

**PHYSICAL PROPERTIES,
CHARACTERIZATIONS & SOLUBILITY STUDY
BETWEEN CALCIUM SULPHATE AND
GLUTAMIC ACID, N, N-DIACETIC ACID,
TETRASODIUM SALT**

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NUR FAIZAH BINTI YOUSOF

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

JANUARY 2015

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Dedication

To my parents for their love and encouragement.

ACKNOWLEDGEMENT

I am grateful and would like to express a sincere gratitude to my supervisor Dr. Syamsul Bahari Bin Abdullah for his germinal ideas, invaluable guidance, continuous encouragement and constant support in making this research possible. He had impressed me with her outstanding professional conduct, his strong conviction for science, and his belief that a degree program is only a start of a life-long learning experience. I am truly grateful for his progressive vision about my training in science, his tolerance of my naïve mistakes, and his commitment to my future career. I also sincerely thanks for the time spent proofreading and correcting my many mistakes.

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ABSTRACT

Sulphate scale is formed due to water injection of seawater to the reservoirs and causes corrosion, equipment damage, formation damage, and flow restriction. Among various types of scale, calcium sulphate is often the predominant scale produced. Thus, Glutamic acid, N, N-diacetic acid, tetrasodium salt (GLDA) is used to study the solubility of calcium sulphate (CaSO_4) in the solvent. Based on the conducted experiments, the solubility of CaSO_4 in GLDA is with a mass ratio of 87:1 and a detail study are carried out to study the physical properties, characterisations, and the interaction mechanism of the solvent. GLDA is an acidic solvent with a pH of 4.11, viscosity of 11.56 mPa.s and is heavier than water as its density is 1.271 g/cm^3 . Besides, based on the result obtained through ICPMS, GLDA contains a high amount of sodium and potassium with 37498 ppm and 12.26 ppm respectively. In CHNS test, the highest amount of atoms is carbon atom with 17.69 w% followed by hydrogen atom with 6.52 w%. Based on the FTIR and NMR spectrum, it showed that the physical interaction hydrogen bonding occurred between GLDA and CaSO_4 . Therefore, Glutamic acid, N, N-diacetic acid, tetrasodium salt is a suitable solvent to investigate the solubility of calcium sulphate.

ABSTRAK

Pembentukan terapan sulfat adalah disebabkan oleh air laut yang akan mengakibatkan berlakunya hakisan, kerosakan peralatan, kerosakan formasi, dan sekatan aliran. Di antara pelbagai jenis terapan, kalsium sulfat adalah jenis terapan sulfat yang paling banyak dihasilkan. Oleh itu, asid glutamik, N, asid N-diacetic, garam tetrasodium (GLDA) digunakan untuk mengkaji kelarutan kalsium sulfat (CaSO_4) dalam pelarut. Berdasarkan ujikaji, keterlarutan CaSO_4 dalam GLDA adalah dengan nisbah jisim 87: 1 dan kajian terperinci dijalankan untuk mengkaji sifat-sifat fizikal, perwatakan, dan mekanisme interaksi pelarut. GLDA adalah pelarut yang berasid dengan pH 4.11, kelikatan 11.56 mPa.s dan ianya lebih berat daripada air kerana ketumpatannya adalah $1,2710 \text{ g / cm}^3$. Selain itu, berdasarkan keputusan yang diperolehi melalui ICPMS, GLDA mengandungi jumlah natrium dan kalium yang tinggi iaitu natrium sebanyak 37 498 ppm dan kalium sebanyak 12.26 ppm. Dalam ujian CHNS pula, jumlah atom yang paling tinggi ialah karbon dengan 17.69 w% diikuti oleh hidrogen atom sebanyak 6.52 w%. Selain itu, berdasarkan spektrum FTIR dan NMR pula, interaksi fizikal ikatan hidrogen berlaku antara GLDA dan CaSO_4 . Oleh itu, asid glutamik, N, asid N-diacetic, garam tetrasodium adalah pelarut yang sesuai untuk dianalisa kebolehlarutan kalsium sulfat.

TABLE OF CONTENTS

SUPERVISOR'S DECLARATION	IV
STUDENT'S DECLARATION	V
<i>Dedication</i>	VI
ACKNOWLEDGEMENT	VII
ABSTRACT.....	VIII
ABSTRAK.....	IX
TABLE OF CONTENTS.....	X
LIST OF FIGURES	XII
LIST OF TABLES	XIII
LIST OF ABBREVIATIONS.....	XIII
LIST OF ABBREVIATIONS.....	XV
1 INTRODUCTION	1
1.1 Motivation and statement of problem	1
1.2 Objectives.....	2
1.3 Scope of this research.....	2
1. Organisation of this thesis	3
2 LITERATURE REVIEW	3
2.1 Overview	5
2.2 Introduction	5
2.2.1 Water Injection.....	5
2.2.2 Scale	7
2.2.3 Scale Forming Mechanism.....	9
2.2.4 Factors affecting the formation of scale.....	10
2.2.5 Scale control techniques.....	12
2.2.6 Chelating agent.....	14
2.3 Previous work on GLDA.....	16
2.4 Summary	17
3 MATERIALS AND METHODS.....	18
3.1 Overview	18
3.2 Chemicals	18
3.2.1 Calcium sulphate (CaSO ₄)	18
3.2.2 Glutamic acid, N, N-Diacetic acid, Tetrasodium salt (GLDA).....	18
3.3 Method	19
3.3.1 Solubility of calcium sulphate in GLDA	19
3.3.2 Gravimetric method.....	20
3.3.3 Test for physical properties	21
3.3.4 Characterization of the solution	24
3.3.5 Solubility verification test	27
3.4 Precautions	27
3.5 Summary	28
4 RESULTS AND DISCUSSIONS.....	29
4.1 Overview	29
4.2 Physical properties	29
4.2.1 Verification of solvent.....	31
4.3 Characterizations.....	31
4.3.1 CHNS analysis	31

4.3.2	Inductively Coupled Plasma Mass Spectrometer (ICPMS)	32
4.4	Interaction Mechanism through Fourier Transform Infrared Spectroscopy	33
4.5	Interaction Mechanism through Nuclear Magnetic Resonance (NMR).....	34
4.6	Solubility Study.....	35
4.6.1	Completely dissolved	36
4.6.2	Partially dissolved	37
4.7	Summary	38
5	CONCLUSION.....	39
5.1	Conclusion.....	39
5.2	Recommendations	40
	REFERENCES	41

LIST OF FIGURES

Figure 2.1: Picture of sulphate scales formed in a pipeline	7
Figure 2.2: Schematic illustration of scale formation schemes (Antony <i>et al.</i> 2011).....	9
Figure 2.3: Effect of temperature on the scale formation (Hoang <i>et al.</i> 2007).....	10
Figure 2.4: Permeability ratio (k/k _o) against the number of pore volume injected for different flow rate (Tahmasebi et al, 2010).	11
Figure 2.6: GLDA and green character (AkzoNobel, 2011)	15
Figure 3.1: Chemical structure of GLDA.	19
Figure 3.2: Method for the solubility of calcium sulphate.....	19
Figure 3.3: Procedure for gravimetric method.....	20
Figure 3.4: Metler Toledo FiveEasy pH meter.	21
Figure 3.5: Brookfield viscometer	22
Figure 3.6: Micromeritics AccuPys II 1340 Gas Pycnometer	22
Figure 3.7: Karl Fischer Titrator.	23
Figure 3.8: CHNS Analyser.....	24
Figure 3.9: ICP-MS.....	25
Figure 3.10: FTIR.	26
Figure 3.11: Nuclear Magnetic Resonance	26
Figure 3.12: KUBOTA Centrifuge.	27
Figure 4.1: FTIR test result.....	33
Figure 4.2: NMR test result for the highlighted hydrogen atom.....	34
Figure 4.3: Before mixing.....	35
Figure 4.4: During the stirring of GLDA-CaSO ₄ at 2 nd hours.	36
Figure 4.5: Completely dissolved amount of CaSO ₄ salts in 10mL of GLDA.....	36
Figure 4.6: The maximum amount of CaSO ₄ (0.145g) dissolved in 10mL GLDA.....	37
Figure 4.7: 0.16g of CaSO ₄ salts in 10mL of GLDA	37

LIST OF TABLES

Table 2.1: The major dissolved constituents in seawater	6
Table 2.2: Scale inhibitors used in He <i>et al</i> (2013) study	13
Table 2.3: Inhibition percent of YMR-antiscalants for CaSO ₄ scales in different pipe systems (Yousef <i>et al.</i> 2015).....	14
Table 4.1: Differences of physical properties between pure GLDA and GLDA with optimum amount of CaSO ₄	30
Table 4.2: The composition of C, H, N, and S atoms in GLDA.....	31
Table 4.3: The value of each element in GLDA	32

LIST OF ABBREVIATIONS

$^{\circ}\text{C}$	<i>degree Celsius</i>
%	<i>Percentage</i>
<i>g</i>	<i>Grams</i>
<i>mol</i>	<i>Moles</i>
<i>rpm</i>	<i>Rotation per minutes</i>
<i>mL</i>	<i>milliliter</i>
μL	<i>microliter</i>
cm^{-1}	<i>inverse of centimeter</i>
cm^3	<i>cubic of centimeter</i>
<i>mPa.s</i>	<i>millipascal seconds</i>
<i>w</i>	<i>weight</i>
<i>ppm</i>	<i>part per million</i>
<i>atm</i>	<i>atmosphere</i>

LIST OF ABBREVIATIONS

CaSO ₄	Calcium sulphate
BaSO ₄	Barium sulphate
SrSO ₄	Strontium sulphate
Ca	Computational fluid dynamics
Ba	Capillary suction probe
Sr	Strontium
Cl	Chloride
SO ₄	Sulphate
HCO ₃	Carbonic acid
Fe	Iron
H ₃ BO ₃	Boric acid
Mg	Magnesium
Ca	Calcium
K	Potassium
Na	Sodium
GLDA	Glutamic acid, N,N-diacetic acid, tetrasodium salts
EDTA	Ethylenediaminetetraacetate
NTA	Nitrilotriacetic acid
DPTA	Diethylenetriamnepentacetic acid
HEDTA	Hydroxyethylenediaminetriacetic acid
CHNS	Carbon, Hydrogen, Nitrogen and Sulphur analyser
ICPMS	Inductively Coupled Plasma Mass Spectrometer
FTIR	Fourier Transform Infrared Spectroscopy
NMR	Nuclear Magnetic Resonance
XRD	X-Ray diffraction
PC	Personal Computer

1 INTRODUCTION

1.1 Motivation and statement of problem

Waterflooding using seawater and production water is one of the main oil recovery processes that have been used in many reservoirs around the world (Salman *et al.*, 2007). However, sulphate scaling is often encountered in this recovery system where seawater rich in sulphate mix with formation water rich in Ca, Ba, and Sr ions. Thus, it produces CaSO₄, barium sulphate (BaSO₄) and strontium sulphate (SrSO₄) with CaSO₄ as a predominant scale in the mixture (Senthilmurugan *et al.*, 2010). The precipitation of the sulphates of calcium, barium, and strontium, together with calcium carbonate, are responsible for the majority of problems encountered with respect to scale formation (Salman *et al.*, 2007).

