjusted to the targeted value using sodium hydroxide or hydrochloric acid solutions.

### 1.4.3 Scaling Brines

Scaling brines are used for static bottle inhibition test and dynamic scale loop test during this work. The reagents used are the same as these used for compatibility test except that the amounts vary. Two scaling brines need to be prepared for inhibition tests. A cationic and anionic brine solutions are prepared separately each are 500 ml. The procedure of scaling brines preparation is the same as that for non-scaling brines, however the concentrations of ions and corresponding salts are given in table 5. Also, in the scaling brine preparation to 500 ml beakers are needed. The first one is used for cationic brine and the second one is used for anionic brine. Both brines are filtered after addition of all salts.

**Table 4 : Ions Concentrations for inhibition test**

<b>Salt</b>	<b>CW (g)</b>	<b>AW(g)</b>	<b>MIX(g)</b>
Nacl	8.83	43.254	52
Kcl	2.268	-	2.268
Mgcl <sub>2</sub> .6H <sub>2</sub> O	4	-	4
Cacl <sub>2</sub> .2H <sub>2</sub> O	39.12	-	39.12
Na <sub>2</sub> SO <sub>4</sub>	-	0.46	0.46
Fecl <sub>2</sub> .4H <sub>2</sub> O	0.01	-	0.01

### 1.4.4 Compatibility Test

Scaling Compatibility of the inhibitor is very important before testing the inhibitor efficiency. If the inhibitor is not compatible, it will aid the formation of scale instead of hindering it. An inhibitor that forms a precipitate or phase separation with the non-scaling brine is said to be not compatible and cannot be used for inhibition efficiency test. To do compatibility test, the oven is set to the intended test temperature for an hour before test to reach stability.

The required number of containers depends on the number of products and dosage concentrations being evaluated. 100 mL glass bottles are used for temperatures below 90 °C.

For tests conducted at temperatures between 90-150 °C, thick walled glass tubes must be used with high temperature, lined caps. Each container is clearly labelled; including the name of the chemical and the dose/concentration. A permanent marker is used to ensure the readability throughout the test.

The brine is added to each container; filled to no greater than 1/2 to 2/3 full to provide room for liquid expansion. Using a pipette or syringe, the inhibitor solution is added to the compatibility brine to reach the required concentration for the particular test. Used dose concentrations are 10 ppm, 100ppm, 1000ppm, 1% v/v and 10% v/v. At the higher doses, i.e. above 1%, the equivalent volume of brine is removed from the container before the inhibitor is added. A blank in every test is included where no inhibitor is added to the brine. observations of visual changes to the brine upon immediate injection of the scale inhibitor in a laboratory is recorded in a notebook. The containers are sealed and mixed by shaking bottles vigorously by hand. The containers are photographed, and the appearance of each tube is documented. Notes include the colour and clarity of the solution and any evidence of incompatibility such as precipitation or phase separation. This observation is considered time = 0 (initial). Then, the containers are placed in preheated oven for 24 hrs.

After 24 hours, the containers are removed from the oven, then Photographed and the appearance of each glass tube is documented. Descriptions in the notebook include the color and clarity of the solution and any evidence of incompatibility such as precipitation or phase separation. This observation is considered time = 24 hr. Compatibility, static bottle test and early results interpretations has been done and will be expressed in this section.

Compatibility test must be done before testing any inhibitor. More than thirteen compatibility tests were done for different chemical compounds. Table 6 illustrates some of the chemicals tested and their response.

**Table 5: Compatibility tests**

<b>Product</b>	<b>T= 0 hr</b>	<b>T= 1 hr</b>	<b>T=24 hr</b>	<b>Note</b>
Graphene	√	×	-	Small crystals formed.
Graphene+5% isopropanol	√	√	×	Small crystals formed.
Graphene+15% isopropanol	√	√	×	Small gathered crystals formed.
.				
.	-	-	-	-
.				
.				
Polyacrylate based polymer	√	√	√	No precipitation. Clear solution was observed

The inhibitor is said to be compatible if it doesn't form a precipitate in the synthetic brine. If a precipitate is formed or a phase separation is formed, then the inhibitor is not compatible and cannot be used for inhibition tests. Figures 2, 3 and 4 show examples of a compatible inhibitor (Polyacrylate based) and a non-compatible inhibitor (graphene). As seen from figure 3, small crystals are formed. 5% and 15% isopropanol were added to the graphene solution to make it compatible, unfortunately nothing changes, and the small crystals are still forming. If graphene can be made compatible by using any solvent, it has the potential to give very good inhibition results. This inhibition potential is ascribed by its structure since it can chelate metal ions leading to inhibition.

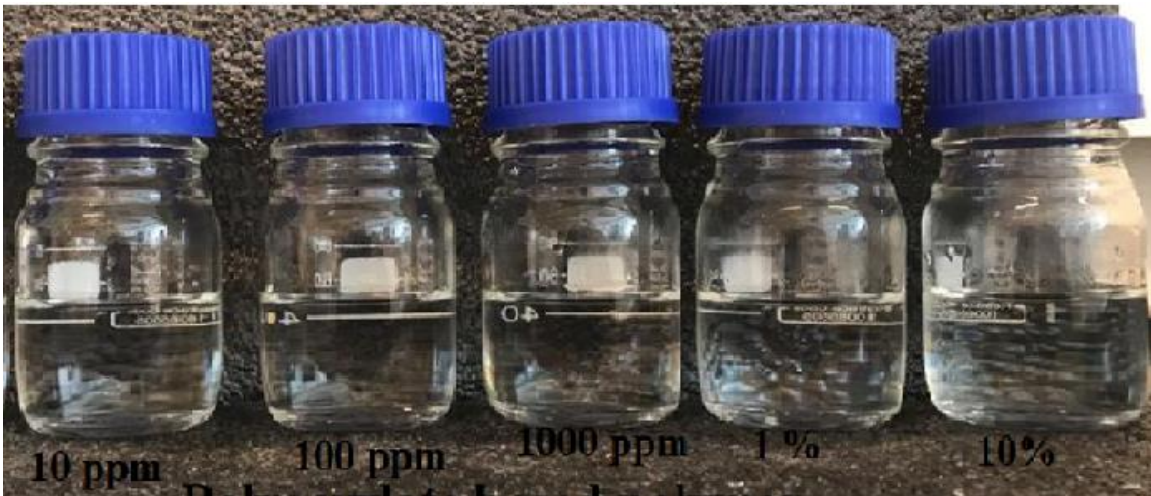


Figure 4: Polyacrylate based inhibitor comp. test

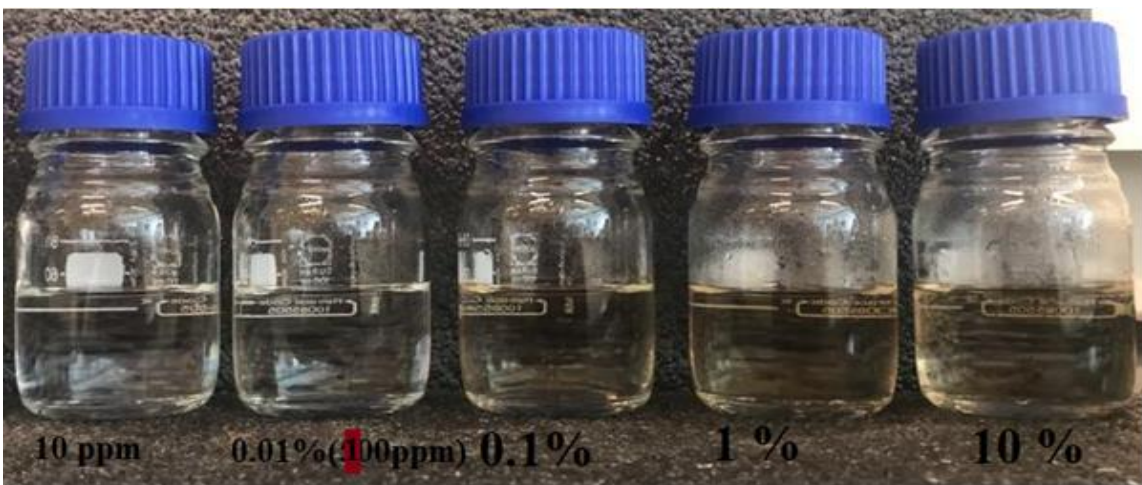


Figure 5: Pure graphene compatibility test

#### 1.4.5 Static Bottle Inhibition Test

After preparation of the cationic and anionic brines, they are filtered through a 0.45  $\mu\text{m}$  filter before use. No bicarbonate should be added to the anionic brine. Two ratios should be examined in order to evaluate scale inhibitor performance when two incompatible waters are mixed in the field: One. the ratio leading to the highest supersaturation and Two. the ratio leading to the

highest expected precipitation. However, in most cases only the ratio leading to the highest supersaturation is evaluated.

#### **1.4.6 pH buffer Preparation**

Buffer solution is used when the pH needs to be adjusted on the range 5.5-6.

The buffer solution is an acetic acid/sodium acetate buffer solution prepared in order to give the required pH (~5.5-6.0). The buffer solution is prepared by dissolving the following amounts of Analar grade reagents into 100mls of distilled water:

- 13.60 g sodium acetate tri-hydrate

- 0.5 g acetic acid.

The required volume of buffer (1 ml buffer/100 ml final brine mixture) is added to the anion brine. The pH of the anion brine and buffer is measured and recorded when combined with an equal volume of the cationic brine

When doing studies at high pH (pH~7) or low pH(pH~2), the pH is adjusted using 0.1 M HCl(aq) and 0.1 M NaOH(aq) solutions.

#### **1.4.7 Test Procedure**

Scaling The required number of test bottles are be numbered; these values correspond to the sample's names provided for chemical analysis. Each test bottle is labelled with the name of the chemical and the dose rate written with permanent marker. Each inhibitor dose rate is tested in duplicate.

50 ml of ‘anion’ solution is added to each test bottle using the dispenser; 50 ml of the ‘anion’ solution should also be added to the blanks. Two ‘control’ test bottles with 50 ml of deionized water instead of ‘anion’ solution are also included.

The ‘anion’ solution in each test bottle is dosed with the required amount of Scale inhibitor intermediate solution (using pipettes) to give the required final dose rate for the test.

The concentration of the inhibitor in the ‘anions’ must be double than that required for the test which accounts for the dilution when mixed with the ‘cations. Inhibitor is not added to the ‘Blank’ and ‘Control’ bottles.

An equal number of test bottles are prepared each filled with 50 ml of ‘cation’ solution using the dispenser. Test bottles are Placed into a water bath/oven at the appropriate test temperature for ~60 mins to reach thermal equilibrium. After 60 mins, the two brines are mixed together by pouring the ‘cations’ into the ‘anions’ and mixed manually. The bottles are Returned to the oven/bath as soon as possible and the timer is Started; this is  $t_0$ .

The test bottles are sampled at defined time intervals. Test bottles are sampled after 2h, 16h and 24h. If required, the pH values can be monitored at the start of the test and upon cooling at the end. The samples taken at different time intervals are sent for chemical analysis to evaluate the performance of the inhibitors.

#### **1.4.8 Dynamic Scale Loop Test**

Scaling This test method utilizes a dynamic scaling loop (i.e.: PMAC model) to determine the scaling potential of synthetic field brines. The test method is also used to select scale inhibitor(s) for the prevention of scale created in the scaling loop with the synthetic field brines. The dynamic scale loop test is used at high temperatures and in the applications of totally anaerobic

conditions. The main characteristics of the dynamic scale loop is little amount of sample, automated gradient concentration tests, automated scale detection and cleaning of scale system and accurate results compared to simple static bottle inhibition test.

The analysis of results is done by plotting the differential pressure versus time data for the blank and each scale inhibitor tested. The best scale inhibitor for a given water composition at a given temperature/pressure is the one which prevents an increase in differential pressure at the lowest concentration (i.e. minimum inhibitor concentration or MIC). This test method maybe used later in this work where we need to test at high temperature and pressure.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Traditional Oilfield Scale Inhibition Techniques**

Oil is one of the most important raw materials encountered. Everyday life activities involve different things that are made from oil or gas. One of the oils' primary importance is that oil is a very versatile source of energy. Oil is also used as a raw material in manufacturing a thousand other products such as paints , plastics, polymers, detergents and even cosmetics [21].

Due to the increase in energy demand, companies are forced to go for deeper wells where harsh environment is faced. Formation of scale is a very common problem in oil and gas industry especially at harsh environments at high temperature and pressure. Scaling is the deposition of mineral salts on the working equipment such as wellbore and tubes.

Scaling is a consequence of supersaturation of the mineral ions in the processing fluid[22]. The supersaturation of ions depends on different factors. The main contributor to ions supersaturation leading to scale formation is the production of formation water from the well which contains high salts concentration[22]. Scale is affected by changes in physical variables such as temperature, pressure and PH. These factors determine the scale type and composition [23].

Scale consequences can be very dramatic and quick and can bring the production capacity to zero in just few hours with a very high cost treatment [24]. Scale deposition in the formation

pores blocks the flow of fluid by reducing the diameter of tubing leading to a high pressure drop and full blockage which leads to loss of production. Scale formation causes additional problems such as energy leakage, acceleration of corrosion and severe accidents that influences safety and economics of production[25].

Several solution techniques have been proposed in the last decades to get rid of scale formed in the oil and gas industry. The solution techniques can be categorized to mechanical and chemical treatments. There are different ways of removing scale in mechanical sense. The simplest is milling technique which depends largely on the location of scale thereby the energy needed to overcome the scale using this technique vary greatly according to the location of scale formed. The chemical treatment method is the easiest and cheapest method to use among these two. The idea of chemical treatment is the introduction of some chemicals called solvents which will dissolve the scale to be washed out as a fluid. The scales encountered is of two types: the acid soluble scales mainly the metal oxides and sulfides, and the acid insoluble scales such as metal sulphates. The chemical treatment is highly affected by the surface to volume ratio of the scale[22].

Iron sulfide is one of the major encountered scales in the oil and gas industry taking place when oil and gas contain substantial amounts of hydrogen sulfide and sulfur. Varying from highly viscous fluid to dry solid, the characteristics of iron sulfide scale depends on temperature pressure and PH. Iron sulfide is formed by the reaction of hydrogen sulfide with iron. Hydrogen sulfide production as a free gas from the sour well is the main source for the  $H_2S$  in the reaction. Other sources of hydrogen sulfide include reduction of sulphate ion, degradation of additives in drilling mud, degradation of sulfur containing compounds and sulfate reducing bacteria-SRB[26]. Sources of iron includes but not limited to formation brines, tubulars, minerals,

treatment fluids and as a corrosion product. iron sulfide comes in different forms (iron to sulfur ratio) depending on temperature, pressure, formation mineralogy, brine and exposure time. Iron sulfide could exist in different form yet in the same well. The different forms of iron sulfide are presented in table 1 below.

**Table 6: different forms of iron sulphide [27]**

<b>SULFIDE SCALE</b>	<b>COMPOSITION</b>
Pyrrhotite	$Fe_7S_8$
Troilite	$FeS$
Mackinawite	$Fe_9S_8$
Pyrite	$FeS_2$
Marcasite	$FeS_2$
Greigite	$Fe_3S_4$

Iron sulfide scales causes many operational problems in the oil and gas industry since they are formed in all types of well such as producer, injector and supply wells where there is iron and hydrogen sulfide. Iron sulfide scales can alter the performance of supply wells and gas wells[28].

Iron sulfide can damage the downhole tools such as logging tool. It has also effects on pipeline valving system. The scale can also lead to the precipitation of asphaltene near wellbore thus reduces the effective permeability of the wellbore. It also blocks the flow in the production tubing and cause damage to wellbore equipment such as heat exchangers, turbines and pumps. Failing to properly handle iron sulfide scale could lead to wellbore shutdown[29]. This review

discusses different types of dissolvers used for iron sulfide. It also outlines the challenges encountered when treating iron sulfide scales.

## **2.2 Calcium carbonate Inhibition**

The formation of mineral scales imposed on reservoirs, downhole equipment and wellhead during oilfield process is becoming a serious problem that leads to equipment damage and production losses. The best solution to overcome this problem is the chemical treatment using scale Inhibitors [30]. The formation of calcium carbonate scales in the reservoirs happens due to different reasons. It may happen due to temperature and pressure changes. In general, the formation of Calcium carbonate scale arises if the concentration of ions in solution exceeds their equilibrium concentration[31]. Calcium carbonate precipitation takes place when bicarbonate ions in the anionic water is mixed with calcium ions in the cationic water that is injected to enhance oil recovery[32]. Scale inhibitors are injected with water into the formation to prevent scale precipitation [33].

Different types of scale inhibitors have been used in the last decade to hinder calcium carbonate scale. Huge intention was on green inhibitors derived from petrochemicals[34]. In a recent review Hasson et al mentioned that the most promising scale inhibitors are those derived from Polyaspartic acid (PASP) [35]. PASP is considered as green inhibitor because it is non-nitrogenous, non-phosphorus and biodegradable [34]. The biodegradability feature of PASP was examined by Thombre et al. Martinod et al studied the inhibition efficiency of PASP using chronoamperometry towards synthetic brines resembling calcium ions of North Sea with a total amount of 14224 ppm of  $Ca^{2+}$ . Their findings indicate that 4 ppm of PASP can reduce the amount of calcium carbonate deposition. Their study was done at room temperature which is

not the case in waterflooding oilfield processes where temperature is high. In addition, their findings propose the formation of Vaterite, a metastable phase of calcium carbonate scale. Recent study of PASP static inhibition efficiency tests was carried out by Liu et al. Liu et al utilized a diluted mineral water containing only 253 ppm of  $Ca^{2+}$  at 80 °C. An inhibition efficiency percentage of 80 % was achieved at these conditions with a dosage of 12 ppm PASP by blocking the active sites of calcium carbonate crystals[36]. SEM and XRD characterizations showed a change in the morphology in the presence of PASP leading to slow down of precipitate formation. Same findings were also stated by Quan et al[37]. Quan et al employed the static bottle test to examine the performance of PASP on a synthetic water which contains 240 ppm of  $Ca^{2+}$ .

The authors reached 90% inhibition at 30 °C and 60 °C with a dosage of 4 ppm and 12 ppm respectively. SEM results showed a considerable change in the morphology which accounted for crystal growth suppression. Moreover, dynamic scale tests revealed that a decrease in calcium carbonate deposition was achieved upon the addition of PASP.

The development of PASP derived inhibitors might be attractive, however these are mostly used in water treatment processes. Polyepoxy succinic acid (PESA) is another green inhibitor used for calcium carbonate scales. Sun et al utilized PESA in a static inhibition efficiency test at 30 °C. The results showed that a 90 % inhibition is reached with a dosage of 10 ppm and with concentrations of 40, 100, 200 ppm of  $Ca^{2+}$  [38]. It is very important to mention here that Liu et al claimed that the performance of PESA is better than that of PASP [39]. According to their study PESA is a very good alternative to PASP for water treatment technology. M. Schweinsberg et al and W. Girasa et al demonstrated the limitations of PESA and PASP in field tests and a further field studies should be carried out[40] . Carboxymethylinulin (CMI) is a

biodegradable polymer that has been tested for calcium carbonate inhibition. Verraest et al. examined the performance of small amounts of CMI in the 0.1 to 200 ppm on the crystallization and inhibition of calcium carbonate scale [41]. Verraest et al concluded that CMI is a good inhibitor since it changes the morphology of Calcium carbonate crystals. They deduced that CMI derived molecules with high polymerization and substitution are the most effective in terms of performance. Demandis et al scrutinized the performance of CMI by monitoring the formation of calcium carbonate scale in a scale sensor by measuring the absorbance. In accordance with Verraest et al, the results showed that at a dosage of 100 to 300 ppm of CMI, the calcium carbonate scale formation was substantially decreased. At high concentrations of CMI i.e. 1000 ppm, CMI was able to dissolve large amounts of calcium carbonate scale. CMI was also inspected by chronoamperometry at 25 °C by Martinod et al in an environment resembling that of North Sea with a total of 14225 ppm of  $Ca^{2+}$ . With a dosage of 30 ppm of CMI, the authors reported the deposition of calcium carbonate scale on the working electrode[42]. Kirboga et al studied the performance of CMI also by constant composition method that helps to understand the growth rate of calcium carbonate crystals. The authors inferred as the negatively charged functional groups increase the effectiveness of CMI increases [43]. Kirboga et al also carried out experiments recently to examine the effect of CMI in morphology and polymorph of crystallized calcium carbonate. It has been found that CMI concentration has the greatest effect in calcium carbonate polymorph and morphology [43].

Another class of scale inhibitor are the natural organic molecules which are environmentally friendly compared to conventional inhibitors. Hoch et al investigated the performance of humic substance towards calcium carbonate scale growth inhibition. They authors used an equal amount of calcium and carbonate ions. They studied the effect of humic and fulvic acid by

adding seed crystals to supersaturated solution. They concluded that some organic acids derived from plants in Florida Everglades that are hydrophobic can decrease the calcite growth at 0.2 ppm dosage[44] . It was also reported that a complete inhibition of calcium carbonate at a dosage of 5 ppm and that was attributed to blocking the active sites of calcium carbonate scale by the adsorbing ligands as was confirmed by the SEM analysis [44]. Another recent study by Gauthier et al. was carried out to evaluate the effect of humic acid in synthetic water containing 100 ppm of Calcium ions at a temperature of 35 °C. their results showed good inhibition of calcium carbonate at concentration of 1 ppm of the inhibitor[45]. Results showed that humic acid was also effective in concentrations as low as 0.2 ppm with an inhibition efficiency of 78 % [45] . Some limitations of humic acid performance towards scaling are the dependence on water quality and concentration range of calcium ions so that humic substances are not used in technical applications [34].Light scattering technique and pH drift method were used by Wada et al. to study the effect of maleic acid, tartaric acid, malonic acid, succinic acid and citric acid on calcium carbonate crystallization. The experiments were implemented at room temperature in synthetic water containing calcium and bicarbonate ions. The results were as follows: Citric acid was found to be quite effective in the inhibition of scale in a synthetic water containing 800 ppm of calcium ions. Calcium carbonate crystal growth inhibition was believed to be due to the adsorption of carboxylic groups on the calcite surface hindering the propagation of calcium carbonate [46]. The experiments showed that the inhibition efficiency of these acids was dependent on the number of carboxylic groups present and conformation circumstances [46] .Citric acid performance was also studied by Reddy et al. using the constant composition technique at room temperature and pH of 8.55. The results showed that moderate crystal growth inhibition was achieved at concentrations of 10 ppm and no inhibition found with dosage in the

range 0.01 to 0.1 of citric acid provided that the calcium ions concentration is 76 ppm [47]. Malaki et al. have also studied the kinetics of vaterite crystal growth in the presence of leucine at room temperature and pH of 8.5 and no effect was reported in the growth mechanism. Same results were also found in the presence of glutamic acid by F. Manoli et al.. Dalas et al. used the same technique to study the calcite crystal growth in the presence of cysteine peptide. Their experiments were conducted at room temperature and at a pH of 8.5. The authors reported an inhibition of calcite crystal growth in the range 22-58% when the concentration of calcium ions ranged from 80 to 120 ppm [48]. These results were attributed to the adsorption of the peptide on the calcium carbonate crystals surface through hydrogen bonding.

Petroyel-L-glutamic acid PGLU was also evaluated towards calcium carbonate inhibition by Kumar et al. The authors used static bottle inhibition test as well as dynamic inhibition test for their experiments. A 100 % inhibition was achieved through static bottle test at a temperature of 70 °C and a dosage of 120 ppm of the inhibitor [49]. The synthetic water used for testing was resembling offshore oil field containing high concentrations of calcium and bicarbonate ions. They also tested the inhibitor at high temperatures in the range 90 to 110 °C and deduced that at high temperatures low concentration of PGLU was not effective and the minimum effective concentration was found to be 160 determined by the dynamic scale loop test. The effectiveness of PGLU was ascribed to the formation of soluble complex molecules with calcium ions and calcium carbonate morphology distortion as the SEM, FTIR and XRD analysis suggested [49].

