Mitigation of Calcium Carbonate ($CaCO_3$) Inorganic Scaling using Green Inhibitors

by

NOOR AFIQAH BINTI AHMAD
(12405)

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Petroleum Engineering)

JANUARY 2012

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Mitigation of Calcium Carbonate Inorganic Scaling Using Green Inhibitors

by

Noor Afiqah binti Ahmad

A project dissertation submitted to the
Petroleum Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(PETROLEUM ENGINEERING)

Approved by,

____
(AP Dr. Ismail M Saaid)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
January 2012

CERTIFICATION OF ORIGINALITY

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

NOOR AFIQAH BINTI AHMAD

ABSTRACT

Scale deposition is one of the most critical and troublesome damage problems in oilfield industry which may lead to loss in productivity and equipments malfunction. Formation of scale may occur in various areas such as in the reservoir area near the wellbore, in the production tubing or in surface equipments. Scale inhibition by scale inhibitor is one of numerous methods to mitigate scale formation. However, nowadays, due to new regulations constructed, utilization of conventional scale inhibitor is limited as its discharged chemicals will definitely give harm to marine ecosystems in the long run. Thus, “green” scale inhibitor need to be developed in order to fulfill its increasing demand in oil and gas industry. Therefore, this project is carried out to identify new potential of “green” scale inhibitor from natural resources based on comprehensive studies on characteristics of existing “green” scale inhibitor in the industry. Candidates of potential resources are Barley, Sweet Potato, Ginger, and Pennywort. Through extensive selection, Barley and Pennywort are chosen to be further studied in this project. Their inhibiting potential and efficiencies will be examined through several methods; Compatibility Test, Calcium Carbonate Threshold Test, and Optical Microscopic Examination. The objectives of those tests are to evaluate the compatibility of candidates with synthetic brine, to examine inhibition potential as well as to determine the threshold concentration of inhibitors, and to observe effect of presence of inhibitors towards morphology of lattice, respectively. The data obtained shows that Barley extract exhibit compatibility with synthetic water at all tested concentrations meanwhile Pennywort extracts only at lower concentrations. Both Barley and Pennywort extracts show the ability to inhibit scale formation as their percentages of inhibition are increasing with escalating concentrations tested. Effect of inhibitors concentrations is still insignificant in this project as size of precipitating particles formed is not further evaluated.

ACKNOWLEDGEMENTS

First and foremost, all praises to Allah for His guidance and blessings for giving an opportunity for the author to accomplish this Final Year Project as part of the requirements for Bachelors of Engineering (Hons.) in Petroleum Engineering at Universiti Teknologi PETRONAS.

My sincere gratitude and appreciation is extended, especially, to the assigned supervisor for this project, AP Dr Ismail M Saaid for the continuous guidance and support provided throughout the progression of this project.

My acknowledgement would be incomplete without giving credit to UTP, especially Petroleum and Geosciences Department laboratory technicians and also Chemical Engineering Department laboratory technicians for giving the author an opportunity to utilize the laboratory and assisting the author in completing the experiment works.

Finally, countless appreciation goes to my family back home for their sacrifices coupled with their continuous encouragement and support in completing this project.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: PROJECT BACKGROUND

1.1 Background Study

Oil and gas industry is a continuously developed industry which expose to any challenges and problems. One of the most common and troublesome damage problems in oil field and can occur in both production and injection well is scale deposition. This problem is probably one of the three biggest water-related production problems after corrosion and gas hydrates formation. Thus, this matter needs to be anticipated in advance in order to uphold oil productivity for future assurance.

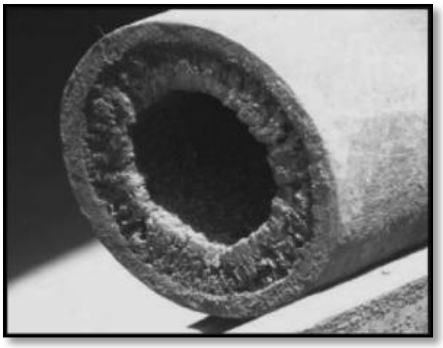


Figure 1: Scale deposits in a conduit.
From *Production Chemicals for the Oil and Gas Industry* (p. 54), by Kelland, M. A., 2009, Norway: Taylor and Francis Group, LLC. Copyright 2009 by the Taylor and Francis Group, LLC

Scale formation is a deposition of sparingly soluble inorganic salts from aqueous solutions. This scale deposit can occur everywhere in the tubing, gravel pack, perforations or in the formation. Scale deposition can occur when the solution equilibrium of the water is disturbed by pressure and temperature changes, dissolved gases or incompatibility between mixing waters.

Inorganic scales consists of many different groups but the most common ones are of carbonate and sulphate scales with presence of alkaline earth metals such as Mg, Ca, Sr, Ba or Ra. Carbonate and sulphate are present as negative ions while the alkaline earth metals are present as positive ions when dissolved in the water. Thus, below are the most common scales encountered in oil and gas industry in the order of prevalence (Kelland, 2009):-

- Calcium Carbonate (Calcite and Aragonite) ($CaCO_3$)
- Sulphate salts of Calcium (Gypsum) ($CaSO_4$), Strontium (Celestite) ($SrSO_4$), and Barium (Barite) ($BaSO_4$)
- Sulphide scales - Iron (II) (FeS), Zinc (ZnS) and Lead(II) (CuS)
- Sodium Chloride (Halite) (KCl)

Scale deposition in production conduit may lead to numerous other undesirable problems if it is untreated. Scale deposits block pore throats at near-well bore region or in the well itself causing formation damage and loss of well productivity. Besides that, wall insulation by scale also may cause unscheduled equipment shutdown or failure to function well. It can also block production flow by clogging perforations or forming a thick lining in the production tubing. The build-up of scale inside well bores causes millions of dollars in damage every year. Thus, these circumstances indirectly contribute to low production and increasing operational cost in order to overcome the problem.

1.2 Problem Statement

After employing inhibitors for scale treatment, the chemicals will be discharged into the sea. This activity will definitely be harmful to marine environment in a long run, consequently, disturbing the equilibrium of ecosystems. Most countries had realized the adverse impacts of discharging the chemicals inappropriately, therefore they are moving forward by generating new regulations to encounter the problem. Thus, due to that implemented law, oilfield industry nowadays is facing severe restrictions concerning discharge of oilfield chemicals into the environment. According to the formulated rule, discharged chemicals should contain no or less toxicity elements and should be biodegradable in order to not destroy the environment any further (Chen, Chen, Montgomerie, Hagen, & Ekpeni, 2011).

Since at present, oilfield industry is still lack of commercialized environmental-friendly or “green” inhibitors for field implementation, thus, this project is significant to be performed as it involves in discovery of new potential “green” inhibitors and indirectly enlarging the study of environmentally-friendly scale inhibitors.

1.3 Objectives of Project

In particular, the objectives of this project are:

1. To identify methods used for $CaCO_3$ scale mitigation with more emphasize on green technology
2. To identify characteristics of existing environmentally-friendly scale inhibitor in industry
3. To identify any potential “green” inhibitors based on characteristics of studied inhibitors from natural resources
4. To analyze those identified candidates of “green” inhibitors for $CaCO_3$ scale
5. To compare shortlisted candidates of “green” inhibitors for $CaCO_3$ scale with studied ‘green’ inhibitors through experimental approaches

1.4 Scope of Study

In general, this project is within production optimization scope for the industry but specifically, scope of study of this project revolves around discovering new potential of “green” inhibitors in natural resources to mitigate inorganic scaling, particularly for $CaCO_3$ scale. There are three phases prepared for this study whereby the first phase is to study and understand the approaches used in order to mitigate $CaCO_3$ scale problems in the industry. Total emphasize will be put on green technology as strict environmental legislation is in compliance nowadays. Concurrently, thorough study on the characteristics of existing “green” scale inhibitors in the industry is carried out as well in this phase. Besides, identification and comprehensive studies on any natural resources which could be potential “green” inhibitors based on characteristics of existing inhibitors are performed. Next in second stage, effectiveness and efficiencies of potential “green” inhibitors candidates are examined through laboratory experiments comparatively to existing “green” inhibitors. Besides, their compatibility with formation water also been evaluated in this project. Potential inhibitors can be assessed on several bases which include their performance, effect on pH and dissolved ion on inhibition and thermal stability. Last but not least, for the final stage, results obtained from experiments are analyzed; hence, any “green” inhibitors which possess huge potential will be promoted for further development research.

As this project consumes two semesters which is approximately nine months to complete, thus, those three phases of this study are conducted during this planned time frame. First phase is performed in the first semester which is roughly from September till December 2011. The second and final phases are resumed in second semester of final year which is from middle of January 2012 till end of March 2012. Meanwhile, the rest of second semester which is around two months (April and May 2012) is fully allocated for documentations and presentations of the overall project.

Based on this timeline plan, this project is feasible and relevant enough to be done and objectives of this project are alleged to be achieved by the end of the second semester.

CHAPTER 2: LITERATURE REVIEW

2.1 Mechanisms of Calcium Carbonate ($CaCO_3$) Scale Formation

Calcium Carbonate, $CaCO_3$, is one of the most common scale depositions found in oilfield production wells and surface facilities. It can be deposited all along the production conduit to the surface equipment, especially in high temperature and high pressure (HTHP) wells, where temperature is up to 250°C and pressure is up to 20000 psi (Chen, et al., 2011).

In the reservoir, there is an existing compound in the formation water which contributes to the formation of calcium carbonate scale which is calcium bicarbonate ($CaHCO_3$). During production, reduction of both pressure and temperature leads to the occurrence of chemical reaction in $CaHCO_{3.}$

$$HCO_3^{2-} \longleftrightarrow CO_3^{2-} + H_2O + CO_2\,(g) \qquad (2.1)$$

According to Le Chatelier's Principle, as the pressure drops, the above equilibrium will move to the right, thus, more CO_2 gas will form in order to increase the pressure (Kelland, 2009). This causes more carbonate ions formed, pH increases and an associated increase in super saturation. Subsequently, in this super saturation condition, calcium carbonate scale will form with the presence of calcium ions, carbonate ions and high temperature as the driving force for $CaCO_3$ self-deposition.

$$Ca^{2+} + CO_3^{2-} \longleftrightarrow CaCO_3\,(s) \qquad (2.2)$$

As the solubility of calcium carbonate decreases with the increasing of temperature, hence, crystallization of $CaCO_3$ will occur more frequent in high temperature. In addition, the kinetics of calcium carbonate is a function of temperature (i.e. slow kinetics at low temperature). Thus, the formation of calcium carbonate will speed up and precipitation may take place at an earlier stage (Chen, et al., 2011).

2.2 Methods of Scale Control

In order to mitigate or prevent formation of scale in oil and gas industry, there are three basic approaches which are generally used. The approaches are tabulated as below:-

Table 1: Methods of Scale Control and Details

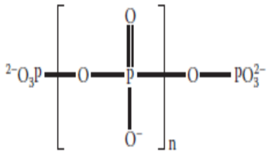
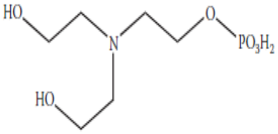
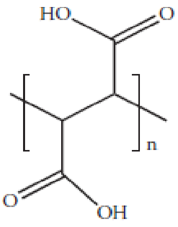
Methods of Scale Control	Details	Advantages / Disadvantages
Desulfation of Injected Seawater	• Prevent only the formation of sulphate and sulphide scales.	Advantages: • Considered as the best alternative for sulphate and sulphide scales mitigation in large production fields • Reduced reservoir souring thus minimizing degree of microbial corrosion
		Disadvantages: • Efficiency of scale removal is depending on the concentration of sulphate ions in the seawater • High cost of treatment • Not applicable for all types of scale
Scale Inhibition	• Most common remedy to treat scale problems in industry • Scale inhibitors used to treat scales are depend on the type of scale formed in the production system • Numbers of methods of scale inhibitor deployment such as through squeeze	Advantages: • Many options on the most suitable scale inhibitor for treatment as there are several types or brands of scale inhibitor in market • Easier to be performed and its operational cost is quite reasonable • Applicable for treatment at all areas such as in the reservoir, surface equipments, and also for scale formation in production tubing

	treatment and continuous injection	Disadvantages: • Chemicals of inhibitors will be discharged into the sea after deployment, thus eventually will create harmful condition for marine environment • Utilization of inhibitors are limited, highly depending on its compatibility with formation water and its hydrothermal stability
Nonchemical Scale Removal	i. High-frequency electric induction • Induced electric will lead the scale particles to form in the produced fluids instead of insulating the walls of surface or topside equipments • Literally, it did not prevent scale formation, yet only altering the location of scale occurrence	Advantage: • Applicable for any types of scale formed
	ii. Lowering ion solubility below that of saturation • Re-dissolving and cleaning pipelines • Break down hard scale	Disadvantages: • Suitable for scale formed in production tubing and in equipments only • Rarely used in oilfield industry
	iii. Magnetic field treatment • Scale prevention through this method may involve a combination of magnetohydrodynamic, agglomeration of ferromagnetic and super paramagnetic microparticles mechanisms.	