Sulphate scale formation is a serious problem in industries such as oil and gas production, water transport, power generation and batch precipitation. It causes corrosion, equipment damage, formation damage and flow restriction which indirectly decreasing the production rate (Said *et al.*, 2009). Thus, according to Bader (2006), the best way to avoid sulphate scale is to prevent it from forming by using scale inhibitor.

However, there is no evidence proving that sulphate in seawater has completely being removed once the inhibitor is used. Besides, according to He *et al.* (2013), some scale inhibitor may function well in neutral conditions, but not certainly function well in acidic conditions. Some scale inhibitors may not compatible with the solution at high temperatures and may cause more severe damage. Therefore, in this study, Glutamic acid, N, N-diacetic acid, tetrasodium salt which is also known as GLDA will be used to dissolve and remove the calcium sulphate from the reservoir.

GLDA is produced from natural and sustainable raw materials. Therefore, this solvent is classified as biodegradable solvent with a high solubility over a wide pH range. Besides, GLDA is a type of chelates which are used extensively to control ions in water-based systems for countless applications. Currently, GLDA have been used to control water hardness ions, to clean surfaces, descaled boilers, processing textile and to prevent scale in heating system and it has been proved to be an effective chelating agent. Besides, GLDA is a readily biodegradable where majority of the molecule originates from a natural, and renewable source. Moreover, it has a high solubility over a wide pH range and is more effective chelating agent as compared to phosphates and phosphonates (AkzoNobel, 2011).

1.2 Objectives

The following are the objectives of this research:

- To study the physical properties of GLDA
- To analyse the characteristics based on CHNS, ICPMS, FTIR and NMR.
- To analyse the dissolution of CaSO_4 in GLDA.

1.3 Scope of this research

In order to fulfil the research objectives, the following scopes have been outlined namely:

- i) The correlation of results obtained from characterisations tests with the chemical formula of GLDA.
- ii) Experimental analysis of the amount of CaSO_4 ranging from 0.02g to 0.16g of CaSO_4 dissolved in GLDA at room temperature and atmospheric pressure.
- iii) The differences between the pure GLDA and GLDA with maximum amount of CaSO_4 salts in terms of its physical properties.

1.4 Organisation of this thesis

The structure of the remainder of the thesis is outlined as follow:

Chapter 1 (this chapter) provides a background description of waterflooding, production water and the common problems take place in industries which is the formation of sulphate scales. Besides, this chapter also provides the background description on Glutamic acid N,N-diacetic acid, tetrasodium salts (GLDA) which is a medium that will be used in this work to dissolve the CaSO_4 . Next, the objectives and scope of this research are also mentioned here. Chapter 1 ends with the organisation of this thesis.

Chapter 2 provides a description on the general overview of scale formation and calcium sulphate scales in more detail. Besides, the scale formation mechanisms, and factors affecting the formation of scales are also being discussed here. A number of journals are referred in order to understand the topic in detail. Besides, this chapter also provide the previous work on GLDA. Based on the previous work, GLDA has been used in many areas including in controlling the water hardness ions, to clean surfaces, to prevent scale in heating system and others. Thus, GLDA is suggested as the removing agent for this type of sulphate scales. This chapter ends with the summary of the literature review.

Chapter 3 gives the information about the chemicals that are being used in this study and the techniques to measure the amount of CaSO_4 that will be dissolved in GLDA. The techniques to measure the dissolution are by using CHNS analysis, ICP-MS, FTIR and NMR. Next, the procedure of the experiments is also being discussed here. This chapter ends with the summary of materials and methods used.

Chapter 4 provides the description of the results based on the experiments conducted. The results are studied in terms of physical properties, characterizations, interaction mechanisms and the solubility study of pure GLDA and GLDA-CaSO₄ mixture. The physical properties studied are density, pH, viscosity, water content and the separation of GLDA solvent. On the other hand, the characterizations and interaction mechanisms of pure GLDA and GLDA-CaSO₄ mixture studies are made using CHNS analysis and ICP-MS as well as FTIR and NMR respectively. The other factors that are being studied here is the solubility study of GLDA-CaSO₄ mixture. This chapter ends with the summary of this subtopic.

Chapter 5 conclude the findings and results obtained through experimental works and analysis. Besides, recommendations and the methods to improve the study are also being discussed here.

2 LITERATURE REVIEW

2.1 Overview

Scaling or the accumulation of materials depositing on the surface of equipment is a complicated phenomenon, which significantly affects a wide range of industrial processes, with serious technical and economic consequences (Hoang *et al.*, 2007). The formation of scale is affected by several parameters including temperature, pressure, flow rate, solution composition and pH. Besides, scaling causes production losses by reducing the volume of equipment. It also leads to emergency shutdowns due to blocked pipelines, increased corrosion and fatigue in metal parts. Periodic shutdowns of plants for mechanical removal of scales are necessary. Costs involved in maintenance and frequent shutdowns of these plants are high (Azimi, 2010). Therefore, scaling removing method in this processes are of great interest.

2.2 Introduction

2.2.1 Water Injection

Water injection is the most commonly used secondary oil recovery method. This is because water is readily available in large volumes and because water is very effective at substantially increasing oil recovery. The main purpose of the water injection is to increase the reservoir pressure to its initial level and maintain it near that pressure (Source: <http://petrowiki.org/>). It is normally used in oil-fields operations for flooding.

Hypersaline chloride-type waters are the common type of water formed in most reservoirs. This type of water contains alkaline cations such as barium, calcium, strontium, and sometimes radium. Although water injection is an expensive method, it could damage reservoirs formation due to incompatible salinity (Jones *et al.*, 1964). The most common option for water injection in offshore and near coastal operations is seawater. It is due to its abundance and acceptable compatibility with the salinity of most reservoirs formation waters (Bader, 2006). Moreover, scientifically it has proved

that water has viscosity, density, and wetting properties that affect efficiently in displacing various types of oils from the reservoir rocks (Source: <http://petrowiki.org/>).

Table 2.1: The major dissolved constituents in seawater
(Source: <http://petrowiki.org/>).

Ion	Cl = 19‰	Percent
Cl	18.980	55.05
Br	0.065	0.19
SO ₄	2.649	7.68
HCO ₃	0.140	0.41
F	0.001	0.00
H ₃ BO ₃	0.026	0.07
Mg	1.272	3.69
Ca	0.400	1.16
Sr	0.008	0.03
K	0.380	1.10
Na	<u>10.556</u>	<u>30.61</u>
Total	34.477	99.99

Seawater can be categorised as incompatible water as it will interact chemically and form precipitate minerals when being mixed with other type of water. The major dissolved ions in seawater are as in Table 2.1. Seawater has a high concentration of sulphate ions and low concentration of barium or strontium ions and formation waters has a low concentrations of sulphate ions and high concentration of calcium, barium and strontium ions. Therefore, mixing of these waters produces precipitation of CaSO₄, BaSO₄ and/or SrSO₄ (Collins, 1975). In most cases, the formation of sulphate and carbonate scales of calcium and barium in scaled-up wells are due to their relative hardness and low solubility (Moghadasi *et al.*, 2004).

2.2.2 Scale

Mineral scale is a serious problem in industries such as oil and gas production, water transport, power generation and batch precipitation. It is formed from inorganic insoluble salts that is precipitated in water and subsequently deposited on any surface it comes in contact with (Said *et al.*, 2009). Moreover, besides corrosion and gas hydrates, scale is one of the biggest water-related production problems. It can cause blockage of pore throats in the near well bore region or in the well itself (Silva *et al.*, 2015).



Figure 2-1: Picture of sulphate scales formed in a pipeline.

Scale deposits are adherent, hard, insoluble in mineral acids or other common solvents, and difficult to remove mechanically (Rhudy *et al.*, 1994). Thus, deposits could cause severe flow restrictions in processing and surface equipment and within the wellborn (Bader, 2006). Besides, scale also cause the loss of well productivity, formation damage and formation of a layer on well equipment surfaces, such as sliding sleeves, manifold or electric submersible pumps, and causing malfunctions of the equipments. Furthermore, it can occur anywhere along the production pipeline by narrowing the internal diameter of the pipes and, finally blocking the flow of the oil (Azimi *et al.*, 2007).

Calcium sulphate scales are the result of mixing of incompatible waters. For example, seawater is often injected into offshore reservoirs for pressure maintenance. Seawater has a high-sulphate content and the formation waters often have a high-calcium contents. Thus, mixing of these waters will results in calcium sulphate deposition (Source: <http://petrowiki.org/>).

Calcium sulphate is often the predominant scale produced although the solubility of CaSO_4 is higher than BaSO_4 and SrSO_4 . This is due to the formation water which often supersaturated with calcium ions, especially in dolomite and limestone reservoir. Managing sulphate scale deposition is more difficult than calcite scales due to the difficulty in removing the scales using a simple operation such as acid wash (Senthilmurugan *et al.*, 2010).