Yang et al. used a polysaccharide inhibitor produced by bacteria called *Xanthomonas campestris*. They studied the inhibition effect at temperature and pH of 25 C and 9 respectively. The initial concentrations of calcium and carbonate ions were 2664 ppm and 2544ppm. Their XRD results showed that all crystals were stacked together, and the degree of stacking was

found to increase as the concentration of the inhibitor increases [50]. The inhibitor concentrations range was from 100 ppm to 1000 ppm which was able to disperse the calcium carbonate crystal and prevent them from cluster as stated by the authors.

A recent emerging class of inhibitors is the plant extracts as anti-scalants. The first plant extract method was developed by Abdel-Gaber et al. Abdel-Gaber et al used fig leaf extract and the inhibition results were good. The solution of the inhibitor was prepared by extraction from grinded and dried fig leaves using boiling distilled water. The authors used chronoamperometry to study the effect of the inhibitor in a synthetic alkaline water similar to that of natural sea water at 40 °C. The minimum concentration of the inhibitor stock solution was reported to be 75 ppm in order to get 85 % inhibition [51]. A.M. Abdel-Gaber tried the same terminology using olive leaf extract. They tried olive leaf extract because it contains phenolic compounds like oleuropein and caffeic acid [51][52][53]. Stock solution of the inhibitor was prepared by boiling distilled water extraction from dried olive leaves. The authors deduced that olive leaves extract works as an inhibitor because it terminates nucleation step. 50 ppm concentration of olive leaf extract was found to be the most effective in terms of inhibition [51]. Soybean extract from Sea weeds was also investigated in static bottle test by N.A.C.E. Standard Test Method. The experiments were done at a temperature of 71 °C and a concentration of 12150 ppm of calcium ions with a dosage of 10 ppm of the inhibitor. The inhibition results from this extract were better than those obtained from polyaspartic acid as claimed by the authors [54]. Another strategy for plant extracts as scale inhibitors is considering the extracts that would complex the metal ions such as Magnesium ions and Calcium ions [34]. Inhibition properties of Punica granatum hull and leaf extract was examined by Abdel-Gaber et al in synthetic brines at room temperature.

The results showed that the hull extract was found to be better than the leaf extract since it contains polyphenols and punicalagin [51] [34].

Recently, natural polymer-based agents, multifunctional groups agents derived from different previous base inhibitors such as polyaspartic acid and effect of Enhanced Oil Recovery chemicals on the efficiency of phosphonate inhibitors. Ying Zhang introduced acyl-amino and hydroxyl groups to the polyaspartic acid to enhance its inhibition efficiency. The new graft copolymer (PASP derivative) was used in a static bottle inhibition test for inhibition of calcium carbonate. The test was done in temperature of 80 °C and pH of 9 using borax buffer solution. In a synthetic brine containing 240 ppm of calcium ions, 91 % inhibition was achieved [55]. QingDu et al. evaluated the performance of a natural polymer-based agent: Starch-graftpolyacrylic acid (St-g-PAA). St-g-PAA manifested both good turbidity removal and effective efficiency results towards calcium carbonate scale. The authors used the static bottle test at concentration of 5 mmol/l of calcium and carbonate ions. In a test temperature of 70 °C the inhibition efficiency was found to be 94% at an optimal St-g-PAA dosage of 40 ppm [54] . Qiwei Wang et al. evaluated the performance of three different inhibitors: tri-phosphonate, penta-phosphonate and polyacrylate based chemicals. They authors examined the performance of the inhibitors in the presence of surfactants and polymers as enhanced oil recovery chemicals. Static bottle test experiments were conducted at 70 °C and a concentration of 3942 ppm of calcium ions[56]. According to the authors findings the inhibition results of tri-phosphonate and penta-phosphonate were better with no EOR chemicals and reached greater than 80 % at a dosage of 2 ppm [56]. As seen from literature, either high dosages of scale inhibitor are needed, or inhibition efficiency is low. In addition, no comprehensive study of the inhibition efficiency

changes with temperature, pH and cationic to anionic ratio(C/A) is reported. This work is intended to get a very high inhibition results yet at very low dosage of inhibitors.

### **2.3 Iron Sulphide Scale Inhibition**

The best chemical to be used for inhibition is chosen after knowing the exact composition and chemical and physical properties of the scale. An effective inhibitor in a specific well won't be effective in other wells due to the difference in the nature of the scale. The commonly used inhibitors are categorized into organic acids and chelating agents.

Several organic acids have been proposed as inhibitors such as acetic acid, formic acid and maleic acid especially at high temperature high pressure environments[57]. The mentioned organic acids have low dissociation constant when compared to HCl. Organic acids are a good choice as inhibitors if the corrosion rate to be minimized, however they need longer contact time with the scale[57].

Chelating agents are chemical compound which react with metal ions to produce a stable complex which is usually water-soluble. Chelating agents have a ring-like structure and can bind the metal in two bonds allowing the metal to be separated. Whether the complex is stable or not is determined by the properties of the metal ions and the agent itself. The stability constant controls the stability of the chelated product. The stability constant depends on several things such as pH, number of rings and nature of the central element[58]. Unlike in acidic solutions, at higher pH(basic solution) the efficiency of the chelating agent is higher since there is no hydrogen ions that occupies the functional groups of the chelating agent[59]. Biodegradability is an important characteristic of chelating agents and should be considered for specific applications of chelating agents. Biodegradability depends mainly on the number of nitrogen

atoms in the chelating agent. A chelating agent having only one nitrogen atom is readily biodegradable, however as the number of nitrogen atoms increases, the biodegradability vanishes. Chelating agents are better choice for scale control than organic and mineral acids since they don't cause corrosion to downhole equipment and they are environmentally friendly. Chelating agents used are mainly aminopolycarboxylic acids that have nitrogen in the center and carboxylic groups as the arms of the chelating agent. Most common chelating agents include ethylenediamine tetra acetic acid (EDTA), hydroxyethyl ethylene diamine tetra acetic acid (HEDTA), hydroxyethyl iminodiacetic acid (HIDA), Glutamic acid N, N-diacetic acid (GLDA), Diethylene triamine Penta acetic acid (DTPA), Nitriiotriacetic acid (NTA), and Methylglycinediacetic acid (MGDA). In the last few years different solutions have been proposed to mitigate scale formation to improve productivity in the oil and gas industry. Finding an ideal scale inhibitor is not an easy task due to many things that will be discussed in this section. An ideal inhibitor should be thermally stable at harsh environment encountered downhole where the temperature can be very high. An ideal inhibitor also should have high inhibiting capacity to get the maximum possible inhibition percentage. It should be less corrosive and shouldn't generate  $H_2S$  gas so the potential of corrosion initiation is minimized. Challenges of scale chemical treatment are related to the nature of the scale itself. The most important challenge is that iron sulfide scales come along with other scales such as iron carbonate and iron oxides. This mixture of different scale types called scale matrix, makes it difficult to dissolve and one should think of different additives depending on the scale matrix encountered. another challenge arises from the fact that iron sulfide particles are oil-wet meaning that they are coated with a layer of oil which work as a barrier between the inhibitor

and the scale thus blocks the inhibitor-scale contact lowering the efficiency of inhibitors. The presence of hydrocarbons with the scale is yet another challenge that should be addressed.

These challenges can be overcome by considering them when preparing a chemical treatment compound. An example is using surfactants and other water-wetting agents in case of scale coated with oil. The main objective of the additives as agents and surfactants is to enhance the contact time between the scale and the inhibitor. To deal with the scale matrix and design suitable chemical treatment procedure, chemical analysis of the scale should be carried out to determine the different compounds involved.

Different chemical inhibitors have been studied over the past years. N. Bhandari et al investigated the performance a polymeric material containing amide group towards iron sulphide inhibition which shows a positive inhibition results at threshold concentrations. In their experiments, they stated that the inhibitor did not prevent iron sulphide from formation instead, they showed that the aggregation and growth of scale were successfully suppressed by the inhibitor. Their lab experiments were carried out under strictly anoxic conditions and at 90 °C. They achieved 60-80 % dispersion at dosages of 100 ppm to 200 ppm of the inhibitor [60].

Wei Li et al. have studied the effect of bio acids such as THPS, EDTA and polyacrylamide (PAM) on FeS inhibition. They found that unlike EDTA, THPS is not effective as was previously thought. They have also concluded that EDTA is a good dissolver, but these inhibition and dissolution properties are largely affected by silica, however the dispersion effects were not affected by Silica. They have reached an inhibition efficiency of 83% at 100 ppm of PAM and 90% at 100 ppm PAM+EDTA [61]. Bader Alharbi et al. have also evaluated the performance of different chemistries for iron and zinc sulphides inhibition under different experimental conditions temperature, pH and ion concentrations. They tested phosphino

polycarboxylic acid (PPCA) which shows positive results towards iron sulfide scale inhibition. Their findings indicated that some of the inhibitors that were effective for zinc sulphide didn't show any inhibition efficiency towards iron sulfide. They noticed that a significant decrease in the amount of inhibitor was noticed in ZnS experiments which was not the case for iron sulphide inhibition. According to these findings, they concluded that it is easier to inhibit FeS rather than ZnS under the same conditions. The inhibition efficiency was improved by increasing the inhibition dosage to 100 ppm for both iron sulphide and zinc sulphide to reach 90 % [62]. Narayan Bhandari et al. make use of a strictly anoxic bottle test setup to investigate the potential inhibition efficiency of different conventional inhibitors such as phosphonates and carboxylic acid polymeric materials and new chemical formulations. Different ionic concentrations were synthesized to mimic the field conditions. They have found that as expected, phosphonate and carboxylic acid polymers did not show inhibition positive tendency towards iron sulphide scale. A novel chemistry formulation was developed which shows inhibition of iron sulphide scale nucleation and growth at early stages affecting dispersion, aggregation and deposition of FeS. They used 10 ppm of  $Fe^{2+}$  and 50 ppm  $S^{2-}$  with dosages of 100 ppm to 600 ppm of the inhibitor which resulted in inhibition percentages ranging from lower than 10% to 90% at 100ppm to 600 ppm respectively[63]. Saebom Ko et al. tested effective iron sulphide dispersants and inhibitors. Polyoxazoline (OX) ,polyvinyl pyrrolidone (PVP), polyacrylamide (PAM) and carboxymethyl cellulose (CMC) were investigated since they are frequently used in oil and gas production activities for different applications. Upon testing, these chemicals showed positive inhibition results by preventing iron sulphide particles from settling. They have concluded that among those chemicals, CMC was the most effective in FeS dispersion even at higher ionic strength. The tested Nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA) and

diethylenetriamine pentamethylene phosphonate (DTPMP) at 70 °C showed an inhibition result greater than 90 % [60]. All these studies show that higher dosages of the inhibitor are needed yet the efficiency of inhibition is not high. In addition, no comprehensive study at different temperature, pH and brine compositions was carried out.

This work will test a novel L-glutamic acid grafted polyacrylamide at different temperature, pH and brine compositions.

## **CHAPTER 3**

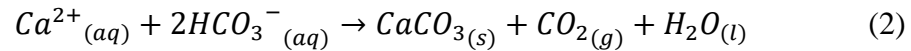
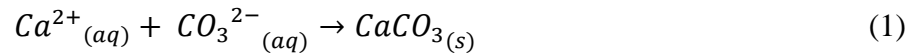
# **EVALUATION OF A NOVEL FUNCTIONALIZED POLYMER MATERIAL AS CALCIUM CARBONATE INHIBITOR AT DIFFERENT TEMPERATURE, PH AND BRINE CONCENTRATIONS**

Calcium carbonate scale forms in production and injection wells and precipitates when there is a pressure and temperature change, mixing of incompatible waters and dehydration. Consequences of calcium carbonate scale can be dramatic leading to production shutdown. To prevent the formation of calcium carbonate, in this work, gallic acid grafted polyacrylamide was synthesized, characterized and tested for calcium carbonate inhibition. Positive compatibility test results were achieved prior to inhibition efficiency test. The inhibition efficiency testing methodology followed is static bottle test in which two incompatible cationic and anionic waters are mixed. The inhibition efficiency was calculated by the amount of calcium ions left in solution that was determined by ICP-OES. The inhibitor was found to be effective at different temperatures (40,60,80 °C), pH (5,7,9) and brine compositions. The inhibition efficiency increases with increasing temperature and pH reaching 95% at 20 ppm inhibitor concentration after 16 hours of reaction time at temperature of 80 °C and pH of 7. At 80/20 cationic to anionic ratio, more scale was formed due to the abundance of calcium ions. The

inhibition efficiency was also higher than that of the 20/80 ratio especially at lower inhibitor dosages. The collected scale particles in the blank samples and at low concentration of the inhibitor were characterized by different instrument including SEM, TEM and EDS. As the characterization techniques proved, the inhibitor is believed to chelate calcium preventing scale formation. SEM results showed the change on scale morphology as the inhibitor is absorbed to the active crystal sites interrupting the microcrystals growth. These findings showed a promising inhibition results at high temperature and different pH and brine concentrations at relatively low inhibitor concentration.

### 3.1 Introduction

Calcium carbonate is considered as one of the most frequent occurring scales in oil and gas industry [56]. Due to the increase in oil demand, companies are forced to go for deeper wells where harsh environment is faced[64]. Formation of scale is a very common problem in oil and gas industry especially at harsh environments at high temperature and pressure. Scaling is a consequence of supersaturation of the mineral ions in the processing fluid[22]. Calcium carbonate scale takes place when  $Ca^{2+}$  is supersaturated with  $CO_3^{2-}$  or  $HCO_3^-$  according to the following chemical equations:



The supersaturation of ions depends on different factors. The main contributor to ions supersaturation leading to scale formation is the production of formation water from the well which contains high salts concentration[22]. Scale is affected by changes in physical variables such as temperature, pressure and PH. These factors determine the scale type and composition [23]. Partial pressure of carbon dioxide plays a crucial role in the mechanism of calcium carbonate deposition. Pressure drop leads to shortage of CO2 in the aqueous phase leading to calcium carbonate deposition as equation (2) suggests. Increase in temperature leads to more

scale deposition since high temperature accelerates the kinetics. The high temperature influences the thermodynamics as well. Since the solubility of calcite decreases at high temperature, the precipitation may happen at earlier stage when high temperature is encountered. The same phenomena happen when the PH increases. High PH leads to lower solubility thus precipitation occurs at earlier stages. Obviously high concentrations of scaling ions (i.e.;  $Ca^{2+}$ ,  $CO_3^{2-}$ , ...) will lead to high precipitation potential. Three main stages (nucleation, crystal growth and precipitation) with enough time and adherence will stick to the surface leading to scale deposition [65].

Scale consequences are dramatic and quick and can bring the production capacity to zero in just few hours with a very high cost treatment [24]. Scale deposition in the formation pores blocks the flow of fluid by reducing the diameter of tubing leading to a high pressure drop and full blockage which leads to loss of production. Scale formation causes additional problems such as energy leakage, acceleration of corrosion and severe accidents that influences safety and economics of production[25].

Scale treatment has been carried out using different solution techniques proposed in the last decades to minimize the effect of scale formed in the oil and gas industry[9]. These are categorized to mechanical and chemical treatments used once the scale forms. There are different ways of removing scale in mechanical sense. The simplest is milling technique which depends largely on the location of scale thereby the energy needed to overcome the scale using this technique vary greatly according to the location of scale formed [66]. The chemical treatment method is the easiest and cheapest method to use among these two. The idea of chemical treatment is the introduction of some chemicals called dissolvers which will dissolve the scale to be washed out as a fluid. The scales encountered is of two types: the acid soluble scales mainly the metal oxides and sulfides, and the acid insoluble scales such as metal sulphates, according to these categories the dissolver chemicals are synthesized[12] .

A more realistic and beneficial approach to overcome scale is the prevention of scale from forming or scale inhibition. Scale inhibition is the best solution for scale in the oil and gas industry however it is not an easy job. Scale inhibition has different challenges since it highly depends on the environment of scale formation, mixture of compounds found in the scale, concentration of ions presents and formation conditions.

Different types of scale inhibitors have been used in the last decade to hinder calcium carbonate scale. The main target of the chemical inhibitors is to sequester the calcium ion, so it will not react with carbonate or bicarbonate ions preventing the formation of calcium carbonate scale. Huge attention was on green inhibitors derived from petrochemicals[34]. In a recent review Hasson et al mentioned that the most promising scale inhibitors are those derived from Polyprotic acid (PASP) [35]. PASP is considered as green inhibitor because it is non-nitrogenous, non-phosphorus and biodegradable [34]. The biodegradability feature of PASP was examined by Thombre et al. Martinod et al studied the inhibition efficiency of PASP using chronoamperometry towards synthetic brines resembling calcium ions of North Sea with a total amount of 14224 ppm of  $Ca^{2+}$ . Their findings indicate that 4 ppm of PASP can reduce the amount of calcium carbonate deposition. Their study was done at room temperature which is not the case in waterflooding oilfield processes where temperature is high. In addition, their findings propose the formation of Vaterite, a metastable phase of calcium carbonate scale. Recent study of PASP static inhibition efficiency tests was carried out by Liu et al. Liu et al utilized a diluted mineral water containing only 253 ppm of  $Ca^{2+}$  at 80 °C. An inhibition efficiency percentage of 80 % was achieved at these conditions with a dosage of 12 ppm PASP by blocking the active sites of calcium carbonate crystals[36]. SEM and XRD characterizations showed a change in the morphology in the presence of PASP leading to slow down of precipitate formation. Same findings were also stated by Quan et al[37]. Quan et al employed the static bottle test to examine the performance of PASP on a synthetic water which contains 240 ppm of  $Ca^{2+}$ . The authors reached 90% inhibition at 30 °C and 60 °C with a dosage of 4 ppm and 12 ppm respectively. SEM results showed a considerable change in the morphology which accounted for crystal growth suppression. Moreover, dynamic scale tests revealed that a decrease in calcium carbonate deposition was achieved upon the addition of PASP.

The development of PASP derived inhibitors might be attractive, however these are mostly used in water treatment processes. Polyepoxy succinic acid (PESA) is another green inhibitor used for calcium carbonate scales. Sun et al utilized PESA in a static inhibition efficiency test at 30 °C. The results showed that a 90 % inhibition is reached with a dosage of 10 ppm and with concentrations of 40, 100, 200 ppm of  $Ca^{2+}$  [38]. It is very important to mention here that Liu et al claimed that the performance of PESA is better than that of PASP [39]. According to their

study PESA is a very good alternative to PASP for water treatment technology. M. Schweinsberg et al and W. Girasa et al demonstrated the limitations of PESA and PASP in field tests and a further field studies should be carried out[40] . Recently, natural polymer-based agents, multifunctional groups agents derived from different previous base inhibitors such as polyaspartic acid and effect of Enhanced Oil Recovery chemicals on the efficiency of phosphonate inhibitors have been studied. Ying Zhang introduced acyl-amino and hydroxyl groups to the polyaspartic acid to enhance its inhibition efficiency. The new graft copolymer (PASP derivative) was used in a static bottle inhibition test for inhibition of calcium carbonate. The test was done in temperature of 80 °C and pH of 9 using borax buffer solution. In a synthetic brine containing 240 ppm of calcium ions, 91 % inhibition was achieved [55].

QingDu et al. evaluated the performance of a natural polymer-based agent: Starch-graftpolyacrylic acid (St-g-PAA). St-g-PAA manifested both good turbidity removal and effective efficiency results towards calcium carbonate scale. The authors used the static bottle test at concentration of 5 mmol/l of calcium and carbonate ions. In a test temperature of 70 °C the inhibition efficiency was found to be 94% at an optimal St-g-PAA dosage of 40 ppm [54] . Qiwei Wang et al. evaluated the performance of three different inhibitors: tri-phosphonate, penta-phosphonate and polyacrylate based chemicals. The authors examined the performance of the inhibitors in the presence of surfactants and polymers as enhanced oil recovery chemicals. Static bottle test experiments were conducted at 70 °C and a concentration of 3942 ppm of calcium ions[56]. According to the authors findings the inhibition results of tri-phosphonate and penta-phosphonate were better with no EOR chemicals and reached greater than 80 % at a dosage of 2 ppm [56]. Yuwei Zuo et al studied the performance of carboxylic polymers that have low molecular weight toward calcium carbonate inhibition. The authors have used polyaspartic acid (PAA) and polyepoxysuccinic acid (PESA) to represent low molecular weight carboxylic polymers. In their static experimental setup, they have found that PAA is better inhibitor than PESA especially at normal temperatures and this was attributed to the number of carboxylic groups in PAA which is higher than that of PESA [67]. Stéphanie C. de Morais et al. investigated the efficiency of sodium hexametaphosphate (SHMP) as calcium carbonate inhibitor under static conditions at different temperatures, pressures and SHMP concentration. Their findings showed almost complete calcium carbonate inhibition at pH 6.5 at dosage of 2.5 ppm SHMP and deformation of calcium carbonate crystals as observed by SEM images [68].

As seen from literature, either high dosages of scale inhibitor are needed, or inhibition efficiency is low. In addition, no comprehensive study of the inhibition efficiency changes with temperature, pH and cationic to anionic ratio(C/A) is reported. In addition, this novel inhibitor was selected due to its potential inhibition properties as it contains carboxylic groups and the fact its easy to synthesize and at the same time very effective and hasn't been tested before. This work is intended to get a relatively high inhibition results yet at quite low dosage of inhibitors. Furthermore, unlike previous studies this work will report a study of the inhibition efficiency at different temperature, pH and C/A.

## 3.2 Experimental

### 3.2.1 Materials

The chemical composition of the synthetic brine is given in table 1. The synthetic brines were prepared using analytical grade chemicals and deionized water, then filtered using 0.45  $\mu\text{m}$  membrane filters in all experiments. The inhibitor was tested at different conditions: Temperatures of 25, 40, 60 and 80  $^{\circ}\text{C}$ , PH of 5,7 and 9. Ratios of cationic to anionic brines were also altered from 50:50 to 80:20 and 20:80 respectively. The influence on the inhibitor efficiency was monitored upon these changes.

**Table 7: Concentration of synthetic brine**

Ion	Conc.(ppm)
Na <sup>+</sup>	19047
K <sup>+</sup>	703
Mg <sup>2+</sup>	1286
Ca <sup>2+</sup>	3942
Sr <sup>2+</sup>	62
Cl <sup>-</sup>	39119
SO <sub>4</sub>	1847
HCO <sub>3</sub>	500
TDS	66530

### 3.2.2 Preparation of Gallic Acid Grafted Polyacrylamide

In a typical synthesis, gallic acid grafted polyacrylamide is synthesized by adding 2.5g of acrylamide in a three-neck flask containing 50ml of distilled water. After that, 3g of gallic acid is dissolved in 50 ml distilled water then added to the 3-neck flask to make the gel-mixture. Then, 20 ml of ethanol was added to the reaction mixture and the temperature was set to 60 °C before the addition of sodium persulfate as the reaction initiator according to eqn 3 below. This mixture was purged with nitrogen for 5 hours and stirred at 450 rpm for 24 hours before collecting the product.