2.3 Scale Inhibition by Several Classes of Calcium Carbonate Scale Inhibitors

Scale inhibitors are water-soluble chemicals that prevent or retard the nucleation or crystallization growth of inorganic scales. Based on studies made in early years of scale inhibitors discoveries, it was generalized that polymers are good nucleation inhibitors and dispersants (Kelland, 2009). As scale crystallization occurs, they will adsorb onto scale crystal surfaces and are expended in the lattice thus retarding further growth of the scale. Besides, threshold levels for each and every inhibitor should be known as their effectiveness of inhibition are also depending on that factor. Only certain inhibitors are able to effectively prevent crystal growth below their threshold levels meanwhile some inhibitors are not. Besides, crystal growth of calcium carbonate inhibition can be achieved by interacting either with its cations or anions. Normally several interactions are necessary to tightly hold the inhibitor on the surface while other molecules with similar functional groups will interact with the lattice ions on the crystal surface. In order to bind well with the anions, opposite charged cations are needed. Thus, to put several cations in a molecule easily is through quaternary ammonium, phosphonium, or sulfonium groups. However, polyquaternary ammonium salts are discovered as poor scale inhibitors, probably due to the mismatch of size between the quaternary groups and the cations in scale lattice, i.e. calcium (Kelland, 2009). Since interacting with anions is quite difficult to achieve, thus by attaching other anionic groups to an organic molecules which can interact well with cations on scale lattice is the other option to prevent scale nucleation. Those anionic groups are Phosphate ions, Phosphonate ions, Phosphinate ions, Carboxylate ions, Sulfonate ions. Mixtures of these ions or existence of two or more of these ions are able to build into structure of good scale inhibitors which by now exist in the industry. The molecules can be prepared in acid forms such as carboxylic acid, phosphonic acid, etc. Thus, most common classes of scale inhibitors containing these ions or acids are Polyphosphates, Phosphate Esters, Polycarboxylates, Polyphosphonates, Polysulfonates, etc (Kelland, 2009). Details on several classes of scale inhibitors are summarized as below:

Table 2: Several Common Classes if Scale Inhibitors with their Characteristics

Types of Classes	Details
Polyphosphates 	• Found in Sodium Tripolyphosphate or Sodium Hexametaphosphate • Mainly used in Boiler Water Treatment • May found in mammalian soft tissue in the form of Citric Acid Phosphate • Thermally Stable and more compatible for oilfield scale inhibition at low calcium concentrations
Phosphate Esters 	• Environmental- friendly for calcium carbonate and calcium sulfate scale • Made by reacting Phosphoric Acid with alcohols • Compatible with high calcium brines • Possess limited thermal stability; up to 110˚C for carbonate scale control • Has limited range of biodegradability due to hydrolysis instability; up to 80˚C
Polycarboxylates 	• Have been used as scale inhibitors almost as long as Polyphosphates • Poorly biodegradable as scale inhibitor in general but can be improved by reducing its molecular weight • Based on Polyacrylic acid, Polymethacrylic acid, and Polymaleic acid • Addition of hydroxyl groups (-OH) to this component are claimed to be significant as it can improves their performance as scale inhibitors and increase their calcium tolerance

2.4 Conventional and “Green” Scale Inhibitors

Phosphonate-based scale inhibitors have been widely used as effective calcium carbonate scale inhibitors for squeeze application. This inhibitor is low in concentration, easily to be detected, good adsorption and desorption along with long squeeze life. However, utilization of this inhibitor has been limited, especially at high temperature due to thermal stability and compatibility with formation water (Chen, et al., 2009).

Scale inhibitors have been used for many years in both squeeze treatment applications and also in the treatment of topside facilities. Once scale inhibitor injection job is complete, they were released into the sea. In recent years, it has become a heightened concern over potential damage to the environment from these discharged chemicals and the impact they may have on marine ecosystems (Wilson D., 2010). As most countries establishing new government regulations to counter this matter, hence, the oil industry faced severe restrictions concerning discharge of oilfield chemicals into the environment. Thus, the best way to overcome the restrictions is to generate more environmentally friendly “green” scale inhibitors to replace the conventional scale inhibitors in the market at present. The challenge for any green inhibitor is not only to meet or exceed these regulations but also to be able to inhibit mixed scale, both downhole and at the surface separations facilities (Wilson D., 2009). Recently, there have been a number of reports of new products that are more environmentally acceptable and that have been studied in the laboratory and/or applied in the field. Those new invented products are Carboxymethyl Inulins (CMIs) and Polyaspartic Acids (Polyaspartate). These products are discovered to be naturally biodegradable, possess good adsorption and desorption properties (Amjad Z., 2009). However, high dosages of “green” scale inhibitor are required for field application in order to create similar effectiveness with conventional inhibitor (David Hasson, et al., 2011).

2.5 Performance Testing Of Scale Inhibitors

Scale inhibitors need to undergo laboratory testing in order to know their capability to function well before they are being commercialized. There are various types of laboratory tests which can be performed depends on the type of the inhibitor itself. The most common types of laboratory tests carried out for new scale inhibitor applications are:-

i. Compatibility Test
ii. Dynamic Tube Blocking Test
iii. Hydrothermal Stability Test

Basically, all tests stated above are specifically tested for calcium carbonate scale inhibitors. Besides, these basic tests are conducted based on the method of scale inhibitors deployment in field application, whether it is through continuous injection or squeeze treatment (Kelland, 2009).

Differences in tests-sequencing based on method of deployments are as follows:-

Table 3: Experimental Tests for Different Method of Deployments

Continuous Injection Method	Squeeze Treatment
1st: Dynamic Tube Blocking Test (DTB) - Primary stage of scale inhibitor testing - In the test, concentrations of the inhibitors are reduced gradually until a given pressure drops occur across the tube - Besides, Minimum Inhibitor Concentration (MIC) which is necessary for complete inhibition	**1st:** Compatibility Test - Need to check whether or not the inhibitor precipitates when mixed with the formation brines which will cause formation damage. - This test is assessed by visually and quantitatively determination of the remaining calcium ions in solution (Bazin B., et al., 2004) **2nd:** Hydrothermal Stability Test

can be determined by this method and also the performance of inhibitors can then be compared. • MIC is the guideline figure in order for the inhibitors to be applied in the field and its effect needs to be monitored once in use. **2nd:** Compatibility Test • Need to be conducted for continuously dosed inhibitors as there is a possibility for the inhibitors to mix with produced fluid in downstream (Kelland, 2009).	• Need to be performed for the reason that any potential squeeze inhibitors must be able to withstand the thermal and aquatic environment in the reservoir for long period of time, usually one to one and a half year, without breakdown. • If the inhibitor breaks down, it shows high possibility that it will lose its inhibiting efficiency during the treatment period (Wilson D., 2010). **OR 2nd:** Thermal Ageing Test • Similar to Hydrothermal Stability Test • Need to ensure the inhibitor is stable at reservoir temperature for estimated squeeze lifetime. • The inhibitor solution is aged in a static bottle and then performance-tested against a nonage sample. Basically, for this test, it can be done concurrently with Static Bottle Test or Jar test and Dynamic Tube Blocking Test (Kelland, 2009).

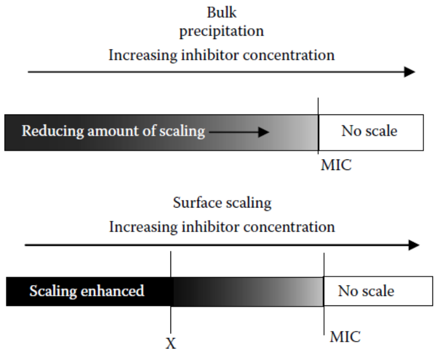
2.6 Mechanism of Inhibitions by Scale Inhibitor

Mechanism of inhibition is depending greatly on several factors such as pH of formation water, temperature, pressure, nucleation time of crystal growth, adsorption and desorption of inhibitor, etc. Yet, the nature, amount and type of interaction of inhibitor with scale crystal surface are hard to be predicted from the aspect of either thermodynamics or kinetic (M.B. Tomson, 2002). Thus, until now, those factors that affecting the mechanism of inhibition are still being studied.

Therefore, several attempts had been done by researchers to predict the effect of inhibitor on mineral scale formation. Below are some mechanisms of inhibition defined in number of studies which had been examined:

Table 4: Mechanisms of Inhibition in different Literatures

Literatures	Mechanisms of Inhibition
(1) Mechanisms of Mineral Scale Inhibitor by M.B Tomson, SPE, G. Fu, M.A. Watson, and A.T. Kan, Rice University	<u>Burton-Caberrara-Frank (BCF) Spiral Growth Mechanism Theory</u> • In this theory, kink sites grow continuously in a spiral, thus overcoming the expected activation energy for nucleation of a new site on a flat particle surface. Consequently, inhibitor inhibits the advance of the spiral. • Besides, only the active growth sites that needs to be poisoned in order to prevent the spiral from growing any further.
	• Meanwhile, on the other hand, there are other different models of inhibition which come up with functions that mechanisms of inhibiting are such as reducing rate of growth by the fraction of surface covered by inhibitor or by the fraction of critical coverage.
(2) Mechanisms of Scale and Corrosion Inhibition by Polyaspartates by C. Estievenart, N. Kohler, F. Ropital,	• Mechanism of inhibition occurs by dispersion of calcium carbonate particles or complexion of calcium ions by inhibitor. • Inhibitor used for the study in exact is Polyaspartate (PASP). • By adding PASP in the solution, morphology of growing calcite crystals is altered. • This situation can be modeled by combining those

and C. Fiaud	mechanisms stated beforehand, which are dispersion, complexion, and another mechanism which is, adsorption. • After the initial calcite crystal form, the added PASP will adsorb on the calcite surface and only allow growth in some favored growing sites. Meanwhile, growth in the axis perpendicular to the quartz is prevented. This shows that calcite growth is being reduced at this moment. Subsequently, PASP will form a complex with calcium, while the carbonate ions had been replaced by carboxylic groups of the polymer. This reaction induces the dissolution of crystal, therefore building a smoother lattice which is also calcium carbonate in different form which is Vaterite.
(3) A Natural Extract as Scale and Corrosion Inhibitor for Steel Surface in Brine Solution by A.M. Abdel-Gaber, B.A Abd-El-Nabey, E. Khamis, D.E Abd-El-Khalek	• Antiscalant acts by inhibiting nucleation step in calcite crystallization. • The inhibitor will bind permanently with calcium ions which existed in the solution and later performing complex nucleus, which adsorb on the surface at early phase of nucleation. Thus, those existing crystal nuclei around them will be poisoned indirectly nucleation phase had been delayed.
(4) Chapter 8: Latest Developments in Oilfield Scale Control, The Science and Technology of Industrial Water Treatment by Zahid	 *Figure 2: Schematic diagram of surface and bulk scaling*

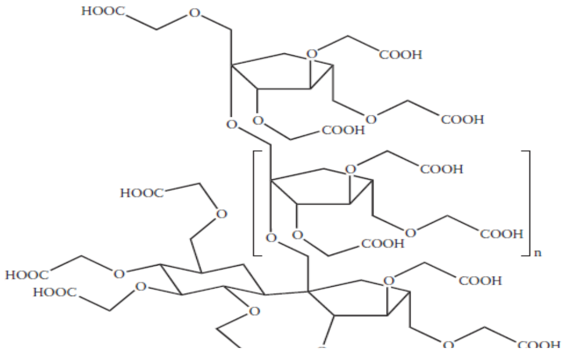
Amjad	*scenarios.* *Retrieved from Yuan, Latest Developments in Oilfield Scale Control, 143, 2010.* • Inhibitor acts by delaying the nucleation and growth of both bulk precipitation and surface scaling of $CaCO_3$ especially at the initial stages. • Inhibitor forms a film on the metal surface which will prevent the adhesion of scale particles onto the surface. • Thus, indirectly, the inhibitor is increasing the nucleation time of $CaCO_3$ in bulk precipitation • Based on Figure 2 above, $CaCO_3$ scale formation can be fully prevented at as low as Minimum Inhibitor Concentration of scale inhibitor. Thus, MIC is the lowest effective concentration for the inhibitor to work efficiently

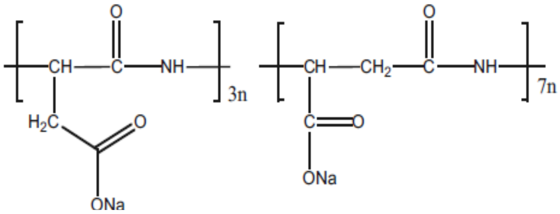
2.7 Characteristics of Studied 'Green' Inhibitors

There are a number of "green" inhibitors which have been studied for calcium carbonate scale removal. However, this study will only look thoroughly on certain inhibitors such as Carboxymethyl Inulin (CMI) and Polyaspartate (PASP). These inhibitors are widely studied in oilfield research industry because of its high potential to be well-developed for future used. The components of the plant materials are mostly possessed of nitrogen or oxygen atoms. Thus the mechanism of inhibition of these extracts may take place either by adsorption on nuclei surface or forming complex mechanism.