However, calcium sulphate scale solubility increases with decreasing temperature, unlike that of barium sulphate scale. The minimum temperature for the calcium sulphate scale to form is 40°C . This can decrease the likelihood of scale after the initial mixing deposition. The reversal in solubility falloff below 40°C accounts for the gypsum scaling observed in surface equipment. This inverse temperature effect can result in the generation of calcium sulphate scale when injecting seawater (Tahmasebi *et al.*, 2010).

Calcium sulphate is two times more soluble than calcium carbonate. This means that the sulphate is much less likely to drop out of solution when both are present. At higher temperatures, calcium carbonate scale, begins to precipitate at lower temperature and can be easily cleaned, chemically using acids or mechanically, by using sponge ball cleaning method. Besides, the solubility of calcium sulphate is strongly affected by the presence and concentration of other ions in the system.

2.2.3 Scale Forming Mechanism

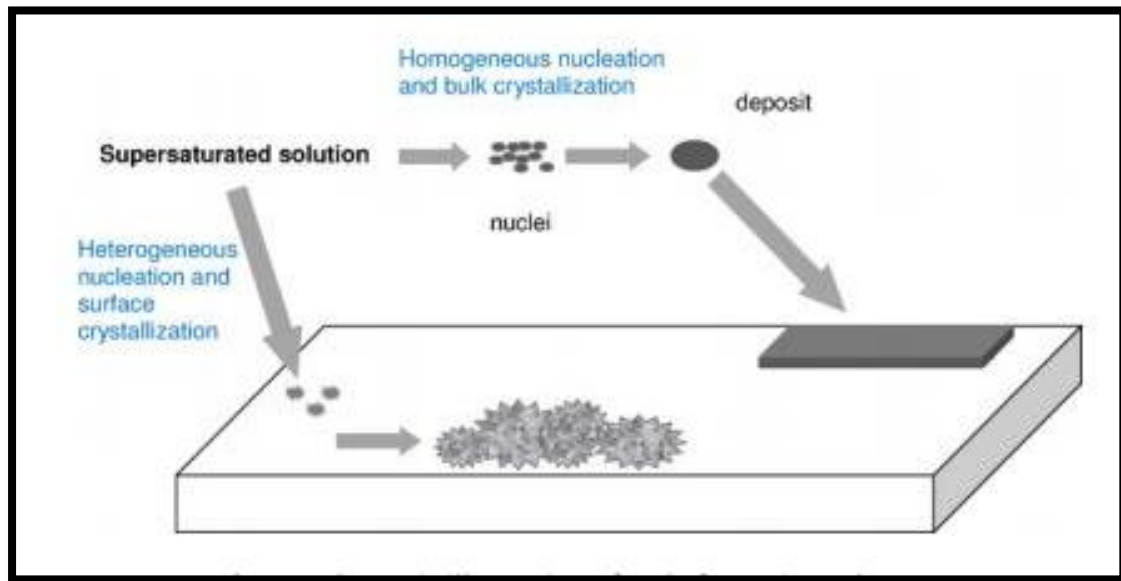


Figure 2.2: Schematic illustration of scale formation schemes (Antony *et al.*, 2011).

Scale formations involve both crystallization and transport mechanisms. Thermodynamically, crystallization or precipitation becomes achievable when the activity of ions in solution is above their saturation limit and the solution is supersaturated. Besides, the other key of determination is through the kinetic of precipitation. When supersaturation exceeds a critical value, nucleation of scale formation on particle surfaces induces growth of crystals, however low concentration of nucleation sites slows crystallization kinetics (Antony *et al.*, 2011).

Besides, scale formation occurs through two crystallization pathways, surface crystallization and bulk crystallization. Surface crystallization occurs due to the lateral growth of the scale deposit on the membrane surface, resulting in flux decline and surface blockage. On the other hand, bulk crystallization start to occur when crystal particles are formed in the bulk phase through homogeneous crystallization and will deposit on membrane surfaces as sediments to form a cake layer that leads to flux decline (Lee *et al.*, 1999).

In addition, supersaturated scale forming conditions leads to scale growth and agglomeration. This is due to the random collision of ions with particles and the production of secondary crystals on the surface of these foreign bodies that are present in the bulk phase (Hasson *et al.*, 2001). A schematic representation of these crystallization processes is illustrated in Figure 2.2.

2.2.4 Factors affecting the formation of scale.

2.2.4.1 Temperature

The formation of various calcium sulphate crystalline forms including the anhydrite, dehydrate or gypsum, and hemihydrates are affected by changes in temperature, pressure and ionic strength. However, it is more sensitive to temperature rather than pressure (Firas *et al.*, 2005). Among the various types of calcium sulphate scales, gypsum is the most common precipitate that formed at the ambient temperature and the formation of all forms of calcium sulphate changes with increasing temperature (Hoang *et al.*, 2007 and Dydo *et al.*, 2003).

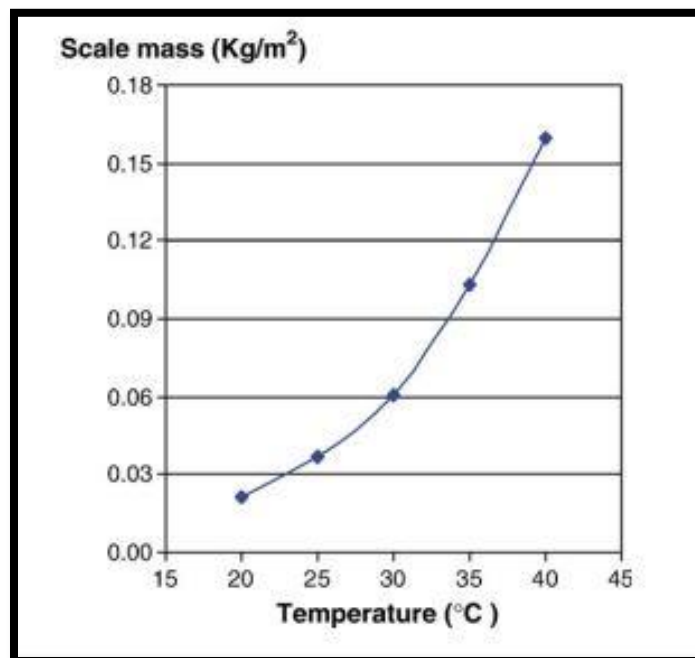


Figure 2.3: Effect of temperature on the scale formation (Hoang *et al.*, 2007).

Based on Hoang *et al.* (2007) and Tahmasebi et al (2010), the permeability declines more rapidly for the temperature range of 20 °C to 90 °C. This is because, the saturation index and the rate of precipitation reaction increases with the increase in temperature. Therefore, high temperature speeds up the scaling process by significantly reducing the induction time, increases the rate of precipitation and a faster permeability decline.

Besides, high temperature also changes the hydrate forms of the scale deposit. At temperatures lower than 40 °C, only calcium sulphate dehydrate is formed. However, hydrated and anhydrous type of scales will be formed at temperature of more than 40 °C (Hoang *et al.*, 2007). Thus, solution temperature proved to have important effects on the formation of calcium sulphate scales.

2.2.4.2 Flow rate

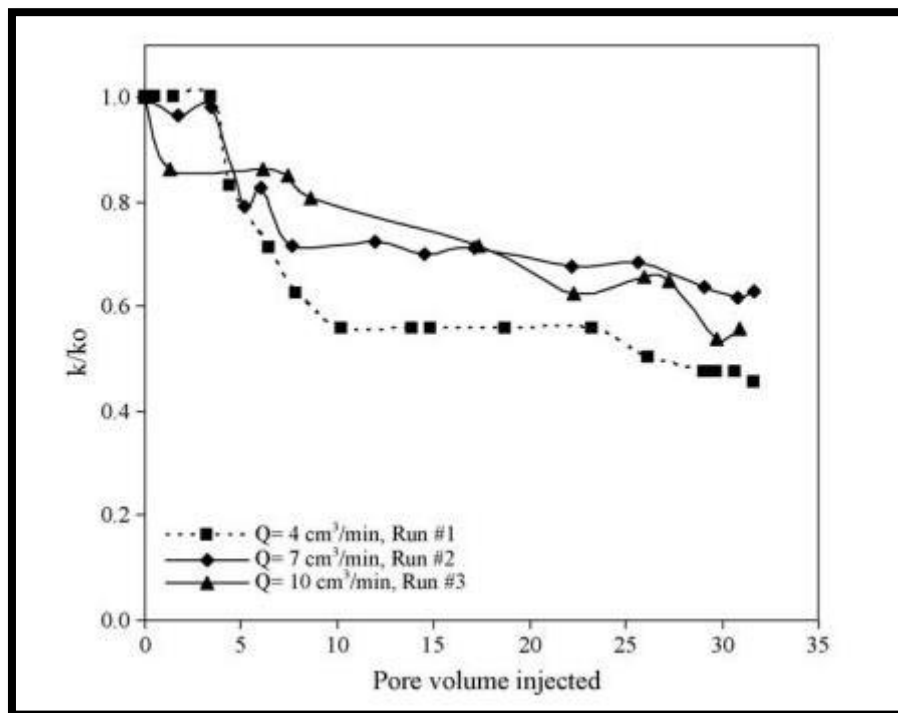


Figure 2.4: Permeability ratio (k/k_o) against the number of pore volume injected for different flow rate (Tahmasebi *et al.*, 2010).

At lower flow rate, the scale deposition and pore plugging near the injected area have a major effect on the permeability decline against higher flow rate. Therefore, at higher flow rate, the mixing of injected solution increased and the size of crystal of calcium sulphate scale formed is reduced due to increased in particle movement and crystal growth.

2.2.4.3 Pressure

At low operating pressure, the initial flux and the concentration polarization remain low, and the degree of surface crystallization is also low. However, the formation of scales favours a high pressure, where both surface crystallization and bulk crystallization method will occur (Antony *et al.*, 2011).

