MITIGATION OF CALCIUM CARBONATE INORGANIC SCALING

By

MOHAMED FAKHRULLAH BIN HARON

(10723)

FINAL REPORT

SUPERVISOR: AP DR ISMAIL M SAAID

Submitted to the Petroleum Engineering Programme
in Partial Fulfilment of the Requirements
for the Bachelor of Engineering (Hons) Degree in Petroleum Engineering

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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Approved by,

(AP Dr. Ismail M Saaid)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2011

CERTIFICATION OF ORIGINALITY

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

MOHAMED FAKHRULLAH BIN HARON

ABSTRACT

Inorganic scale is a very common problem in the oil and gas industry. Common types of scale include calcium carbonate, magnesium carbonate, calcium sulphate, barium sulphate, strontium sulphate and radium sulphate. Carbonate deposits depend on changing operational conditions such as pressure and temperature whereas sulphate scale deposits depend on mixing incompatible waters and seawater rich in sulphate. The focus of this project will be on calcium carbonate scale which is one of the most common types of scale. Unresolved calcium carbonate scale problem may lead to loss in production and damage to equipments which will eventually lead to severe economic loss. In order to tackle the scale problem, scale inhibitors are introduced into wells. Example of conventional scale inhibitors which is widely used is diethylenetriaminepentakis (methylenephosphonica acid) or DTPMP. The problems with conventional scale inhibitors are most of them are harmful towards the environment. This project will look into green alternatives for calcium carbonate scale inhibitors. The green alternatives consist of gambir extracts, aloe vera gels and green tea extracts. Laboratory tests will be performed to evaluate their potential in inhibiting the formation of calcium carbonate deposits. Comparisons in terms of their effectiveness in delaying the deposition of calcium carbonate will be made between the three materials for calcium carbonate scale inhibitors.

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Chapter 1: Project Background

1.1 Background Study

1.1.1 Inorganic Scale

Oil and gas industry is a challenge-laden industry filled with many problems and challenges. One of the most common challenges faced especially on the operation side is scale deposition, either in the formation or in the production system. Scale mitigation and prevention programs are critical for sustained oil production.

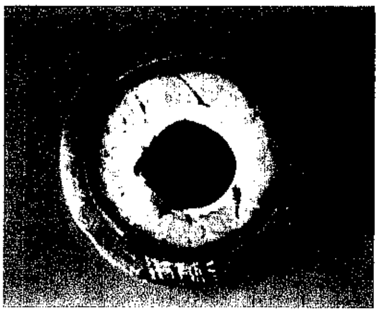

Figure 1: Scale deposits in a conduit

Inorganic scales are mineral deposits in salt from aqueous solutions of minerals in brines due to disturbance in thermodynamic and chemical equilibrium resulting in supersaturation. Inorganic scales consists of many different groups but the most common ones are of the carbonate and sulphate scales with the presences of alkaline earth metals such as Mg, Ca, Sr, Ba or Ra (ExproBase, 2010). Carbonate and sulphate are present as negative ions while the alkaline earth metals are present as positives ions when dissolved in the water, resulting in these common scale types:

- Calcium carbonate, $CaCO_3$
- Magnesium carbonate, $MgCO_3$
- Calcium sulphate, $CaSO_4$
- Barium sulphate, $BaSO_4$
- Strontium sulphate, $SrSO_4$
- Radium sulphate, $RaSO_4$

Carbonate deposits depend on changing operational conditions such as pressure and temperature whereas sulphate scale deposits depend on mixing incompatible waters and seawater rich in sulphate.

1.2 Problem Statement

Calcium carbonate is one of the most common scales found in the oil and gas industry. The formation of scale deposits upon tubing, casing, perforations and formation face can lead to reduced production rate of oil and gas wells due to the narrowing of production conduit internal diameter (Hinrichsen, 1998). Besides loss in production, formation of scale may cause equipments in the well to malfunction when they occur on equipments such as electric submersible pumps or sliding sleeves. The deposition of scale on the formation face could also block pore throats in the near-well bore region or in the well itself causing formation damage and perforation blockage.

Based on the problems posed by scale deposition, it is clear as to why mitigation plan for scale deposition is vital in an operation. Unresolved scale problem may lead to loss in production and damage to equipments which will ultimately lead to severe economic loss. In the North Sea, BP estimated that they lose 4 million barrels of oil annually due to scale and about 20% of their well losses are due to scale damage (Graham, et al, 2002).

Most scale inhibitors from conventional organic phosphates and phosphonates are quite harmful the environment. Since scale problem is one of the most common problems in the oil and gas industry, it is important to study on green scale inhibitors to reduce the harm done to the environment from the usage of toxic scale inhibitors.

1.3 Objectives of Project

The objectives of this project are:

1. To identify and evaluate a list of potential green inhibitors for $CaCO_3$ scale.
2. To compare the performances of green inhibitors with reported works.
3. To recommend green $CaCO_3$ inhibitor with further potential to be explored based on the laboratory experiments conducted.

Scope of Study

The scope of study revolves around the mitigation plan to resolve inorganic scaling, particularly for $CaCO_3$ scale. The study will be in two stages, where the first stage is to study and understand the approach used in order to mitigate $CaCO_3$ scale problems in a well. More emphasize will be put on green technology as strict environmental legislation is in compliance nowadays. Based on the study, potential green inhibitors will be listed and studied upon more thoroughly. The second stage is to analyze the potential green inhibitors using laboratory experiments in order to determine their effectiveness and efficiency as compared to conventional inhibitors. Inhibitors can be evaluated on several bases which include performance, effect of pH and dissolved ion on inhibition and thermal stability. As a result of the experiments conducted, green inhibitor with huge potential will be recommended for further research. The project is within the scope of well production and optimization study as inorganic scale is a common problem in production and injection well.