Based on literature study, characteristics of both CMI and PASP inhibitors are as below:

Table 5: Characteristics of Commercialized Green Inhibitors

Scale Inhibitor	Characteristics	References
CMI	• *Chemical Structure*  *Figure 3: Chemical Structure of CMI biopolymer.* • *Active components for inhibition*: Carboxylate groups (R-CO_2^-) • *Origin of polymer*: Synthesized from derivatives of inulin which extracted from Chicory roots (polysaccharides), undergo carboxymethylation process with Sodium Monochloroacetate • *Compatibility with formation water (brine):* Calcium tolerance is higher than that of Phosphonate (Conventional Antiscalant) • *Thermal Stability*: Stable up to 110˚C (without presence of surfactant) • *Toxicity*: Negligible • *Mechanism of Inhibition*: Adsorption on crystal surfaces - Inhibitor molecules will adsorb on the most energetic and favorable sites of the solute ions - Once adsorbed, they will inhibit $CaCO_3$ crystal	*Retrieved on December 16, 2012, from: http://www.aidic.it/isic18/webpapers/112Boels.pdf* (B. Bazin, 2004) (Luciaan Boels, et al., 2011)

	growth by suppressing, or even blocking the movements of ions along the step - Thus, through suppression, it prevents the displacement of crystal growth and indirectly poisons all crystals on surface, and inhibit their further growth for certain period - Therefore, induction time for $CaCO_3$ scale formation will also be sufficiently longer than that of inhibition without additives	
PASP	• *Chemical structure*  *Figure 4: Chemical Structure of Polyaspartate.* • *Active components for inhibition*: Carboxylate group • *Origin*: Synthesized from Aspartic acid through Thermal Polycondensations with or without acid catalyst • *Thermal Stability*: 60˚C (depends on condition of experiments) • *Mechanism of inhibition*: Adsorption, Dispersion of calcium carbonate and Complexation of calcium ions - *Refer explanation in literature review; 2.5: Mechanism of Inhibitions by Scale Inhibitor (Mechanisms of Scale and Corrosion Inhibition by Polyaspartates)*	*Retrieved on December 21, 2012 from: http://academic.scranton.edu/faculty/cannm1/polymer/polymermodule.html* (David Hasson, et al., 2011)

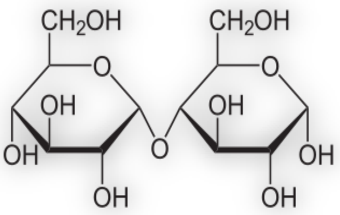
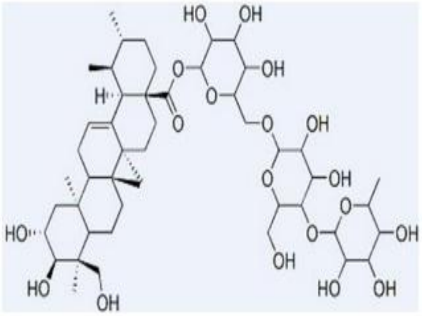
Besides CMI and PASP, aqueous plant extracts are also been investigated in discovering their potential for new ‘green’ scale inhibitors. They are organic in nature and contain Protein, Terpenes, Tannins, Limonide, Nemocin, Carotene, Thiamine (Vitamin B1), Ascorbic acid, Riboflavin (Vitamin B2), Amino acids, Flavonoids, etc. (Quaraishi, 2004). Therefore, with this finding, it is easier to investigate other new resources which have the potential of inhibiting calcium carbonate scale.

2.8 Characteristics of Potential Resources of $CaCO_3$ Scale Inhibitors

As one of the objectives of this project is to identify any potential “green” inhibitors based on characteristics of studied inhibitors, thus, several natural resources are studied on their characteristics as to be selected as candidates of “green” scale inhibitors. Based on information declared earlier on, there are numbers of natural resources which contain high inulin content such as Barley, Sweet Potato, Ginger, Garlic, Cinnamon, etc (FarmAfripedia). Thus, these plants can be considered to be further study as to select the candidates of “green” scale inhibitors. Besides, plants with high content of Protein, Amino Acids (i.e. Tannins, etc) and Riboflavin (Vitamin B2) are also qualified to be examine further in this project. Examples of plants which contain those components as stated are Pennywort, Onions, Cabbage, etc. Nevertheless, considering suitability, potential and availability of preparation methods and other factors in short listing candidates, therefore, selected plants which are decided to be further investigated are Pennywort and Barley. Further details on the characteristics of reviewed resources are as tabulated below:-

Table 6: Characteristics of Potential Resources for Inhibitors

Potential Resources	Characteristics	References
 Barley Grains	• Barley is a type of cereal grain with plenty of nutlike flavor and a tempting chewy, pasta-like consistency • Barley is naturally high in maltose, which possibly helpful in scale	*Retrieved on December 21, 2012, from: http://www.foodsubs.com/GrainBarley.html* (Barley: In Depth Nutrient Analysis)

	inhibition since maltose is a type of disaccharides  *Figure 5: Chemical Structure of Maltose contained in Barley.* • Barley contains several vitamins and minerals including niacin (Vitamin B3), thiamine (Vitamin B1), selenium, iron, magnesium, zinc, phosphorus and copper, as well as high content of dietary fiber • Besides, barley also possesses high content of inulin which possibly useful potential for scale inhibitor	(FarmAfripedia) *Retrieved on December 21, 2012 from: http://en.wikipedia.org/wiki/Maltose* (Foundation, 2001-2011)
 **Pennywort** ***(Cerella Asiatica)***	 *Figure 6: Chemical structure of Pennywort.* • A type of herbaceous plant which originate from moist areas • This herb works by preventing a	*Retrieved on December 21, 2012, from: http://rls8994.hubpages.com/hub/Pennywort-Tea-And-Its-Many-Benefits*

	rowdy manner of the absorption of nutrition and alters this process through an enhanced sequence of nutrient digestion • Pennywort contains vitamins B1, B2, B3, and B6 as well as the minerals, calcium, magnesium, sodium, manganese, and zinc • Besides, it has properties of being antibacterial, and anti-inflammatory	

CHAPTER 3: RESEARCH METHODOLOGY

3.1 Project Activities

The overall planning for this project is as shown in Figure 1 below.

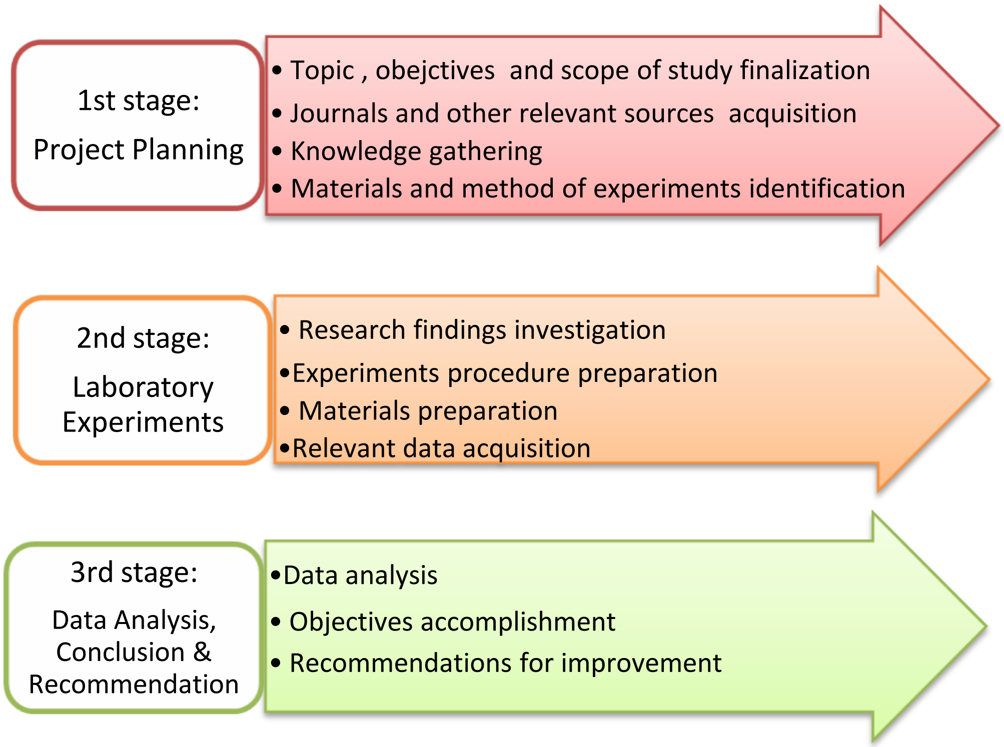


Figure 7: Stages and Planned Activities of Project

Figure 7 shows the stages and planned activities for this project in general. Specifically, three (3) experiments had been planned for this project within specified time spans which taking approximately three months to be completed in second stage. Planned experiments are conducted to examine and assess thoroughly inhibiting potential of Barley and Pennywort extract towards calcium carbonate scale. Besides, their performance will be compared with existing green scale inhibitor which is Polyaspartate (PASP). After data acquisition, the results will be analyzed to come up with a conclusion and recommendations which is the outcome of this project.

3.2 Experimentation Overview

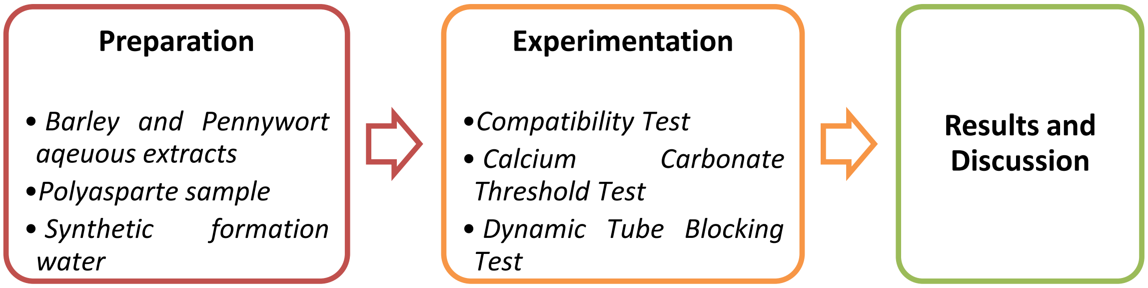


Figure 8: Overall Experimentation Flow

Figure 8 summarized the experimentation flow of this project. Additional details will be explained further.

3.2.1 Compatibility Test

Compatibility Test is a preliminary test conducted to examine compatibility of tested scale inhibitor (Barley and Pennywort extract) with synthetic formation water in different concentrations of inhibitors and at test conditions. Specifically in this investigation, compatibility of PASP with formation water also been conducted for comparison purposes. Generally, steps of executing this experimentation are as shown in **Figure 9** below. Further details on the process of this experiment will be explained next.

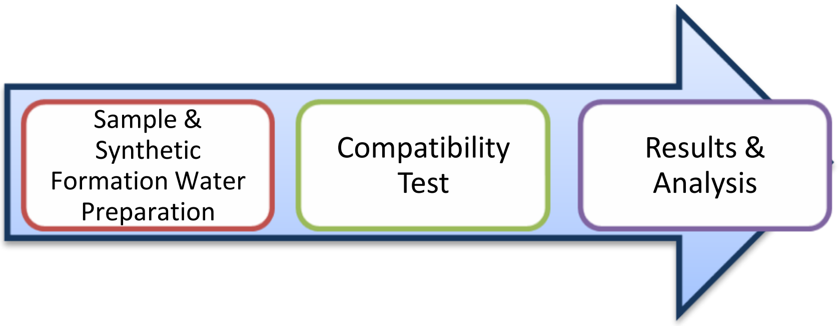


Figure 9: Stages of performing Compatibility Test

Sample and Synthetic Formation Water Preparation:

- *Preparation of Barley Extract* (Sati Al-dalain, 2008)

  Barley grains are obtained and they are cleaned, dried and grounded into a fine powder using Mortar Grinder. Barley powders are weighted, added and soaked in boiled water for six (6) hours then filtered through a sieve and stored in dark bottles immediately.

Figure 10: Barley grain

Figure 11: Barley powder

- *Preparation of Pennywort Extract* (A.M Abdel-Gaber et al., 2011)

  Fresh leaves of pennywort are obtained and dried in oven at 50˚C overnight. Dried leaves were then grounded to powdery form using Mortar Grinder. Some amount of distilled water was boiled. Pennywort powder are weighted and added to some volume of boiled distilled water, depending on desired concentration for particular experiments. The solution is left for cooling in some times then filtered using sieve. Filtered solution is stored in clean bottles and labeled.