2.2.5 Scale control techniques

According to Bader (2006), the best way to avoid sulphate scale is to prevent it from forming by using scale inhibitor. Scale inhibitor is used to refer to a chemical that stops or interferes with inorganic scale nucleation, and precipitation of them. The application of scale inhibitors has been an economical method used to mitigate calcium sulphate. The use of scale inhibitors may act either as chelating agents to form a soluble complex or as threshold inhibitors, which block the development of the supercritical nuclei or as retarders of the growth of the calcium sulphate crystals.

Mineral scale formation can be prevented during the process of acid stimulation by simply adding an acid-soluble and effective scale inhibitor into the acid system. In addition, combining scale inhibition and acid stimulation into a single package inherently reduces well intervention costs and well downtime, and therefore achieves significant economic benefits (He *et al.*, 2013).

Moreover, according to He *et al.* (2013), some scale inhibitor may function well in neutral conditions, but not certainly function well in acidic conditions. Some of them may even be not compatible with the solution at high temperatures while some may cause severe damages to the reservoir. Besides, the selection of scale inhibitors depends on temperature, pH value of the solution, and compatibility with solution. Six different types of scale inhibitors used by He *et al.* (2013) are as shown in Table 2.2.

Table 2.2: Scale inhibitors used in He *et al.* (2013) study.

Abbreviated Name	Active Ingredient	Approximate Activity, %
A	Phosphinopolycarboxylic acid	29
B	Sulfonated polymer	31
C	Polyacrylic acid	19
D	P tagged sulfonated polymer	45
E	Diethylenetriamine penta(methylene phosphonic acid)	18
F	Bis-hexamethylene triamine-penta(methylene phosphonic) acid	12

In addition, maleic anhydride and acrylic acid are also among the scale inhibitors (Zhang *et al.*, 2012). Maleic anhydride based polymers are considered as an effective in desalination of seawater through multi-stage flash evaporation (MSF) process and is used as enhancer for this process. However, temperature plays an important role in determining the effectiveness of the inhibitors (Source: <http://www.oilfieldwiki.com/>). Table 2.3 below shows that with the increase in temperature of pipes from 60 °C to 70 °C, the inhibition efficiency decreases by 7-11% whereas further 5 °C increase in temperature decreases the inhibition efficiency up to 12-15% (Yousef *et al.*, 2015).

Table 2.3: Inhibition percent of YMR-antiscalants for CaSO₄ scales in different pipe systems (Yousef *et al.*, 2015).

Temperature (°C)	YMR 142-A	YMR-68	YMR-74	YMR-63	YMR 135-S
<i>Copper pipes</i>					
60	95.29	96.58	98.20	95.47	93.90
65	90.84	93.63	95.98	91.33	87.67
70	81.40	87.88	90.74	84.04	76.33
75	65.12	77.73	78.55	74.56	59.63
<i>Steel pipes</i>					
60	92.82	97.31	98.84	97.19	92.38
65	89.31	95.01	97.03	95.37	88.40
70	83.77	89.14	91.41	89.06	81.31
75	73.71	77.02	78.25	73.79	70.98

2.2.6 Chelating agent

Chelates are chemical agents that interact with metal ions and hard water ions such as Ca²⁺, Mg²⁺. Chelating agents have been widely used in various applications because of their ability to form metal complexes that are reasonably stable and therefore reduce the metal ion reactivity. It has been used in washing and treatment of contaminated soil/sediment, softener for commercial detergents, in food industry and medicine as heavy metal detoxification agent, dissolution of calcium anhydrate sulphate scale from reboilers and heater tubes (Rabie *et al.*, 2011).

There are various types of chelating agents such as ethylenediaminetetraacetate (EDTA), Nitrilotriacetic acid (NTA), diethylenetriamnepentacetic acid (DPTA), hydroxyethylenediaminetriacetic acid (HEDTA) and glutamic acid diacetic acid (GLDA). However, EDTA is the most widely used, strong, cost effective and the general purpose chelating agent. However, EDTA is not readily biodegradable and its phosphate can cause pollution via eutrophication and are therefore not environmentally friendly (Source: <http://www.subsport.eu>).

Besides, HEDTA which is a solvent having the similar efficiency as EDTA are useful in dealing at low pH for a high solubility performance. It is also being used to stabilize iron ions at high pH. Another type of strong chelating agent is DTPA. It is used in peroxide bleaching of pulp and is more suitable to be used under oxidising conditions. EDTA, DTPA and HEDTA are non-biodegradable chelating agents, while NTA and GLDA are bio-degradable chelating agents. NTA has a high temperature stability and is widely used in cleaning processes and detergent application. However, NTA is not as strong as EDTA (AkzoNobel, 2011).

On the other hand, GLDA is the latest, stronger and green chelate as compare with others. GLDA possesses excellent biodegradability with more than 60% of GLDA degraded within 28 days (Kolodynska, 2011). Besides, it is a readily biodegradable, with a high solubility over a wide pH range. Compared to EDTA and NTA, GLDA performs better in cleaning the hard surfaces. It has an improved biodegradability property and exhibit as a more effective chelating agent as compared to phosphates and phosphonates (AkzoNobel, 2011). Therefore, since GLDA is a safe and readily biodegradable chelating agent, it can be used as alternative for NTA, EDTA, phosphates and phosphonates.

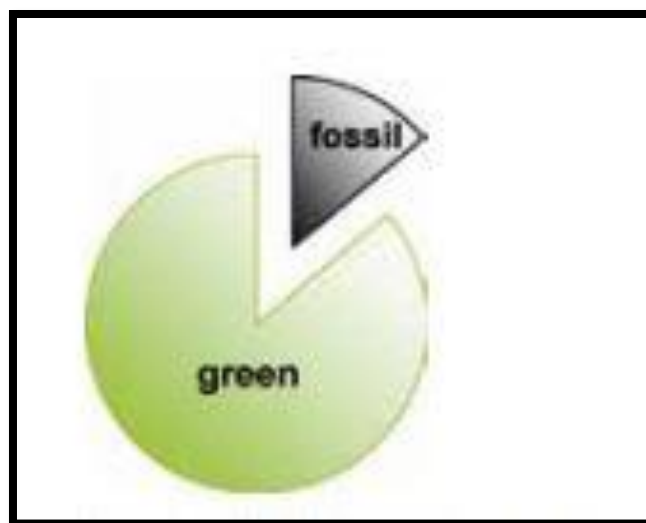


Figure 2.6: GLDA and green character (AkzoNobel, 2011)

2.3 Previous work on GLDA

Glutamic Acid, N, N-Diacetic Acid, Tetrasodium salt (GLDA) is a type of chelates which are used extensively to control ions in water-based systems for countless applications. Currently, GLDA have been used to control water hardness ions, to clean surfaces, descaled boilers, processing textile and to prevent scale in heating system and has been proved to be effective. Besides, GLDA is also being used as a medium to control the metal reactivity.

In addition, GLDA has been used to remove heavy metals from industrial sludge which is generated from a local battery company. The metals found in the battery sludge are cadmium, nickel, copper, and zinc. Those metals are harmful and toxic to human beings and to environments. Accumulation of these metals in living organisms can cause various diseases and disorders (Wu *et al.*, 2015).

Moreover, they are also the important processing tools for reducing the detrimental effect of metals in pulp bleaching for paper manufacturing, improving personal care formulations, stabilizing food products and for pharmaceutical formulations. Finally, they are also used extensively in metalworking areas, ranging from metal plating, dosing essential elements to plants and supplying iron for the development of photographic films and paper using silver halide technology. Besides, according to Wu *et al.* (2015), GLDA has been used to remove heavy metals from industrial sludge.

2.4 Summary

Scales formation such as the formation of CaSO_4 causes many problems in industries such as oil and gas production industry. Water injection which uses seawater as its medium to increase the reservoir pressure is the main contributor to the scale problems. Seawater contains a high concentration of sulphate ions where as production water contains a high concentration of calcium ions. Thus, the mixing of these two types of waters produces CaSO_4 scale.

Deposits of CaSO_4 scales can cause the loss of well productivity, corrosion as well as the blockage of the pipeline which results in the narrowing of the internal diameter of the pipes. Initially, scale is formed from the nucleation of particles surfaces which induces the growth of crystals. Later, these small crystals will grow, agglomerate and sediment to form cake layer. This process is known as crystallization or precipitation.

Besides, formation of scale is affected by several parameters such as temperature, pressure, and flow rate. Among these three parameters, temperature is the most influencing factor that promotes the formation of CaSO_4 scales. Higher temperature speeds up the scaling process and increases the rate of precipitation. However, higher flow rate increases the particle movement which prevents the agglomeration of the crystals and reduced the formation of CaSO_4 scales.

Therefore, scale inhibitors are used in order to prevent the formation of scales. Examples of scale inhibitors are sulfonated polymer, maleic anhydride and acrylic acid. However, these inhibitors are not compatible at high temperature and can cause severe damage to the reservoir. Thus, GLDA which is a type of chelating agent is used in this study to remove the CaSO_4 scales. The studies will be based on their physical properties effects, characterizations, interaction mechanisms between GLDA and CaSO_4 as well as the solubility study of GLDA- CaSO_4 mixture. Therefore, experiments are done to know detail on the outlook from those aspects.

3 MATERIALS AND METHODS

3.1 Overview

This paper presents the chemicals and procedure of the experiments that will be carried out in order to achieve the objectives of this work. The purpose of this experiment is to analyse the dissolution of CaSO_4 in GLDA and to study the physical properties of GLDA.

The salt of CaSO_4 will be stirred in GLDA for 24 hours and followed by 1 hour of sedimentation. Later, CHNS analyser, Inductively Coupled Plasma Mass Spectrometer (ICPMS), Fourier Transform Infrared Spectroscopy (FTIR), and Nuclear Magnetic Resonance (NMR) will be used to study the dissolution of the salts in the GLDA.

3.2 Chemicals

3.3.1 Calcium Sulphate (CaSO_4)

The salt used is calcium sulphate (CaSO_4) with the purity of 0.98. The molar weight of CaSO_4 is 136.14 g/mol. It appears as a white solid and odourless. It has a melting point of 1460 °C.