2.2 Scale Inhibitors

Scale inhibitors are chemicals that prevent or retard the nucleation and crystal growth of inorganic scales. They function either by binding to the insoluble scale forming mineral thus keeping them in solution or by modifying the crystal structure of the precipitate to prevent the forming of scale. Scale inhibitors are deployed in the oilfield using various methods which include continuous injection and squeeze treatment. This project will involve two types of scale inhibitors; conventional and the potential green inhibitor. Conventional $CaCO_3$ scale inhibitors which include phosphates and phosphonates have poor biodegradability and risks of causing environment disequilibrium due to the enrichment of environment in nutrients from water discharges (Holt, et al, 2009). Example of a conventional $CaCO_3$ scale inhibitor is diethylenetriaminepentakis (methylenephosphonica acid) or DTPMP. DTPMP is one of the widely-used phosphonate scale inhibitor in the oil industry due to it being an excellent carbonate and sulphate scale inhibitor.

Green inhibitor is environmentally-friendly inhibitor which reduces the negative impacts on the environment due to its application. The criteria needed for an inhibitor to be considered as "green" include little or no toxicity to human health and environment, biodegradable and utilizing renewable resources (Gupta, 2004). Less toxic organic phosphorous compounds such as carboxyhydroxymethylphosphonic acid and dibutylphosphorodithoic acid have been introduced to replace conventional organic phosphates and phosphonates. Recent development in green technology also has introduce alternative classes of compounds which are acrylate based polymers (e.g. polyacrylic acid, polyacrylamide and various polyacrylates), poly amino acids (e.g. polyaspartates) and carboxylated plant polysaccharides (e.g. carboxylated inulins).

2.2.1 Diethylenetriamine penta (methylene phosphonic acid) (DTPMP)

DTPMP is a phosphonic acid and has excellent scale and corrosion inhibition and also good thermal tolerance ability. DTPMP can inhibit scale formation of carbonate, sulphate and phosphate. DTPMP is more efficient in alkaline environment and high temperature than other organophosphines. (Sorbie and Laing, 2004)

DTPMP operates through a crystal growth retardation mechanism and is significantly affected by the presence of Ca and Mg ions in solutions. DTPMP has poor biodegradability and high levels of phosphonates are increasingly restricted in terms of release to the environment.

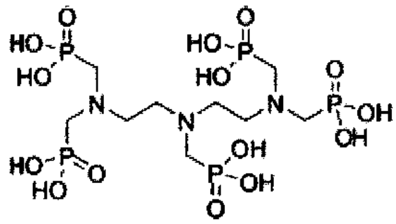

Figure 2: DTPMP (Wikipedia, 2011)

Table 1: Specifications of DTPMP (Wanjiechem, 2011)

Specifications	
Molecular formula	$C_9H_{28}N_3O_{15}P_5$
Molar mass	573.20
Appearance	Brown transparent liquid
Active acid	48.0 – 52.0%
Phosphorus acid (as PO33-)	3.0% max
Chloride (as Cl-)	12 – 17%
Density (20 centigrade)	1.35 – 1.45 g/cm^3
pH (1% solution)	2.0
Fe ppm	35 max

2.2.2 Polyaspartates (PASP)

Polyaspartates are highly biodegradable alternatives for scale inhibitors. Polyaspartates are prepared from L-aspartic acid through 3 different syntheses that are based on intermolecular dehydration: thermal polycondensations without or with and acid catalyst and bulk polycondensations with catalyst (Baraka-Lokmane, et al, 2008).

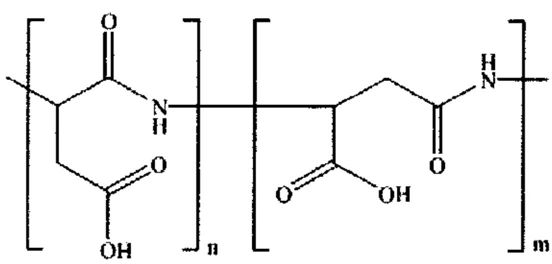

Figure 3: Structural formula of PASP (Estievenart, et al, 2002)

Polyaspartates can inhibit both carbonate and sulphate based scales based on laboratory studies demonstrated using jar tests and the tube blocking tests (Inches, et al, 2007). Besides that, polyaspartates can function both as scale and corrosion inhibitor under oil field conditions as shown by laboratory tests (Inches, et al, 2007).

Based on test results for polyaspartates biodegradability, polyaspartates produced by catalytic process are highly biodegradable regardless of the molecular weight of the polymer (Ross, et al, 1996). Biodegradability of polyaspartates was followed by the respiration and growth of biomass in the presence of polyaspartic acid sodium salt (Estievenart, et al, 2002).

2.2.3 Carboxy Methyl Inulin (CMI)

The carboxy methyl inulins are derivatives from inulin which is a natural ß poly-fructoside with a glucose unit at the reducing end, extracted from chicory roots. Carboxylate groups are introduced into the polysaccharide by carboxy methylation with sodium monochloro acetate as reagent in alkaline medium (Bazin, et al, 2004). Carboxy methyl inulin based product (DS 2.5 and DP 10), is inherently biodegradable with more than 20% biodegradation according to OECD 306 test method and has very low ecotoxicity (Bazin, et al, 2004). It has an excellent ecotoxicity profile for fresh and seawater species.