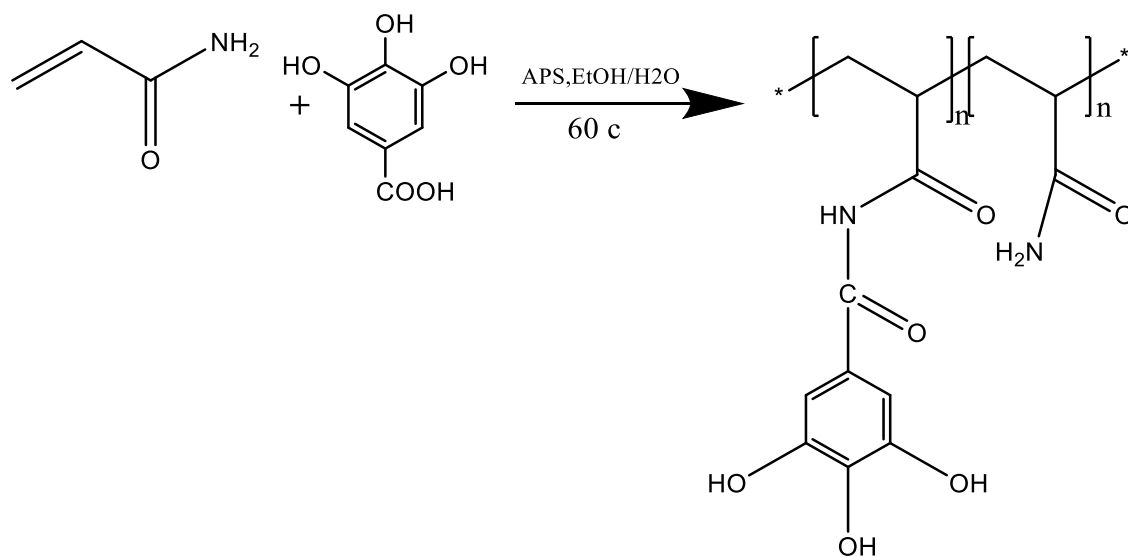
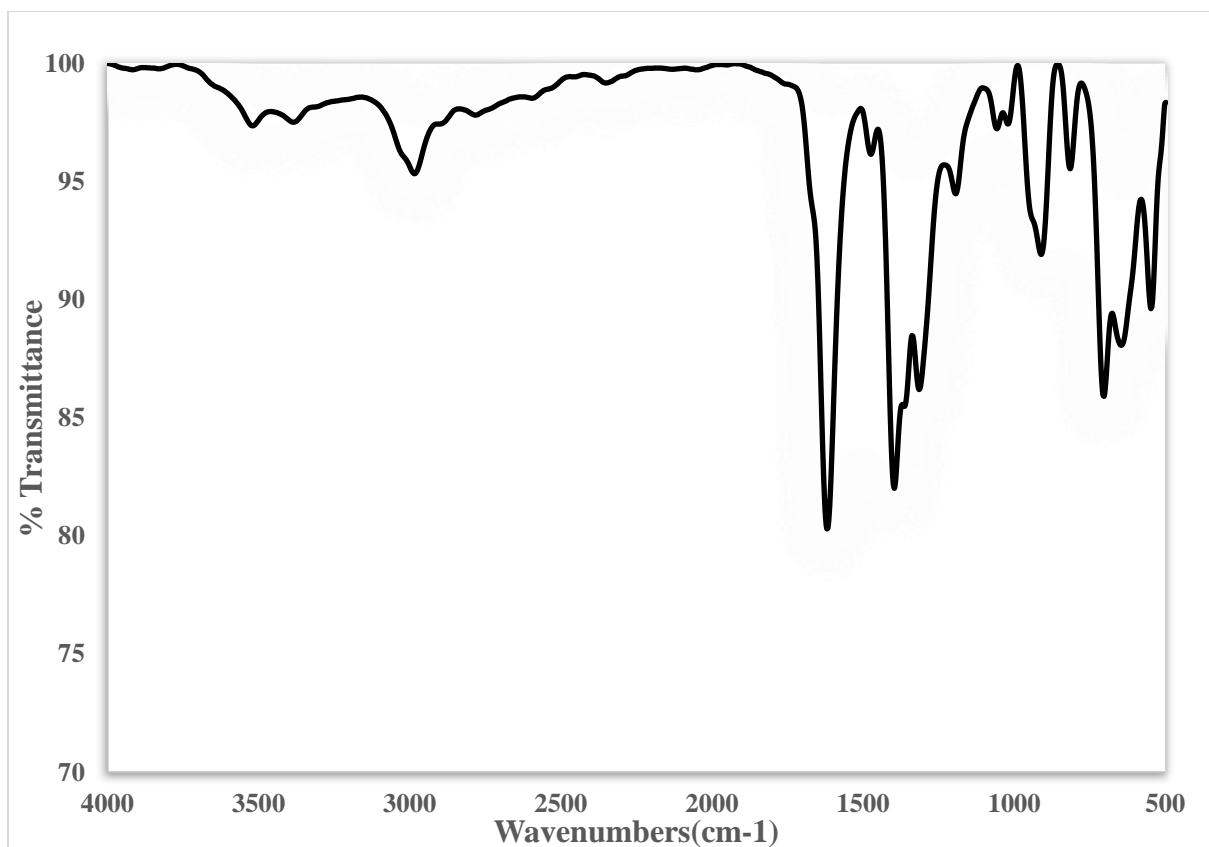


Figure 6: Preparation of GAGP

### 3.2.3 GAGP Fourier Transform Infrared Spectroscopy

A small quantity of solid dried gallic acid grafted polyacrylamide was utilized and used to measure infrared spectra of the synthesized inhibitor. Potassium bromide method was deployed in the range of 500  $cm^{-1}$  to 4000  $cm^{-1}$ . FTIR results are represented in figure 1.

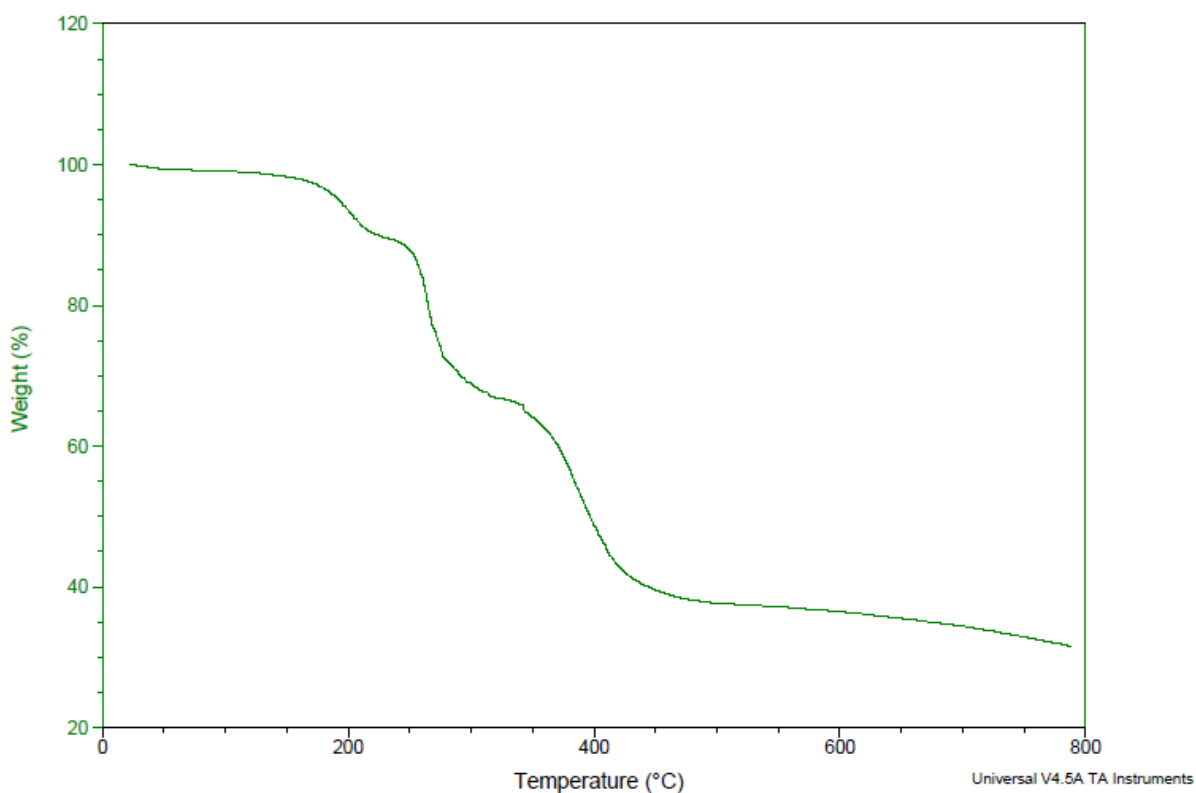


**Figure 7: FTIR of gallic acid grafted copolymer**

The characteristic peak at around 1550  $\text{cm}^{-1}$  is attributed to the carboxylic group  $\text{COO}^-$  [69]. The peak at 1473  $\text{cm}^{-1}$  corresponds to the  $\text{C} - \text{H}$  that are in the  $\text{C} - \text{H}_2$  groups while the peak at 2984  $\text{cm}^{-1}$  is ascribed to the adsorbed surface molecules [36-37]. It can be easily inferred that the peak at 3500  $\text{cm}^{-1}$  is the characteristic of hydroxyl. It is also observed that the peak at 1618.37  $\text{cm}^{-1}$  is the characteristic peak of carbonyl, and those of 1193  $\text{cm}^{-1}$  and 1057  $\text{cm}^{-1}$  are attributed to  $\text{C} - \text{O}$  bond. Peaks of 1396  $\text{cm}^{-1}$  and 1313 is the characteristics of aromatic Skelton stretching vibrations while the peaks at 910  $\text{cm}^{-1}$  and 814.73  $\text{cm}^{-1}$  are characteristics of external plane bending vibration of  $\text{CH}_2$  and  $\text{CH}$  of double bond alkene. The weak peaks from 703.44  $\text{cm}^{-1}$  to 546.71  $\text{cm}^{-1}$  is due amide linkage. All those characteristic signals show the successful synthesis of the gallic acid grafted copolymer containing carboxyl and hydroxyl groups.

### 3.2.4 GAGP Thermogravimetric Analysis

SDT Q600 model thermogravimetric analyzer was used to examine thermal stability of the synthesized polymer material under nitrogen atmosphere up to 800 °C susceptible to 20°C /min heating ratio. The thermal properties of the polymer are represented in figure 2. It is easily inferred that the weight of the polymer remained constant below 200 °C. The weight of the polymer then decreases dramatically as the temperature increases from 200°C to 400 °C reaching a weight loss of around 60 % at 400 °C. After 400 °C, the weight of the polymer decreases slightly as the temperature increases to a value of almost 30 % at 800°C. The polymer possessed high thermal stability and can be tested at temperatures up to 200°C.

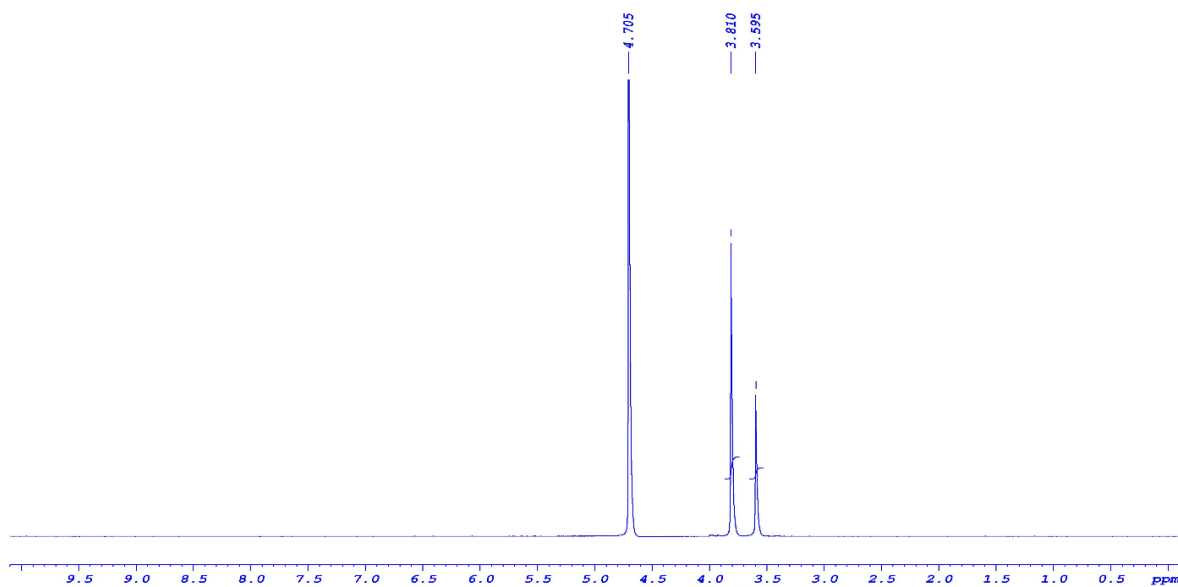


**Figure 8: TGA curve of the synthesized polymer**

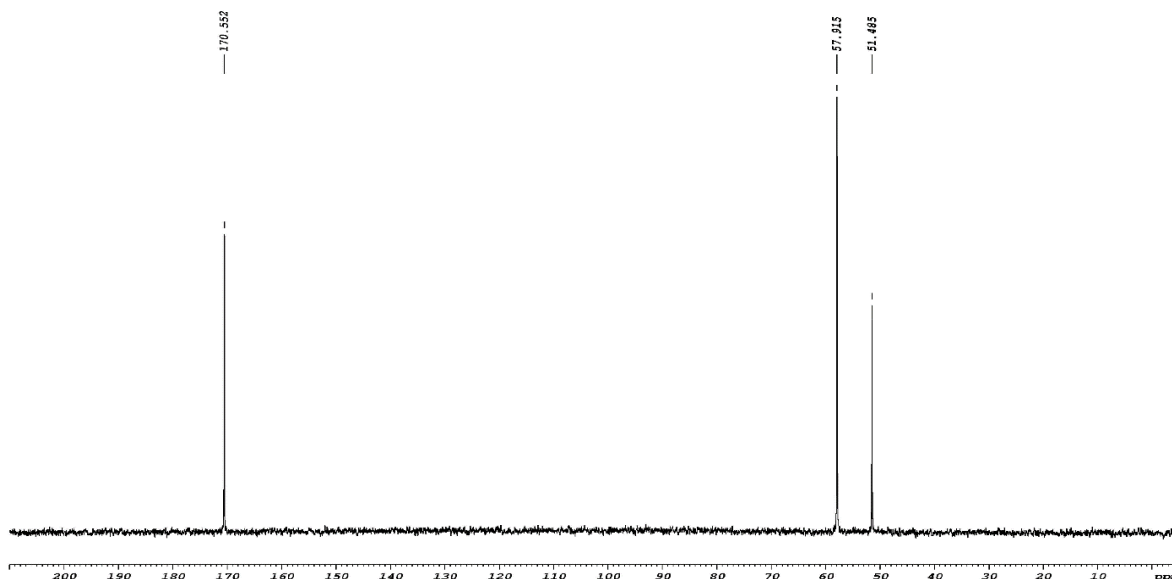
### 3.2.5 GAGP Nuclear Magnetic Resonance

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the collected sample of the inhibitor product were carried out by means of Bruker NMR 400 MHz spectrometer at room temperature using  $\text{D}_2\text{O}$  as the solvent with a dosage of 20-30 mg. Figure 3 shows the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of GAGP. The  $^1\text{H}$  NMR signal at 4.70 ppm is the solvent residual peak of  $\text{D}_2\text{O}$ .

a



b



**Figure 9:**  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  NMR (b) spectra of GAGP.

The characteristic peaks of methine group (CH) appear at 4.58 ppm in  $^1\text{H}$  NMR and 51.01 ppm in  $^{13}\text{C}$  NMR. The characteristic peaks of methylene group (CH<sub>2</sub>) appear at 2.65 ppm in  $^1\text{H}$  NMR and 22.30 ppm in  $^{13}\text{C}$  NMR. In addition, the  $^1\text{H}$  NMR signal at 1.24 ppm and  $^{13}\text{C}$  NMR signal at 19.49 ppm are assigned to methyl group (CH<sub>3</sub>). The characteristic peaks of methine group associated with carboxyl group (CHCOOH) appear at 3.47 ppm in  $^1\text{H}$  NMR and 60.56 ppm in  $^{13}\text{C}$  NMR. The characteristic peaks of methine group associated with hydroxyl group (CHOH) appear at 4.15 ppm in  $^1\text{H}$  NMR and 65.93 ppm in  $^{13}\text{C}$  NMR. The appearance of methyl group, methine group associated with carboxyl group and hydroxyl group confirms the introduction of threonine successfully. The  $^{13}\text{C}$  NMR signals at 162.68, 171.05, 172.83 and 177.42 ppm are assigned to four kinds of carbonyl groups of the copolymer, respectively. All above characteristic signals demonstrate that the graft copolymer has been successfully prepared.

### 3.2.6 Static Bottle Test

Firstly, Static inhibition test was carried out in this study under static conditions as described in the National Standard of the People's Republic of China (GB/T 16632-2008). To carry out the test, the cationic and anionic brines are prepared by dissolving the respective salts into DI water. The amounts of salts added (Table 2) was calculated to maintain the total composition given in table 1.

**Table 8: Salts added for CW & AW preparation**

SALT	CW (G)	AW(G)	MIX(G)
NaCl	7.93	14.92	24.56
KCl	0.67	-	0.67
MgCl <sub>2</sub> .6H <sub>2</sub> O	5.38	-	5.38
CaCl <sub>2</sub> .2H <sub>2</sub> O	7.23	-	7.23
NaHCO <sub>3</sub>	-	0.34	0.34
Na <sub>2</sub> SO <sub>4</sub>	-	1.37	1.37
PH	7.85	8.44	7.83

To test the scale inhibitor efficiency, the ratio leading to the highest supersaturation and the ratio leading to the highest precipitation are tested. The usual practice which was followed in this study is to test the ratio leading to the highest supersaturation. The required number of test bottles were labeled; these labels correspond to the sample's names provided for chemical

analysis. Each test bottle is labelled with the name of the chemical and the dose rate written with permanent marker.

To the six glass bottles, 50 ml of 'anion' solution was added to each test bottle using the dispenser; 50 ml of the 'anion' solution was also be added to the blanks.

The 'anion' solution in each test bottle is dosed with the required amount of scale inhibitor intermediate solution (using pipettes) to give the required final dose rate for the particular test. The concentrations tested in this study were 0.02 ppm, 0.1ppm, 0.2ppm,2ppm and 20ppm. The concentration of the inhibitor in the 'anions' was double than that required for the test which accounts for the dilution when mixed with the 'cations. Inhibitor is not added to the 'Blank' bottles.

An equal number of test bottles were prepared each filled with 50 ml of 'cation' solution using the dispenser. Test bottles were placed into a pre-heated oven at the appropriate test temperature for ~60 mins to reach thermal equilibrium. After that, the two brines were mixed together by pouring the 'cations' into the 'anions' and mixed manually. The bottles were returned to the oven as soon as possible and the timer is started; this is  $t_0$ . The test bottles were sampled at defined time intervals. Test bottles were sampled after 2h,16h and 24h. The pH values were monitored at the start of the test and upon cooling at the end. The samples taken at different time intervals are sent for chemical analysis to evaluate the performance of the inhibitors. This procedure was carried out in each experiment to evaluate the inhibitor at different conditions. The inhibitor was tested at 25 C, 40 C, 60 °C and 80 °C without altering the pH. The temperature was then set to 80 °C and the inhibitor was tested at 5, 7 and 9. The test was also performed at

different cationic/ anionic (C/A) compositions. C/A of 80/20 and 20/80 by volume was implemented.

The inhibition efficiency,  $\varepsilon$  was calculated using the calcium ions remaining in the solution after the test by the following equation:

$$\varepsilon = \frac{C_2 - C_1}{C_0 - C_1}$$

Where  $C_2$  is the  $Ca^{2+}$  remaining in the filtrate after the reaction at different time intervals,  $C_1$  is the remaining  $Ca^{2+}$  in the blank sample and  $C_0$  is the concentration of  $Ca^{2+}$  used before the test.

### 3.2.7 Calcium Carbonate Characterization

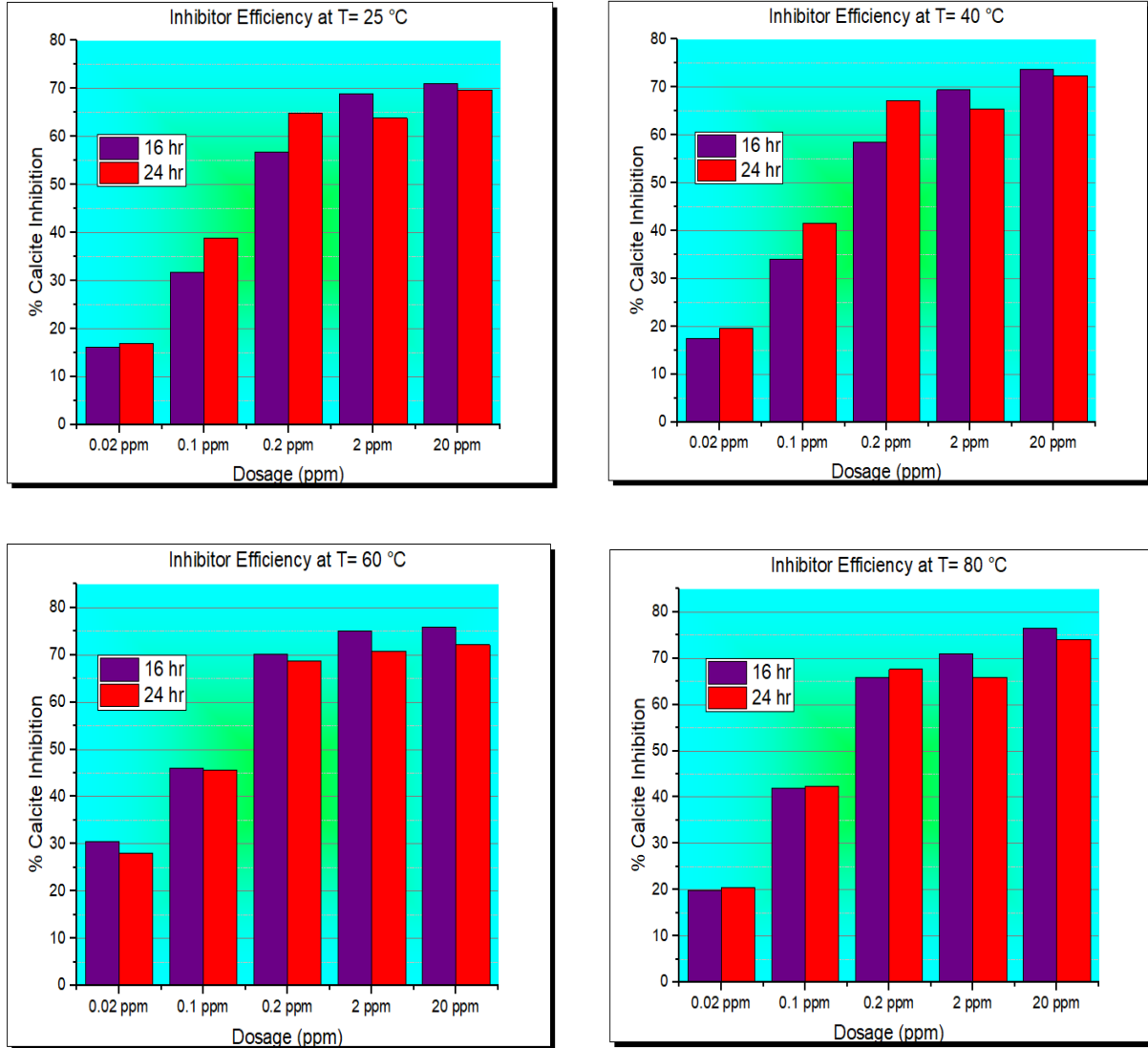
Sample  $CaCO_{3(s)}$  precipitate was collected by filtering the solutions of blank, 0.02 ppm and 0.1 ppm inhibitor using 0.45  $\mu m$  membrane filters. The collected solid material was washed with DI water to remove potential contaminants, then dried over night at 40 C to be ready for instrumental characterization. The shape and surface morphology of the solid precipitate were examined by scanning electron microscopy SEM. Elemental composition of collected samples was tested by Energy Dispersive X-Ray analysis EDX. High resolution images of the collected precipitate were achieved by Transmission electron microscopy TEM.

## 3.3 Results and Discussion

### 3.3.1 Influence of Temperature on Calcium Carbonate Inhibition

**Error! Reference source not found.** shows the fluids hydrogen index. The influence of temperature change on the efficiency of the inhibitor was tested at 25C, 40C, 60°C and 80 °C.

Aliquots of the test solutions, about 15 ml free from scale was sampled at 2 hr, 16 hr and 24 hr for  $Ca^{2+}$  ICP analysis. The results are reported in figures 1 to 4.