3.3.2 Glutamic Acid, N, N-Diacetic Acid, Tetrasodium Salt (GLDA)

The chemical name for GLDA is L-glutamic acid N,N-diacetic acid, tetra sodium salt with a chemical formula of $\text{C}_9\text{H}_9\text{NO}_8\text{Na}_4$.

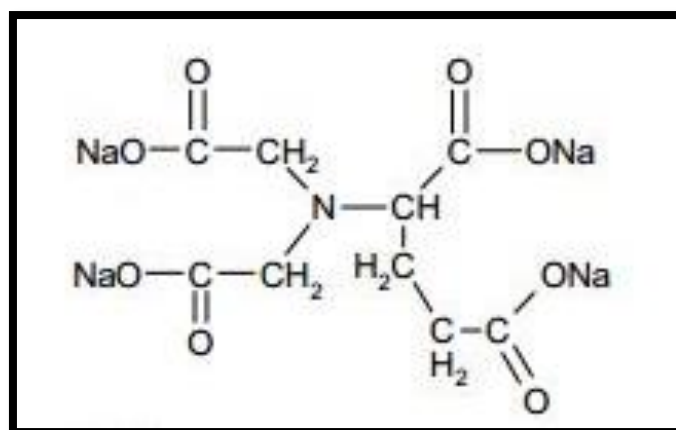


Figure 3.1: Chemical structure of GLDA.

3.3 Method

3.3.1 Solubility of calcium sulphate in GLDA.

0.02g of CaSO_4 powder is mixed with 10mL of GLDA.

The mixture is stirred using a magnetic stirrer for 24 hours at room temperature with a stirring speed of 1200rpm.

After 24 hours, the mixture is left for another 1 hour of sedimentation.

The steps are repeated with 0.04g, 0.06g, 0.08g, 0.1g, 0.12g, 0.14g and 0.16g of CaSO_4 under the same conditions.

Figure 3.2: Method for the solubility of calcium sulphate

The method of preparing the samples are followed based on Figure 3.2. 0.1g of CaSO_4 and 10mL of GLDA are mixed using a magnetic stirrer at a stirring speed of 1200 rpm and room temperature of 27 °C for 24 hours. The dissolution of CaSO_4 in the chelating agent is observed. The experiment is repeated using a different amount of CaSO_4 of 0.04g, 0.06g, 0.08g, 0.1g, 0.12g, 0.14g and 0.16g of CaSO_4 at the same temperature, stirring speed and amount of GLDA.

The screening of the solubility of CaSO_4 in GLDA is visually identified. The solubility of CaSO_4 is determined when all the salt has been totally dissolved in GLDA after 24 hours of stirring.

3.3.2 Gravimetric method

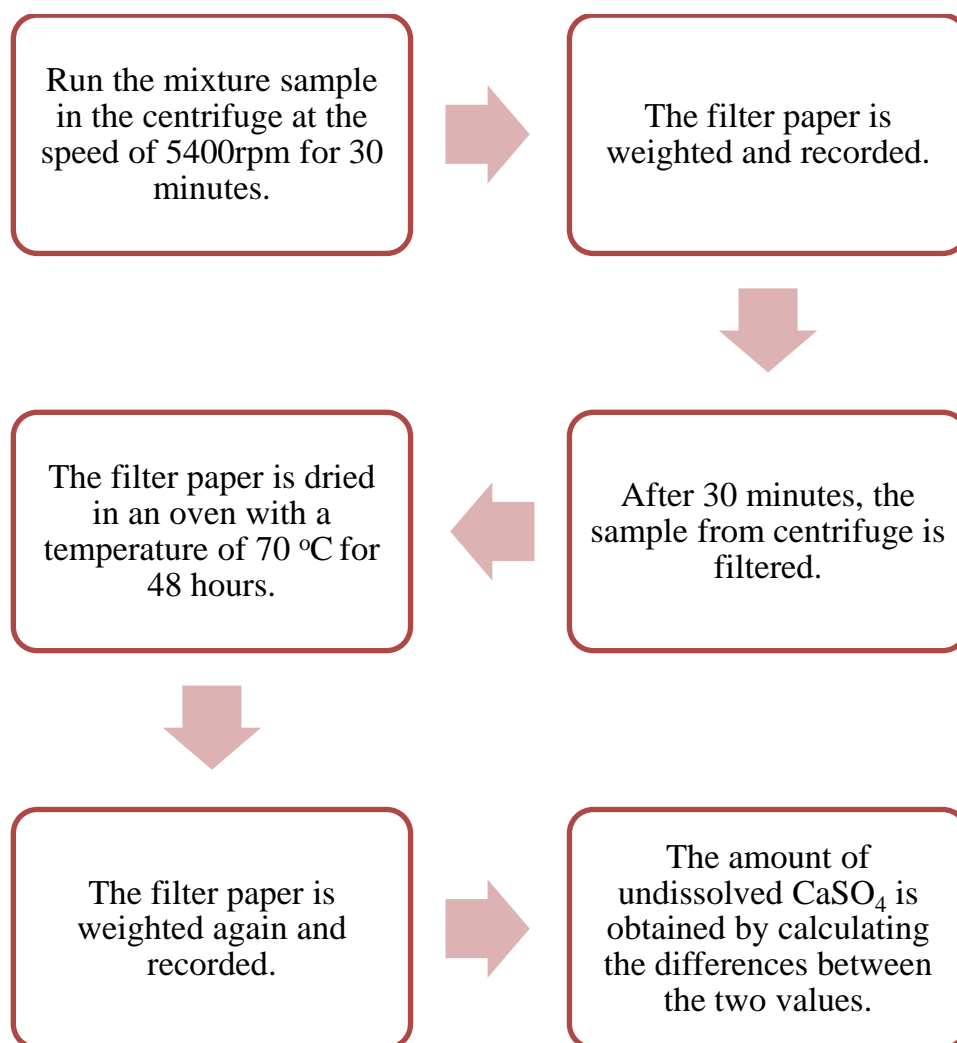


Figure 3.3: Procedure for gravimetric method

This method is only carried out after the solubility of CaSO_4 in GLDA is found and only for the samples with undissolved CaSO_4 . Firstly, the sample is run in the centrifuge at the speed of 5400rpm for 30 minutes. Later, the weight of the filter paper is measured and recorded. Next, the sample is filtered with the filter paper to obtain the undissolved CaSO_4 salt only. The filter paper is dried in an oven with the temperature of $70\text{ }^\circ\text{C}$ for 48 hours as the solution is thick. Lastly, the weight of filter paper is measured again and recorded. The amount of undissolved CaSO_4 is obtained by calculating the differences of the weight before and after.

3.3.3 Tests for Physical properties

3.3.3.1 pH test



Figure 3.4: Metler Toledo FiveEasy pH meter

pH is measured using Metler Toledo FiveEasy pH meter. Firstly, the pH meter is calibrated using a calibration buffer in order to improve its measurement accuracy. Then, the sensor of the pH meter is rinsed with distilled water and dried. Later, the sensor is dipped in the 10 mL of pure GLDA and GLDA- CaSO_4 mixture. The pH value appeared on the screen is recorded.

3.3.3.2 Viscosity



Figure 3.5: Brookfield viscometer

Viscosity is measured using Brookfield viscometer. Firstly, the calibration is done on the viscometer. Next, the sample is poured in the viscometer sample container. The spindle is immersed into the sample to the groove on the spindle shaft. Later, the spindle is attached to the viscometer. The torque speed is set to 10 percent at the temperature of 28.9 °C. The value of viscosity is recorded.

3.3.3.3 Density



Figure 3.6: Micromeritics AccuPyc II 1340 Gas Pycnometer

The density of solvent is identified using Micromeritics AccuPys II 1340 Gas Pycnometer as in Figure 3.6. Firstly, calibration is done on the gas pycnometer in order to increase the accuracy of the density obtained. Later, deionized water is used to fill up the cup, weighted and recorded. Next, the cap chamber is removed, the sample cup is placed in the cell chamber and the cap is replaced. Start button on the PC is clicked and the results appeared on the screen is recorded. Density of deionized water obtained is made as reference value for the GLDA sample. The same method is repeated for GLDA sample.

3.3.3.4 Water content analysis



Figure 3.7: Karl Fischer Titrator

The amount of water in the GLDA sample is determined using Karl Fischer titrator, Metrohm brand. Firstly, the vial is half-full with the sample. The reagent used in this analysis is hydranal 5. Next, the stirred time is set and the analysis is run. Once the titration is completed, the titrator beeped and the percentage of water in the sample is displayed on the instrument panel. The value is recorded.

3.3.4 Characterisation of the solution

The solution with the optimum amount of CaSO_4 is tested with various types of tests such as CHNS analysis, Inductively Coupled Plasma Mass Spectrometer (ICPMS), Fourier Transform Infrared Spectroscopy (FTIR), and Nuclear Magnetic Resonance (NMR) to study the characteristics of the mixture of CaSO_4 with GLDA.

3.3.4.1 CHNS analysis



Type of Equipment	Vario Macro CHNOS Analyzer
Brand	Elementary Germany

Figure 3.8: CHNS Analyser

Figure 3.8 shows the equipment used to determine and analyse C, H, N and S atoms presents in GLDA.

Firstly, the sample is burned in excess oxygen and the combustion products are collected. Later, the mass of these combustion products is used to calculate the composition of the sample.

3.3.4.2 ICP-MS analysis

Figure 3.9 shows the equipment used to analyse the elements in GLDA.



Type of Equipment	Inductively Coupled Plasma Mass Spectrometer
Brand	Agilent 7500 Series

Figure 3.9: ICP-MS

10mL of sample is pipette into the centrifuge tube and 10 μ L of internal standard is added. The sample is shaken well and the sample is placed in the analyser. Next, the analysis is run.

3.3.4.3 FTIR analysis

Figure 3.10 shows the equipment used to identify the type of bonding based on their peak frequency. The spectral range of this FTIR spectrometer is between 7800 to 350 cm^{-1} .