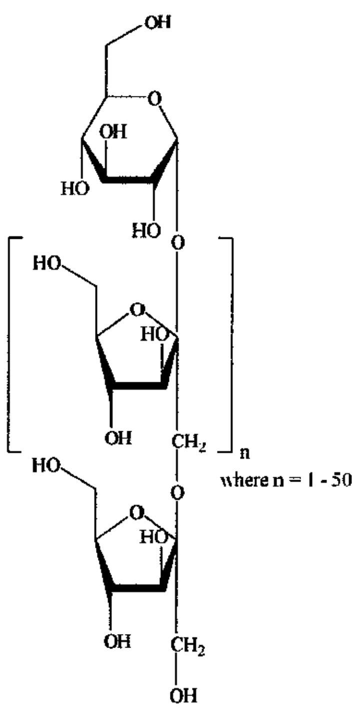

Figure 4: Structure of CMI (B. Bazin, et al, 2004)

Inulin has an excellent calcium tolerance so it can be used in various oilfield conditions. Preliminary static and dynamic adsorption experiments performed on limestone core material with CMI inhibitor dispersed in sea water show that its behaviour is quite similar with polyacrylates but with superior adsorbing properties (Bazin, et al, 2004). Acidic conditions improve the inhibitor adsorption.

2.2.2 Aloe Vera

Aloe Vera is a xerophile plant originated in tropical or subtropical zones such as Sudan. The leaf epidermis has a thick cuticle or rind and underneath it contains mesophyll which is differentiated by clorenchimas cells and parenchyma. The cellular parenchyma encircles a jellied transparent and mucilaginous material which is referred to as gel. (Wikipedia, 2011)

The scale inhibitor is derived from the gel which contains various chemical compounds such as amino acids, glucosides, minerals and vitamins. The aloe gel constitutes hydrocarbon chain structure having carboxyl and alcohol functional groups. These functional groups interact with divalent ions which cause scale such as Ca++ and Mg++. Aloe-derived gel has reactivity with calcium to form gels which encapsulate the calcium as the calcium ions serve as a bridge to form ionic liaisons between two carboxyl groups belonging to two different chains in close contact (Viloria, et al, 2010).

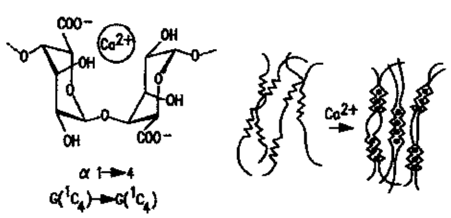

Figure 5: How chains of the gel interact with Ca^{++} to get together

(Viloria, et al, 2010)

The interaction strength between calcium and other oxygen atoms in the polysaccharides shows coordination through the calcium empty orbital. Oxygen atoms of the hydroxyl groups, the ring oxygen atom and the oxygen atoms of sugars combined by hydrogen bridges participate in the combining process through free electrons. The acid group presence from gels of aloe vera such as carboxylic acid (-COOH) in soluble protein molecules interacts with calcium ions (Ca^{+2}), controlling crystallization.

Table 2: Aloe Vera gel characterization (Viloria, et al, 2010)

Aloe Vera gel characterization	
Property	**Average**
Chemical Structure	Hydrocarbon chain structure with carboxyl (COOH) and alcohol (OH) functional groups
Elemental composition	C 29.0-32.0; H 4.2-6.5; O 44.0-55.0; N 0.4-0.8; S 0.3-1.6; Ca 2.3-5.2; Mg 0.8-1.0; P 0.3-0.4
Average molecular weight, determined by viscosimetry	25 KDa (kilo-Dalton)
Thermal stability	Up to 125°C

Table 3: Aloe Vera gel aqueous solution characterization

(Viloria, et al, 2010)

Aloe Vera gel aqueous solution characterization	
Property	**Average**
pH	3.8
Calcium	3.75% wt/wt
Magnesium	0.9% wt/wt
Acidity (TAN)	18.33 meq KOH/g
Intrinsic viscosity	0.4 dL/g
Fluid type	Newtonian
Critical Concentration	15% wt/wt

2.2.3 Gambir Extracts

Gambir extracts from *Uncaria gambir* leaves is to be investigated as an inhibitor for $CaCO_3$ scale formation. Gambir extract is identified as a potential inhibitor of scale formation because it contains chemical compounds such as tannic acid, catechin and quercetin which are effective inhibitors of scale formation of $CaCO_3$ (Suharso, et al, 2011).

Gambir extracts operate by adsorbing onto the active growth sites of the $CaCO_3$ crystal surface and inhibit the regular outgrowth of the crystal during $CaCO_3$ crystal growth thus changes the morphology and reduces the size of $CaCO_3$ crystals. Based on investigation using bottle-roller batch method, the presence of 50-250 ppm of this inhibitor effectively inhibits 60-100 % of the formation of calcium carbonate under the experiment conditions (Suharso, et al, 2011).

Figure 6: Uncaria Gambir plant (Wikipedia, 2011)

Table 4: Gambir extracts properties (Suharso, et al, 2011)

Gambir extracts properties	
Chemical Compounds	**Percentage (approx.)**
Tannic acid	40%
Catechin	25%
Quercetin	12%

2.2.4 Green Tea Extracts

Figure 7: Green tea extract

Green tea extract is an herbal derivative from green tea leaves (*Camellia sinensis*). It contains high content of polyphenols and the main antioxidative ingredient in green tea extract is green tea catechins (GTC). Other than antioxidative ingredients, other components include three kinds of flavonoids; namely, kaempferol, quercetin and myricetin (Wikipedia, 2011). Catechin and quercetin are effective inhibitors of $CaCO_3$ scale formation (Suharso, et al, 2011).

The structure and functional group of green tea extract is phenolic and carboxyl. Carboxyl and phenolic functionalities are usually contained in humic substances which behave as negatively charged colloids or anionic polyelectrolytes in natural waters. Some studies have reported on the influence of natural organic compounds on the precipitation of various scale forming salts (Reynolds, 1978). When added, polyelectrolytes decreased the growth of crystals by interacting on the crystallization of calcium carbonate through adsorption of polyelectrolytes on submicronic crystals of calcite where carboxylate functions adsorb on the calcite crystals occupying cationic sites thus modified the ongoing processes.

Experiment result shows that further increase in the green tea extract concentration by a factor of two and one half (from 10 to 25 ppm) results in a tenfold increase in the ability of GTE to delay $CaCO_3$ precipitation under the experiment conditions but it failed to give complete inhibition even at significantly higher concentrations (Amjad, 2006).