**Figure 10: Influence of temperature on CaCO<sub>3</sub> inhibition**

Due to the inverse solubility behavior of calcium carbonate, it was noted that the scale formation increases as the temperature increases. In fact, a very small amount of scale was formed at 25 °C and the inhibitor efficiency was not impressive reaching a maximum of only 70 %. As the

temperature increased to 40, a relatively large amount of scale formed, and the efficiency increased from around 20% at 0.02 ppm of the inhibitor to around 75% at 20 ppm. The inhibition efficiency was further improved at 60 °C where 30 % inhibition was reached at 0.02 ppm of the inhibitor. The efficiency then increases to 76% at a dosage of 20 ppm of the inhibitor. The highest amount of scale formation was found to be at 80 °C. The inhibition efficiency jumped from 20% at 0.02 ppm to around 77% at 20 ppm. It can be easily seen that while the efficiency is higher after 16 hours of reaction at higher dosage of the inhibitor, the 24-hour efficiency is higher in case of lower inhibitor dosage. This happens because at lower inhibitor concentration, the inhibitor will not interact with the scale formed hence the crystal growth is not hindered so the scale will continue to form enabling the inhibitor to function. The opposite happens at higher inhibitor dosage where the inhibitor is believed to interact with the scale formation leading to crystal growth slow down after the 16 hr. which explains why the inhibition efficiency is higher at 16 hr. than that of 24 hr. The mechanism by which the inhibitor works is explained by the functional groups of the gallic acid grafted copolymer. The amine group will chelate the calcium ions preventing it from carbonate and bicarbonate contact thus mitigating scale formation. This chelation will produce water soluble product since the nitrogen atom of the amine and the oxygen atom contains lone pairs and are electronegative.

### 3.3.2 Influence of pH on Calcium Carbonate Inhibition

The influence of pH on the calcium carbonate inhibition was examined, the result is in figure4.

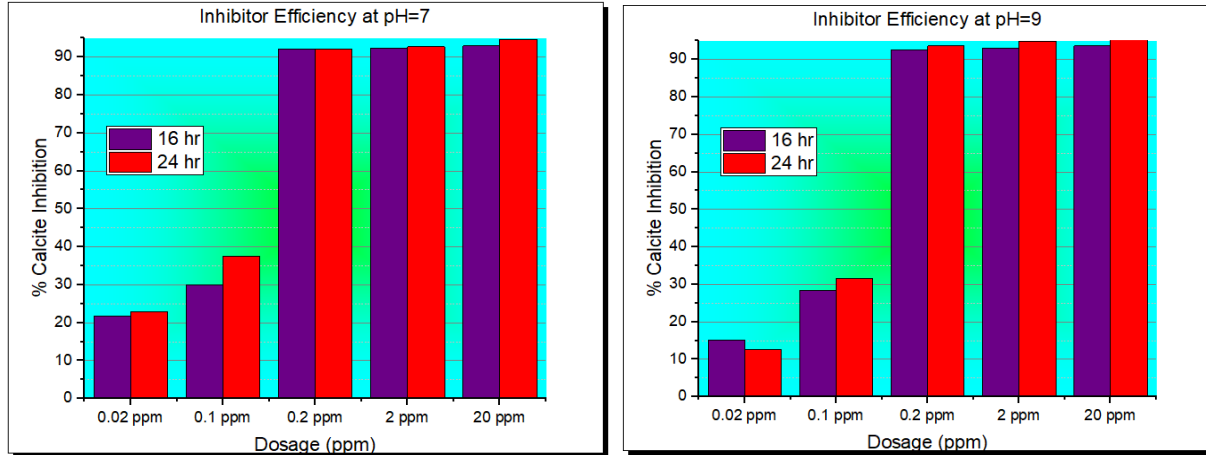


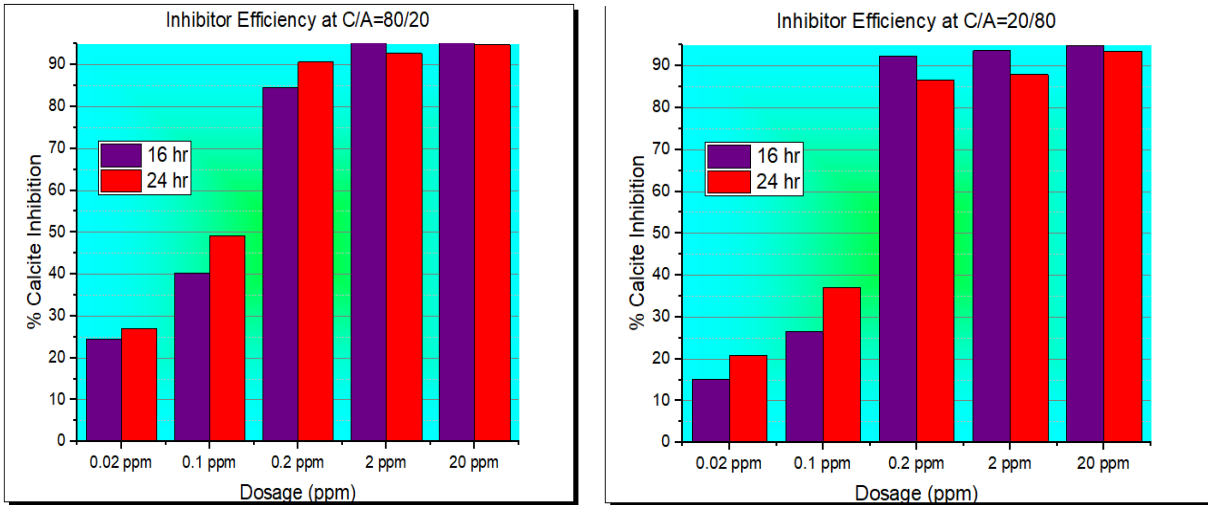
Figure 11: Influence of pH on CaCo3 Inhibition

The pH of the test brines was found to be 7.4. One drop of 10 % HCl was used to lower the pH to 7. Lowering the pH increased the inhibition efficiency to 94% at 20 ppm dosage after 24 hours of the test. The inhibition efficiency was very low at 0.02 ppm of inhibitor at a value of 20 %. There was a slight increase at 0.1 ppm of inhibitor followed by a substantial increase to above 90% at 0.2 ppm inhibitor concentration. The pH was then increased to 9 by addition of 200  $\mu$ L of NaOH by trial and error. At pH=9, the inhibition efficiency was relatively lower compared to pH= 7 starting by 12 % at 0.02 ppm inhibitor dosage, increasing slightly to 35% at 0.1 ppm then sharp increase to more than 90%. The maximum efficiency attained was 95% at 20 ppm.

### 3.3.3 Influence of (C/A) Composition on Calcium Carbonate Inhibition

The influence of cationic to anionic brine ratio was also tested. The temperature was kept at 80  $^{\circ}$ C and two ratios were examined. Without altering the pH, 80 ml of cationic brines were mixed with 20 ml of anionic brines containing different inhibitor concentrations and one blank solution

as done for other experiments. The opposite was also tested where 20 ml of cationic brines were added to 80 ml of anionic. The results of this test are represented in figure 5.

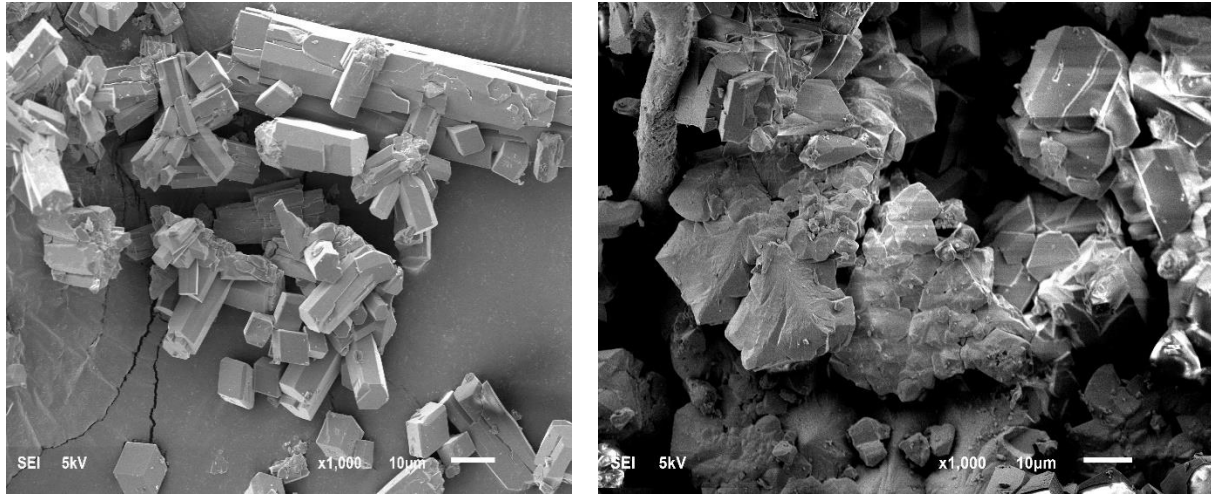


**Figure 12: Influence of (C/A) composition on CaCo<sub>3</sub> inhibition**

When the cationic brine is 80 and the anionic brine is 20, the inhibition efficiency starts at 25% with a dosage of 0.02 ppm of the inhibitor, increasing to 50% at 0.1 ppm of the inhibitor. The efficiency then goes up to 95% at the highest inhibitor concentrations (i.e. 2 ppm and 20 ppm). The same behavior is recognized for the 20 cationic/80 anionic case except that in this case the inhibition efficiency starts at a much lower proportion at 15 % and lower than 40% when the inhibitor dosage is 0.02 ppm and 0.1ppm respectively. This is attributed to the higher amount of calcium ions which provide higher potential of scale formation thus efficiency of inhibitor is increased in the 80/20 proportion.

### 3.3.4 Investigation of Inhibition Mechanism

To further understand the chemistry behind  $CaCO_3$  inhibition, scale samples collected after the static bottle test were characterized. SEM and EDS pictures in the presence and absence of gallic acid grafted acrylamide are depicted in figure 8 and 9.



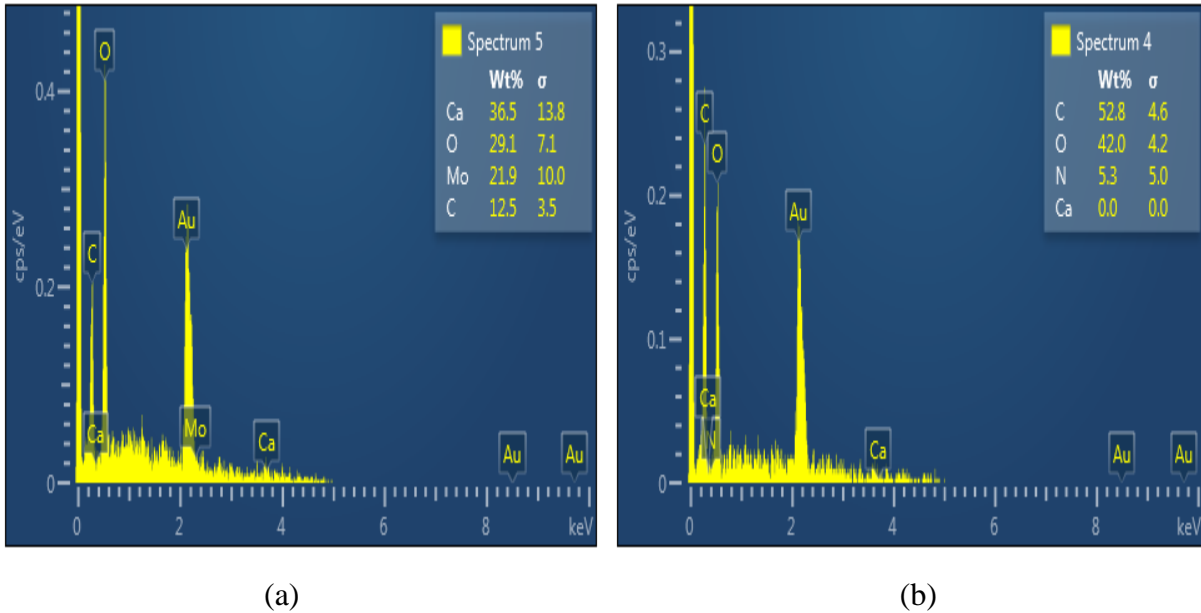
(a)

(b)

**Figure 13: SEM results of CaCO<sub>3</sub> precipitate (a) without inhibitor (b) at 0.1 ppm**

Generally, the amount of scale formation in the presence of the inhibitor was found to be much less than that of the blank samples especially at higher dosages of inhibitor (i.e. 0.1 ppm and 2ppm). The SEM results of calcium carbonate in figure 6 (a) in the absence of the inhibitor showed regular aragonite structure as long strip crystals with glassy surface that forms at elevated temperatures. However, figure 6 (b) the crystals were interrupted upon the absorption of the inhibitor into the surface of the crystals thereby hindering the normal crystal growth of calcium carbonate[72]. The aragonite formation is consistent with literature since magnesium ions were present [34-35]. The rule of the inhibitor was to occupy the active crystal growth sites by the inhibitor with the help of the functional groups destroying the crystal lattice. The functional groups cause more internal stress inside the crystals leading to microcrystalline inhibition which prevents scale formation. SEM characterization results points out that in addition to the calcium ions chelation, the inhibitor contributed in crystal growth distortion. At lower inhibitor concentrations, the effect on the crystals was not much and some crystal structures remained unchanged especially at a dosage of 0.02 ppm.

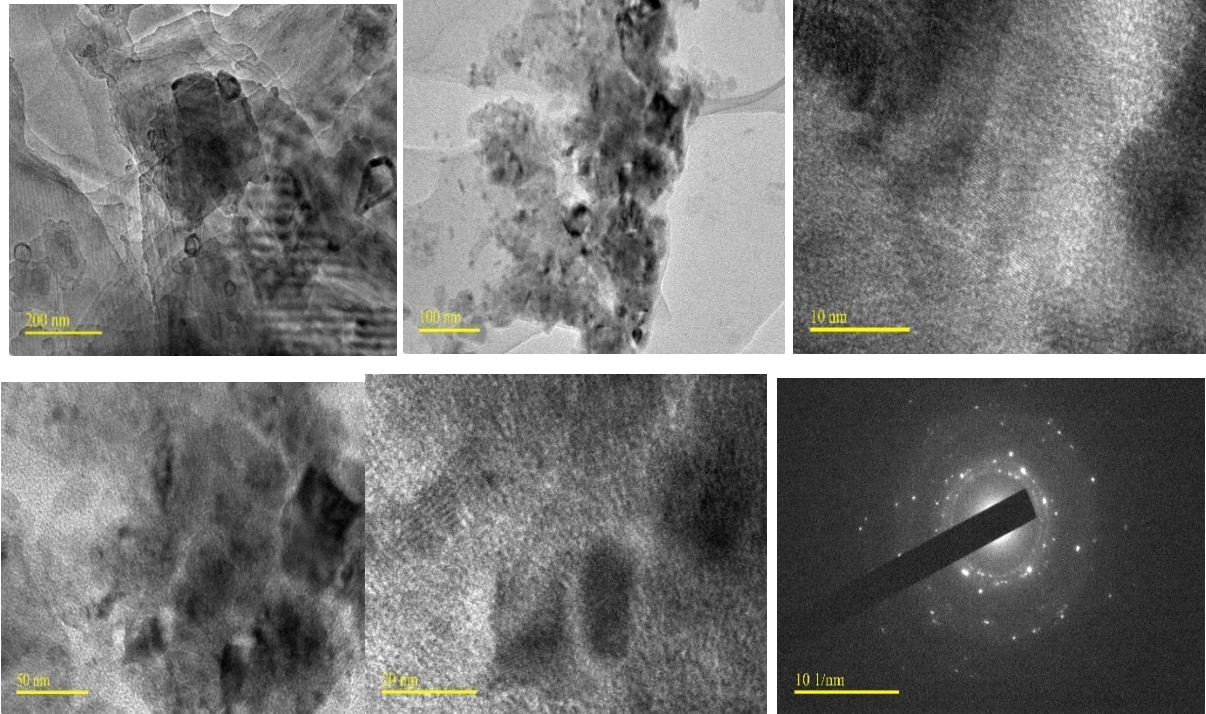
Energy Dispersive X-Ray analysis EDX was also performed to have an idea about the elements present in the scale sample. Results are shown in figure 7.



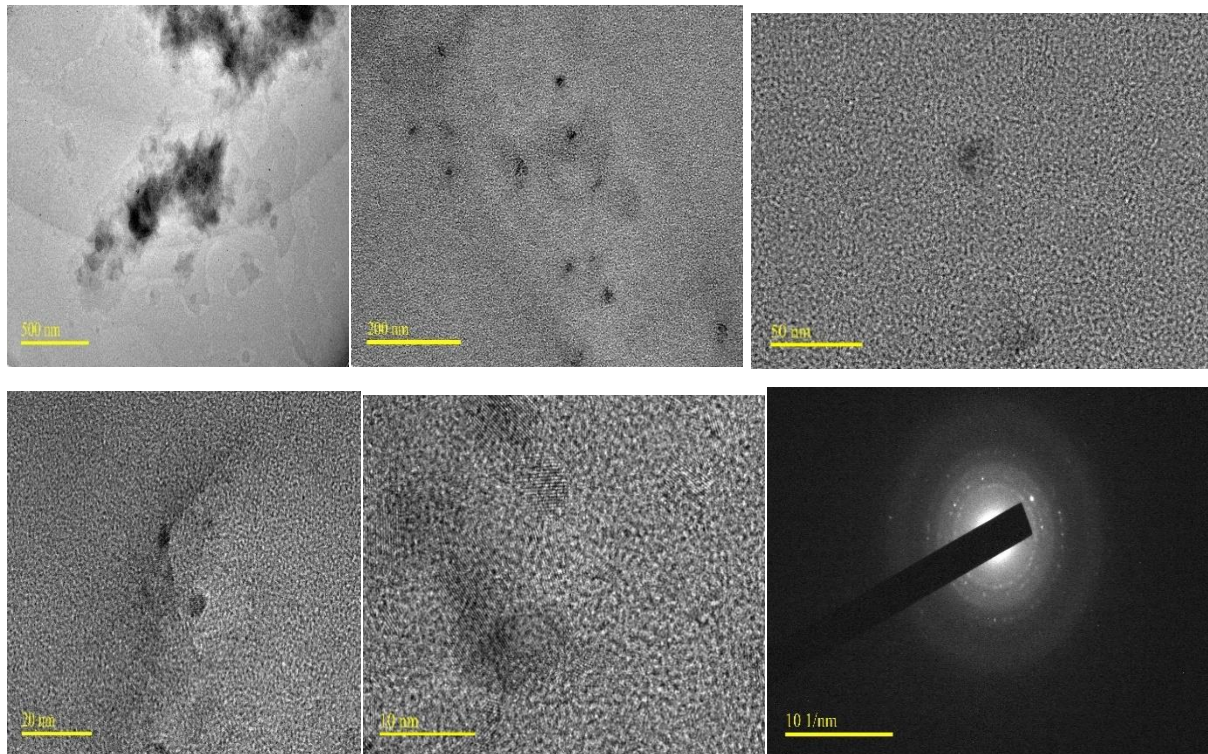
**Figure 14:EDS results of CaCO<sub>3</sub> precipitate (a) without inhibitor (b) at 0.1 ppm of inhibitor**

Trace amounts of Mg and cl were spotted by EDS in crystal type shown in figure7. The column shaped structure formed in the blank samples in figure 7 (a) was developed into compact structure at inhibitor concentration of 0.1 ppm. The columns were changed to distorted spheroid particles and the packed structure was evolved into loosely packed particles.

Images of the scale formed were taken by transmission electron microscopy and results are shown in figure8.The images are consistent with SEM characterization supporting the inhibition mechanism explained above.



(a)



(b)

**Figure 15: TEM images of CaCO<sub>3</sub> precipitate (a) without inhibitor (b) at 0.1 ppm of inhibitor.**

## **CHAPTER 4**

### **DEVELOPMENT OF A NOVEL IRON SULPHIDE SCALE**

#### **INHIBITOR FOR OILFIELD APPLICATION**

##### **4.1 Introduction**

Iron sulphide scale formation is a very common problem in oil and gas industry especially at harsh environments. Scale can be found as a single mineral however, most of the time it is usually found as a mixture of different scale types. Several organic compounds such as unsaturated hydrocarbons, organic acids and their salts, aromatic compounds, paraffins and sulfur containing compounds affects scale formation in downhole environment. The most widely common scales are sulfates (barium sulfate and calcium sulfate ), oxides and hydroxides( iron oxide and magnesium hydroxide ), and sulfides ( iron sulfide) [74]. Scaling is a consequence of supersaturation of the mineral ions in the processing fluid[22]. The supersaturation of ions depends on different factors. The main contributor to ions supersaturation leading to scale formation is the production of formation water from the well which contains high salts concentration[22]. Scale is affected by changes in physical variables such as temperature, pressure and PH. These factors determine the scale type and composition [23]. Scale consequences can be very dramatic and quick and can bring the production capacity to zero in just few hours with a very high cost treatment [24]. Scale deposition in the formation pores blocks the flow of fluid by reducing the diameter of tubing leading to a high pressure drop

and full blockage which leads to loss of production. Scale formation causes additional problems such as energy leakage, acceleration of corrosion and severe accidents that influences safety and economics of production[25].

Iron sulfide is one of the major encountered scales in the oil and gas industry taking place when oil and gas contain substantial amounts of hydrogen sulfide and sulfur. Varying from highly viscous fluid to dry solid, the characteristics of iron sulfide scale depends on temperature pressure and PH. Iron sulfide is formed by the reaction of hydrogen sulfide with iron. Hydrogen sulfide production as a free gas from the sour well is the main source for the H<sub>2</sub>S in the reaction. Other sources of hydrogen sulfide include reduction of sulphate ion, degradation of additives in drilling mud, degradation of sulfur containing compounds and sulfate reducing bacteria-SRB[26]. Sources of iron include but not limited to formation brines, tubulars, minerals, treatment fluids and as a corrosion product. iron sulfide comes in different forms (iron to sulfur ratio) depending on temperature, pressure, formation mineralogy, brine and exposure time. Iron sulfide could exist in different form yet in the same well. The different forms of iron sulfide are presented in table 1 below.

**Table 9: different forms of iron sulphide**

SULFIDE SCALE	COMPOSITION
<b>Pyrrhotite</b>	$Fe_7S_8$
<b>Troilite</b>	$FeS$
<b>Mackinawite</b>	$Fe_9S_8$
<b>Pyrite</b>	$FeS_2$
<b>Marcasite</b>	$FeS_2$

Iron sulfide scales cause many operational problems in the oil and gas industry since they are formed in all types of well such as producer, injector and supply wells where there is iron and hydrogen sulfide. Iron sulfide scales can alter the performance of supply wells and gas wells[28].It can also damage the downhole tools such as logging tool. It has also effects on pipeline valving system. The scale can also lead to the precipitation of asphaltene near wellbore thus reduces the effective permeability of the wellbore. It also blocks the flow in the production tubing and cause damage to wellbore equipment such as heat exchangers, turbines and pumps. Failing to properly handle iron sulfide scale could lead to wellbore shutdown[29].Chemical inhibitors are the chemical compounds used to inhibit and prevent scale formation. Chemical inhibition involves the use of organic and inorganic materials to control the scale. The best chemical to be used for inhibition is chosen after knowing the exact composition and chemical and physical properties of the scale. An effective inhibitor in a specific well won't be effective in other wells due to the difference in the nature of the scale. The commonly used inhibitors are categorized into organic acids and chelating agents.

Several organic acids have been proposed as inhibitors such as acetic acid, formic acid and maleic acid especially at high temperature high pressure environments[57]. The mentioned organic acids have low dissociation constant when compared to HCl. Organic acids are a good choice as inhibitors if the corrosion rate to be minimized , however they need longer contact time with the scale[57].