Figure 12: Dried Pennywort leaves

Figure 13: Grounded Pennywort leaves

Selected concentrations to be examined for inhibitors in this test are 100 ppm, 1000 ppm, 10000 ppm, and 50000 ppm. In order to prepare those concentrations of aqueous extracts, Barley and Pennywort powder need to be weighed 0.01 g, 0.1 g, 1 g, and 5 grams respectively and added to 100 ml of boiled distilled water using heater and beaker. Summary on details of aqueous extracts preparation are given in **Table A1** *(Refer Appendix I)*. Meanwhile, PASP is prepared with similar concentrations (100 ppm, 1000 ppm, 10000 ppm, and 50000 ppm) as well. Next, preparation for synthetic formation water is made. Formulation of synthetic water for this test is prepared based on composition of high salinity formation water as shown in **Table A2** (Hasson & Semiat, 2005) *(Refer Appendix I)***.** However, synthetic water formulated only contains calcium ions for simplification purposes. Preparation of the water with 30, 000 ppm calcium ions need 110.05 grams of Calcium Chloride dihydrate, $CaCl_2.2H_2O$ to be dissolved and mixed into 1 L of distilled water. Detail calculations to clarify previous statement are as shown in **Appendix II**.

Compatibility Test Experiment (N. Kohler, 2004)*:*

13 mL of synthetic formation water ($CaCl_2.2H_2O$ solution) is measured and filled in four (4) test tubes. 3 mL of Barley aqueous extract (100pm) is then being measured using measuring cylinder and be added to one of the test tubes and then labeled. Any observations witnessed at the initial mixing of tested scale inhibitor and high calcium formation water are recorded. All previous steps are repeated with other concentrations of Barley aqueous extract (1000 ppm, 10000 ppm, 50000 ppm). Then, mixtures with Pennywort aqueous extract and PASP are prepared similarly as well. Next, all twelve labeled test tubes are placed in an oven simultaneously with the temperature adjusted to 95˚C (approximate to normal field temperature) for 24 hours. Finally, observations and changes to the mixtures after 24 hours ageing are recorded for further analysis. Outcomes of the investigation will be presented in next section of this report.

Note: *It is not advisable to store those aqueous extracts for more than three (3) days, thus perform the test as soon as possible.*

3.2.2 Calcium Carbonate Threshold Test

Main objective of this test is to evaluate the capability and performance of potential inhibitors under formulated synthetic water conditions to inhibit calcium carbonate, $CaCO_3$ scale precipitation by determining threshold concentration for both additives. In addition, the parameter is checked comparatively on both aqueous extracts of Barley and Pennywort as well as PASP by analyzing remaining calcium content in mixture of scaling water and additive.

Stages of conducting this experimentation are similar as Compatibility Test execution to some extent.

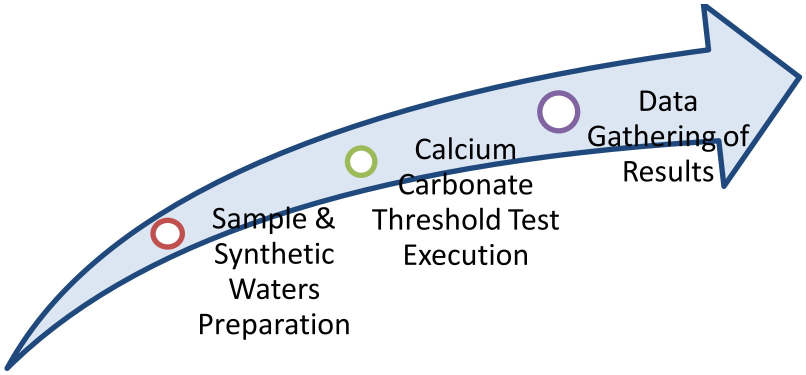


Figure 14: Stages of Calcium Carbonate Threshold Test Execution

Sample and Synthetic Waters Preparation:

Barley and Pennywort aqueous extracts are made up to several concentrations of 10 ppm, 30 ppm, and 50 ppm. Details on the concentration measurements are shown in **Table A1.** Likewise, PASP is prepared with the same concentrations as well. Next, two synthetic waters are made, one containing the scaling cations (Ca^{2+}) and the other containing anions (CO_3^{2-}). These solutions primarily formulated by using Calcium

Chloride dihydrate, $CaCl_2.2H_2O$ and Sodium Carbonate, Na_2CO_3 respectively. Composition of both cation and anion synthetic waters are as shown in **Table A2** referring to Normal Salinity of Formation Water. Since both waters are mixed in 50:50 ratio later on, thus, in precise, concentrations of these waters are fixed to 3500 ppm and 175 ppm correspondingly. Detail calculations on weight of $CaCl_2.2H_2O$ and Na_2CO_3 powders required to prepare 1 L of stock solution are similar with the one calculated for preparation of synthetic formation water in Compatibility Test with only difference in desired concentration of ions **(Appendix II).** As a result, 0.3091 grams of Na_2CO_3 is required to be added to 1 L of distilled water to facilitate the preparation of anion synthetic water with 175 ppm of carbonate ions. Meanwhile, 12.839 grams of $CaCl_2.2H_2O$ is required for 1 L of distilled water to make stock solution of cation water with 3,500 ppm of calcium ions.

Calcium Carbonate Threshold Test Experiment (N. Kohler, 2004)*:*

Six (6) 100 mL beakers are filled up with Barley aqueous extract of 6 mL in volume. Each beaker is filled up with different concentrations of extracts; 10 ppm, 30 ppm, and 50 ppm respectively. Next, 25 mL of anion water (Na_2CO_3 solution) is added to the beakers after the inhibitor solution and then mixed. The cation water ($CaCl_2.2H_2O$ solution) is then added with mixture as much as 25 mL and mixed them well. Simultaneously, all six beakers are placed in a water bath shaker which was adjusted to 60 revolutions per minute at 90°C for approximately four (4) hours. The experiment is repeated twice more by adding in different additives of similar concentrations (Pennywort extract and PASP) in each run. Heated and shaken solutions are then filtered immediately using Whatman filter paper and calcium remaining in solution is analyzed by titration with EDTA solution to identify the percentage of inhibition exhibits by tested scale inhibitors.

- Flow of Titration using Ethylenediaminetetraacetic acid (EDTA) Solution

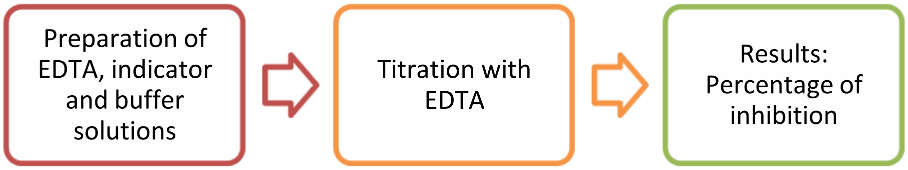


Figure 15: Steps performing EDTA Titration

Preparation of 0.01M EDTA, Indicator and Buffer Solutions:

- *0.01M EDTA Solution*

  EDTA dry-salt is obtained and 5 grams is dried in an oven overnight at temperature of 80˚C. 4 grams of dried EDTA salt is weighed and added slowly to 1 L of deionized water. Next, 0.2 grams of Magnesium Chloride, $MgCl_2.6H_2O$ is weighed and added to the mixture. The mixture is stirred well until all solute is fully dissolved. 0.01 M EDTA stock solution is stored in glass bottle (Kinard, 2010).

- *Ammonia-Ammonium Chloride, NH_3-NH_4Cl Buffer Solution (pH 10)*

  67.5 grams of Ammonium Chloride, NH_4Cl is weighed and dissolved in 570 mL concentrated Ammonia, NH_3 aqueous in a beaker. The mixture is stirred and diluted simultaneously with distilled water to 1 L. The buffer solution is stored in covered glass bottle (Outreach, 2010).

- *Eriochrome Black T Indicator Solution*

  0.2 grams of Eriochrome Black T is weighed and dissolved into 15 mL of triethanolamine and 5 mL of absolute ethanol. The mixture is mixed and stirred well. The indicator solution is stored in glass bottle (Jeffery, J.Bassett, J.Mendham, & Denney, 1989).

Note: *All tasks must be conducted in fume hood as chemicals used are harmful and corrosive. Direct inhalation should be avoided.*

Titration with EDTA Solution (Jeffery, J.Bassett, J.Mendham, & Denney, 1989)*:*

10 mL of filtered solution which had been prepared previously is filled into a conical flask. Then, 15 mL of NH_3-NH_4Cl buffer solution is added to the sample and mixed them well. Next, three to four drops of Eriochrome Black T indicator solution is dripped in and swirled the solution to dissolve it. The solution turned into wine red in colour. Distilled water is added up to 100 mL to dilute the solution. Subsequently, wine red solution is titrated slowly with EDTA solution. The endpoint of titration is a colour change from wine red to sky blue. The titration is repeated twice or more with further sample until concordant results (titres agreeing within 0.1mL) are obtained. The titration is also repeated with using other filtered solutions at different concentrations. All titration results are recorded and presented in next section of this report.

3.2.3 Optical Microscopic Examination

This examination was performed in order to observe the effect on morphology of $CaCO_3$ crystals, the precipitate formed from previous experiment (Calcium Carbonate Threshold Test) with influence of different concentrations of different additives. The morphology of lattice is analyzed by Scanning Electron Microscope (SEM) with magnification of 1000x. All micrographs obtained from this observation will be presented in next section.

3.3 Materials and Tools

The materials for this project require potential inhibitors which derived from local natural resources. Besides that, certain chemicals are also needed for the preparation of solutions.

Materials needed:

- Barley grains
- Fresh Pennywort leaves
- Ethylenediaminetetraacetic acid (EDTA) dry-salt
- Calcium Chloride dihydrate, $CaCl_2.2H_2O$
- Sodium Carbonate, Na_2CO_3
- Magnesium Chloride, $MgCl_2.6H_2O$
- Triethanolamine
- Absolute Ethanol
- Eriochrome Black T powder
- Ammonium Chloride, NH_4Cl
- Deionized water
- Distilled water
- Concentrated Ammonia, NH_3 aqueous

The equipments and tools are based on the tests required. List of tools and equipments needed are as listed:

For preparation of extracts and solutions:

- Heater stirrer
- Electronic scale
- Aluminium foil
- Spatula
- Beakers
- Sieve
- Glass bottles
- Magnetic bar

For experimentations:

- Mortar Grinder
- Laboratory oven
- Water bath shaker
- Burette
- Conical flasks
- Pipette
- Test tubes
- Test tubes rack
- Burette stand
- Whatman filter paper
- Tube Blocking Rig

Figure 16: Water Bath Shaker

Figure 17: Mortar Grinder

3.4 Project Milestone (Gantt Chart)

Refer next page.

Timeline for 1st Semester (September 2011)

No	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	*Topic Selection / Proposal*	■	■					**MID SEMESTER BREAK**								
2	*Preliminary Research Work*		■	■	■	■										
3	*Submission of Proposal Defense (Preliminary) Report*						🟥									
4	*Proposal Defense (Oral Presentation)*								🟩	🟩						
5	*Input Data Acquisition & Lab Experiments Familiarization and Planning*										■	■	■			
6	*Submission of Interim Draft Report*													🟥		
7	*Submission of Interim Report*														🟥	
	Timeline for 2nd Semester (January 2012)															
1	*Lab Experiments and Data Acquisition*	■	■	■	■	■	■	**MID SEMESTER BREAK**								
2	*Submission of Progress Report*								🟥							
3	*Lab Experiments, Data Acquisition and Analysis*								■	■	■	■	■			
4	*Pre-EDX*											🟩				
5	*Submission of Draft Report*												🟥			
6	*Submission of Dissertation (Soft Bound)*													🟥		
7	*Submission of Technical Paper*													🟥		
8	*Oral Presentation*														🟩	
9	*Submission of Dissertation (Hard Bound)*															🟥

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Compatibility Test

4.1.1 Results

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

Table 7: Compatibility of candidate scale inhibitors with high calcium content of synthetic formation water at ambient and temperature of 95˚C

Candidate Scale Inhibitors	Concentration (ppm)	Initial observation at ambient temperature	Observation after 24 hours at 95˚C
Barley Extract	100	Clear solution	Clear solution
	1000	Clear solution	Clear solution
	10000	Hazy solution	Clear solution
	50000	Hazy solution	Clear solution
Pennywort Extract	100	Clear solution	Clear solution
	1000	Clear solution	Clear solution
	10000	Hazy solution	Deposit
	50000	Hazy solution	Deposit
PASP	100	Clear solution	Clear solution
	1000	Clear solution	Clear solution
	10000	Hazy solution	Deposit
	50000	Deposit	Deposit