2.2.1 Table for Comparisons of Listed Scale Inhibitors

Table 5: Scale Inhibitors Comparison

INHIBITORS	APPLICATION	LIMITATIONS	HIGHLIGHTS	REFERENCES
DTPMP	Used in industry as scale inhibitor, deflocculant, sequestrant, water stabilizer in cooling water, boiler, oil-drilling, detergent under high pH (10~11)(dosage: 3mg/L), also applied as stabilizer of hydrogen peroxide (dosage 20 to 50 mg/L)	DTPMP works better at higher temperature Does not operate at lower pH values (< 4.5) Efficiency reduces in low Ca^{2+} Magnesium lowers inhibition efficiency	Very effective inhibitor for carbonate and sulphate based scales Tube blocking test result shows low flow rate tests gave inhibition time higher than low flow rate tests.	(Bazin, et al, 2005), (Wajiechem, 2011), (Sorbie and Laing, 2004)
PASP	Green inhibitor that inhibits both carbonate and sulphate based scale. Also acts as corrosion inhibitor under oil field conditions	Polymers obtained by thermal polymerisation without solvents is less efficient in terms of scale inhibition and biodegradability	Squeeze lifetime of PASP is better than CMI and comparable with DTPMP Efficient scale inhibitors in testing conditions of higher temperature and under flow	(Kohler, et al, 2004), (Baraka – Lokmane, 2008), (Estievenart, et al, 2002)
CMI	Green inhibitor that can be applied in various oilfield conditions	Lower adsorption lifetime compared to phosphonate in similar test conditions	Excellent ecotoxicity profile for fresh and seawater species	(Kohler, et al, 2004), (Baraka – Lokmane, 2008)
Aloe Vera	Field tests at two wells of Venezuelan Oilfields (98% water and high scale tendency; 74% water and high scale tendency) for $CaCO_3$ scale problems at wellhead and bottom hole	Thermally stable up to temperature of 125°C	Field tests result show better performance than commercial inhibitors Can be applied at low and high calcium concentrations and does not precipitate due to hydrolysis	(Viloria, et al, 2010), (Castillo, et al, 2009)

Gambir Extract	$CaCO_3$ inhibitor investigation using bottle-roller batch method with solution concentration from 0.1 to 0.6M at 80°C	Higher concentration of the growth solution lowers the ability to inhibit the scale formation of $CaCO_3$	Based on experiment conducted, effectively inhibits 60-100% at 50-250 ppm	(Suharso, et al, 2011)
Green Tea Extract	Investigated in an experiment using supersaturated aqueous solutions	Failed to give complete inhibition even at significantly higher concentrations	Experiment results show that green tea extract strongly delays the onset of $CaCO_3$ precipitation. Further increase of its concentration by a factor of two and one half (from 10 to 25 ppm) results in a tenfold increase in the ability to delay the precipitation	(Amjad, 2006)

Chapter 3: Methodology

3.1 Project Activities

The layout for this project is as below:

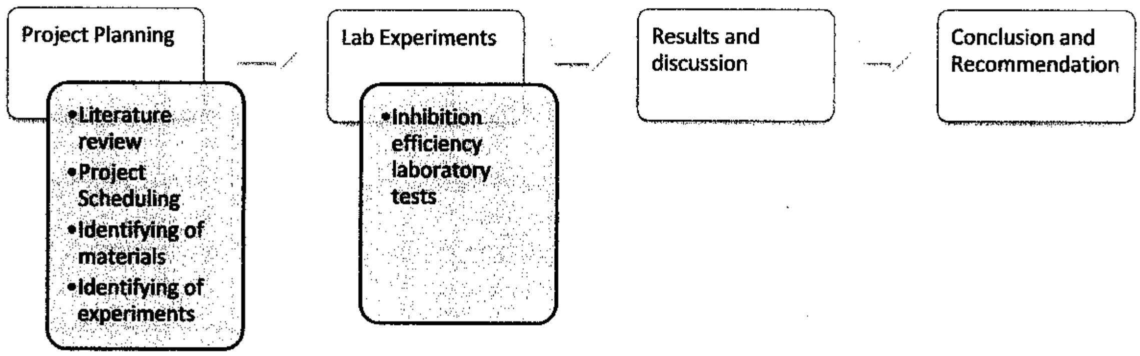

Figure 8: Project Flow

Based on the flow chart, the first phase of this project will be more on researches from journals and technical papers. Studies will be done on the mechanism of scale inhibitors and potential green scale inhibitors based on their properties. Next, laboratory experiments and tests using water bath shaker to evaluate the scale inhibitors' efficiency and compatibility tests will be done to evaluate the performance of the inhibitors. After obtaining the data required, the result will be analyzed to come up with a conclusion and recommendation which is the outcome of this project.

3.2 Project Experiments Flow

Figure 9: Project Experiments Flow

3.2.1 Preparation (Extraction from natural resources)

3.2.1.1 Aloe Vera

Obtain a crop of *Aloe Vera* plants. The *Aloe Vera* gel is isolated and purified. Then process the gel to sterilize and stabilize. The sterilized and stabilized *Aloe Vera* gel is then dissolved in H_2O. At temperature of between 60°C and 90°C, stir continuously to prevent enzymatic reactions or bacteria agent actions that cause organic material degradation. Formulate the solution of the gel in water having a concentration between 5% and about 50% wt/wt. Observe for abrupt change in solution conductivity and viscosity especially at concentration of 15% wt/wt. This concentration is there desirable.