Type of Equipment

Thermo-Nicolet

Brand

AVATAR 380

Figure 3.10: FTIR

This equipment uses OMNIC software. Firstly, the instrument is calibrated. The setting is set to analyse the absorbance. The background is analysed. Later, a drop of sample is put on the tester and the sample is analysed. The result for the sample is equals to its differences. The peak for the pure GLDA is compared with GLDA-CaSO₄ mixture.

3.3.4.4 NMR analysis



Type of Equipment

Nuclear Magnetic Resonance

Brand

Bruker Ultra Shield Plus 500

Figure 3.11: Nuclear Magnetic Resonance

Figure 3.11 shows the equipment used to identify the structure and the unknown substances. Firstly, the tube containing the sample is inserted in the new sample depth gauge. Next, the parameters are chosen and the analysis is started.

3.3.5 Solubility verification test

The mixture of GLDA and CaSO_4 is tested using the centrifuge in order to identify the homogeneity of the mixed solution. 10mL of GLDA- CaSO_4 mixture is prepared in the centrifugal vial. The centrifuge is set to 5600 rpm for 60 minutes. Later, CaSO_4 sedimentation is determined through visual observation.



Model

Kobota

Figure 3.12: KUBOTA Centrifuge

3.4 Precautions

Precaution steps taken during conducting the experiments are to ensure the accuracy of the results obtained as well as to avoid from any accidents to happen. Therefore, one of the precaution steps taken is to take the GLDA sample to be used in every experiment from small bottle. This is to avoid the contamination of pure GLDA source. Besides, an accurate weighing machine must be used in order to decrease the probability of errors.

3.5 Summary

This chapter presents the methods and materials used in this study. Besides, it explains the procedures of all the equipment used and the methods to obtain accurate results. Later, the results obtained will be discussed in terms of physical properties, characterizations, interaction mechanisms and solubility study of pure GLDA and GLDA- CaSO₄ in the next chapter.

4 RESULTS AND DISCUSSIONS

4.1 Overview

This section shows the results obtained through the experiments that have been carried out in the previous subtopic. The main objective of this study is to analyse the solubility of CaSO_4 in GLDA (GLDA-CaSO_4). The studies are done on both pure GLDA and GLDA-CaSO_4 in order to study their differences in terms of their physical properties, characterizations, interaction mechanisms, and solubility study of GLDA-CaSO_4 .

Density, pH, viscosity, water content and separations are the criteria of physical properties that are being studied in this chapter. Besides, the characterisations of pure GLDA and GLDA with 0.145g of CaSO_4 are done through few tests such as CHNS analysis, and Inductively Coupled Plasma Mass Spectrometer (ICPMS) while, Fourier Transform Infrared Spectroscopy (FTIR), and Nuclear Magnetic Resonance (NMR) tests are carried out to study its interaction mechanisms.

4.2 Physical Properties

The physical properties studies are done on two samples, pure GLDA and GLDA with the optimum amount of CaSO_4 . The optimum amount of CaSO_4 that can be dissolved based on current experiments is 0.145g. Physical properties are properties that can be measured without changing the chemical identity of the substance (Source: www.boundless.com). Thus, the physical properties studied are density, pH, viscosity, water content and separation. The purpose of studying the differences of these two samples is to know the effect of CaSO_4 on the physical properties of GLDA.

Table 4.1: Differences of physical properties between pure GLDA and GLDA with optimum amount of CaSO₄.

Properties	Pure GLDA	GLDA + CaSO ₄
Density	1.2710 ± 0.0002 g/cm ³	1.2846 ± 0.0001 g/cm ³
pH	4.11 ± 0.01	4.52 ± 0.01
Viscosity	11.56 mPa.s	-
Water Content		62.3 w%
Separation		No separation

Based on Table 4.1, GLDA with CaSO₄ shows a higher value of density and pH as compared with pure GLDA. Generally, density is the most fundamental physical properties of any material. It is defined as the ratio of an object mass to its volume. Besides, it is a function of the mass of the atoms making up the materials (Source: <http://engineershandbook.com/>). The density of pure GLDA is 1.2710 g/cm³ and GLDA-CaSO₄ is 1.2846 g/cm³. The differences is 0.0316 g/cm³ indicates that CaSO₄ has actually been dissolved in the GLDA.

On the other hand, pH for pure GLDA and GLDA-CaSO₄ are 4.11 and 4.52 respectively with a difference of 0.41. Basically, the pH of CaSO₄ in water is 7.7 which is a weak base. pH is defined as the negative logarithm of the hydrogen ion concentration. The H⁺ ion from the GLDA neutralises the OH⁻ ion from the CaSO₄. Thus, the total number of H⁺ ion in the GLDA is decreased after being mixed with CaSO₄. Therefore, the mixture of acidic GLDA with CaSO₄ produced a slightly lower (weak) acidic property.

Besides, the other physical property that is being studied is viscosity. The viscosity of both pure GLDA is 11.56 mPa.s. On the other hand, the viscosity of GLDA-CaSO₄ cannot be identified due to equipment failure. However, based on visual observation, the solution is still viscous as the pure GLDA. Therefore, it shows that CaSO₄ does not affect the viscosity of the GLDA.

On the other hand, the water content and separation of the sample GLDA-CaSO₄ and pure GLDA remain unchanged. Based on the test carried out, it was found out that the water content in GLDA and GLDA-CaSO₄ is 62.3 w%. Solubility of CaSO₄ in GLDA neither increases nor decreases the amount of water. Therefore, it indicates that there is no chemical reaction between them and is only bounded to the molecules.

4.2.1 Verification of Solvent

GLDA solvent is a mixture of GLDA compounds and water. However, based on Table 4.1, it shows that there is no separation of water and GLDA compounds after it has been tested with centrifugation process. Moreover, GLDA-CaSO₄ solvent also shows the same results. Therefore, it indicates that GLDA and GLDA-CaSO₄ is a homogeneous solvent as it cannot be separated and appears as single phase.

4.3 Characterisations

The studies on the characterisations of pure GLDA and GLDA with 0.145g of CaSO₄ are done through few tests such as CHNS analysis, Inductively Coupled Plasma Mass Spectrometer (ICPMS), Fourier Transform Infrared Spectroscopy (FTIR), and Nuclear Magnetic Resonance (NMR) to study the characteristics of the mixture of CaSO₄ with GLDA.

4.3.1 CHNS analysis

Table 4.2: Composition of C, H, N, and S atoms in GLDA.

Element	W%
C	17.69
H	6.52
N	2.88
S	0.11

CHNS test functions as a medium to study the organic element in the sample. Based on Table 4.2, pure GLDA contains the highest number of carbon (C) atoms with 17.69 w% from the overall mass, followed by hydrogen (H) atoms and nitrogen (N) atoms with 6.52 w% and 2.88 w% respectively. The total weight percent of these 3 elements is 27.09 w%, and the rest 72.91 w% is the weight percent of other elements which is also found in GLDA which is sodium (Na) atoms. Thus, it can be concluded that the value obtained through CHNS test correlate with the number of atoms of the elements in GLDA with a chemical formula $C_9H_9NO_8Na_4$.

4.3.2 Inductively Coupled Plasma Mass Spectrometer (ICPMS)

Table 4.3: Value of elements in GLDA

Element	Value (ppm)
Na	37 498
K	12.260
Mg	6.17
Ca	0.7
Fe	0.5777
Ca	0.1818
Ba	0.0421

ICPMS test is used as an element analysis for inorganic elements. Based on Table 4.3, GLDA contains the highest amount of sodium atom with 37498 ppm. However, other elements appear to be in small amount as they are not literally attached to the GLDA molecules but appears as impurities in the solvent.

4.4 Interaction Mechanism through Fourier Transform Infrared Spectroscopy (FTIR).

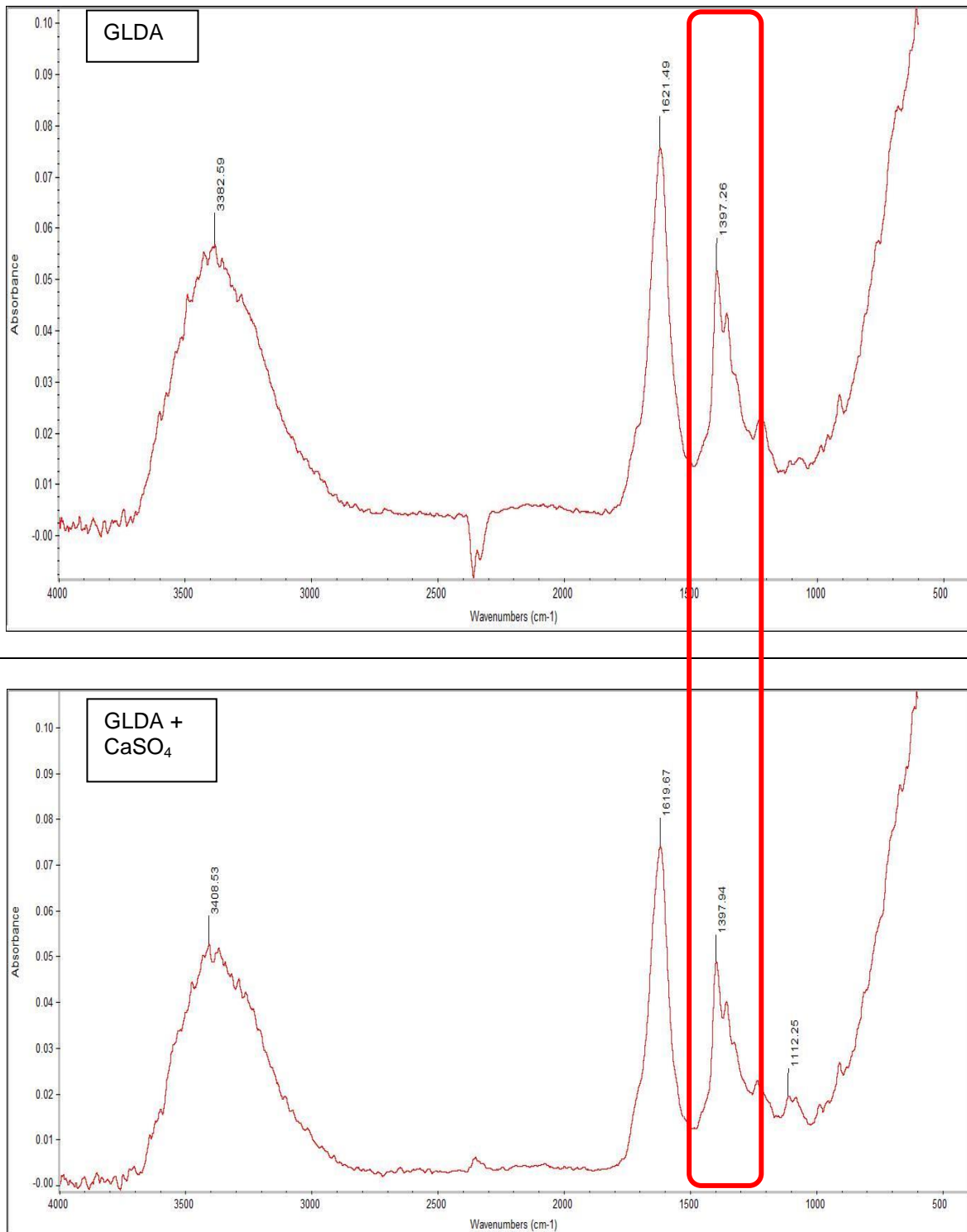


Figure 4.1: FTIR test result.