Chelating agents are chemical compound which react with metal ions to produce a stable complex which is usually water-soluble. Chelating agents have a ring-like structure and can bind the metal in two bonds allowing the metal to be separated. Whether the complex is stable

or not is determined by the properties of the metal ions and the agent itself. The stability constant controls the stability of the chelated product. The stability constant depends on several things such as pH, number of rings and nature of the central element[58]. Unlike in acidic solutions, at higher pH (basic solution) the efficiency of the chelating agent is higher since there is no hydrogen ions that occupies the functional groups of the chelating agent[59]. Biodegradability is an important characteristic of chelating agents and should be considered for specific applications of chelating agents. Biodegradability depends mainly on the number of nitrogen atoms in the chelating agent. A chelating agent having only one nitrogen atom is readily biodegradable, however as the number of nitrogen atoms increases, the biodegradability vanishes. Chelating agents are better choice for scale control than organic and mineral acids since they don't cause corrosion to downhole equipment and they are environmentally friendly. Chelating agents used are mainly aminopolycarboxylic acids that have nitrogen in the center and carboxylic groups as the arms of the chelating agent. Most common chelating agents include ethylenediamine tetra acetic acid (EDTA), hydroxyethyl ethylene diamine tetra acetic acid (HEDTA), hydroxyethyl iminodiacetic acid (HIDA), Glutamic acid N, N-diacetic acid (GLDA), Diethylene triamine Penta acetic acid (DTPA), Nitriolotriacetic acid (NTA), and Methylglycinediacetic acid (MGDA). In the last few years different solutions have been proposed to mitigate scale formation to improve productivity in the oil and gas industry. Finding an ideal scale inhibitor is not an easy task due to many things that will be discussed in this section. An ideal inhibitor should be thermally stable at harsh environment encountered downhole where the temperature can be very high. An ideal inhibitor also should have high inhibiting capacity to get the maximum possible inhibition percentage. It should be less corrosive and shouldn't generate  $H_2S$  gas so the potential of corrosion initiation is minimized.

Challenges of scale chemical treatment are related to the nature of the scale itself. The most important challenge is that iron sulfide scales come along with other scales such as iron carbonate and iron oxides. This mixture of different scale types called scale matrix, makes it difficult to dissolve and one should think of different additives depending on the scale matrix encountered. another challenge arises from the fact that iron sulfide particles are oil-wet meaning that they are coated with a layer of oil which work as a barrier between the inhibitor and the scale thus blocks the inhibitor-scale contact lowering the efficiency of inhibitors. The presence of hydrocarbons with the scale is yet another challenge that should be addressed.

These challenges can be overcome by considering them when preparing a chemical treatment compound. An example is using surfactants and other water-wetting agents in case of scale coated with oil. The main objective of the additives as agents and surfactants is to enhance the contact time between the scale and the inhibitor. To deal with the scale matrix and design suitable chemical treatment procedure, chemical analysis of the scale should be carried out to determine the different compounds involved.

Different chemical inhibitors have been studied over the past years. N. Bhandari et al investigated the performance a polymeric material containing amide group towards iron sulphide inhibition which shows a positive inhibition results at threshold concentrations. In their experiments, they stated that the inhibitor did not prevent iron sulphide from formation instead, they showed that the aggregation and growth of scale were successfully suppressed by the inhibitor. Their lab experiments were carried out under strictly anoxic conditions and at 90 C. They achieved 60-80 % dispersion at dosages of 100 ppm to 200 ppm of the inhibitor [60].

Wei Li et al. have studied the effect of bio acids such as THPS, EDTA and polyacrylamide (PAM) on FeS inhibition. They found that unlike EDTA, THPS is not effective as was

previously thought. They have also concluded that EDTA is a good dissolver, but these inhibition and dissolution properties are largely affected by silica, however the dispersion effects were not affected by Silica. They have reached an inhibition efficiency of 83% at 100 ppm of PAM and 90% at 100 ppm PAM+EDTA [61]. Bader Alharbi et al. have also evaluated the performance of different chemistries for iron and zinc sulphides inhibition under different experimental conditions temperature, pH and ion concentrations. They tested phosphino polycarboxylic acid (PPCA) which shows positive results towards iron sulfide scale inhibition. Their findings indicated that some of the inhibitors that were effective for zinc sulphide didn't show any inhibition efficiency towards iron sulfide. They noticed that a significant decrease in the amount of inhibitor was noticed in ZnS experiments which was not the case for iron sulphide inhibition. According to these findings, they concluded that it is easier to inhibit FeS rather than ZnS under the same conditions. The inhibition efficiency was improved by increasing the inhibition dosage to 100 ppm for both iron sulphide and zinc sulphide to reach 90 % [62]. Narayan Bhandari et al. make use of a strictly anoxic bottle test setup to investigate the potential inhibition efficiency of different conventional inhibitors such as phosphonates and carboxylic acid polymeric materials and new chemical formulations. Different ionic concentrations were synthesized to mimic the field conditions. They have found that as expected, phosphonate and carboxylic acid polymers did not show inhibition positive tendency towards iron sulphide scale. A novel chemistry formulation was developed which shows inhibition of iron sulphide scale nucleation and growth at early stages affecting dispersion, aggregation and deposition of FeS. They used 10 ppm of  $Fe^{2+}$  and 50 ppm  $S^{2-}$  with dosages of 100 ppm to 600 ppm of the inhibitor which resulted in inhibition percentages ranging from lower than 10% to 90% at 100ppm to 600 ppm respectively [63]. Saebom Ko et al. tested effective iron sulphide dispersants and inhibitors.

Polyoxazoline (OX), polyvinyl pyrrolidone (PVP), polyacrylamide (PAM) and carboxymethyl cellulose (CMC) were investigated since they are frequently used in oil and gas production activities for different applications. Upon testing, these chemicals showed positive inhibition results by preventing iron sulphide particles from settling. They have concluded that among those chemicals, CMC was the most effective in FeS dispersion even at higher ionic strength. The tested Nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA) and diethylenetriamine pentamethylene phosphonate (DTPMP) at 70 showed an inhibition result greater than 90 % [60]. All these studies show that higher dosages of the inhibitor are needed yet the efficiency of inhibition is not high. In addition, no comprehensive study at different temperature, pH and brine compositions was carried out.

## **4.2 Experimental**

### **4.2.1 Materials**

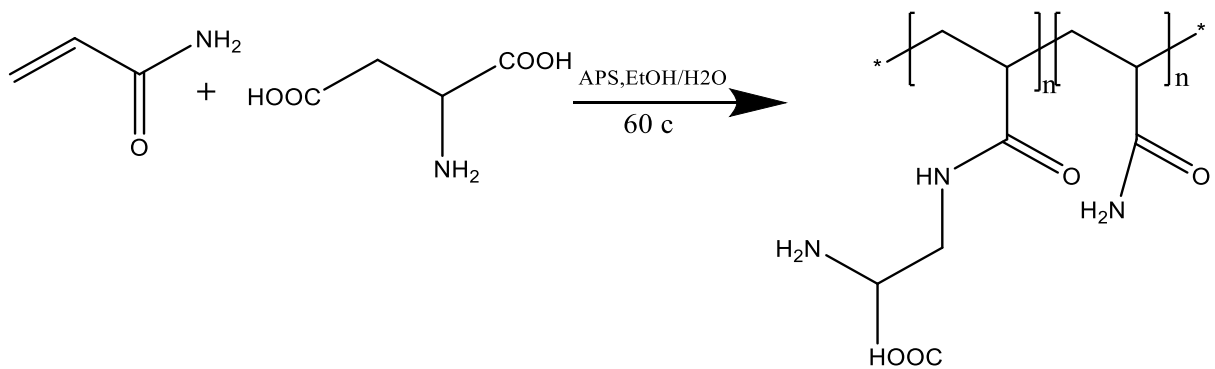
The chemical composition of the synthetic brine is given in table 2. The synthetic brines were prepared using analytical grade chemicals and deionized water, then filtered using 0.45  $\mu\text{m}$  membrane filters in all experiments. The inhibitor was tested at different conditions: Temperatures of 40 C, 60 °C and 80 °C, PH of 6.7 and 8.5. Ratios of cationic to anionic brines were also altered from 50:50 to 80:20 and 20:80 respectively. The influence on the inhibitor efficiency was monitored upon these changes.

**Table 10: Concentration of brine components in the study**

Component	Concentration
NaCl	1 M
Ca <sup>2+</sup>	25mM
Fe <sup>2+</sup>	30 ppm
S <sup>2-</sup>	90 ppm

#### 4.2.2 Preparation of The Inhibitor

In a typical synthesis, L-glutamic acid grafted polyacrylamide is synthesized by adding 2.5g of acrylamide in a three-neck flask containing 50ml of distilled water. After that, 2.6g of L-glutamic acid is dissolved in 50 ml distilled water then added to the 3-neck flask to make the gel-mixture. Then, 20 ml of ethanol was added to the reaction mixture and the temperature was set to 60 °C before the addition of sodium persulfate as the reaction initiator according to figure 1 below. This mixture was purged with nitrogen for 5 hours and stirred at 450 rpm for 24 hours before collecting the product.



**Figure 16: L-glutamic acid grafted polyacrylamide synthesis**

### 4.2.3 Anaerobic Inhibition Test

Brine solutions were prepared according to Saebom Ko et al. In a typical brine synthesis, 55.22 g of NaCl was dissolved in 1000 ml of deionized water. In the meantime, 14.701 g of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  was dissolved in 100 ml deionized water which gives 1 M  $\text{Ca}^{2+}$ . From the 1 M  $\text{Ca}^{2+}$ , 12.5 ml was taken into 500 ml deionized water which gives the 25 mM  $\text{Ca}^{2+}$  for background solution. The pH was adjusted using sodium acetate/ acetic acid buffers. The background solution was then sparged with nitrogen for 3 hours before the addition of  $\text{Fe}^{2+}$  and  $\text{S}^{2-}$  brine solutions for inhibition testing.  $\text{FeCl}_2$  and  $\text{Na}_2\text{S}$  were used to prepare 30 ppm and 90 ppm of  $\text{Fe}^{2+}$  and  $\text{S}^{2-}$  respectively by dissolving 0.032 g of  $\text{FeCl}_2$  in 500 ml of the background brines. The other 500 ml of the background brine was utilized for  $\text{S}^{2-}$  preparation by dissolving 0.11 g of  $\text{Na}_2\text{S}$ . These two brines were then sparged for another 2 hours separately at the same time. Valved port caps were used to stop air from entering the stock bottles to maintain the anaerobic condition. The purging setup was connected by polyether ketone tubes which reduces the possibility of oxygen permeation. Transfer of stock brine solutions into the test bottles was carried out using gas tight syringes inside a glove bag after purging the glove bag for at least 10 times. Figure 2 shows the schematic diagram of the experimental setup.

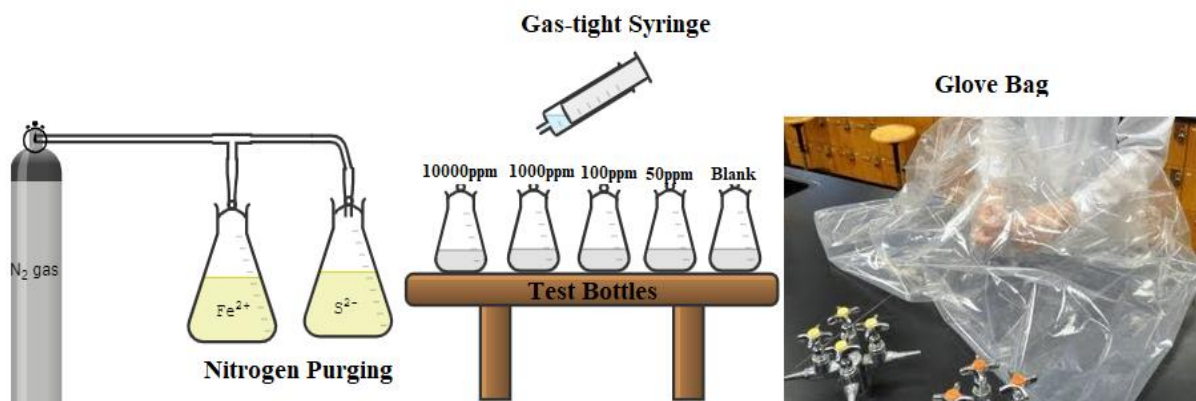


Figure 17: Schematic diagram of experimental setup

The required number of test bottles were labeled; these labels correspond to the sample's names provided for chemical analysis. Each test bottle is labelled with the name of the chemical and the dose rate written with permanent marker. To the five glass bottles, 50 ml of ' $Fe^{2+}$ ' solution was added to each test bottle using the gas-tight syringe; 50 ml of the ' $S^{2-}$ ' solution was also be added to the blanks. The ' $Fe^{2+}$ ' solution in each test bottle is dosed with the required amount of scale inhibitor intermediate solution (using gas-tight syringe) to give the required final dose rate for the particular test. The concentrations tested in this study were 50 ppm, 100ppm, 1000ppm and 10000ppm. The concentration of the inhibitor in the ' $Fe^{2+}$ ' was double than that required for the test which accounts for the dilution when mixed with the ' $S^{2-}$ '. Inhibitor is not added to the 'Blank' bottles.

An equal number of test bottles were prepared each filled with 50 ml of ' $S^{2-}$ ' solution using the gas-tight syringe inside the glove bag. Test bottles were placed into a pre-heated water bath at the appropriate test temperature for ~60 mins to reach thermal equilibrium. After that, the two brines were mixed by pouring the ' $S^{2-}$ ' into the ' $Fe^{2+}$ ' and mixed manually. The bottles were returned to the water bath immediately and the timer is started; this is  $t_0$ . The test bottles were sampled at defined time intervals. Test bottles were sampled after 2h, 16h and 24h. The pH values were monitored at the start of the test and upon cooling at the end. The samples taken at different time intervals are sent for chemical analysis to evaluate the performance of the inhibitors. This procedure was carried out in each experiment to evaluate the inhibitor at different conditions. The inhibitor was tested at 40 °C, 60 °C and 80 °C without altering the pH. The temperature was then set to 80 °C and the inhibitor was tested at 6.7, and 8.5. The test was also performed at different cationic/ anionic (C/A) compositions. C/A of 80/20 and 20/80 by volume was implemented.

The inhibition efficiency,  $\varepsilon$  was calculated using the iron ions remaining in the solution after the test by the following equation:

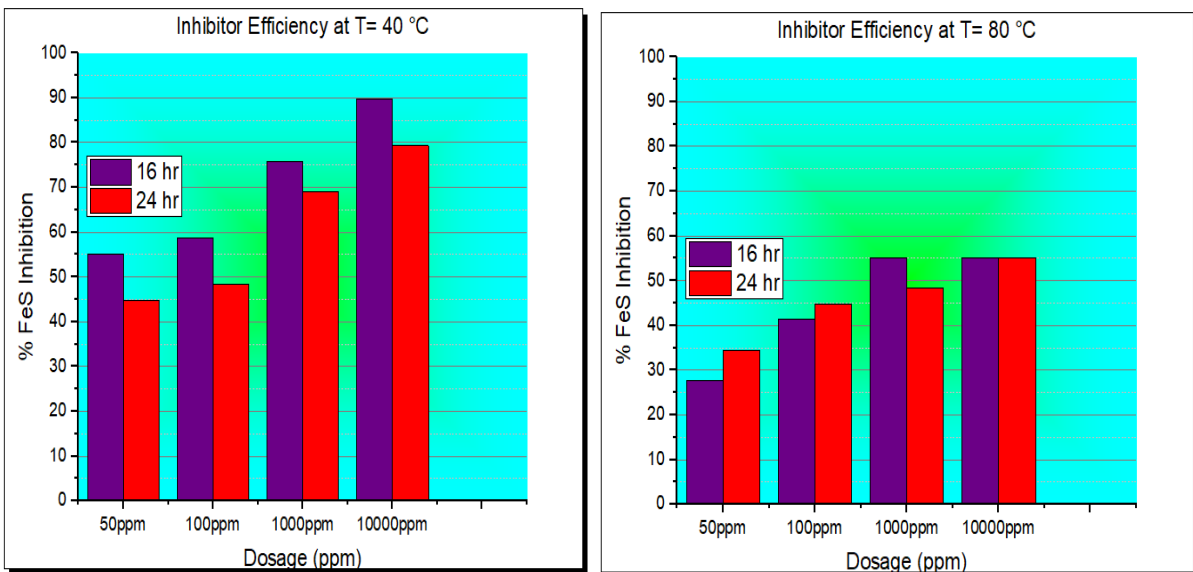
$$\varepsilon = \frac{Z_2 - Z_1}{Z_0 - Z_1}$$

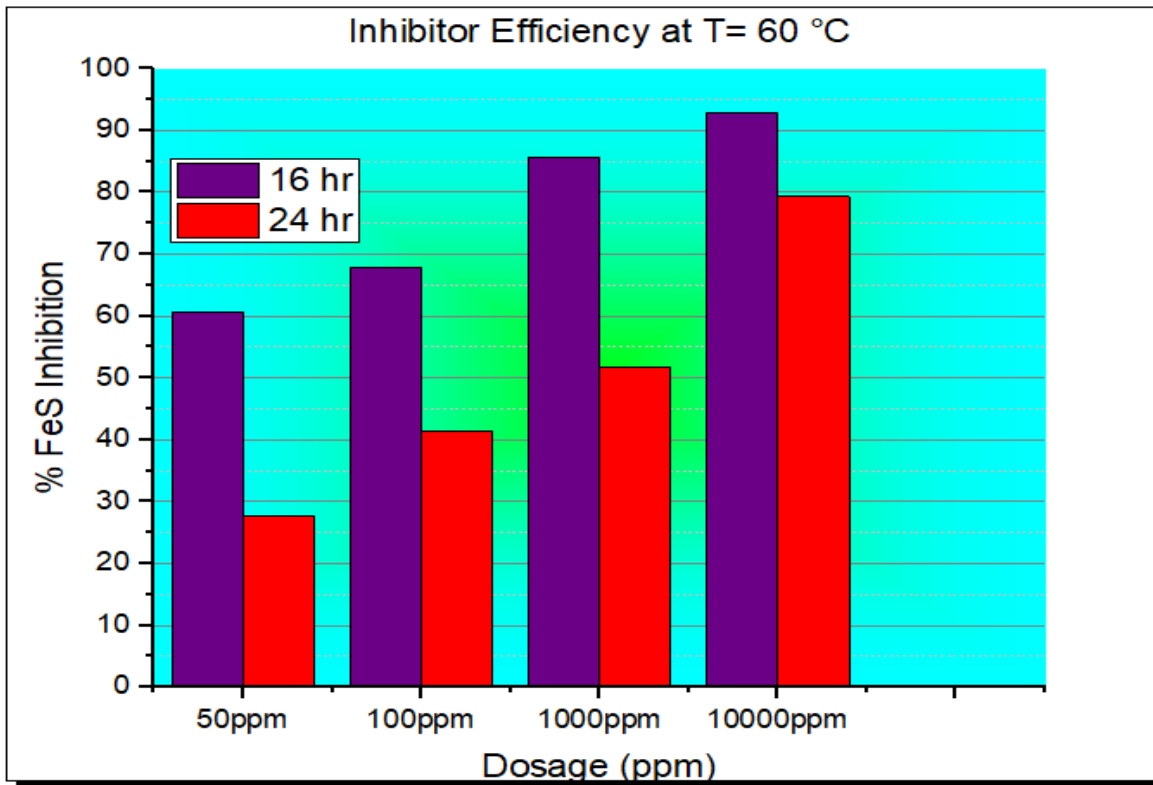
Where  $Z_2$  is the  $Fe^{2+}$  remaining in the filtrate after the reaction at different time intervals,  $Z_1$  is the remaining  $Fe^{2+}$  in the blank sample and  $Z_0$  is the concentration of  $Fe^{2+}$  used before the test.

### 4.3 Results and Discussion

#### 4.3.1 Influence of Temperature on FeS Inhibition

The influence of temperature on inhibition efficiency upon iron sulphide scale was studied and the results at 40°C, 60 °C and 80 °C are presented in figure 3. Aliquots of the test solutions, about 15 ml free from scale was sampled at 2 hr, 16 hr and 24 hr for  $Fe^{2+}$  ICP analysis.

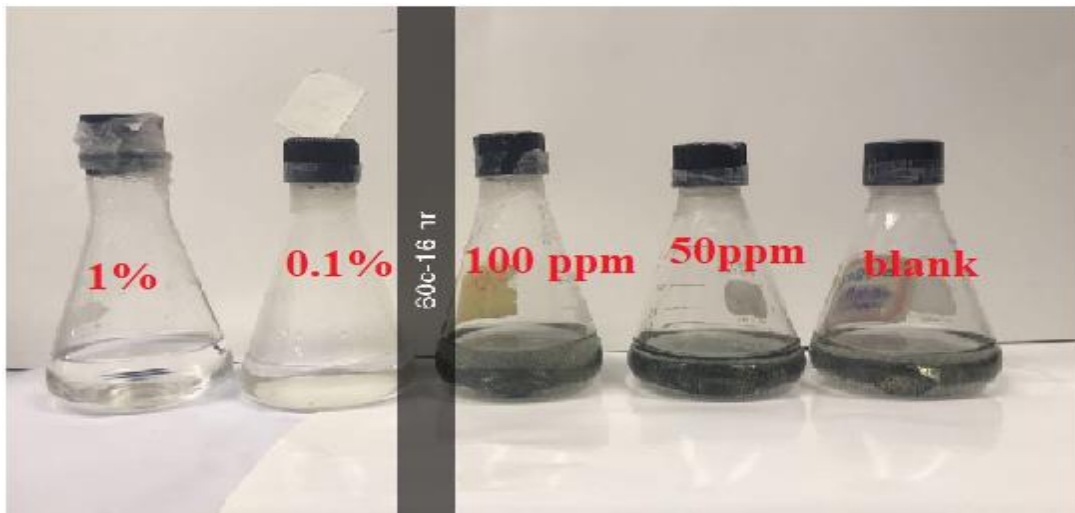




**Figure 18: Influence of temperature on FeS inhibition**

As seen from figure3, the inhibition efficiency increases with increasing the inhibitor dosage at the three temperatures 40C,60 °C and 80 °C. At 40 °C, the efficiency starts at 55% at 50 ppm inhibitor concentration, then increases to the highest value at 10000 ppm recording a value of 90%. It is easily recognized that the inhibition efficiency after 16 hours reaction is always higher than that of the 24-hour reaction. This phenomenon can be explained by the fact that in 24 hours, the nucleation growth of iron sulphide is mitigated and no more FeS is formed thus not much value for the inhibitor. At 80 °C, the inhibition efficiency starts at 26 % at 50 ppm inhibitor concentration after 16 hours of reaction, then increases to 55% at 10000 ppm inhibitor dosage. Surprisingly, at this temperature the inhibition efficiency after 24 hours reaction is always greater than that at 16 hours. Looking at the 60 °C results, the gap between the 16 hours results and 24

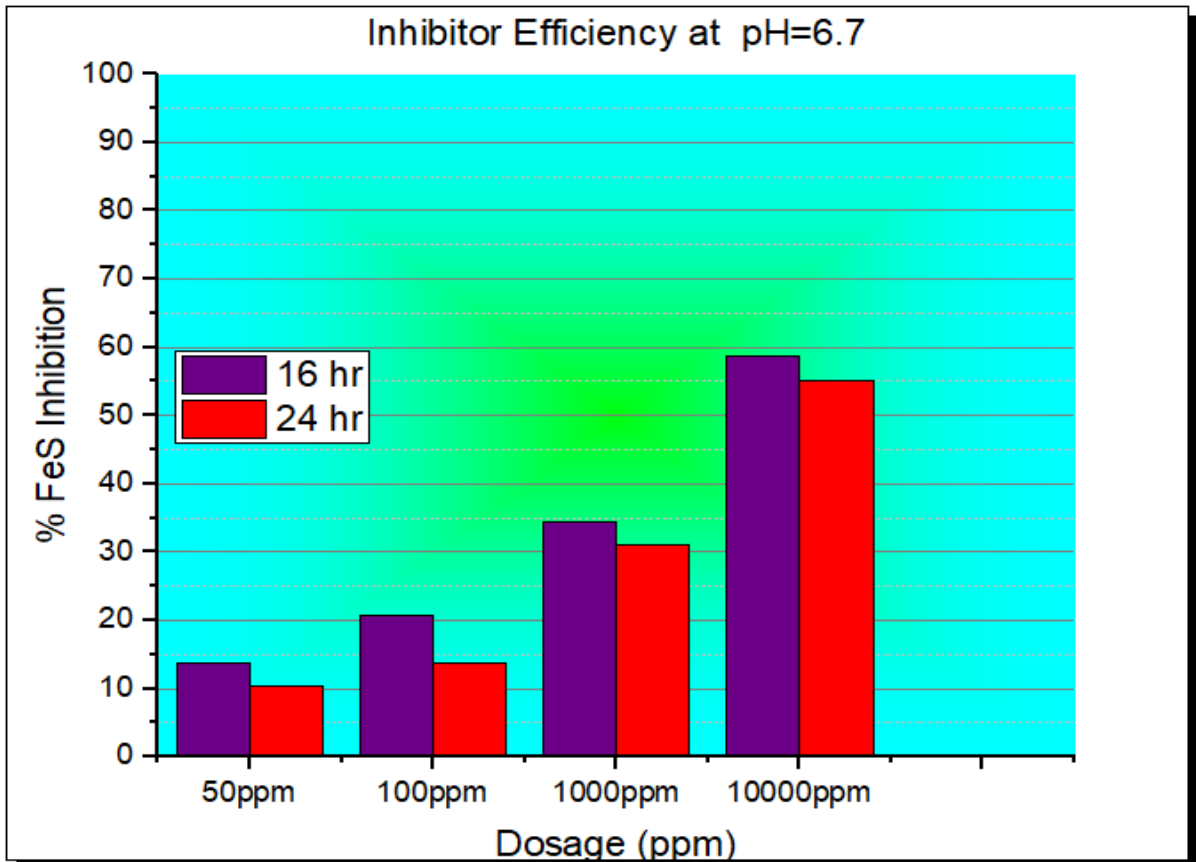
hours is the largest among the three temperatures. After 16 hours and at 50 ppm inhibitor concentration, the inhibition efficiency is 60 % while the 24 hours reaction time the efficiency is only just above 25%. The inhibition efficiency then increases to hit the highest ever recorded figure among the three temperatures which is 92% at 10000 ppm inhibitor concentration. The visualization of the efficiency test at 60 °C is represented in figure 4.