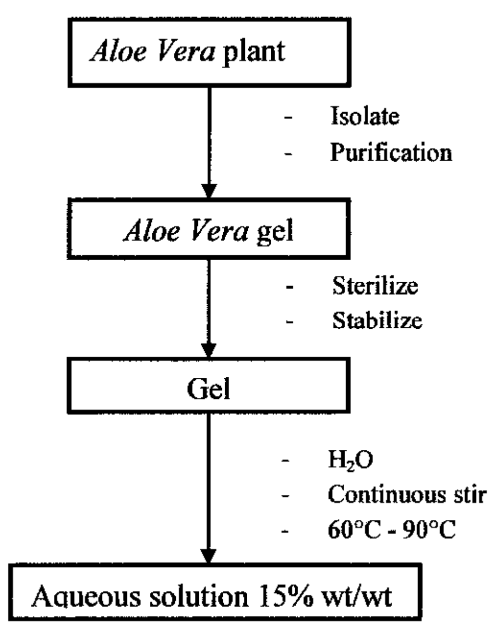

Figure 10: Obtaining Aloe Vera gel extract

3.2.1.2 Gambir Extract

Obtain extract of Gambir from dry leaves of *Uncaria Gambir*. Heat 100g of powdered Gambir in water with total volume of 1L at a temperature of 80°C for 1 hour then keep it for 1 night. Filter the solution and identify the filtrate to investigate the chemical compounds such as tannic acid, catechin and quercetin in the Gambir extract.

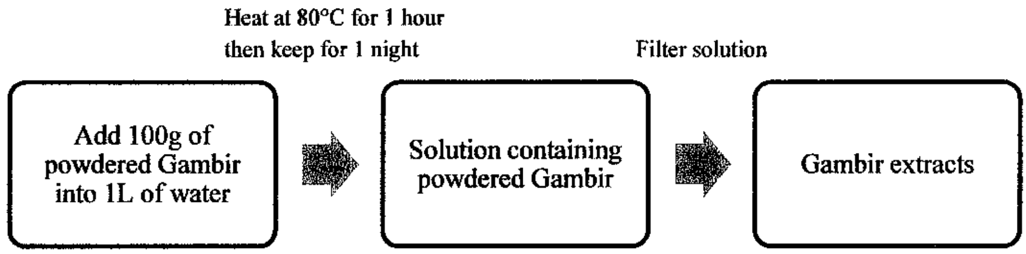

Figure 11: Gambir extracts preparation

3.2.1.3 Green Tea Extract

Obtain green tea leaves. Boil a kettle filled with 1 cup of filtered water and remove the water from heat once it boils. Measure 1 tsp. of green tea leaves and add them to a heated cup. The temperature of the boiled water in the kettle should be around 160°F. Pour hot water over the green tea leaves in the cup such that it covers the leaves and is filled only 1 inch above the leaves. Let it stand for approximately 20 seconds.

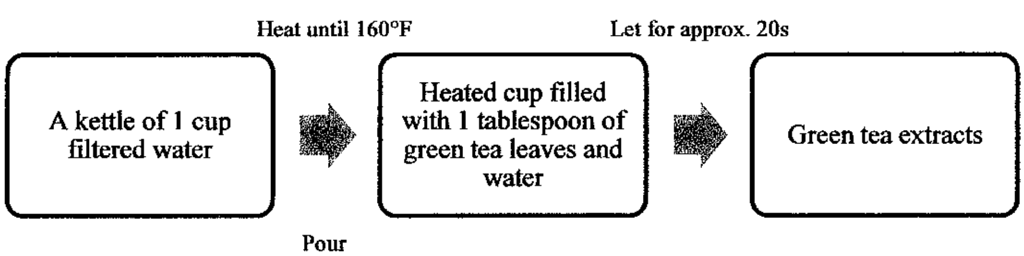

Figure 12: Green tea extract preparation

3.2.2 Inhibition Efficiency Laboratory Test

In order to evaluate the efficiency of Gambir extracts, Aloe vera and green tea extract as calcium carbonate scale inhibitor, laboratory test is performed. The experiment is made up of two parts which are preparation of seed crystal and the crystallization experiment. The seed crystal will be used for the crystallization experiment.

Preparation of seed crystal:

The seed crystal was prepared by mixing $CaCl_2$ anhydrate solution (1M) with Na_2CO_3 solution (1M) each in 50 ml water. Then the mixture was shaken to form seed crystals. The seed crystals is then filtered and washed thoroughly with distilled water and dried at room temperature for at least 2 days.

Crystallization experiment:

200 ml of 0.1 M $CaCL_2$ was mixed with 200 ml of 0.1 M Na_2CO_3 at temperature of 80°C to prepare a growth solution of 0.1 M $CaCO_3$. The mixture was shaken to form homogeneous solution. Then, the solution was filtered and the filtered solution was placed into 6 beakers, each containing 50 ml of the solution. 100 mg of seed crystals which were prepared earlier were added into each beaker. The beakers were then placed in water bath shaker which was adjusted at 60 rev/min and at the temperature of 80°C for 90 minutes. Every 15 minutes, a beaker was taken. The precipitate formed was washed thoroughly with distilled water and dried in the oven for 1 day at the temperature of 80°C. The weight of the crystals formed was measured and recorded. The experiment was repeated for several times but the Na_2CO_3 solution in the first step was treated by adding different additives (Gambir extracts, Aloe Vera and green tea extracts) in each run. For each additive, the amount added was 10 mg (50 ppm), 20 mg (100 ppm) and 40 mg (200 ppm) in different runs.

3.3 Materials and tools

The materials for this project will require potential inhibitors derived from local natural resources such as local herbs and plants will be looked at. Besides that, certain chemicals will also be needed for the formation of calcium carbonate crystal.

Materials needed:

- Aloe Vera
- Gambir extracts
- Green tea extracts
- Calcium Chloride anhydrite solution ($CaCl_2$)
- Sodium Carbonate solution (Na_2CO_3)

The equipments and tools will be based on the tests required. For the experiment preparation which is the of extraction of *Aloe Vera* gel, *Gambir* extracts and green tea extracts from their natural resources, the tools needed are knife, beakers and spatula. The tools needed for inhibition efficiency test are beakers, conical flasks, filter papers, funnel and spatula. The equipments that are needed include heater stirrer, electronic scale, laboratory oven and water bath shaker.