FTIR analysis is used to identify organic functional groups and the specific organic compounds (Source: <http://www.eag.com/>). Figure 4.1 shows the FTIR test results for pure GLDA and GLDA with CaSO_4 . The highlighted peaks are the peak for C-H bond. The wavelength for C-H peak is 1397.26 cm^{-1} while the wavelength for the mixture is 1397.94 cm^{-1} . The wavelength shifted to the left with 0.68 cm^{-1} depicted that there is hydrogen bonding occurred between the C-H bonds.

4.5 Interaction Mechanism through Nuclear Magnetic Resonance (NMR).

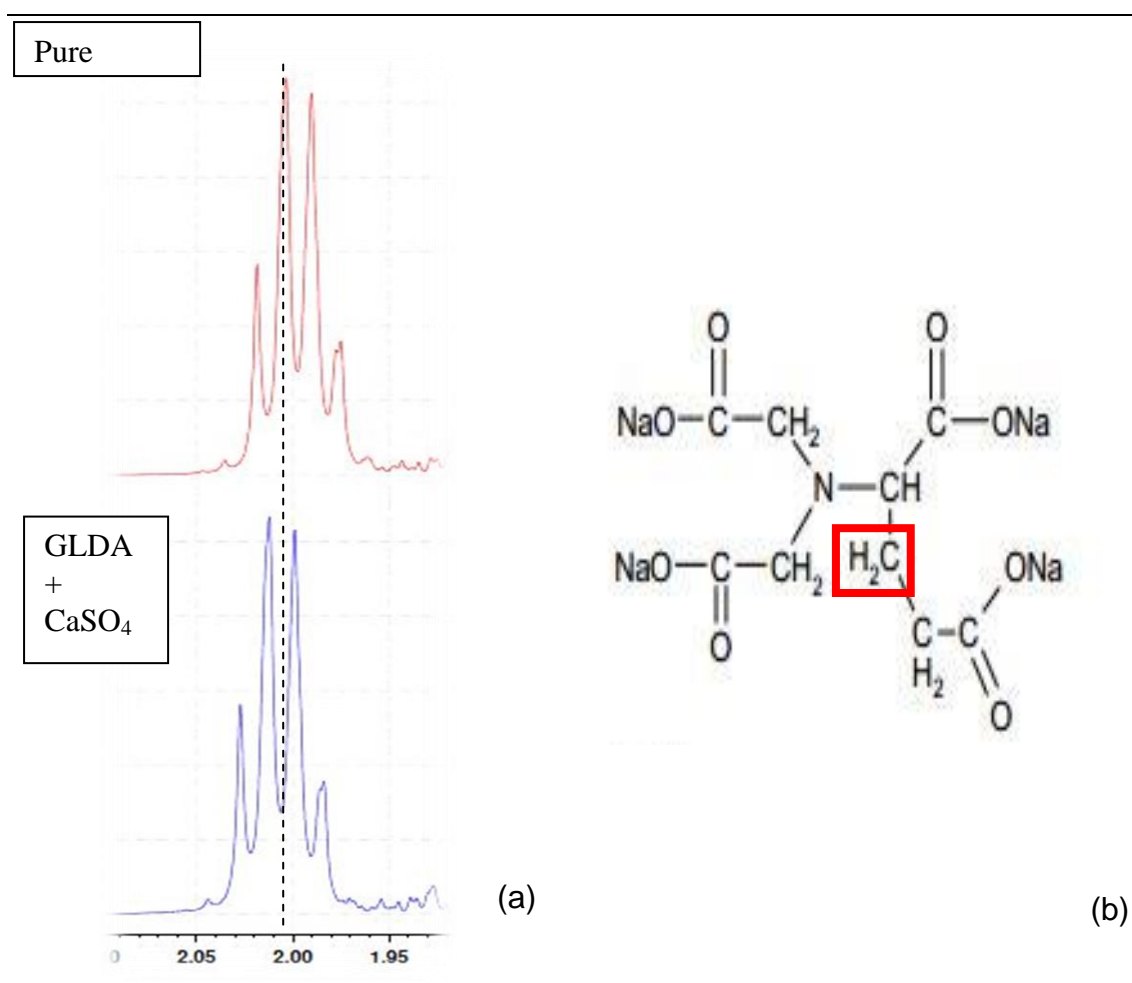


Figure 4.2: NMR test result for the highlighted hydrogen atom.

NMR spectroscopy is an analytical chemistry technique used in determining the content and its molecular structure (Hoffman *et al.*, 2013). From Figure 4.2 (a), the result shows that the molecular structure for these four peaks indicates the CH₂ group at the position highlighted as in Figure 4.2 (b). The chemical shifted to the left with 0.01ppm depicted that there is hydrogen bonding occurred on that CH₂ group between targeted solute which is CaSO₄ and GLDA as solvent.

4.6 Solubility Study

The solubility studies are carried out on the mixture GLDA-CaSO₄ that was obtained from the experiment conducted. The purpose of this study is to know the ability of GLDA in dissolving CaSO₄ and is measured in terms of the maximum amount of CaSO₄ dissolved in GLDA at the studied condition (27 °C and 1 atm).

The mass of CaSO₄ salts in 10mL of GLDA differed in each experiment and is mixed for 24 hours. Figure 4.3 below shows the solution condition before the mixing, while Figure 4.4 shows the mixing process of GLDA-CaSO₄ using magnetic stirrer after 2 hours.

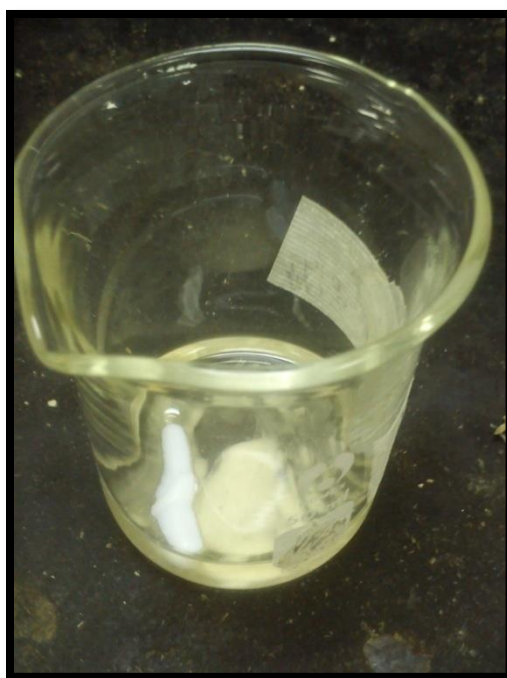


Figure 4.3: Before mixing

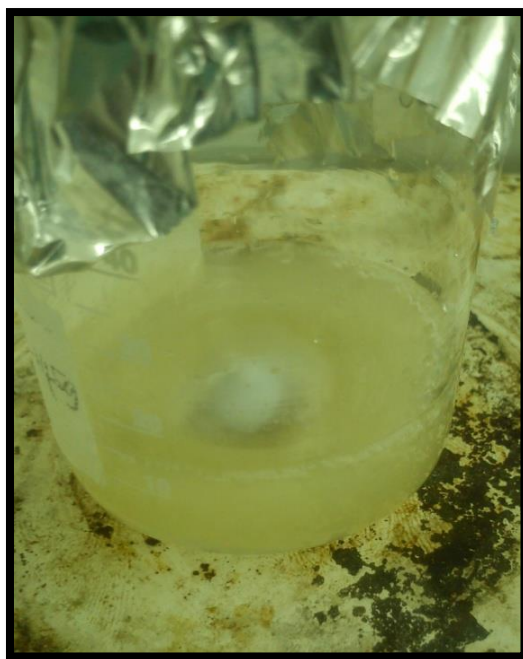


Figure 4.4: During the stirring of GLDA-CaSO₄ at 2nd hours.

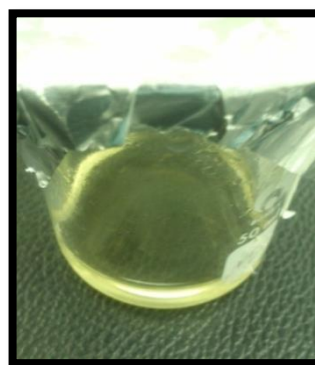
4.6.1 Completely dissolved



0.10 g CaSO₄



0.12 g CaSO₄



0.14 g CaSO₄

Figure 4.5: Completely dissolved amount of CaSO₄ salts in 10mL of GLDA

Figure 4.5 shows the amount of CaSO_4 that are completely dissolved in 10mL of GLDA. All the mixture samples appear as light yellowish liquid which is almost similar to the color of pure GLDA. Since all the CaSO_4 salts dissolved in the GLDA and the maximum amount of CaSO_4 is not determined yet, the solutions are considered as unsaturated solution.