**Figure 19: visualization of the efficiency test at 60 °C**

### **4.3.2 Influence of pH on FeS Inhibition**

The influence of pH on the inhibition efficiency was also studied and represented in figure 5.



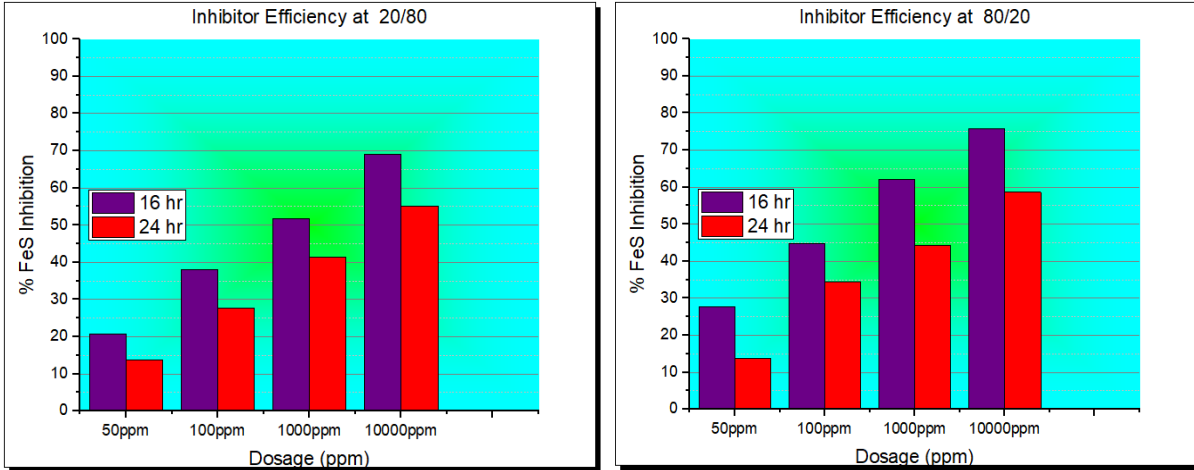
**Figure 20: Influence of pH on FeS inhibition**

At 6.7 pH value, the inhibition efficiency was affected negatively. At 16 hours reaction time, the efficiency is around 12 % while at 24 hours of reaction the efficiency is 10% both at 50 ppm inhibitor concentration. The highest efficiency at 6.7 pH is just below 60% at 10000 ppm inhibitor dosage. It is easily seen that the inhibition efficiency after 16 hours reaction is higher than that of the 24 hours for all inhibitor concentration dosages.

### 4.3.3 Influence of Brines Composition on FeS Inhibition

The influence of brine compositions on the inhibition was also studied and represented in figure 6. Two ratios of  $Fe^{2+}$  to  $S^{2-}$  were studied namely 20/80 and 80/20. The temperature was kept at 80 °C and two ratios were examined. Without altering the pH, 80 ml of  $Fe^{2+}$  brines were

mixed with 20 ml of  $S^{2-}$  brines containing different inhibitor concentrations and one blank solution as done for other experiments. The opposite was also tested where 20 ml of  $Fe^{2+}$  brines were added to 80 ml of  $S^{2-}$ .



**Figure 21: Influence of Brines composition on FeS inhibition**

In the case of 20/80, the efficiency starts at 20% in the 16 hours duration at 50ppm inhibitor concentration. The efficiency then increases to just below 70% at the highest inhibitor concentration dosage of 10000ppm. The same phenomena found at previous experiments is recognized here when the 16 hours reaction time have higher efficiencies than those of the 24-hour duration at all inhibitor dosages. The 80/20 ratio records an efficiency of slightly above 25% at 16 hours and an inhibitor concentration of 50ppm. The efficiency increases to 75% at 10000ppm. Like the 20/80 ratio, the efficiencies of the 16 hours duration is higher than those of the 24 hours. It is clearly seen from the figure that the 80/20 ratio is better giving higher efficiencies especially at high inhibitor concentrations. This is explained by the fact that in the 80/20 ratio, the availability of more  $Fe^{2+}$  facilitates formation of more FeS scale which can be inhibited leading to higher inhibition efficiency.

## CHAPTER 5

### A NOVEL CORROSION INHIBITOR FOR CARBON STEEL

#### IN 1M HCL

##### 5.1 Introduction

Carbon steel corrosion is considered one of the essential corrosion types that need to be dealt with due to carbon steel wide use industrially. It has been reported that the annual cost of corrosion is more than two trillion dollars which constitutes around 3.5% of global GDP [75]. The high cost of corrosion, makes it very crucial to think of protective material that could reduce the cost. One of the most applicable ways to reduce cost is the use of chemical inhibitors since they are more effective and cost competitive [2-3]. Over the years, organic molecules have been applied as metallic corrosion inhibitors but they found to be not applicable due to their toxicity and the fact they are not stable at higher temperature specially in acidic media [4-5]. Naturally occurring materials containing heteroatoms like oxygen, nitrogen and phosphorus has been employed as potential metallic corrosion inhibitors [6-9]. Reports indicated that the efficiency chromate and dichromate-based corrosion inhibitors can't be compared [84]. However, now there are a lot of recent environmental rules require a replacement of toxic inhibitors such as sodium chromate ( $\text{Na}_2\text{CrO}_4$ ) inhibitor [84], with what called “*green chemicals*” “*green chemicals*”. In this experimental work, corrosion inhibition of steel and aluminum will be studied as proposed in the research hypothesis. Even though there are a lot of

metallic corrosion inhibitors have been commercialized, most of them are carcinogenic or toxic in nature[11-12] . Up to now, Molybdate salts are the most commercial corrosion inhibitors used as replacement of chromates in industrial applications, but their cost is very high [87].

According to [14-15] the corrosion inhibitors such as Gluconates and gluconic acids can be used for cooling water systems contains mild steel as nontoxic, effective and eco-friendly ones. In additions, there are reports that represent their ability and environmental compatibility to reduce the corrosion[16-17]. For example, Rajendran's et al.[92] studied the Ca-gluconate efficiency as corrosion inhibitor for mild steel in cooling water systems of about 60 ppm ions of chlorine.

Ferrous gluconate has been studied as corrosion inhibitor for protection of aluminum from saline corrosive environment by using weight loss technique and the results indicated that the corrosion inhibition occurs on surface of the aluminum and followed Langmuir adsorption isotherm with 1.0 g/mL inhibitor concentration for an optimum efficiency [92].

## **5.2 Experimental**

### **5.2.1 Materials**

Gallic acid and polyacrylamide were obtained from Fisher Scientific and carbon steel (CS) with the wt.% elemental composition given in Table 1. Here, the steel samples were cut into 2.8 cm x 2.8 cm x 0.8 cm, for weight loss, and 1 cm x 1 cm, cold-mounted with an epoxy/hardener mixture (for electrochemical) techniques. The CS coupons were all wet polished using silicon carbide abrasive papers from 120 to 1000 grit, then thoroughly rinsed with purified water,

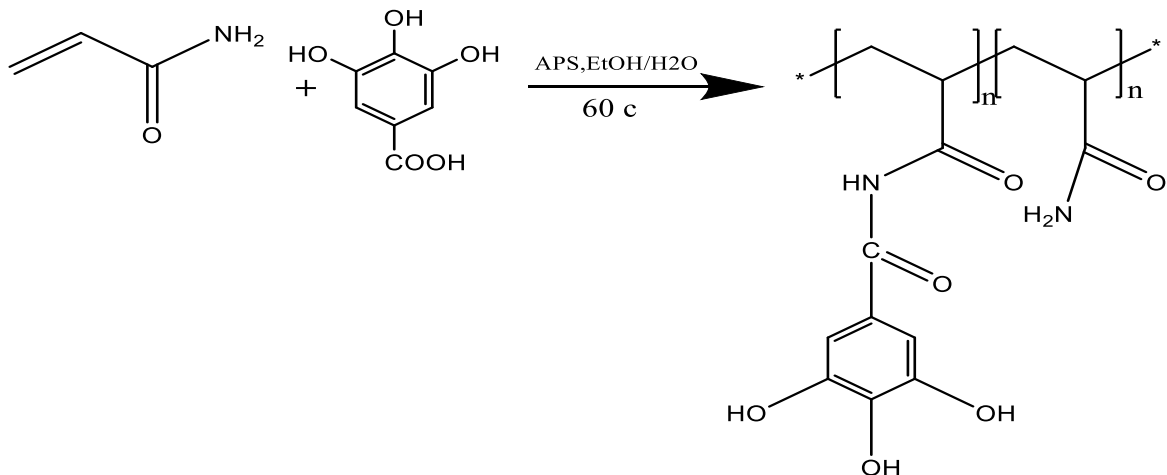
degreased with acetone, dried, and stored in a moisture-free desiccator. The density of CS is 7.87 g/cm<sup>3</sup>.

**Table 11: Concentration of carbon steel used in the study**

Element	Fe	Cr	C	Si	Mn	Cu	Ni	Mo	Al	Nb	V
Composition (wt. %)	<96.2	0.121	0.125	0.125	0.52	1.830	0.296	0.091	0.079	0.043	0.078

### 5.2.2 Inhibitor Preparation

Gallic acid grafted polyacrylamide was synthesized by adding 2.5g of acrylamide in a three-neck flask containing 50ml of distilled water. After that, 3g of gallic acid is dissolved in 50 ml distilled water then added to the 3-neck flask to make the gel-mixture. Then, 20 ml of ethanol was added to the reaction mixture and the temperature was set to 60 °C before the addition of sodium persulfate as the reaction initiator according to eqn 3 below. This mixture was purged with nitrogen for 5 hours and stirred at 450 rpm for 24 hours before collecting the product.



**Figure 22: GAGP Synthesis**

### 5.2.3 Weight Loss

The analysis of weight loss is the simplest and the longest established method of approximating the corrosion losses in equipment and plant. A certain coupon either metal or alloy is introduced into the environment or process under consideration and taken out after many hours. After that, the coupon is cleaned of the product of corrosion and is weighed again. The difference in the weight is converted to a metal loss (ML) or rate of corrosion (CR), as follows:

$$\text{Corrosion rate (CR)} = \frac{\text{weight loss (g)} * K}{\text{alloy density} \left( \frac{\text{g}}{\text{cm}^3} \right) * \text{Exposed Area (A)} * \text{Exposure Time (hr)}}$$

Where the value of the K depends on the unit of corrosion rate as shown in the following table:

Values of the K based on the Units of the area and corrosion rate

**Table 12: K values for corrosion rate calculation**

Desired Corrosion Rate Unit (CR)	Area Unit (A)	K-Factor
mils/year (mpy)	in <sup>2</sup>	5.34 x 10 <sup>5</sup>
mils/year (mpy)	cm <sup>2</sup>	3.45 x 10 <sup>6</sup>
millimeters/year (mmy)	cm <sup>2</sup>	8.76 x 10 <sup>4</sup>

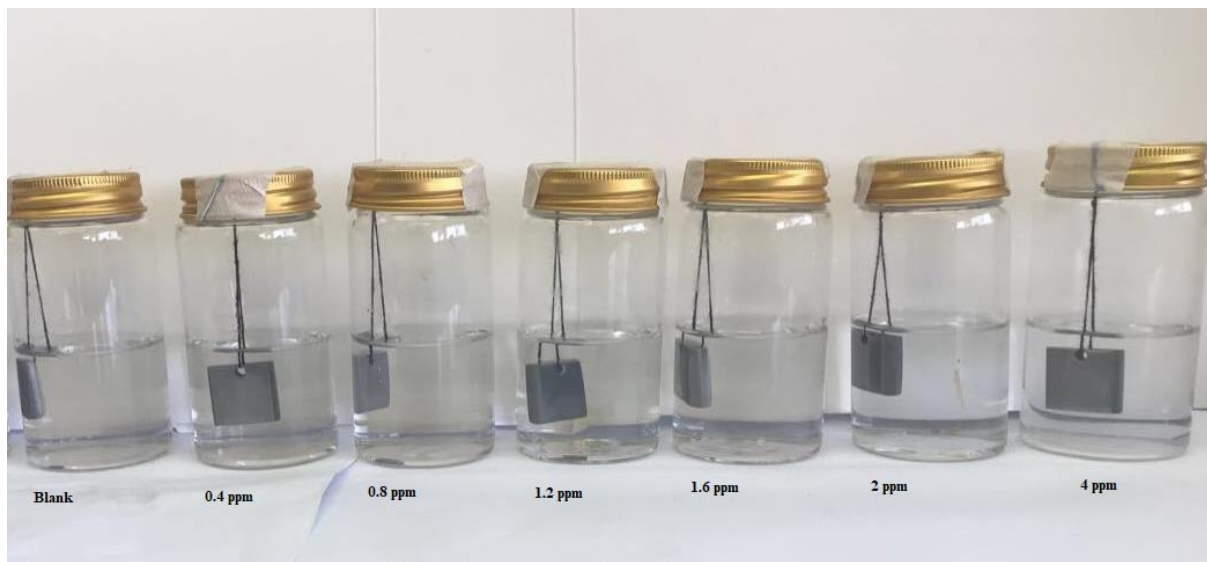
$$Metal\ Loss\ (ML) = \frac{weight\ loss(g) * K}{alloy\ density\ \left(\frac{g}{cm^3}\right) * Exposed\ Area\ (A)}$$

Where the value of the k depends on the unit of metal loss as shown in the following table2:

**Table 13: Values of K based on the units of the area and metal loss**

Desired Metal Loss Unit (ML)	Area Unit (A)	K-Factor
mils	in <sup>2</sup>	61.02
mils	cm <sup>2</sup>	393.7
Millimeters	cm <sup>2</sup>	10.0

Firstly, different concentrations of the inhibitor were tested from 0.4 ppm to 4 ppm as shown in the following figure. The best concentrations were recorded and tested at higher temperatures.

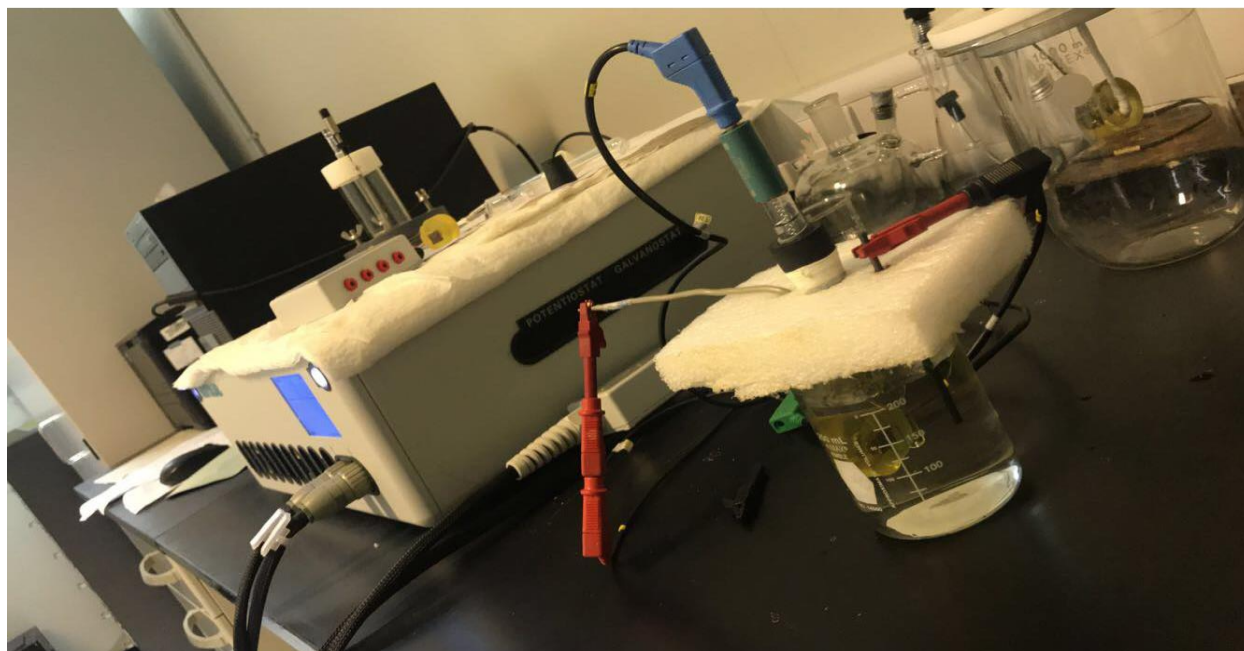


**Figure 23: weight loss at inhibitor concentration**

### 5.2.4 Electrochemical Experiment

The electrochemical experiment was conducted using a Gamry Potentiostat/Galvanostat (Model G-600) instrument with a three electrodes cell system. A cold-mounted CS specimen with 1 cm<sup>2</sup> as the exposed surface area was employed as the working electrode. Silver/silver

chloride electrode (Ag/AgCl) was used as the reference electrode while the graphite rod was used as the counter electrode. Four electrochemical techniques; electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP), electrochemical frequency modulation (EFM), and linear polarization resistance (LPR), were carried out to study the efficacy of GAGP against the CS corrosion in 1M HCl at room temperature. The test samples were firstly submerged for 1 h in the testing media at open circuit potential (OCP) to accomplish a steady state condition before performing the electrochemical techniques. The EIS determinations were performed under a potentiostatic condition at 10 mHz to 100 kHz frequency range and 10 mV amplitude after the 3600 s open circuit potential. This was followed by the LPR technique, taken at 10 mV  $E_{corr}$  at 0.125 mV/s scan rate. Then, EFM was performed with 1 Hz as a base frequency, multiplier A of 2, multiplier B of 5, the cycle of 32 and amplitude of 10 mV. And finally, the PDP measurement carried out at a voltage range of -0.25 V to +0.25 V vs. EOC, with a 0.50 mV/s scan rate. Data analysis and curve fittings were done using the Gamry EChem Analyst 5.5 software. The electrochemical setup used is shown in the following figure.



**Figure 24: Electrochemical cell setup**

To minimize the IR drop, the working electrode should be close to the reference electrode but should not touch. This principle was maintained in every experiment as represented in the following figure.

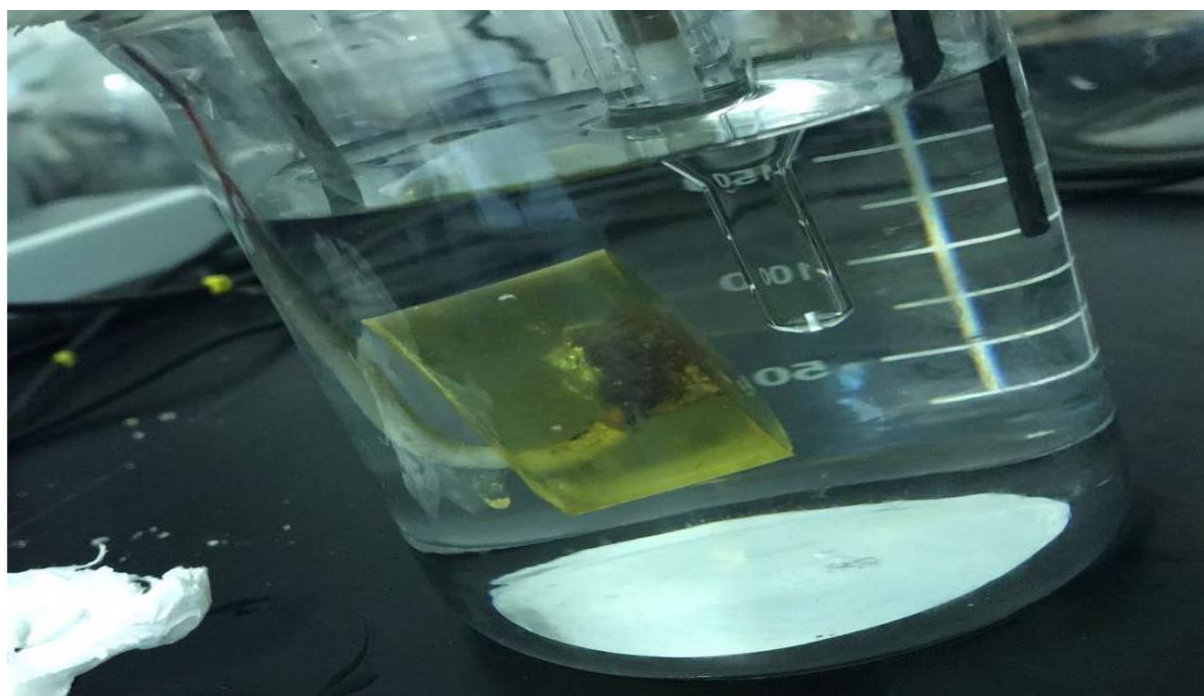
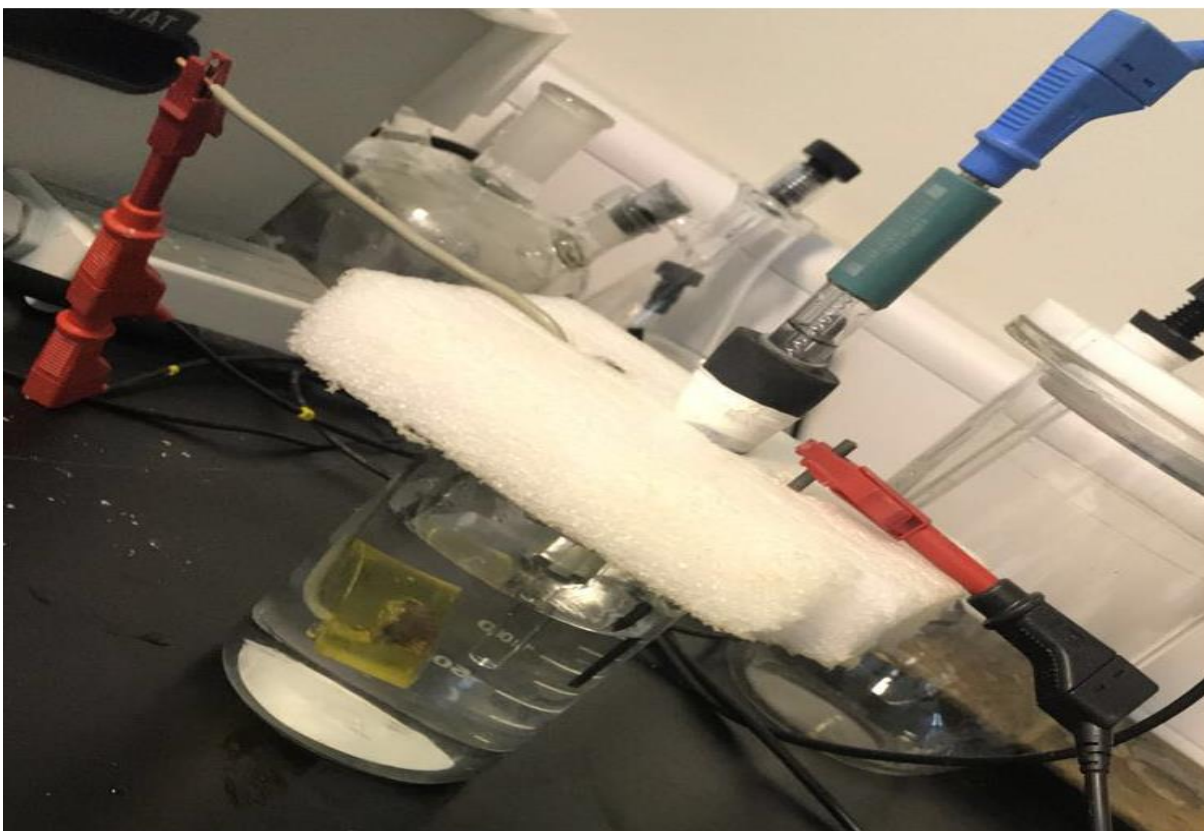


Figure 25: IR drop minimizing.