List of equipments and tools needed:

- Heater stirrer
- Electronic scale
- Laboratory oven
- Water bath shaker
- Beakers
- Knife
- Spatula
- Conical flasks
- Filter papers
- Funnel

Figure 13: Water Bath Shaker

3.4 Gantt Chart

Table 6: Project timeline

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Topic selection/confirmation														
2	Preliminary Research Study														
3	Project Flow Planning														
4	Submission of Preliminary Report														
5	Study on $CaCO_3$ Scale Deposition and Scale Inhibition														
7	Acquiring Input Data														
8	Lab Experiments Familiarization and Planning														
9	Report preparation														
10	Submission of Interim Report														

Table 7: Key Milestone

	1st Semester				2nd Semester			
Milestone	Feb	Mar	Apr	May	June	Jul	Aug	Sept
Completion of material preparation								
Completion of inhibitors evaluation								
Completion of comparison of scale inhibitors								
Report documentation								

Chapter 4: Results and Discussion

4.1 Results

Based on the laboratory test performed, these are the results of the test.

No Additives

Table 8: Amount of precipitation for no additives

Time (minutes)	Amount of precipitation (gram)
0	0.100
15	0.107
30	0.110
45	0.113
60	0.114
75	0.115
90	0.115

Below is the amount of precipitation versus time without additives:

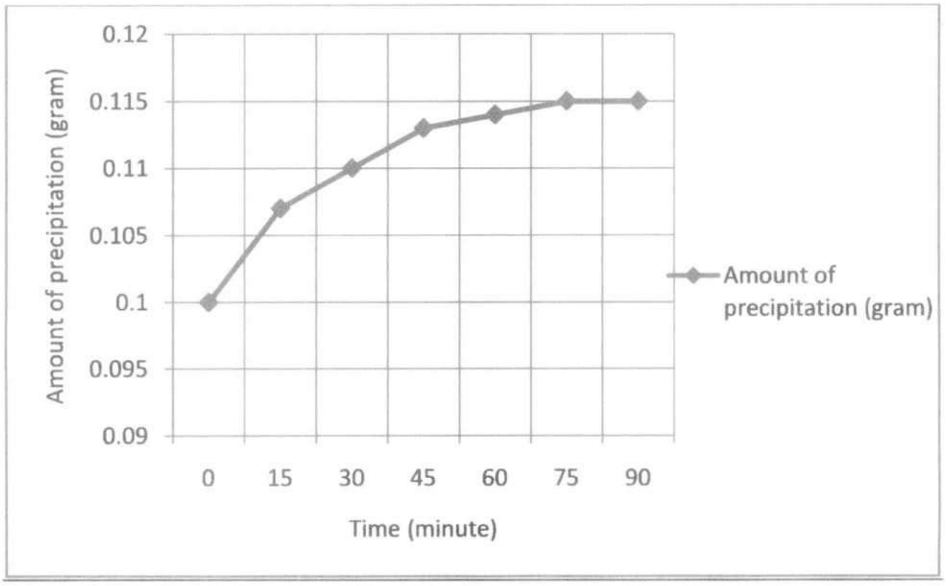

Figure 14: Precipitation amount versus time graph without additives

Based on the results obtained, figure 14 shows the amount of $CaCO_3$ precipitated versus time for the various concentrations of the gambir extracts used. From the figure, it is shown that the amount of $CaCO_3$ precipitated increases as time goes on but the rate of precipitation slowed down after 60 minutes for the test without any inhibitors as the precipitation reaction has reached equilibrium.

Gambir Extracts

Table 9: Amount of precipitation for Gambir extracts inhibition efficiency test

Gambir Concentrations	50 ppm	100 ppm	200 ppm
Time (minutes)	Weight of $CaCO_3$ Precipitates (gram)		
0	0.100	0.100	0.100
15	0.106	0.104	0.102
30	0.108	0.106	0.103
45	0.110	0.107	0.105
60	0.112	0.108	0.106
75	0.114	0.110	0.107
90	0.114	0.111	0.107

Below is the amount of precipitation versus time for all the concentrations of Gambir extracts:

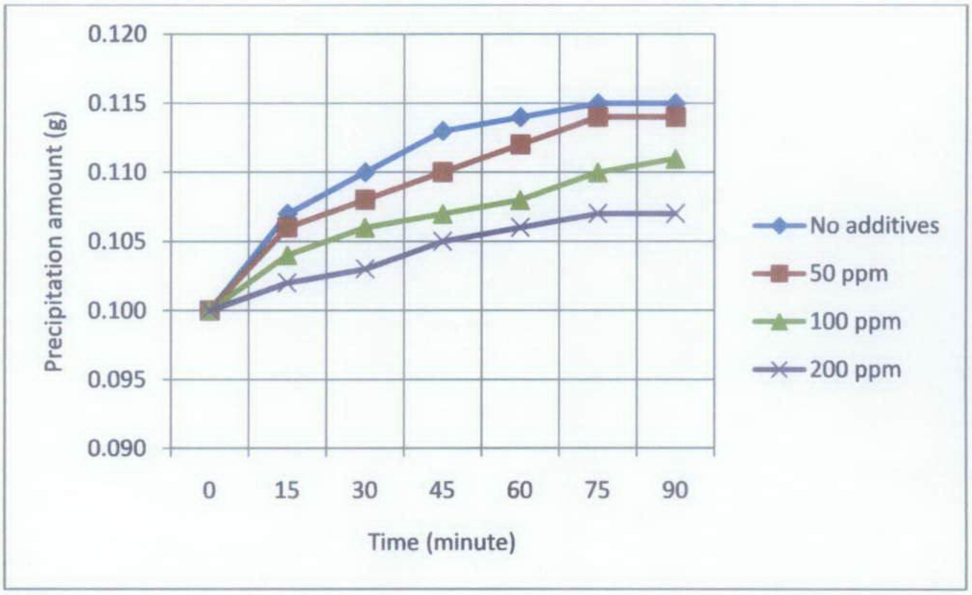

Figure 15: Precipitation amount versus time graph for Gambir extracts

The result for inhibition efficiency tests for Gambir extracts is shown in the figure 15 where the effect of gambir extracts on the precipitation of $CaCO_3$ is displayed. Various concentrations of gambir extracts added has different effect on the amount of $CaCO_3$ precipitated. For the concentration of 50 ppm, the effect is not as drastic as compared to the concentration of 200 ppm gambir extracts used.