On the other hand, Figure 4.6 below shows the saturated GLDA- CaSO_4 solution with 0.145g of CaSO_4 . The solution appears to be in pale-yellow color liquid and it contains the maximum amount of CaSO_4 salts.

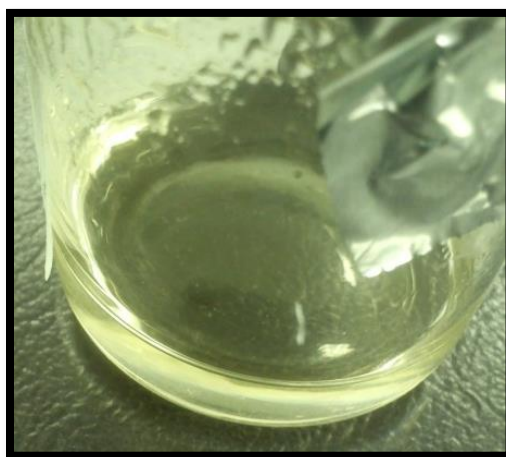


Figure 4.6: The maximum amount of CaSO_4 (0.145g) dissolved in 10mL GLDA.

4.6.2 Partially dissolved



Figure 4.7: 0.16g of CaSO_4 salts in 10mL of GLDA.

Partially dissolved solution is when there is still undissolved solute in the solvent. In this study, the mass of CaSO_4 salts of more than 0.145g starts to sediment at the bottom of the beaker as the solution has achieved a concentrated level. Therefore, the mass ratio of the saturated solution of pure GLDA to CaSO_4 is 87:1, while its volume ratio is 160:1.

4.7 Summary

This paper presents the physical properties, characterization and the interaction mechanisms study and solubility study of pure GLDA, and GLDA- CaSO_4 . The density and pH for both pure GLDA and GLDA- CaSO_4 differ from each other. However, viscosity and water content of GLDA and GLDA- CaSO_4 remains unchanged. Therefore, it indicates that CaSO_4 has been dissolved in GLDA.

On the other hand, the characterisations of pure GLDA and 10 mL of GLDA with 0.145g of CaSO_4 are identified through CHNS analysis and Inductively Coupled Plasma Mass Spectrometer (ICPMS) where it contains a high number of carbon atoms and a high sodium atoms number which are 17.69 w% and 37498 ppm respectively. Besides, C-H bonds and hydrogen bonding at CH_2 were detected through Fourier Transform Infrared Spectroscopy (FTIR), and Nuclear Magnetic Resonance (NMR) tests.

5 CONCLUSION

5.1 Conclusion

Sulphate scale formation is a serious problem in industries such as oil and gas production, water transport, power generation and batch precipitation. It causes corrosion, equipment damage, formation damage and flow restriction which indirectly decreasing the production rate. The most common oilfield scales are calcium carbonate, barium sulphate, strontium sulphate, calcium sulphate and iron sulphide. However, calcium sulphate is often the predominant scale produced due to the formation water which often supersaturated with calcium ions.

Therefore, GLDA which is a type of chelating agent is proposed in this study in order to remove CaSO_4 scale. The objective of this study which is to study the physical properties of GLDA, to analyse the characteristics based on CHNS, ICPMS, FTIR and NMR and the dissolution of CaSO_4 in GLDA is achieved.

Through experiments, the optimum amount of CaSO_4 salt that can be dissolved in 10 mL GLDA at atmospheric pressure and room temperature is determined to be 0.145g. Based on the physical properties tests, CaSO_4 only affects the pH and density of GLDA after it is being mixed. However, it does not affect water content and the GLDA- CaSO_4 mixture does not separate after being tested with centrifugation process. Therefore, it shows that CaSO_4 has been dissolved in GLDA without any chemical reaction happens between GLDA solvent and CaSO_4 .

Besides, based on the characterization analysis, it can be concluded that the bonding formed are between carbon and hydrogen bonds (C-H bonds) and at one of the CH_3 molecules in the GLDA structure. In addition, GLDA also contains a high number of carbon atoms and a high sodium atoms number which are 17.69 w% and 37498 ppm respectively. Thus, based on the results obtained, it proves that CaSO_4 physically bonded with GLDA molecule.

5.2 Recommendations

In order to obtain a more accurate result, the use of standard analysis method such as X-Ray Diffraction (XRD) is necessary. XRD is a technique to characterise the crystalline materials. Since, GLDA contains inorganic component such as sodium ion. Thus, it can provide information on the structures, phases, preferred crystal orientations and other structural parameters (Source: <http://www.eag.com>). Besides, since the gravimetric method used in this experiment does not gives an accurate result. Therefore, a new method should be used in order to quantify the amount of undissolved salts.

REFERENCES

- AkzoNobel Functional Chemicals Chelates. 2011. Dissolvine GL Technical brochure. *AkzoNobel*.
http://www.coastsouthwest.com/wpcontent/uploads/2013/05/GL_technical_brochure.pdf (30 December 2014).
- Antony A., Low J.H., Gray S., Childress A.E., Le-Clech P., and Leslie G. 2011. Scale formation and control in high pressure membrane water treatment systems: A review. *Journal of Membrane Science*. **383**: 1-16.
- Azimi G. 2010. Evaluating the potential of scaling due to calcium compounds in hydrometallurgical processes.
- Bader, M.S.H. 2006. Sulfate scale problems in oil fields water injection operations. *Desalination* **201**:100–105.
- Boundless. 2014. Physical and Chemical Properties of Matter. <https://www.boundless.com/chemistry/textbooks/boundless-chemistry-textbook/introduction-to-chemistry-1/physical-and-chemical-properties-of-matter-28/physical-and-chemical-properties-of-matter-181-1817/> (4January 2015).
- Collins, A.G. 1975. *Geochemistry of Oil-Field Waters*, Elsevier, Amsterdam
- Dydo P.,and Turek J. 2003. Scaling analysis of nanofiltration system fed with saturated calcium sulfate solutions in the presence of carbonate ions. *Desalination*. **159**: 245-251.
- Engineer's Handbook. 2004. Engineering Materials. <http://engineershandbook.com/Materials/physical.htm> (4January 2015).
- Firas A.A., Hime G., Alvarez A., and Farajzadeh R. 2005. External filter cake erosion: mathematical model and experimental study. Paper SPE94635 presented at the 6th European formation damage SPE conference, Scheveningen, Netherland.

Hasson D., Drak A., and Semiat R. 2001. Inception of CaSO₄ scaling on RO membranes at various water recovery levels. *Desalination*. **139**: 73-81.

He. J., Arensman D., and Nasr-El-Din H.E. 2013. Effectiveness of Calcium Sulfate Scale Inhibitors In Spent Hydrochloric Acid/Seawater System. *Petroleum & Environmental Biotechnology*.**4**: 1-6.

Hoang T.A., Ang H.M., and Rohl A.L. 2007. Effects of temperature on the scaling of calcium sulphate in pipes. *Powder Technology*. **179**: 31-37.

Jones, F.O., Jr., and Pet, J. 1964. *Technol.* **441**.

Kolodynska D. 2011. The chelating agents of a new generation as an alternative to conventional chelators for heavy metal ions removal from different waste waters. *Desalination*.: 339-371.

Lee S., Kim J., and Lee C.H. 1999. Scale formation mechanism in various nanofiltration modules. *Journal of Membrane Science*. **163**: 63-74.

Moghadas, J., Steinhagen H. M., Jamialahmadi, M., and Sharif, A. 2004. Model study on the kinetics of oil field formation damage due to salt precipitation from injection. *Journal of Petroleum Science and Engineering*. **43**: 201–217.

PetroWiki. 2014. Scale problems in production. http://petrowiki.org/Scale_problems_in_production (27 December 2014).

PetroWiki. 2014. Waterflooding. SPE International. <http://petrowiki.org/Waterflooding> (27 December 2014).

Rabie A., Mahmoud M. A., and Din H. N. 2011. Reaction of GLDA with Calcite: Reaction Kinetics and Transport Study. *Society of Petroleum Engineers*.

Rhudy, J.S., Hardy, J.A., and Barthorpe, R.T. 1994. Scale control in the south brae field. *SPE Production and Facilities*. **9**: 127–131.

Said, M.E., Ramzi, M., and Moghny, T.A. 2009. Analysis of oilfield waters by ion chromatography to determine the composition of scale deposition. *Desalination*. **249**: 748-756.

Salman, M., Qabazard, H., and Moshfeghian, M. 2007. Water scaling case studies in Kuwaiti oil field. *Journal of Petroleum Science and Engineering*. **55**: 48-55.

Senthilmurugan, B., Ghosh, B., Kundu, S.S., Haroun, M., and Kameshwari, B. 2010. Maleic acid based scale inhibitors for calcium sulfate scale inhibition in high temperature application. *Journal of Petroleum Science and Engineering*. **75**: 189–195.

Silva, I.B., Neto, J.C.Q., and Petri, D.F.S. 2015. The effect of magnetic field on ion hydration and sulfate scale formation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. **465**: 175-183.

Tahmasebi H.A., Kharrat R., and Soltanieh M. 2010. Dimensionless correlation for the prediction of permeability reduction rate due to calcium sulphate scale deposition in carbonate grain packed column. *Journal of the Taiwan Institute of Chemical Engineers*. **41**: 268-278.

Wu Q., Cui Y., Li Q., and Sun J. 2015. Effective removal of heavy metals from industrial sludge with the aid of a biodegradable chelating ligand GLDA. *Journal of Hazardous Materials*. **283**: 748-754.

Yousef M. R., and Hussain K. F. 2015. Application and evaluation of novel acrylic based CaSO₄ inhibitors for pipes. *Desalination*. **355**: 33-44.

Zhang Q., Ren H., Wang W., Zhang J., and Zhang H. 2012. Molecular simulation of oligomer inhibitors for calcite scale. *Particuology*. **10**: 266-275.