## 5.3 Results and Discussion

### 5.3.1 Effect of Inhibitor Concentration

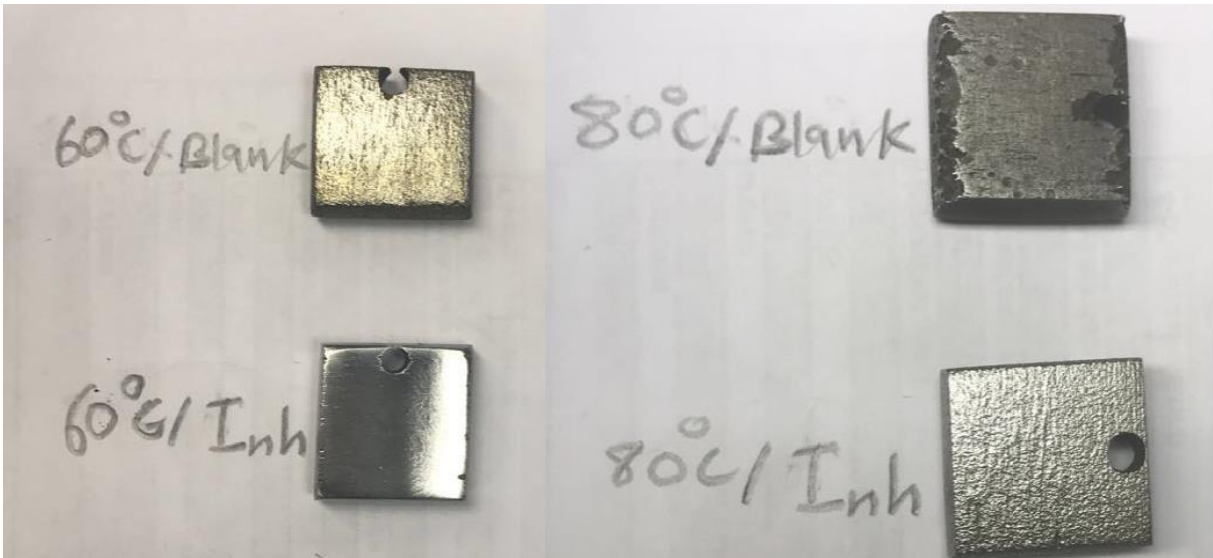
To evaluate the effect of inhibitor concentration upon inhibitor efficiency, different concentrations of the inhibitor were tested. Firstly, those concentrations were tested for 1-day immersion, however the weight loss was found to be very small. To get relatively high weight loss, the immersion test was done for 3 days. Figure shows the experiment for different concentrations.



Figure 26: Specimens before test at different temperatures



Figure 27: wt loss exp. at different concentrations



**Figure 28: Specimens after the test at 60 C and 80 C**

Weight loss and corrosion rate were evaluated and tabulated in tables 4 & 5.

**Table 14: Weight loss at different inhibitor concentrations**

wt loss.(hrs)	Blank	0.4 ppm	0.8 ppm	1.2 ppm	1.6 ppm	2 ppm	4 ppm
wt.loss (1day)	0.0250	-	-	-	-	0.008	-
<b>wt.loss(3 days )</b>	0.1190	0.0240	0.0220	0.0210	0.02	<b>0.019</b>	0.024
wt.loss(5 days )	0.3040	-	-	-	-	0.038	-

To assess the corrosion damage to the metals, corrosion rate was calculated using the weight loss method. Initially the total surface area of the specimens and the mass loss during the test were determined. The average corrosion rate was determined for the different cases of concentrations and inhibitors using this equation:

$$\text{Corrosion rate (CR)} = \frac{K \times W}{A \times T \times D} \quad \text{where;}$$

- *K* is a constant related to the unit of corrosion rate. Different *K* values correspond to different corrosion rate units as the following table suggests.

Corrosion Rate Units Desired	Constant (K) in Corrosion Rate Equation
mils per year (mpy)	$3.45 \times 10^6$
inches per year (ipy)	$3.45 \times 10^3$
inches per month (ipm)	$2.87 \times 10^2$
millimetres per year (mm/y)	$8.76 \times 10^4$
micrometres per year (um/y)	$8.76 \times 10^7$
picometres per second (pm/s)	$2.78 \times 10^6$
grams per square meter per hour (g/m <sup>2</sup> ·h)	$1.00 \times 10^4 \times D$
milligrams per square decimeter per day (mdd)	$2.40 \times 10^6 \times D$
micrograms per square meter per second (µg/m <sup>2</sup> ·s)	$2.78 \times 10^6 \times D$

- $W$  is the mass loss of the specimen in grams.
- $A$  is the surface area of the specimen in  $cm^2$ .
- $T$  is the exposure time in hours.
- $D$  is the density in  $g/cm^3$

Surface Area (A) can be calculated from the dimensions shown in figure X. Accounting for the mounting hole the surface area is:

$$A = 2.7 \times 2.7 + 2.7 \times 4 \times 0.7 = 22 \text{ cm}^2$$

Density of Mild Steel  $D = 7.87 \text{ g/cm}^3$ .

- Exposure time = 24 hr
- Weight loss = 0.119 g (average loss of the blank samples of Experiment#1)
- Taking  $K = 3.45 \times 10^6$  to get the corrosion rate in mpy.

Substituting these values in in equation (1) gives:

$$\text{Corrosion rate (CR)} = \frac{K \times W}{A \times T \times D} = \frac{3.45 \times 10^6 \times 0.00315}{4.4295 \times 24 \times 7.85} = 32.235 \text{ mpy.}$$

**Table 15: corrosion rate at different inhibitor concentrations**

T(hr)	CR(mpy)						
	Blank	0.4 ppm	0.8 ppm	1.2 ppm	1.6 ppm	2 ppm	4 ppm
24	20.62507	-	-	-	-	6.60002	-
72	32.72512	6.600024	6.050022	5.775021	5.500019704	5.22502	6.600024
120	50.16018	-	-	-	-	6.27002	-

To calculate the efficiency the following formula was used

$$\% \text{Eff} = \frac{CR_0 - CR_I}{CR_0} \times 100$$

Where;

$W_0$  is the weight loss of the sample without inhibitor (Blank).

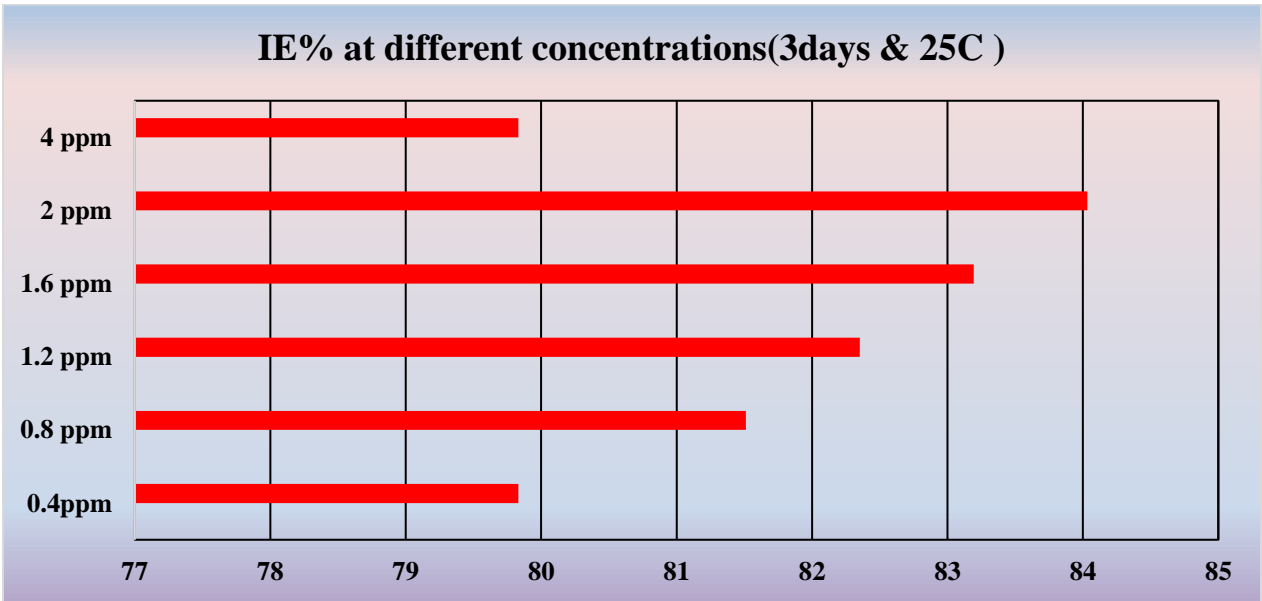
$W$  is the weight loss of the sample when the inhibitor is present.

For 2 ppm for Carbon Steel  $\% \text{Eff} = \frac{W_0 - W}{W_0} \times 100 = \frac{0.003 - 0.001}{0.003} \times 100 = 84\%$

**Table 16: Efficiency at different inhibitor concentrations**

%Eff with Time(hr)	Blank	0.4 ppm	0.8 ppm	1.2 ppm	1.6 ppm	2 ppm	4 ppm
Eff(1 day)	-	-	-	-	-	68.00	-
Eff (3 days)	-	79.83	81.51	82.35	83.19	84.03	79.83
Eff(5 days)	-	-	-	-	-	87.50	-

The efficiency was plotted at different concentrations. The efficiency was found to increase with increasing inhibitor concentration. The highest inhibitor efficiency is at 2 ppm which is 85 %. The efficiency decreases after 2 ppm indicating that the optimum inhibitor concentration is 2 ppm.



**Figure 29: Efficiency at different concentrations**

The optimum inhibitor concentration was taken to be tested for immersion time of 1 day, 3 days and 5 days. The weight loss increases with immersion time increase.

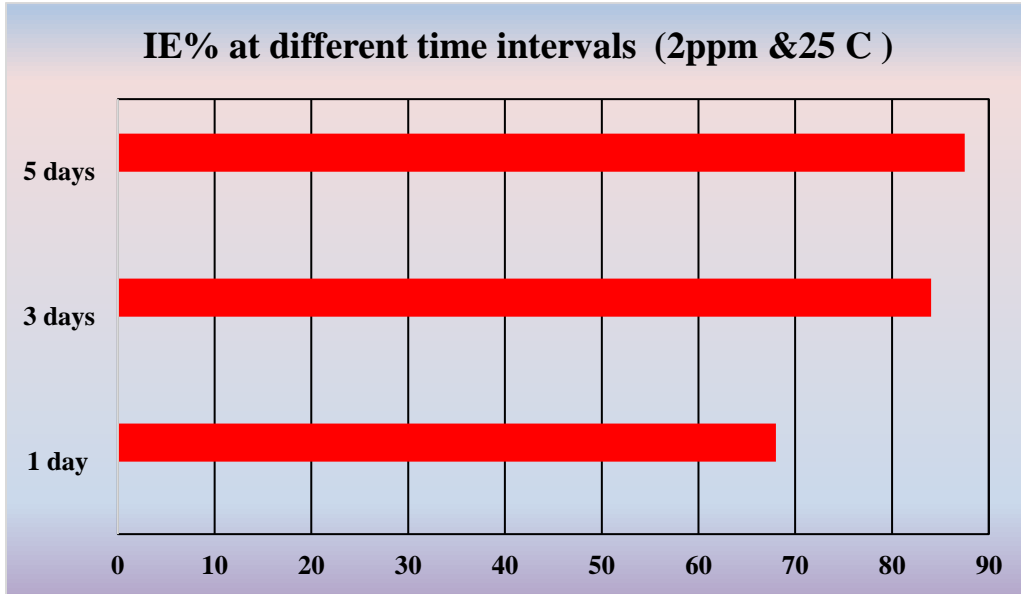


Figure 30: Efficiency at different time intervals

### 5.3.2 Effect of Temperature

The optimum concentration was also tested at 40C, 60°C and 80°C.

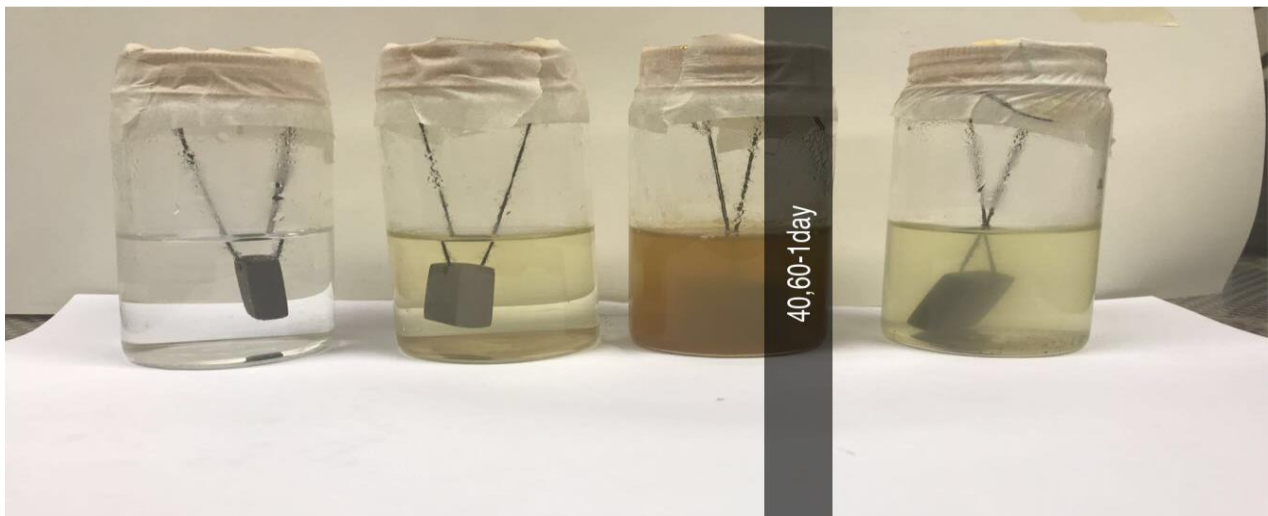
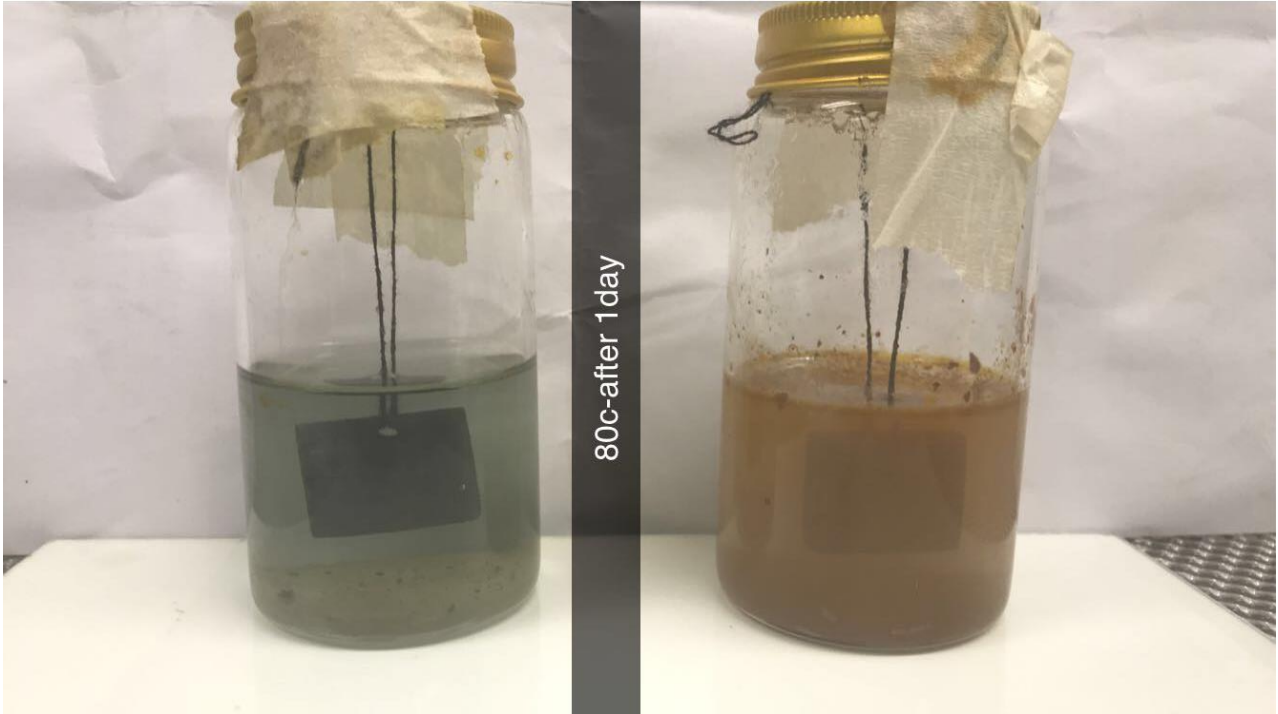


Figure 31: Exp at 40 C and 60 °C.



**Figure 32: Exp at 80 °C**

As the temperature increases, the weight loss increases. At 80 C, the highest weight loss is attained.

**Table 17: weight loss at diff Temp**

wt loss.(T(c))	Blank	2 ppm
wt.loss (40 C)	0.1190	0.0210
<b>wt.loss(60 C)</b>	0.9980	0.1520
wt.loss(80 C)	1.4230	0.2130

**Table 18:Corr rate Temp**

T( hr)	CR(mpy)	
	Blank	2 ppm
24	98.17535	17.32506
24	823.3529	125.4004
24	1173.979	175.7256

**Table 19::Eff. at diff T**

%Eff(at C)	2 ppm
Eff(40 C)	82.35
Eff (60 C)	84.77
Eff(80 C)	85.03

The calculated efficiency was plotted at different temperatures. The highest efficiency was achieved at 80 °C. The achieved value is 87%. The efficiency was found to increase with temperature increase.

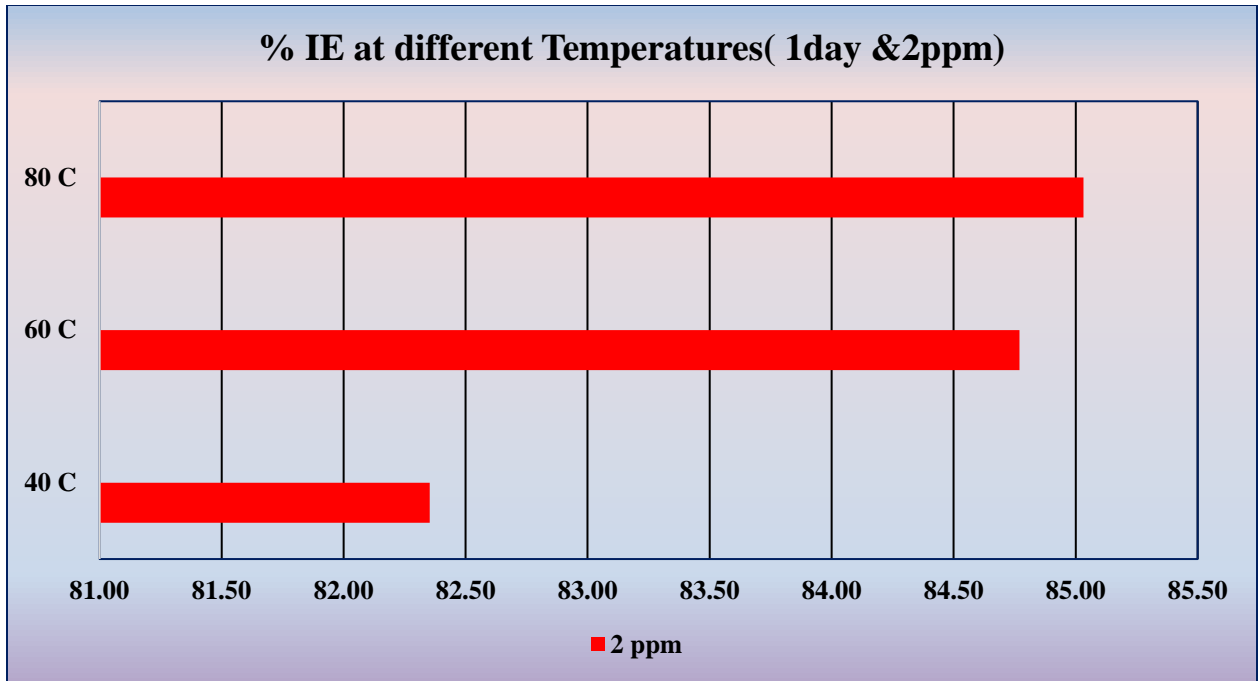


Figure 33: Efficiency at different temperatures

## CHAPTER 6

### Conclusions and Recommendations

The formation of mineral scales imposed on reservoirs, downhole equipment and wellhead during oilfield process is becoming a serious problem that leads to equipment damage and production losses. The best solution to overcome this problem is the chemical treatment using scale Inhibitors. Herein, A novel gallic acid grafted acrylamide polymer containing carboxylic and acrylamino groups was successfully synthesized and characterized by means of FTIR, NMR and TGA. The TGA results showed that the inhibitor is thermally stable at elevated temperatures. The inhibitor was then tested for compatibility and showed positive results of compatibility even at high concentrations with no precipitates or phase separation taking place. The synthesized inhibitor was evaluated by means of static bottle test under various conditions (i.e. temperature, pH and cationic to anionic brine ratios). It was found that higher amount of scale forms at higher temperatures. The effectiveness of the inhibitor increases with temperature reaching a peak at 80 C. The influence of pH on the inhibitor efficiency was also investigated and it was concluded that as the pH increases the inhibition efficiency increases. The ratio of cationic to anionic ratio lead to high inhibition efficiency in case of higher cationic to anionic ratio because of the presence of more calcium ions that facilitates scale formation which in turn can be inhibited. To further investigate the inhibition mechanism, the collected scale samples were characterized by SEM, EDS and TEM. Characterization techniques revealed that in

addition to the successful chelation of calcium by the inhibitor, the absorption of the inhibitor to the active crystal growth sites hindered crystal growth which improved inhibition efficiency. The results of this work proved the potential of the inhibitor efficiency at different temperature, pH and brine concentrations yet at relatively low inhibitor dosages. In addition, functionalized polymer inhibitor was synthesized and evaluated towards iron sulphide scale inhibition. A strictly anoxic setup was utilized at different experimental conditions. This study has shown that the functionalized material has the potential to inhibit iron sulphide formation especially at specific conditions (i.e. temperature of 60 °C). The inhibitor is believed to not only hinder the nucleation growth of iron sulphide but also prevent iron sulphide particles from settling especially at moderate concentration dosages. When evaluated at different temperature, pH and brine composition, the inhibitor revealed no big difference. The inhibitor provides a promising result for metal sulphide scales. Finally, GAGP was successfully synthesized and tested towards carbon steel corrosion. Weight loss results were in full agreement with electrochemistry results. The inhibitor was found to be effective up to 80 °C.