The higher the concentration of gambir extracts used, the less amount of $CaCO_3$ precipitated. The addition of 50 ppm concentration of gambir extracts yield the ability to inhibit the scale formation to be around 7%, for the concentration of 100 ppm is 27% while for the concentration of 200 ppm, the ability to inhibit the scale formation is around 53%. Generally, the addition of the gambir extracts can inhibit the growth of $CaCO_3$ formation. Based on the results, the higher the amount of gambir extracts added, the greater is the inhibition of $CaCO_3$ precipitation.

The effect of Gambir extracts on the inhibition of $CaCO_3$ can be related with the ability of the inhibitor molecules to adsorb onto the active growth sites of the crystal surface and inhibit the regular outgrowth of $CaCO_3$ crystals (Suharso, et al, 2011). Other than adsorbing onto the active growth sites of crystal surface, the inhibitor may also become a heterogeneous nucleator which controls and stabilizes the precipitating polymorph. Due to this, Suharso et al. reported a change in the structure and morphology of the crystal formed.

Aloe Vera

Table 10: Amount of precipitation for Aloe Vera inhibition efficiency test

Aloe Vera Concentrations	50 ppm	100 ppm	200 ppm
Time (minutes)	Weight of $CaCO_3$ Precipitates (gram)		
0	0.100	0.100	0.100
15	0.105	0.104	0.101
30	0.106	0.104	0.102
45	0.108	0.105	0.102
60	0.109	0.106	0.103
75	0.109	0.107	0.104
90	0.110	0.107	0.104

Below is the amount of precipitation versus time for all the concentrations of Aloe Vera extracts:

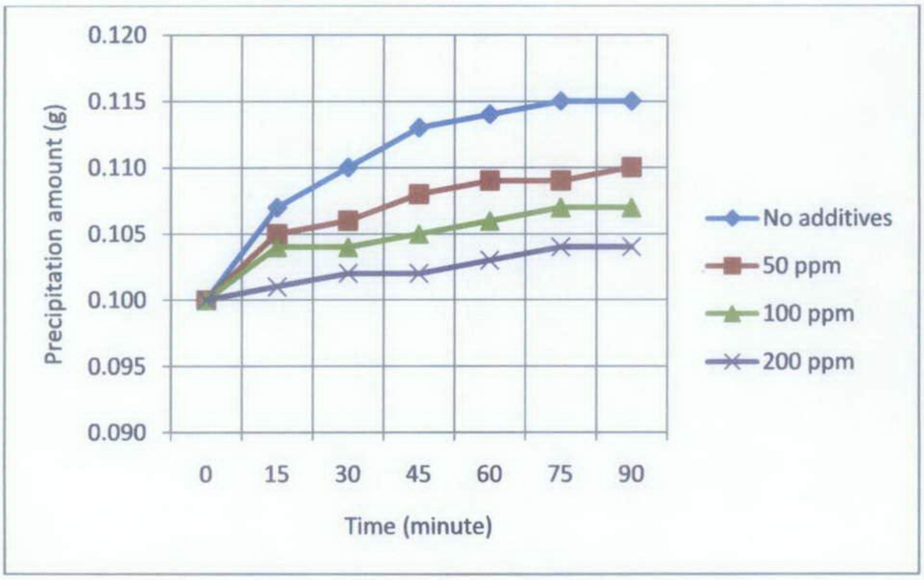

Figure 16: Precipitation amount versus time graph for Aloe Vera extracts

For aloe vera, the result of its efficiency in inhibiting the precipitation of $CaCO_3$ is shown in figure 16. Generally, the higher the concentration of aloe vera used, the less the amount of $CaCO_3$ precipitated during the laboratory test. With the concentrations of 50 ppm, aloe vera is able to inhibit around 33% of the formation of $CaCO_3$. As for the concentration of 100 ppm, the inhibition percentage is around 53.3%. Finally, aloe vera is able to inhibit the precipitation of $CaCO_3$ at around 73.3% at the concentration of 200 ppm. The results show that the higher the amount of aloe vera used, the greater is the inhibition of $CaCO_3$ precipitation.

Aloe vera displays the ability to inhibit the formation of $CaCO_3$ through precipitation due to its characteristics having reactivity with calcium to form gels which encapsulate the calcium. Other than that, the biopolymer adsorption in specific faces of the $CaCO_3$ is also an important element to control the crystallization process. Biomacromolecules also can lead to $CaCO_3$ crystal polyforms where the crystallization with biopolymers induces the phase transition of calcite crystal into aragonite.

There are plenty of advantages from using aloe vera derived scale inhibitor. Firstly is cost reduction. The process in preparing aloe vera derived scale inhibitor does not require chemical synthesis for its composition. Other than that, the composition and method for making and using aloe vera as scale inhibitor does not harm the nature and is environmentally friendly. In addition, the use of aloe vera as scale inhibitor encourages national economy through the encouragement of agro-industry.