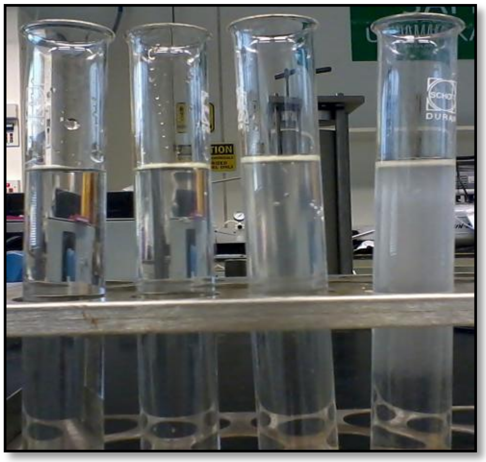


Figure 18: Mixture of Barley Extract at ambient temperature

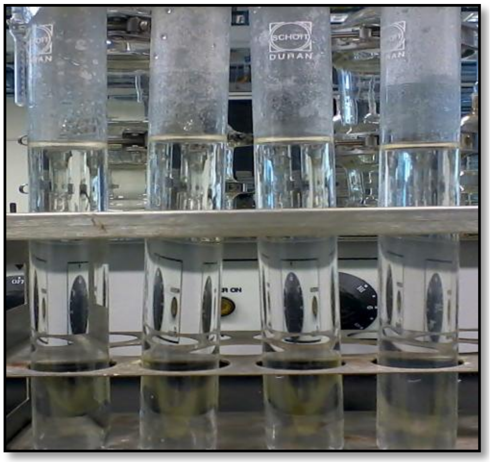


Figure 19: Mixture of Barley extract after 24 hours at 95˚C

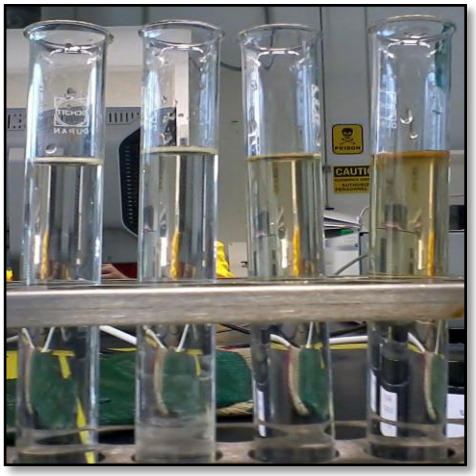


Figure 20: Mixture of Pennywort extract at ambient temperature

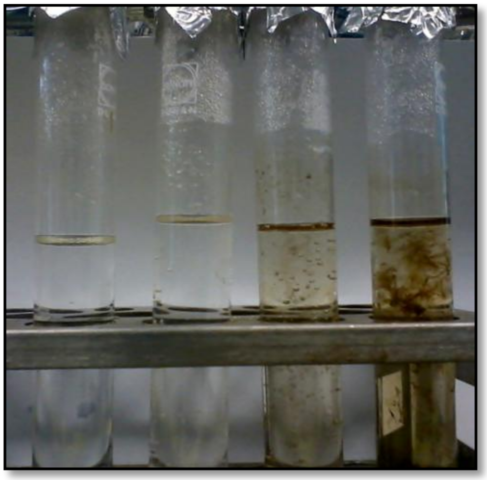


Figure 21: Mixture of Pennywort extract after 24 hours at 95˚C

**From left to right: 100 ppm, 1000 ppm, 10000 ppm, 50000 ppm

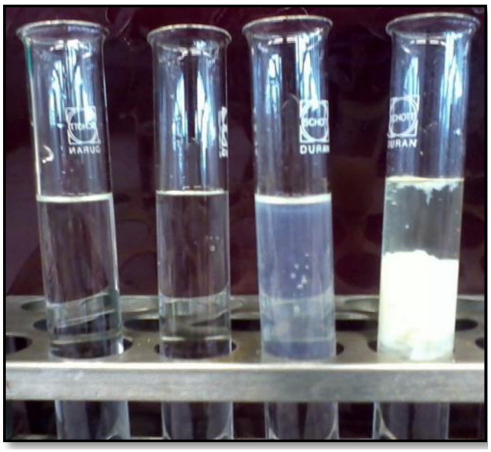


Figure 22: Mixture of PASP at ambient temperature

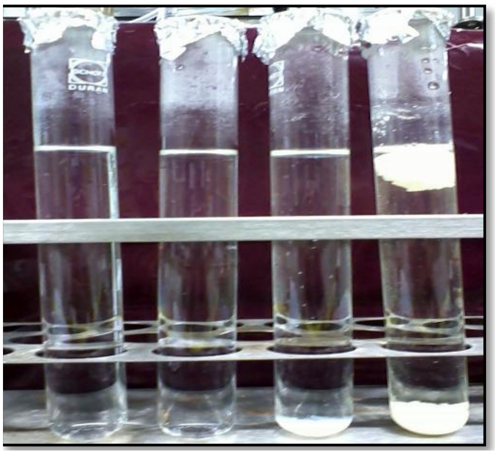


Figure 23: Mixture of PASP after 24 hours at 95˚C

**From left to right: 100, 1000, 10000, 50000 ppm

4.1.2 Discussions

In reality, brine chemistry can adversely impact scale inhibitors in some ways. Salinity that possessed in brine may shield the anionic charges on the polymer functional groups in scale inhibitors. Consequently, it leads to osmotic compression of the polymer and expelling the components of the solution. Plus, the functional groups in polymeric scale inhibitors have a strong binding potential with divalent cations (positive ions with charge of two) such as calcium. Therefore, with this strong ability, calcium can form and precipitate from the brine. This situation may happen at calcium concentrations as low as 250 ppm, which is below the average calcium content in produced water (Holt, Sanders, Rodrigues, & Vanderhoof, 2009). Due to that reason, there goes the purpose of this test which aims to examine the compatibility of possible inhibitors at different concentrations with synthetic waters. With this test, identification of which additives are worth and qualified to be further studied in future can be done. So, based on those statements reported by Holt et al. (2009) previously, it is assumed that all mixtures are compatible with formulated formation water at lower concentrations while incompatibility is displayed at higher concentrations of additives where precipitation or deposit is presumed to form.

Meanwhile, on the application perspective of scale inhibitors in the industry, incompatibility between scale inhibitors and formation water under field temperature potentially caused formation damage which will further affecting the production of the reservoir. Hence, compatibility with formation water should be the one of the main concerns in deciding the best scale inhibitors to be deployed in field application. For an inhibitor to be safely deployed for field applications through any deployment methods (i.e. Squeeze Treatment, Continuous Injection, etc.), it should be compatible with formation water at field condition and at appropriate concentration which is up to ten (10) percent of volume (Chen, Chen, Montgomerie, Hagen, & Ekpeni, 2011). For instance, addition of 5 mL additives into 25 mL of high calcium content of synthetic formation water is applied in this experiment. Formulated high calcium content of formation water was used to compare the compatibility of candidate scale inhibitors with formation water as average reservoir temperature of 95˚C. The results are summarized in **Table 7**.

Table 7 shows the compatibility of all additives (Barley extract, Pennywort Extract, and PASP) in different concentrations with high calcium content of synthetic formation water at both ambient and field temperature, 95˚C. From the figure, it is shown that mixtures are compatible for all additives, at lower concentrations of 100 ppm and 1000 ppm. Visibly clear solutions were observed at both ambient and after been aged for 24 hours at applied field temperature. At initial condition, haziness solutions were observed in mixtures of Barley and Pennywort extracts at higher concentrations (10000 ppm and 50000 ppm). However, the haziness in both concentrations of Barley extract solutions disappeared after 24 hours of heating to 95˚C and clear solution was achieved. On the other hand, mixtures of Pennywort extract at higher concentrations displayed incompatibility as deposit was observed at 95˚C after 24 hours of heating. Besides, 10000 ppm of PASP mixture displayed similar observation with higher concentrations mixtures of Pennywort extract where initially; haziness was observed as well then turned out having deposit after 24 hours of heating. Meanwhile 50000 ppm of PASP mixture exhibit incompatibility with formation water at both ambient condition and at 95˚C after 24 hours. Deposit was observed at both initial mix and after ageing.

Briefly, Barley extract is compatible with formulated formation water at all tested concentrations meanwhile Pennywort extract and PASP are only compatible with the formation water at lower concentrations of 100 ppm and 1000 ppm. Higher concentrations of Pennywort extract and PASP displayed incompatibility with synthetic formulated water.

Throughout this experimentation, there are several possible errors that are believed to slightly affect the results of this test. Considering only calcium content in scaling water formulated can be considered as one of the errors that might affect the whole result of the investigation as it is the main component of this experimentation besides those possible inhibitors. Absence of other ions in the water might give some effects on the result shown by the additives. Besides, methods of preparing aqueous extracts might be one of the errors made as well. Some extraction methods are adapted from other journals which are not specifically designed to extract compositions for scale inhibiting agent. Components extracted may possibly not genuinely function to inhibit formation of scale. In addition, inaccurate measurements either in preparation or mixing stage of the solutions due to equipments' limitations can also be suspected to contribute as error in this investigation which indirectly affecting final result of experiment. Inconsistency in mixing the additives to synthetic water is also believed to be one the errors made. The solutions might not be homogenously mixed and react well throughout the experiment. Thus, pretentious final outcomes of the test should be expected. Besides, machinery error should also be concerned in this experimentation. This is because, constant temperature of 95˚C is difficult to be achieved because the oven is frequently opened by others as they are utilizing the same oven as well at the time of experimentation. It is merely an unpreventable event in conducting laboratory experiments. Consequently, results of the test may perhaps be affected.

Despite of those inaccuracies and elusiveness of results obtained, it can be concluded that hypothesis or assumption made beforehand is tolerably acceptable for Pennywort extract and PASP. However, it slightly deviates for Barley extract since mixtures of this additive are compatible with formulated formation water at all concentrations.

4.2 Calcium Carbonate Threshold Test

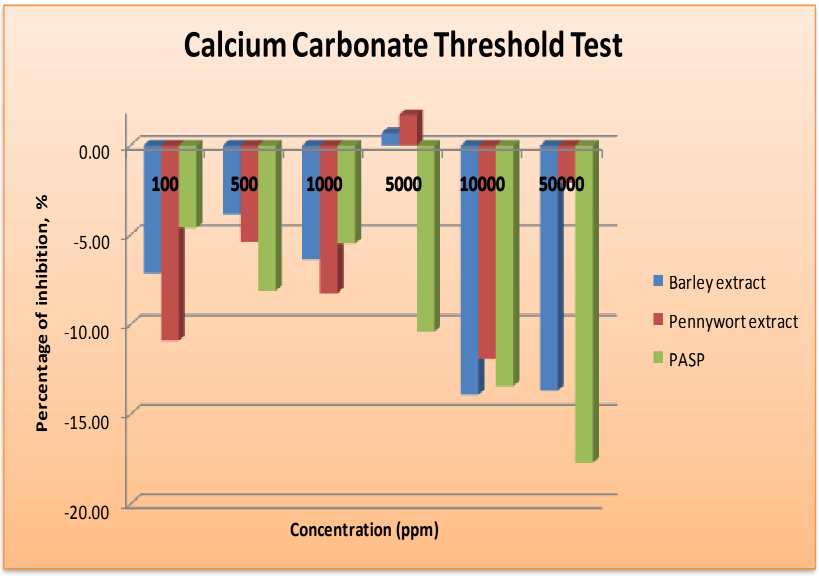
4.2.1 Results

Results obtained at initial stage for this experimentation were contradicted with hypothesis made earlier on. Hypothetically, remaining calcium ions in the solutions should be increasing with addition of additives in the solutions to indicate presence of inhibition effect of that particular additive towards scale nucleation. However, based on **Table 8** and **Figure 24** below, it can be seen that almost all values for percentage of inhibition displayed by all additives are in negative values. Apparently inhibition effect does not exist and cannot be justified with these findings.

Table 8: Inhibition Percentage of Tested Scale Inhibitors

Sample	Concentration (ppm)	Avg. volume of EDTA titrated (ml)	Weight of EDTA titrated (g)	Weight of remaining Ca2+ in solution (g/L)	Percentage of inhibition (%)
No additive	**N/A**	**39.65**	**0.148**	**1.59**	**N/A**
Barley Extract	100	36.85	0.137	1.48	-7.11
	500	38.15	0.142	1.53	-3.84
	1000	37.15	0.138	1.49	-6.36
	5000	39.95	0.149	1.60	0.70
	10000	34.15	0.127	1.37	-13.92
	50000	34.25	0.127	1.37	-13.67
Pennywort Extract	100	35.35	0.132	1.42	-10.90
	500	37.55	0.140	1.50	-5.35
	1000	36.40	0.135	1.46	-8.25
	5000	40.35	0.150	1.62	1.71
	10000	34.95	0.130	1.40	-11.90
	50000	38.85	0.145	1.56	-2.07
PASP	100	37.85	0.141	1.52	-4.59
	500	36.45	0.136	1.46	-8.12
	1000	37.50	0.140	1.50	-5.48
	5000	35.55	0.132	1.42	-10.39
	10000	34.35	0.128	1.38	-13.42
	50000	32.65	0.122	1.31	-17.70

Figure 24: Percentage of Inhibition vs. Concentration (ppm)



Findings are considered irrelevant as most of values acquired are negative values, however, there are still positive inhibition obtained from the experimentation which is for addition of Barley and Pennywort extracts to mixtures at 5000 ppm. With that reason, it is believed that such situations occurred because of several factors which will be investigated through extensive studies. As a result, several faults that lead by some misconceptions are the cause of this irregular outcome and it will be elaborate further soon.