## References

- [1] S. Gao, B. Brown, D. Young, S. Nestic, and M. Singer, "Paper No. 11027," no. 11027, pp. 1–16.
- [2] A. Neville *et al.*, "Scale formation and control in oil and gas fields: A review," *Desalination*, vol. 338, no. 1, pp. 6199–6207, 2014.
- [3] T. Chen, Q. Wang, and F. Chang, "New insight into the mechanisms of iron sulfide deposition in carbonate reservoir during acid stimulation," *NACE - Int. Corros. Conf. Ser.*, vol. 2018-April, 2018.
- [4] "What is Scale Formation? - Goes Heating System." [Online]. Available: <http://goesheatingsystems.com/what-is-scale-formation/>. [Accessed: 16-Nov-2019].
- [5] J. Li, M. Tang, Z. Ye, L. Chen, and Y. Zhou, "Scale formation and control in oil and gas fields: A review," *J. Dispers. Sci. Technol.*, vol. 38, no. 5, pp. 661–670, 2017.
- [6] M. Amiri and J. Moghadasi, "The effect of temperature on calcium carbonate scale formation in iranian oil reservoirs using oli scalechem software," *Pet. Sci. Technol.*, vol. 30, no. 5, pp. 453–466, 2012.
- [7] C. Dai *et al.*, "A unified experimental method and model for predicting scale inhibition," in *Proceedings - SPE International Symposium on Oilfield Chemistry*, 2019, vol. 2019.
- [8] H. Wang, Y. Zhou, Q. Yao, S. Ma, W. Wu, and W. Sun, "Synthesis of fluorescent-tagged scale inhibitor and evaluation of its calcium carbonate precipitation

- performance,” *Desalination*, vol. 340, no. 1, pp. 1–10, 2014.
- [9] P. Rodgers *et al.*, “Multifunctional chemical for simultaneous dissolution of iron sulfide, corrosion inhibition, and scale inhibition,” in *Proceedings - SPE International Symposium on Oilfield Chemistry*, 2019, vol. 2019.
- [10] X. Gu *et al.*, “Preparation and application of polymers as inhibitors for calcium carbonate and calcium phosphate scales,” *Int. J. Polym. Mater. Polym. Biomater.*, vol. 62, no. 6, pp. 323–329, 2013.
- [11] Z. Kiaei and A. Haghtalab, “Experimental study of using Ca-DTPMP nanoparticles in inhibition of CaCO<sub>3</sub> scaling in a bulk water process,” *Desalination*, vol. 338, no. 1, pp. 84–92, 2014.
- [12] H. Wang, Y. Zhou, Q. Yao, Y. Bu, Y. Chen, and W. Sun, “Study on calcium scales inhibition performance in the presence of double-hydrophilic copolymer,” *Int. J. Polym. Mater. Polym. Biomater.*, vol. 64, no. 4, pp. 205–213, 2015.
- [13] M. Xue *et al.*, “Acrylic acid-allylpolyethoxy carboxylate copolymer: An effective and environmentally friendly inhibitor for carbonate and sulphate scales in cooling water systems,” *Int. J. Green Energy*, vol. 12, no. 11, pp. 1151–1158, 2015.
- [14] Z. Belarbi, J. Gamby, L. Makhloufi, B. Sotta, and B. Tribollet, “Inhibition of calcium carbonate precipitation by aqueous extract of *Paronychia argentea*,” *J. Cryst. Growth*, vol. 386, pp. 208–214, 2014.
- [15] K. Harouaka, A. T. Kan, and M. Tomson, “Calcite deposition kinetics and the effect of phosphonate and carboxylate inhibitors at 150 °C,” *Appl. Geochemistry*, vol. 109, p.

104393, Oct. 2019.

- [16] A. V. A. de Souza, F. Rosário, J. Cajaiba, A. Velloso Alves de Souza, F. Rosário, and J. Cajaiba, “Evaluation of calcium carbonate inhibitors using sintered metal filter in a pressurized dynamic system,” *Materials (Basel)*, vol. 12, no. 11, pp. 1–13, Jun. 2019.
- [17] Z. Xu, Y. Zhao, J. Wang, and H. Chang, “Inhibition of calcium carbonate fouling on heat transfer surface using sodium carboxymethyl cellulose,” *Appl. Therm. Eng.*, pp. 1074–1080, Feb. 2019.
- [18] M. Barber and S. Heath, “A new approach to testing scale inhibitors in mild scaling brines – are dynamic scale loop tests needed?,” in *Proceedings - SPE International Symposium on Oilfield Chemistry*, 2019, vol. 2019.
- [19] M. Mpelwa and S.-F. Tang, “State of the art of synthetic threshold scale inhibitors for mineral scaling in the petroleum industry: a review,” vol. 16, pp. 830–849, 2019.
- [20] D. Liu, “Research on Performance Evaluation and Anti-scaling Mechanism of Green Scale Inhibitors by Static and Dynamic Methods,” 2011.
- [21] G. Of, “An Introduction to THE PETROLEUM INDUSTRY,” 1991.
- [22] M. Nergaard and C. Grimholt, “An Introduction to Scaling causes , problems and solutions,” no. november, 2010.
- [23] X. Wang, Q. Qu, S. Berry, J. Cutler, and B. Hughes, “SPE 165199 Iron Sulfide Removal : A Nonacidic Alternative to Hydrochloric Acid Treatment,” 2013.
- [24] A. R. Al Salami, A. A. Monem, Z. Development, and C. Zadco, “SPE 137906

- Downhole and Topside Scale Challenge ‘ Removal , Prevention and Inhibition Strategy ,” 2010.
- [25] M. El-said, M. Ramzi, and T. Abdel-moghny, “Analysis of oil fi eld waters by ion chromatography to determine the composition of scale deposition,” *DES*, vol. 249, no. 2, pp. 748–756, 2009.
- [26] T. Chen, Q. Wang, and F. F. Chang, “New Mechanisms of Iron Sulfide Deposition during Acid Stimulation in Sour Gas Carbonate Reservoir,” 2018.
- [27] M. S. Kamal, I. Hussein, M. Mahmoud, A. S. Sultan, and M. A. S. Saad, “Journal of Petroleum Science and Engineering Oil fi eld scale formation and chemical removal : A review,” vol. 171, no. January, pp. 127–139, 2018.
- [28] I. Wells, “SPE 16907 Diagnosis and Removal of Microbial/Fines Plugging in Water Injection Wells,” pp. 303–306, 1987.
- [29] S. Elkatatny and K. Fahd, “SPE-183914-MS New Formulation for Iron Sulfide Scale Removal,” no. March, pp. 6–9, 2017.
- [30] A. Khormali and D. G. Petrakov, “Laboratory investigation of a new scale inhibitor for preventing calcium carbonate precipitation in oil reservoirs and production equipment,” *Pet. Sci.*, vol. 13, no. 2, pp. 320–327, 2016.
- [31] A. T. Kan and M. B. Tomson, “Scale Prediction for Oil and Gas Production,” 2012.
- [32] V. Tantayakom, T. Sreethawong, H. S. Fogler, F. F. De Moraes, and S. Chavadej, “Scale inhibition study by turbidity measurement,” *J. Colloid Interface Sci.*, vol. 284, no. 1, pp. 57–65, Apr. 2005.

- [33] R. Vazquez and M. Krstic, "Boundary control and estimation of reaction–diffusion equations on the sphere under revolution symmetry conditions," *Int. J. Control*, vol. 92, no. 1, pp. 2–11, Jan. 2019.
- [34] M. Chaussemier *et al.*, "State of art of natural inhibitors of calcium carbonate scaling. A review article," *Desalination*, vol. 356, pp. 47–55, Jan. 2015.
- [35] F. Hasson and S. Keeney, "Enhancing rigour in the Delphi technique research," *Technol. Forecast. Soc. Change*, vol. 78, no. 9, pp. 1695–1704, Nov. 2011.
- [36] M. Liu, H. Su, and T. Tan, "Synthesis and properties of thermo- and pH-sensitive poly(N- isopropylacrylamide)/polyaspartic acid IPN hydrogels," *Carbohydr. Polym.*, vol. 87, no. 4, pp. 2425–2431, Mar. 2012.
- [37] Z. Quan, Y. Chen, X. Wang, C. Shi, Y. Liu, and C. Ma, "Experimental study on scale inhibition performance of a green scale inhibitor polyaspartic acid," *Sci. China, Ser. B Chem.*, vol. 51, no. 7, pp. 695–699, Jul. 2008.
- [38] Y. SUN, W. XIANG, and Y. WANG, "Study on polyepoxysuccinic acid reverse osmosis scale inhibitor," *J. Environ. Sci.*, vol. 21, no. SUPPL. 1, 2009.
- [39] L. Liu *et al.*, "Fatigue and sleep quality are associated with changes in inflammatory markers in breast cancer patients undergoing chemotherapy," *Brain, Behavior, and Immunity*, vol. 26, no. 5. pp. 706–713, Jul-2012.
- [40] M. Schweinsberg, W. Hater, and J. Verdes, "New Stable Biodegradable Scale Inhibitor Formulations for Cooling Water: Development and Field Tests."
- [41] D. L. Verraest, J. A. Peters, H. van Bekkum, and G. M. van Rosmalen,

- “Carboxymethyl inulin: A new inhibitor for calcium carbonate precipitation,” *J. Am. Oil Chem. Soc.*, vol. 73, no. 1, pp. 55–62, Jan. 1996.
- [42] A. Martinod, A. Neville, and M. Euvrard, “Experimental investigation of scaling control by a non-phosphorous polymer: Polyaspartic acid,” *Desalin. Water Treat.*, vol. 7, no. 1–3, pp. 86–92, 2009.
- [43] S. Kirboga and M. Öner, “The inhibitory effects of carboxymethyl inulin on the seeded growth of calcium carbonate,” *Colloids Surfaces B Biointerfaces*, vol. 91, no. 1, pp. 18–25, Mar. 2012.
- [44] A. R. Hoch, M. M. Reddy, and G. R. Aiken, “Calcite crystal growth inhibition by humic substances with emphasis on hydrophobic acids from the Florida Everglades,” *Geochim. Cosmochim. Acta*, vol. 64, no. 1, pp. 61–72, Jan. 2000.
- [45] G. Gauthier *et al.*, “Application of the Fast Controlled Precipitation method to assess the scale-forming ability of raw river waters,” *Desalination*, vol. 299, pp. 89–95, Aug. 2012.
- [46] N. Wada, K. Kanamura, and T. Umegaki, “Effects of carboxylic acids on the crystallization of calcium carbonate,” *J. Colloid Interface Sci.*, vol. 233, no. 1, pp. 65–72, Jan. 2001.
- [47] M. M. Reddy and A. R. Hoch, “Calcite crystal growth rate inhibition by polycarboxylic acids,” *J. Colloid Interface Sci.*, vol. 235, no. 2, pp. 365–370, Mar. 2001.
- [48] E. Dalas, A. Chalias, D. Gatos, and K. Barlos, “The inhibition of calcium carbonate crystal growth by the cysteine-rich Mdm2 peptide,” *J. Colloid Interface Sci.*, vol. 300,

no. 2, pp. 536–542, Aug. 2006.

- [49] T. Kumar, S. Vishwanatham, and S. S. Kundu, “A laboratory study on pteroyl-1-glutamic acid as a scale prevention inhibitor of calcium carbonate in aqueous solution of synthetic produced water,” *J. Pet. Sci. Eng.*, vol. 71, no. 1–2, pp. 1–7, Mar. 2010.
- [50] W. Yang, Y. Fang, J. Liang, and Q. Hu, “Optimization of ultrasonic extraction of *Flammulina velutipes* polysaccharides and evaluation of its acetylcholinesterase inhibitory activity,” *Food Res. Int.*, vol. 44, no. 5, pp. 1269–1275, Jun. 2011.
- [51] A. M. Abdel-Gaber, B. A. Abd-El-Nabey, E. Khamis, and D. E. Abd-El-Khalek, “Investigation of fig leaf extract as a novel environmentally friendly antiscalant for CaCO<sub>3</sub> calcareous deposits,” *Desalination*, vol. 230, no. 1–3, pp. 314–328, Sep. 2008.
- [52] M. Bonoli, A. Bendini, L. Cerretani, G. Lercker, and T. Gallina Toschi, “Qualitative and Semiquantitative Analysis of Phenolic Compounds in Extra Virgin Olive Oils as a Function of the Ripening Degree of Olive Fruits by Different Analytical Techniques,” *J. Agric. Food Chem.*, vol. 52, no. 23, pp. 7026–7032, Nov. 2004.
- [53] G. Maciejewska *et al.*, “Atypical calcium coordination number: Physicochemical study, cytotoxicity, DFT calculations and in silico pharmacokinetic characteristics of calcium caffeates,” *J. Inorg. Biochem.*, vol. 103, no. 9, pp. 1189–1195, Sep. 2009.
- [54] T. D. Baugh, J. Y. Lee, K. Winters, J. Waters, and J. Wilcher, “A fast and information-rich test method for scale inhibitor performance,” in *Offshore Technology Conference, Proceedings*, 2012, vol. 2, pp. 1104–1113.
- [55] Z. Zhang *et al.*, “Inhibition of calcium carbonate fouling on heat transfer surface using

- sodium carboxymethyl cellulose,” *Environ. Technol. (United Kingdom)*, vol. 135, no. 7, pp. 273–279, 2018.
- [56] Q. Wang *et al.*, “Laboratory study on efficiency of three calcium carbonate scale inhibitors in the presence of EOR chemicals,” *Petroleum*, vol. 4, no. 4, pp. 375–384, 2018.
- [57] V. A. Sander, G. B. Facorro, L. Piehl, E. Rubi, D. Celis, and A. B. Motta, “Effect of DHEA and metformin on corpus luteum in mice,” 2006.
- [58] T. Almubarak, J. H. Ng, H. Nasr-el-din, and A. Texas, “SPE-185636-MS Oilfield Scale Removal by Chelating Agents : An Aminopolycarboxylic Acids Review,” no. Iii, 2017.
- [59] C. N. Fredd and H. S. Fogler, “The Influence of Chelating Agents on the Kinetics of Calcite Dissolution,” vol. 197, no. 204, pp. 187–197, 1998.
- [60] S. Ko, X. Wang, A. T. Kan, and M. B. Tomson, “Identification of novel chemicals for iron sulfide scale control and understanding of scale controlling mechanism,” in *Proceedings - SPE International Symposium on Oilfield Chemistry*, 2019, vol. 2019.
- [61] W. Li *et al.*, “Development of novel iron sulfide scale control chemicals,” *Soc. Pet. Eng. - SPE Int. Oilf. Scale Conf. Exhib. 2018*, 2018.
- [62] B. Alharbi, N. Aljeaban, A. Graham, and K. S. Sorbie, “Iron sulfide and zinc sulfide inhibition and scale inhibitor consumption,” *Soc. Pet. Eng. - Abu Dhabi Int. Pet. Exhib. Conf. 2019, ADIP 2019*, 2019.
- [63] N. Bhandari, M. Bhandari, I. Littlehales, and J. Fidoe, “Development of a novel iron sulfide scale inhibitor for onshore US application,” *Proc. - SPE Int. Symp. Oilf. Chem.*,

vol. 2019, 2019.

- [64] H. Lu, B. McCabe, J. Brooks, S. Heath, and S. Stevens, "A novel phosphonate scale inhibitor for scale control in ultra high temperature environments," in *Proceedings - SPE International Symposium on Oilfield Chemistry*, 2019, vol. 2019.
- [65] Y. Tang, W. Yang, X. Yin, Y. Liu, P. Yin, and J. Wang, "Investigation of CaCO<sub>3</sub> scale inhibition by PAA, ATMP and PAPEMP," *Desalination*, vol. 228, no. 1–3, pp. 55–60, Aug. 2008.
- [66] T. Satti, K. Young, and S. Grover, "Detecting catastrophic failure events in large-scale milling machines," *Int. J. Mach. Tools Manuf.*, vol. 49, no. 14, pp. 1104–1113, Nov. 2009.
- [67] Y. Zuo, W. Yang, K. Zhang, Y. Chen, X. Yin, and Y. Liu, "Experimental and Theoretical Studies of Carboxylic Polymers with Low Molecular Weight as Inhibitors for Calcium Carbonate Scale," *Crystals*, vol. 10, no. 5, p. 406, May 2020.
- [68] S. C. de Morais *et al.*, "Effect of pH on the efficiency of sodium hexametaphosphate as calcium carbonate scale inhibitor at high temperature and high pressure," *Desalination*, vol. 491, Oct. 2020.
- [69] Z. Zhu, M. Li, and E. Jin, "Effect of an allyl pretreatment of starch on the grafting efficiency and properties of allyl starch- g -poly(acrylic acid)," *J. Appl. Polym. Sci.*, vol. 112, no. 5, pp. 2822–2829, Jun. 2009.
- [70] X. J. Zhang, T. Y. Ma, and Z. Y. Yuan, "Titania-phosphonate hybrid porous materials: Preparation, photocatalytic activity and heavy metal ion adsorption," *J. Mater. Chem.*,

- vol. 18, no. 17, pp. 2003–2010, Apr. 2008.
- [71] T. Z. Ren, Z. Y. Yuan, and B. L. Su, “Surfactant-assisted preparation of hollow microspheres of mesoporous TiO<sub>2</sub>,” *Chem. Phys. Lett.*, vol. 374, no. 1–2, pp. 170–175, Jun. 2003.
- [72] S. Naserifar, S. Zybin, C.-C. Ye, and W. A. G. Iii, “trioxide (MTO<sub>3</sub>N) green energetic materials from DFT and ReaxFF molecular modeling †,” 2016.
- [73] G. Liu *et al.*, “Scale Inhibition by a Carboxylate-Terminated Double-Hydrophilic Block Copolymer in Industrial Recycling Water,” *J. Water Chem. Technol.*, vol. 41, no. 2, pp. 73–80, 2019.
- [74] A. A. Umar, N. Solids, S. W. Oil, and S. Modeling, “Silicate Scales Formation During ASP Flooding : A Review Silicate Scales Formation During ASP Flooding : A Review,” no. August, 2016.
- [75] E. Bowman *et al.*, “International Measures of Prevention, Application, and Economics of Corrosion Technologies Study,” *NACE Int.*, p. A-19, 2016.
- [76] F. Mansfeld, “Electrochemical impedance spectroscopy (EIS) as a new tool for investigating methods of corrosion protection,” *Electrochim. Acta*, vol. 35, no. 10, pp. 1533–1544, Oct. 1990.
- [77] G. Gece, “The use of quantum chemical methods in corrosion inhibitor studies,” *Corrosion Science*, vol. 50, no. 11. Pergamon, pp. 2981–2992, 01-Nov-2008.
- [78] M. Ormellese, F. Bolzoni, L. Lazzari, A. Brenna, and M. Pedefferri, “Organic substances as inhibitors for chloride-induced corrosion in reinforced concrete,” *Mater.*

*Corros.*, vol. 62, no. 2, pp. 170–177, Feb. 2011.

- [79] E. M. Sherif and S. M. Park, “2-Amino-5-ethyl-1,3,4-thiadiazole as a corrosion inhibitor for copper in 3.0% NaCl solutions,” *Corros. Sci.*, vol. 48, no. 12, pp. 4065–4079, Dec. 2006.
- [80] M. A. Quraishi and D. Jamal, “Technical note: CAHMT - A new and eco-friendly acidizing corrosion inhibitor,” *Corrosion*, vol. 56, no. 10, pp. 983–985, Mar. 2000.
- [81] S. M. Powell, H. N. McMurray, and D. A. Worsley, “Use of the scanning reference electrode technique for the evaluation of environmentally friendly, nonchromate corrosion inhibitors,” *Corrosion*, vol. 55, no. 11, pp. 1040–1051, Mar. 1999.
- [82] P. Bommersbach, C. Alemany-Dumont, J. P. Millet, and B. Normand, “Formation and behaviour study of an environment-friendly corrosion inhibitor by electrochemical methods,” *Electrochim. Acta*, vol. 51, no. 6, pp. 1076–1084, Nov. 2005.
- [83] G. Blustein, A. R. Di Sarli, J. A. Jaén, R. Romagnoli, and B. Del Amo, “Study of iron benzoate as a novel steel corrosion inhibitor pigment for protective paint films,” *Corros. Sci.*, vol. 49, no. 11, pp. 4202–4231, Nov. 2007.
- [84] M. R. Ali, C. M. Mustafa, and M. Habib, “Effect of Molybdate, Nitrite and Zinc Ions on the Corrosion Inhibition of Mild Steel in Aqueous Chloride Media Containing Cupric Ions,” *J. Sci. Res.*, vol. 1, no. 1, pp. 82–91, Dec. 2008.
- [85] “International Journal of Engineering Research and Applications: Ingenta Connect Table Of Contents.” [Online]. Available:  
<https://www.ingentaconnect.com/content/doi/22489622/2016/00000006/00000001;jse>

- ssionid=1g6ii80bn45i4.x-ic-live-02. [Accessed: 20-Nov-2020].
- [86] H. Demiral, I. Demiral, F. Tümsek, and B. Karabacakoğlu, “Adsorption of chromium(VI) from aqueous solution by activated carbon derived from olive bagasse and applicability of different adsorption models,” *Chem. Eng. J.*, vol. 144, no. 2, pp. 188–196, Oct. 2008.
- [87] “(4) (PDF) Review of Corrosion Inhibitors for Industrial Applications.” [Online]. Available:  
[https://www.researchgate.net/publication/345439454\\_Review\\_of\\_Corrosion\\_Inhibitors\\_for\\_Industrial\\_Applications](https://www.researchgate.net/publication/345439454_Review_of_Corrosion_Inhibitors_for_Industrial_Applications). [Accessed: 20-Nov-2020].
- [88] “(4) (PDF) Inhibition of corrosion of carbon steel in a dam water by sodium molybdate - Zn<sup>2+</sup> system.” [Online]. Available:  
[https://www.researchgate.net/publication/267830055\\_Inhibition\\_of\\_corrosion\\_of\\_carbon\\_steel\\_in\\_a\\_dam\\_water\\_by\\_sodium\\_molybdate\\_-\\_Zn2\\_system](https://www.researchgate.net/publication/267830055_Inhibition_of_corrosion_of_carbon_steel_in_a_dam_water_by_sodium_molybdate_-_Zn2_system). [Accessed: 20-Nov-2020].
- [89] I. B. Singh, G. Venkatachari, and K. Balakrishnan, “Inhibition effect of sodium borogluconate on mild steel with and without nitrite ions in low chloride containing water,” *J. Appl. Electrochem.*, vol. 24, no. 2, pp. 179–183, Feb. 1994.
- [90] “Community News: Voestalpine awarded major contract for pipeline project in the United Arab Emirates,” *Mater. Corros.*, vol. 66, no. 11, p. 1363, Nov. 2015.
- [91] S. Karim, C. M. Mustafa, M. Asaduzzaman, and M. Islam, “Corrosion Inhibition of Mild Steel by Calcium Gluconate in Simulated Cooling Water,” 2010.

- [92] S. RAJENDRAN, B. V. APPARAO, and N. PALANISWAMY, “Technical note  
Calcium gluconate as corrosion inhibitor for mild steel in low chloride media  
,” *Br. Corros. J.*, vol. 33, no. 4, pp. 315–317, Jan. 1998.

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