Green Tea Extract

Table 11: Amount of precipitation for green tea extracts inhibition efficiency test

GTE Concentrations	50 ppm	100 ppm	200 ppm
Time (minutes)	Weight of $CaCO_3$ Precipitates (gram)		
0	0.100	0.100	0.100
15	0.107	0.105	0.102
30	0.108	0.106	0.103
45	0.109	0.108	0.103
60	0.113	0.110	0.105
75	0.114	0.110	0.106
90	0.114	0.112	0.107

Below is the amount of precipitation versus time for all the concentrations of green tea extracts:

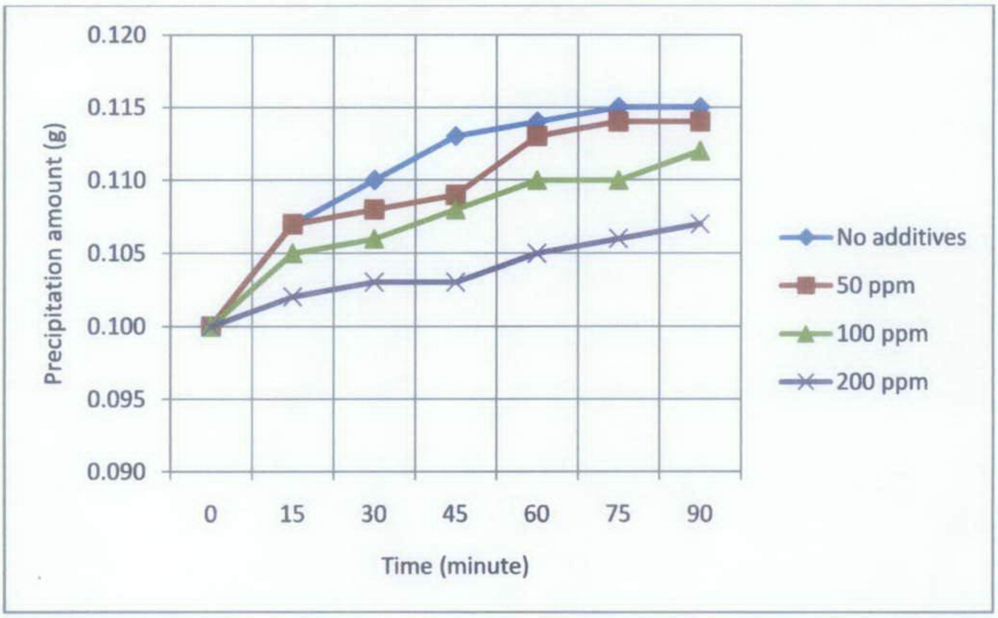

Figure 17: Precipitation amount versus time graph for green tea extracts

Figure 17 displays the result for the effect of inhibition on the precipitation of $CaCO_3$ with the use of $CaCO_3$ scale inhibitor from green tea extracts. As the graph shows, the weight of the final $CaCO_3$ precipitation differs for each different concentration of green tea extracts added where the higher the concentration of green tea extracts added, the lower is the amount of $CaCO_3$ precipitated. For the concentration of 50 ppm of green tea extracts added, the inhibition is around 6%. As for the concentration of 100 ppm of green tea extracts added, the inhibition takes an increase to be around 20%. While for the highest concentration of green tea extracts added which is 200 ppm, the inhibition of $CaCO_3$ precipitation is around 53.3%.

As pointed earlier, green tea extract contain some effective components to inhibit the formation of $CaCO_3$ scale which are catechin and quercetin. Besides that, the structure and functional group of green tea extracts which is phenolic and carboxyl act as negatively charged colloids or anionic polyelectrolytes. These polyelectrolytes interact on the crystallization of $CaCO_3$ through adsorption on submicronic crystals of crystals and occupying cationic sites thus resulting in decreased growth of crystals.

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

Based on the results obtained for inhibition efficiency laboratory tests using Gambir extracts, Aloe Vera and green tea extracts, the three materials play some role in inhibiting the formation of calcium carbonate under the experiment conditions. The inhibition ability depends on the concentration of additives added into the growth solution.

Of the three additives used, Aloe Vera showed the potential to be the most effective calcium carbonate scale inhibitor from the three candidates. Aloe Vera exhibits an inhibition of 73.3% at 200 ppm which is the highest as compared to 53.3% each for Gambir extracts and green tea extracts.

In conclusion, the results show that Gambir extracts, Aloe Vera and green tea extracts have the potential to be further studied as an alternative for calcium carbonate scale inhibitor.

1. Gambir extracts, aloe vera and green tea extracts all showed potentials to be effective calcium carbonate scale inhibitor through the laboratory tests.
2. Based on the results, aloe vera is the most effective calcium carbonate scale inhibitor among the three alternative sources.
3. Advance research and studies on gambir extracts, aloe vera and green tea extracts as $CaCO_3$ scale inhibitor are needed to further explore their potential.

5.2 Recommendations

Based on the laboratory tests done, it has been shown that Gambir extracts, Aloe Vera and green tea extracts all show potentials to be effective calcium carbonate scale inhibitors. In order to further research and discover their potentials, extensive studies and experiments will have to be performed on them as calcium carbonate scale inhibitor. Here is a list of recommendations to further study their potentials as calcium carbonate scale inhibitor:

1. Conduct experiment of their efficiency as calcium carbonate scale inhibitor according to the pressure and temperature of a real oil and gas well. Some materials tend to behave differently in higher pressure and temperature conditions.

2. Find the Minimum Inhibitor Concentration (MIC) refers to the minimum concentration of the inhibitor needed for effectively inhibits scale formation. Equipments such as Tube Blocking Test can find the MIC of each scale inhibitors.

3. Explore the compatibility of each additive with chemicals usually associated with a real oil and gas well. The negative characteristics of these compounds should be tested as well which include the reaction of inhibitor with ions normally dissolved in oilfield brines and also possibilities to form emulsions if aqueous inhibitor solution is contacted with crude oil.

4. Compare the alternative calcium carbonate scale inhibitors performance with conventional calcium carbonate scale inhibitors.

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