Comprehensive studies and analysis made and it is discovered that theoretically, PASP should act as threshold scale inhibitors in field application. It is able to perform efficiently at concentrations far below the stoichiometric amount of calcium ions in any formation water (Estievenart, Kohler, Ropital, & Fiaud, 2004). Therefore, it is understood that PASP will show its inhibiting effect although at very low concentrations of application. Technically, in the absence of PASP, three forms of calcium carbonate crystals are present, calcite in majority, with also aragonite and vaterite, whereas in their presence, the vaterite crystals predominate. Thus, with less existence of calcite crystals, their growth could be limited indirectly retarding scale formation (Estievenart, Kohler, Ropital, & Fiaud, 2004). It can also be concluded that, amount of calcium carbonate scale formed should be lesser with presence of PASP in escalating concentrations. So, it is can be presumed that other tested additives (Barley and Pennywort) should work similarly as PASP if they possess the inhibiting capability.

For that reason, contradiction in results obtained with hypothesis made earlier is now discovered. Based on reported information stated previously and also evaluation on obtained outcomes, a misconception of knowledge is one of the major factors which lead to experimentation faultiness thus yield to acquisition of abnormal results. Apparently, this experiment had been performed with invalid selection of testing concentrations thus leading to unreliable outcomes gained. The concentrations used are unsuitable as they are considerably high for this test therefore not validating the objective of this test; to identify threshold concentration for additives to display their inhibiting effect. Selected concentrations should presume to be much lower than concentration of calcium ions in synthetic water used. Preferable concentrations for addition of PASP are in the range of 1- 10 ppm depending on solutions to be treated as well. In contrast, suggested concentrations for tested inhibitors such as Barley and Pennywort are relatively higher which should range from 5 to 100 ppm as those additives are merely rudimentary elements compare to developed scale inhibitor, PASP.

Quality of tested mixtures is also assumed to be one of the main interests in ensuring reliability and acceptability of outcomes obtained. This is because, time restriction had caused prolonged execution of the experiment. Sample of mixtures prepared are no longer in their best state to be tested hence affecting final results of experimentation. In fact, anomalous readings obtained for 5000 ppm of Barley and Pennywort extract could be due to this reason as well. These mixtures are titrated immediately after preparation and observed to yield more favorable results; which is positive inhibition. On the other hand, delayed titration made for other prepared mixtures due to time constraint produced contrary outcomes. Thus, it proves that quality of tested mixtures plays an essential role as well to ensure more reliable and relevant results are achieved.

Conclusive method of experimentations must be acquired and verified in order to obtain more accurate and precise results. Unresolved uncertainties regarding experimentation procedures (e.g. duration of mixing, suitable mixing rate, etc.) at planning stage had lead to the occurrence of those errors thus finally it fails the test by some means. These major mistakes such as invalid concentrations chosen, defective tested mixtures, and unresolved uncertainties should not be happening if careful and lucid decision is made at first place. Thus, should be more precautions are taken in order to prevent recurrence of similar circumstances.

Due to irrelevant outcomes found earlier, experimentation was repeated once more with much lower range of additives' concentrations which are 10 ppm, 30 ppm, and 50 ppm. All other factors such as rotation speed, testing temperature, and titration method are maintained as before. Results of the test are as shown below:

Initially, amount of calcium ions in mixture of both cation and anion waters are given by;

Cation water contains 3500 ppm of Ca^{2+} *= 3.5 g/L of* Ca^{2+}

Next, volume of 0.01M EDTA solution titrated into mixtures of additives and synthetic waters is tabulated:

Table 9: Mixtures with No additive

Additive	Concentration (ppm)	Initial Reading of burette (mL)	Final Reading of burette (mL)	Avg. volume of EDTA titrated (mL)
No additive	N/A	0	39.7	39.65
		0	39.6	

Table 10: Mixtures with Barley extract

Additive	Concentration (ppm)	Initial Reading of burette (mL)	Final Reading of burette (mL)	Avg. volume of EDTA titrated (mL)
Barley	10	0	40.4	40.45
		0	40.5	
	30	0	41.5	41.50
		0	41.5	
	50	0	41.6	41.65
		0	41.7	

Table 11: Mixtures with Pennywort extract

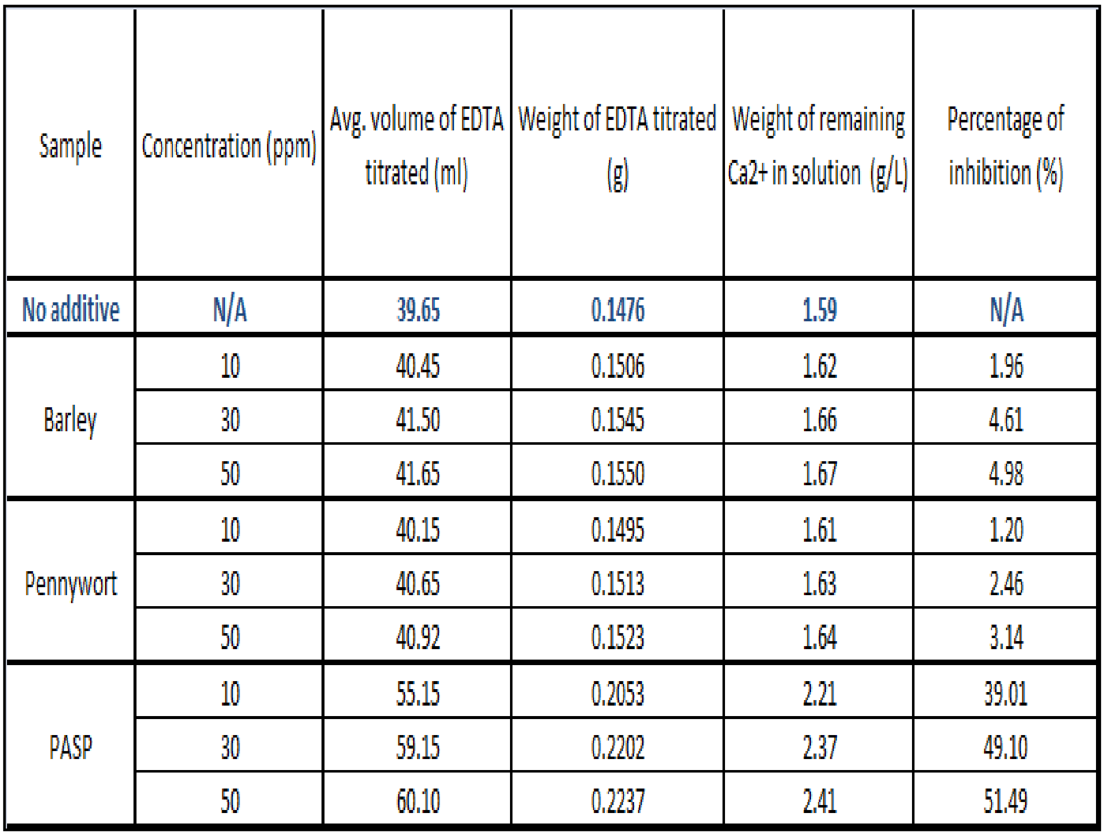
Additive	Concentration (ppm)	Initial Reading of burette (mL)	Final Reading of burette (mL)	Avg. volume of EDTA titrated (mL)
Pennywort Extract	10	0	40.1	40.15
		0	40.2	
	30	0	40.6	40.65
		0	40.7	
	50	0	40.9	40.92
		0	40.9	

Table 12: Mixtures with Polyaspartate (PASP)

Additive	Concentration (ppm)	Initial Reading of burette (mL)	Final Reading of burette (mL)	Avg. volume of EDTA titrated (mL)
PASP	10	0	55.1	55.15
		0	55.2	
	30	0	59.1	59.15
		0	59.2	
	50	0	60.1	60.10
		0	60.1	

4.2.2 Results Analysis

Table 13: Inhibition Percentage of Tested Scale Inhibitors



Sample	Concentration (ppm)	Avg. volume of EDTA titrated (ml)	Weight of EDTA titrated (g)	Weight of remaining Ca2+ in solution (g/L)	Percentage of inhibition (%)
No additive	N/A	39.65	0.1476	1.59	N/A
Barley	10	40.45	0.1506	1.62	1.96
	30	41.50	0.1545	1.66	4.61
	50	41.65	0.1550	1.67	4.98
Pennywort	10	40.15	0.1495	1.61	1.20
	30	40.65	0.1513	1.63	2.46
	50	40.92	0.1523	1.64	3.14
PASP	10	55.15	0.2053	2.21	39.01
	30	59.15	0.2202	2.37	49.10
	50	60.10	0.2237	2.41	51.49

For instance, Percentage of Inhibition, % of 10 ppm Barley Extract towards formation of calcium carbonate, $CaCO_3$ scale is calculated as shown:

From average volume of 0.01 M EDTA solution titrated which is 40.45 mL, weight of EDTA component in that particular volume is obtained;

Molecular weight of EDTA dry-salt = 372.24 g/mol

Molecular weight of Ca^{2+} *= 40.078 g/mol*

*Therefore, 0.01 M of EDTA solution * 372.24 = 3.7224 g/L*

Subsequently, in 40.45 mL of 0.01 M EDTA solution

$$\frac{40.45}{1000} \times 3.7224\ g = \mathbf{0.1506\ \boldsymbol{grams\ of\ EDTA}}$$

Since 1 mole of EDTA is equivalent with 1 mole of Ca^{2+}, thus

372.24 grams of EDTA = 40.078 grams of Ca^{2+} ions

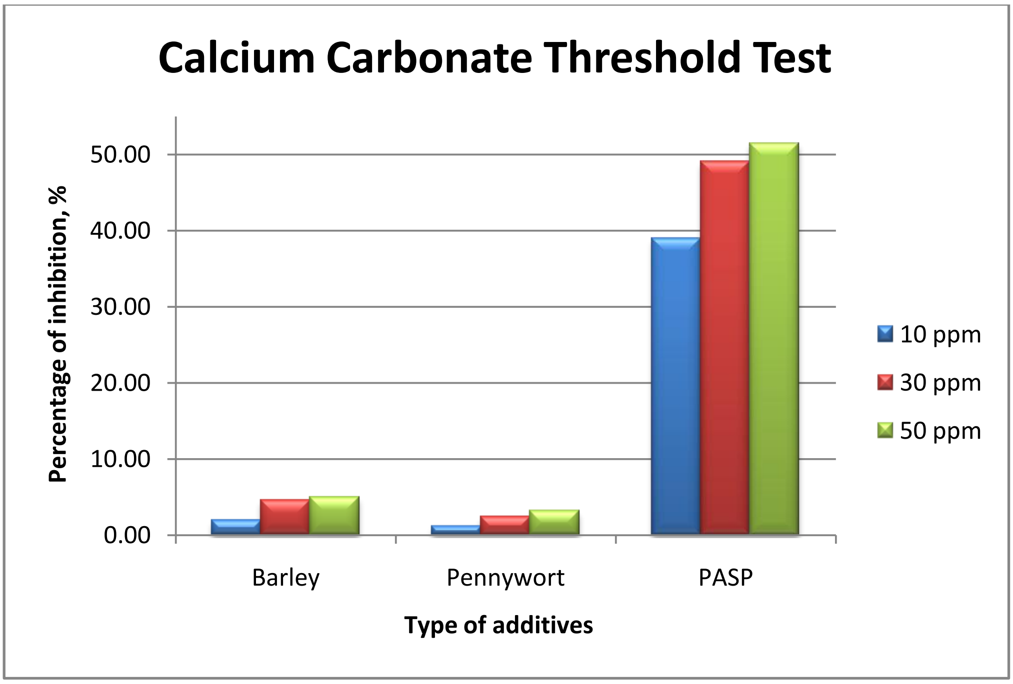
*as **0.1506 grams of EDTA titrated, hence, there are 0.0162 grams of Ca^{2+} ions in 10 mL of sample solution.***

Given that calcium content in sample solution with no additive is as much as 0.0159 grams, thus, it means that percentage of difference of calcium content in two comparative sample solutions will determine the percentage of inhibition of the additive towards $CaCO_3$ formation in the solution

$$\frac{0.0162 - 0.0159}{0.0159} \times 100\% = \ 1.96\ \%\ \boldsymbol{of\ inhibition}$$

As a result, percentages of inhibition for Barley, Pennywort extract and PASP versus concentrations (ppm) are illustrated as below:

Figure 25: Percentage of Inhibition for Barley, Pennywort and PASP



4.2.3 Discussions

Evaluation on the capabilities and performances of tested additives under formulated synthetic water conditions to inhibit calcium carbonate, $CaCO_3$ scale precipitation is the main objective of this test which declared previously. Their potentials can be determined by validating the hypothesis which made earlier. Hypothetically, the higher the concentration of additives added, the greater the amount of remaining calcium ions left in the mixtures which indicate presence of inhibition effect of that particular additive towards scale nucleation. Identification of threshold concentrations for both Barley and Pennywort is the subsequent measure to verify their capabilities in inhibiting scale nucleation.

Figure 25 above shows the percentage of inhibition for Barley, Pennywort and PASP comparatively. In general, addition of all additives in scaling waters can inhibit the growth of $CaCO_3$ formation. Inhibition efficiencies of all additives are increased as the concentrations of additives are increased. This means higher concentrations yielded more remaining calcium ions in mixtures during laboratory test. However, the inhibitor cannot stop the scale formation of $CaCO_3$ totally over the concentration range studied. Hence, it is believed that Barley and Pennywort extracts are promising scale inhibitors studied. This shows that hypothesis made earlier is acceptably valid as both Barley and Pennywort have the potential to inhibit the growth of scale crystals in scaling water formulated. Due to unavailability of specific information regarding mechanism of inhibition by both tested additives as they are newly investigated as potential scale inhibitors, these findings should be further investigated in order to distinguish the exact inhibition mechanisms deployed by both potential inhibitors in retarding scale formation. Besides, precise and accurate functional groups which actually react in inhibiting nucleation of scale also need to be identified. By that identification, enhancement of active inhibition component can be studied further and conducted later in future thus improves their capability to mitigate growth of calcium carbonate scale.

As both Barley and Pennywort have the ability to inhibit scale nucleation, thus determining their threshold concentrations is the following measure of this test. Threshold concentration is a minimum concentration level where the additives start to inhibit scale nucleation. Since both additives display increasing inhibition efficiencies in **Figure 25**, thus it can be concluded that threshold concentrations for both might located approximately below 10 ppm concentration of additives. Should be at threshold concentration of additives, their inhibition efficiencies are approximately less than 1% which is a very small value to indicate the initiation of scale nucleation inhibition by active components in additives. Further investigation on inhibition of lower concentrations (i.e. below 10 ppm) additives are not performed in this test due to equipment limitation experienced. It is almost impossible to weigh the sample powder to a measurement of less than 0.001 g prior to preparation of lower than 10 ppm concentration due to the condition of the powder itself which is a very light material. Besides, inaccuracy of measurement should be taken into account if lower concentrations are tested in this experiment. Thus, arduous measurement to prepare very low concentrations of samples in the laboratory leads to the inability to define the exact value of threshold concentrations for both additives. Hence, by concluding threshold concentrations for both Barley and Pennywort to initiate the inhibition of scale crystals growth are below 10 ppm is considerably acceptable for this experimentation.

From **Figure 25** as well, it can be seen that Barley shows better inhibition effect compare to that of Pennywort at all concentrations tested although the percentages are very low. This situation happened might possibly due to simple components compositions contained in tested additives thus leads to insufficient interactions being formed to inhibit more of scale crystals' growth. Preferably molecules with large numbers of inhibiting components will help better in inhibition of scale crystals growth. Due to this, both Barley and Pennywort might need additional chemical process in order to enhance its composition to function as improved scale inhibitors which similarly done to CMI as declared previously. Improved components might influence their inhibiting potential to be higher than as obtained in recent studies.

On the other hand, PASP displayed very high inhibition efficiency compare to both Barley and Pennywort because it is a commercialized scale inhibitor which present in the industry. Its efficiency should be undeniably far better than other additives tested. At similar concentrations, PASP supposedly shows higher efficiency which ranges from 70 to 80 percent based on other studies. Due to limited equipments to prepare very low concentrations of PASP, errors might occur indirectly influenced the final result of PASP inhibition. Nonetheless, outcomes for

PASP obtained in this experiment are still considered valid as it still shows high effectiveness.

In every experiment done, errors and inaccuracies are inevitable. Several errors that might possibly occur during this experimentation are as explained. Inaccuracy of measurements is the most predicted human error to be experienced in this test as lots of measuring involved such in titration and weighing powder samples. These inaccuracies are alleged to contribute to any imprecise results obtained. Besides, machinery errors due to limitation of equipments such as inconsistency of testing temperature might also contributing to inaccuracy, and elusiveness of outcomes.

As a conclusion, Barley and Pennywort possess the inhibiting potential to mitigate growth of scale nucleation as they generate more calcium ions in the mixture with increasing concentrations of the extracts, which also means that less calcium carbonate scale formed. Besides, threshold concentrations of both additives also can be generalized as below 10 ppm as at higher concentrations, inhibition efficiencies of both potential inhibitors are gradually increasing. Advance and comprehensive studies on active components of additives identification and distinguishing mechanisms of inhibition for both Barley and Pennywort are crucial in order to develop and improve their capabilities as promising scale inhibitors. In addition, comprehensive studies should be done prior to experimentation execution in order to evade mistakes and irrelevant results obtained at the end of testing.

4.3 Optical Microscopic Examination

4.3.1 Results

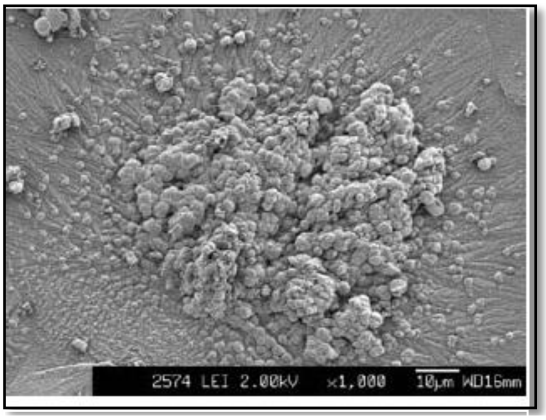


Figure 26: Morphology of $CaCO_3$ precipitation in the absence of additive

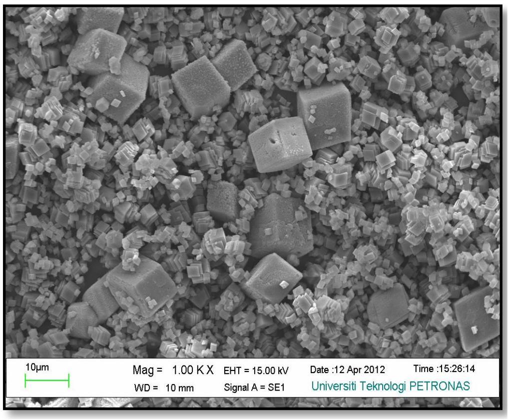


Figure 27: In presence of Barley 10 ppm

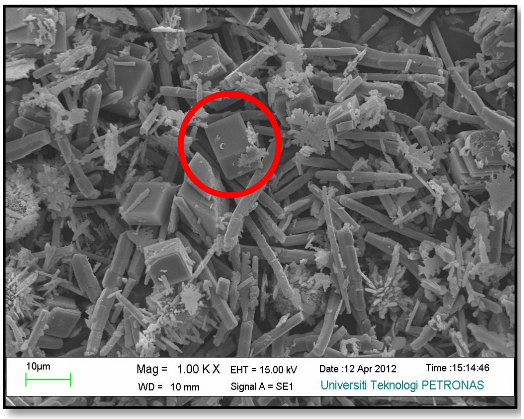


Figure 28: In presence of Barley 30 ppm

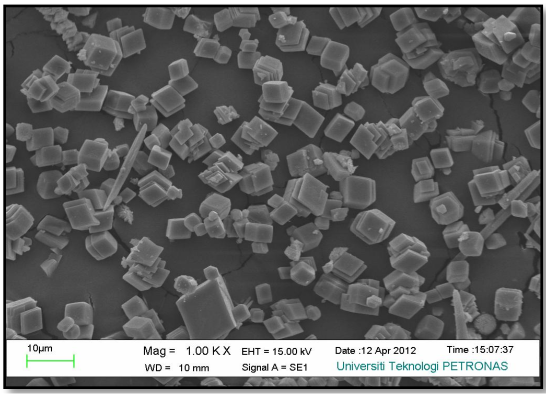


Figure 29: In presence of Barley 50 ppm

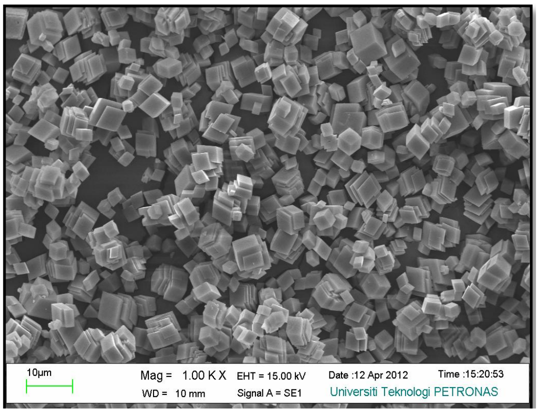


Figure 30: In presence of Pennywort 10 ppm

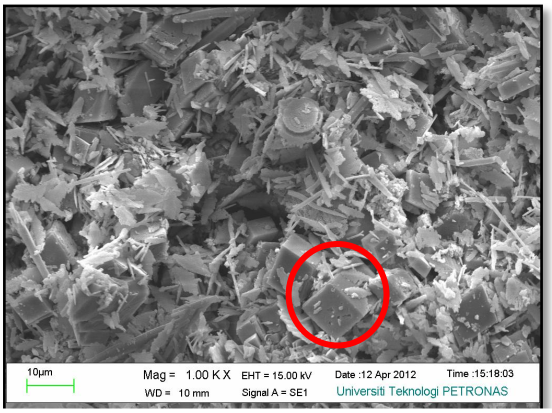


Figure 31: In presence of Pennywort 30 ppm

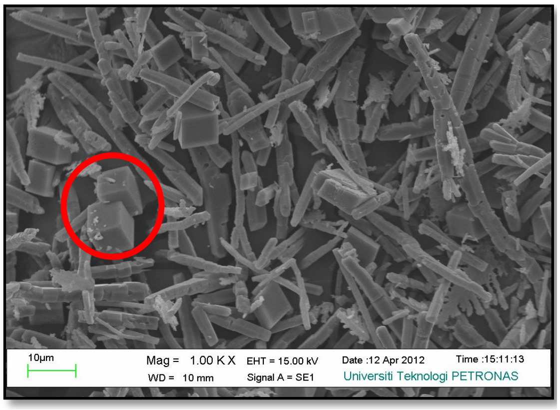


Figure 32: In presence of Pennywort 50 ppm

4.3.2 Discussions

According to Suharso (2009), lattice distortion occurs with presence of inhibitor, thus the crystal structure and morphology are then changed significantly. These changes happen because during $CaCO_3$ crystal growth, the inhibitor molecules may adsorb onto the active growth sites of the crystal surface and inhibit the regular outgrowth of $CaCO_3$ crystals. The inhibitor may also act as a heterogeneous nucleator which acts to control and stabilize the precipitating polymorph. Concurrently, from **Figure 26** comparatively to **Figure 27-32**, it is clear that the extracts of Barley and Pennywort are able to adsorb on the surface of $CaCO_3$ crystals thus changed the morphology of crystals formed. Since the exact mechanism of inhibition for Barley and Pennywort extracts are yet to be studied, it is assumed that their inhibition mechanisms might be similar to the mechanism applied by Polyaspartate which studied by C. Estievenart et al. (2004). However, in this experimentation, the impact of inhibitors' concentrations is insufficient to significantly change the size of $CaCO_3$ crystals hence from figures shown, size of crystals obtained are almost the same comparatively. Meanwhile, effect of PASP addition on morphology of crystals formed cannot be studied for this experiment because the crystals are excessively small and hard to be collected. Presence of impurities in the crystals samples which agitate the results of experiment in some way should be avoided in future studies. In order to further study on the impact of concentrations of additives towards size of morphology formed, advance experimental method can be conducted such as using particle size analyzer.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Barley and Pennywort are selected as candidates of “green” inhibitors at early stage of project among other studied resources. They are examined in order to identify their inhibition capability and potential towards formation of calcium carbonate scale through some tests which namely Compatibility Test, Calcium Carbonate Threshold Test and Optical Microscopic Examination accordingly. Their performances are evaluated comparatively to existing “green” scale inhibitor which is Polyaspartate (PASP). Through Compatibility Test performed it is found that Barley shows more convincing results than that of Pennywort where it displays compatibility with tested scaling water at all testing concentrations, 100 ppm, 1000 ppm, 10000 ppm and 50000 ppm. Pennywort only compatible with tested water at lower concentrations of 100 ppm and 1000 ppm. Furthermore, Barley keep on giving optimistic outcomes as it exhibit better inhibiting potential compare to Pennywort at increasing concentrations of additives. Average percentage of inhibition of Barley is approximately 3.85% meanwhile 2.27% for Pennywort. Their capabilities and potential in inhibiting formation of $CaCO_3$ scale formation are then proved by the results obtained through Optical Microscopic Examination using Scanning Electron Microscope (SEM). From the assessment, it is verified that addition of additives in scaling water will affect the morphology of $CaCO_3$ precipitation formed. However, the impact of additives concentrations is still insignificant as size of particles is not further evaluated in this test.

In conclusion, the results show that both Barley and Pennywort extracts have the potential to be further studied as an alternative for calcium carbonate scale inhibitor.

1. Barley and Pennywort extracts all showed potentials to be effective calcium carbonate scale inhibitor through the laboratory tests.

2. Based on the overall results, Barley is the most effective calcium carbonate scale inhibitor compare to another resource studied.

3. Advance researches and extensive studies on Barley and Pennywort 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 Barley and Pennywort extracts both 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.

Recommendations to further study their potentials as calcium carbonate scale inhibitor are as below:

1. Perform studies and researches on the active inhibiting components in Barley and Pennywort in order to acknowledge and enhanced their potential as alternative “green” scale inhibitors and suggest suitable enhancement method for those components.

2. Find the exact threshold concentration for Barley and Pennywort extracts to inhibit scale nucleation which aids to identify Minimum Inhibitor Concentration (MIC) of both extracts in Dynamic Tube Blocking Test

3. Study the impact of concentrations towards size of precipitating particles formed by using size particles analyzer in order to understand more the mechanisms of inhibition applied by Barley and Pennywort.

4. Compare the alternative calcium carbonate scale inhibitors performance with other conventional calcium carbonate scale inhibitors (i.e. Polyphosphates, etc.) as a bench mark of performance to produce competitive “green” scale inhibitor in future.

REFERENCES

1. A.M Abdel-Gaber et al. (2011). A natural extract as Scale and Corrosion Inhibitor for Steel Surface in Brine Solution. *Desalination* , 1-2.
2. Amjad, Z. (1996). Scale Inhibition in Desalination Applications: An overview. *Corrosion96 - The Nace International Annual Conference and Exposition* (p. 4). NACE Inthernational.
3. B. Bazin, N. K. (2004). A New Class of Green Mineral Scale Inhibitors for Squeeze Treatments. *Society of Petroleum Engineering* (pp. 1-12). United States of America: SPE.
4. B. Bazin, N. K. (2002). An Integrated Approach for the Design of Squeeze of Mineral Scale Inhibitors. *SPE* , 1-6.
5. *Barley: In Depth Nutrient Analysis*. (n.d.). Retrieved December 15, 2012, from The World's Healthiest Foods: http://www.whfoods.com/genpage.php?tname=nutrientprofile&dbid=91
6. C. Estievenart, N. K. (2004). Mechanisms of Scale and Corrosion Inhibition by Polyaspartates. *Corrosion 2004* (pp. 1-21). Texas: NACE International.
7. Chen, T., Chen, P., Montgomerie, H., Hagen, T., & Ekpeni, H. (2011). Development of Environmentally Friendly Calcium Carbonate Scale Inhibitor for HTHP Squeeze Application in the Oil and Gas Field Water Treatment. *NACE International Corrosion 2011 Conference & Expo* , 1-10.
8. David Hasson, et al. (2011). State of the Art of Friendly "Green" Scale Control Inhibitors: A Review Article. *I&EC Research* , 7601-7067.
9. David Wilson, K. H. (2010). Development of A 'Green' Hydrothermally Stable Scale Inhibitor For Topside and Squeeze Treatment. *NACE International Corrosion 2010 Conference & Expo* (pp. 1-13). Texas: NACE International.
10. Dorine L. Verraest, J. A. (1996). Carboxymethyl Inulin: A New Inhibitor for Calcium Carbonate Precipitation. *JAOCS* , 55-62.
11. Duangkamol Taemchuay, T. R. (2008). A Study on Antibacterial Activity Of Crude Extracts Of Asiatic Pennywort And Water Pennywort Against Staphylococcus Aureus. *KMITL Sci. J.* , 2.
12. Erling Notto Halvorsen, A. M. (2009, April 20-22). New Method for Scale Inibitor Testing. *SPE International Symposium and Oilfield Chemistry* . The Woodlands, Texas, United States: SPE.

13. Estievenart, C., Kohler, N., Ropital, F., & Fiaud, C. (2004). Mechanisms of Scale and Corrosion Inhibition by Polyaspartates. *Corrosion 2004* (pp. 1-21). Texas: NACE International.

14. FarmAfripedia. (n.d.). *Root/Tuber Crops with High Starch or Inulin Content.* Retrieved December 13, 2011, from FarmAfripedia.

15. Foundation, T. G. (2001-2011). *Barley*. Retrieved December 15, 2012, from The World's Healthiest Foods: http://www.whfoods.com/genpage.php?tname=foodspice&dbid=127

16. Hasson, D., & Semiat, R. (2005). *Scale Control in Saline and Wastewater Desalination.* Haifa: Israel Institute of Technology.

17. Holt, S., Sanders, J., Rodrigues, K., & Vanderhoof, M. (2009). Biodegradable Alternatives for Scale Control in Oilfield Applications. *SPE International* , 1-10.

18. HubPages. (2011). *Pennywort Health Benefits*. Retrieved December 21, 2012, from HubPages: http://rls8994.hubpages.com/hub/Pennywort-Tea-And-Its-Many-Benefits

19. Jeffery, G., J.Bassett, J.Mendham, & Denney, R. (1989). Complexation Titration - Metal Ions Indicator. In G. Jeffery, J.Bassett, J.Mendham, & R. Denney, *Vogel's Textbook of Quantitative Chemical Analysis Fifth Edition* (p. 317). New York: LONGMAN Scientific & Technical.

20. Kelland, M. A. (2009). Scale Control. In M. A. Kelland, *Production Chemicals for the Oil and Gas Industry* (pp. 53-87). Norway: Taylor and Francis Group, LLC.

21. Kinard, W. F. (2010). *Determination of Calcium Oxide by Titration with a Chelating Ligand, Ethylenediamminetetraacetic Acid (EDTA)*. Retrieved 2 10, 2012, from Chemistry 221 Laboratory Quantitative Analysis: http://kinardf.people.cofc.edu/221LabCHEM/CHEM221L%20Calcium%20Determination%20by%20EDTA%20Titration.htm

22. Luciaan Boels, et al. (2011). Carboxymetyl Inulin Biopolymers: A Green Alternative for Phosphonate Calcium Carbonate Growth Inhibitors. *Crystal Growth & Design* , 4155-4165.

23. M.B. Tomson, S. G. (2002). Mechanisms of Mineral Scale Inhibition. *SPE Oilfield Scale Symposium* (pp. 1-12). United Kingdom: Society of Petroleum Engineering.

24. Mazen A. Ateyyat, M. A.-M.-R. (2009). Aqueous extracts of some medicinal plants are as toxic as Imidacloprid to the sweet potato whitefly, Bemisia tabaci. *Journal of Insect Science:* , 2.

25. N. Kohler, B. B. (2004). Green Inhibitors For Squeeze Treatments: A Promising Alternative. *CORROSION 2004* , 1-19.

26. Outreach. (2010). *Determination of Total Calcium and Magnesium Ion Concentration*. Retrieved 2 17, 2012, from Science Outreach University of Canterbury: http://www.outreach.canterbury.ac.nz/chemistry/documents/magnesium_calcium.pdf

27. Quaraishi, M. A. (2004). Naturally Occurring Products As Corrosion Inhibitors. *Corrosion 2004* (pp. 1-12). Texas: NACE International.

28. S. Baraka-Lokmane, K. S. (2008). Application of Environmentally Friendly Scale Inhibitors in Carbonate Coreflooding Experiments. *INternational Symposium of the Society of Core Analysts* (pp. 1-12). Abu Dhabi: scaweb.org.

29. Sati Al-dalain, M. S.-k. (2008). Inhibitory Effect of Aqueous Extracts of Barley and Fenugreek on Ulcer Induction in Rats. *World Applied Sciences Journal* , 332.

30. Tao Chen, P. C. (2011). Development of Environmentally Friendly Calcium Carbonate Scale Inhibitor for HTHP Squeeze Application in the Oil and Gas Field Water Treatment. *NACE International Corrosion 2011 Conference & Expo* , 1-10.

31. W.Hater. (2002). *Environmental Compatible Scale Inhibitor For The Mining Industry.* Retrieved December 13, 2012, from Henkel Surface Technologies: www.henkel-water.com

32. Yuan, M. (2010). Latest Developments in Oilfield Scale Control. In Z. Amjad, *The Science and Technology of Industrial Water Treatment* (pp. 143-144). Intl Water Assn.

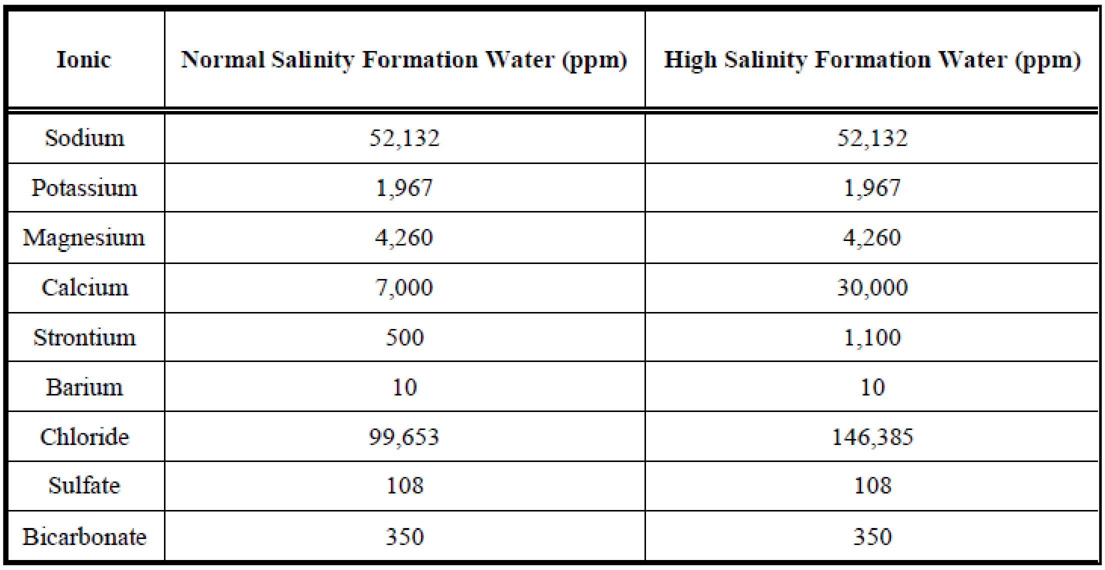
APPENDICES

Appendix I

Table A1: *Summary on aqueous extracts preparation*

Experiment	Concentration (ppm)	Volume of distilled water (mL)	Weight of Barley / Pennywort powder (g)
Compatibility Test	100	100	0.01
	1000	100	0.1
	10000	100	1
	50000	100	5
$CaCO_3$ Threshold Test	10	100	0.001
	30	100	0.003
	50	100	0.005

Table A2: *Composition of Formation Water*



Ionic	Normal Salinity Formation Water (ppm)	High Salinity Formation Water (ppm)
Sodium	52,132	52,132
Potassium	1,967	1,967
Magnesium	4,260	4,260
Calcium	7,000	30,000
Strontium	500	1,100
Barium	10	10
Chloride	99,653	146,385
Sulfate	108	108
Bicarbonate	350	350

Appendix II

Molecular weight of Calcium Chloride dihydrate, $CaCl_2.2H_2O = 147.02$ *g/mol*

Molecular weight of calcium ion, $Ca^{2+} = 40.078$ *g/mol*

Therefore, concentration of Ca^{2+} *in* $CaCl_2.2H_2O$ *is given by;*

$$\frac{40.078\ g/mol}{147.02 g/mol} \times 100\% = 27.26\%$$

Hence, concentration of $CaCl_2.2H_2O$ *that needed to give 30, 000 ppm of* Ca^{2+} *is*

30, 000 ppm = 30, 000 mg/L = 30 g/L

$$\frac{100\%}{27.26\%} \times \frac{30g}{L} = \mathbf{110.05} \boldsymbol{g/L}$$

which means 110.05 grams of $CaCl_2.2H_2O$ *is required to be added to 1 L of distilled water to facilitate the preparation of synthetic formation water with 30, 000 ppm of calcium ions.*