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RESEARCH REPORT UMP GRANT
Laporan Prestasi Skim Geran UMP

Final	/	Progress	

Progress Period : ____________________ √ *Please tick*

PROJECT DETAILS *(Keterangan Projek)*

A	**Grant No**	UIC 170801
	Faculty/CoE	Faculty of Chemical & Natural Resources Engineering
	Project Title	Development of Glutamic Acid and Fluorine-Based Ionic Liquid For Solid Scale Dissolution
	Project Leader	Dr Fatmawati Adam
	Project Member	1. Prof Zulkafli Bin Hassan 2. Dr Norhayati Binti Abdullah 3. Dr Norida Binti Ridzuan

PROJECT ACHIEVEMENT *(Pencapaian Projek)*

B

ACHIEVEMENT PERCENTAGE				
Project progress according to milestones achieved up to this period	**0 - 25%**	**26 - 50%**	**51 - 75%**	**76 - 100%**
Percentage (please state %)				100%

EXPENDITURE *(Perbelanjaan)*

C

Budget Approved *Peruntukan diluluskan*	**Amount Spent** *Jumlah Perbelanjaan*	**Balance** *Baki*	**% of Amount Spent** *Peratusan Belanja*
RM 20 000	**RM 19 200.00**	**RM 800.00**	**96 %**

RESEARCH OUTPUT *(Output Penyelidikan)*

D

NO OF PUBLICATION

KPI FOR NO OF PUBLICATION

	ISI	Scopus	Index Proceedings	Others
KPI	-	-	-	
Achievement				

The contribution of funder (UMP, MOHE, MOSTI, Industry etc.) as the fund provider must be acknowledged at all times in all forms of publications. Please state the grant number (RDU/UIC) and grant name.

Number of articles/ manuscripts/books *(Please attach the First Page of Publication)*	**ISI**	**Scopus**
	1. 2.	1. 2.
Conference Proceeding *(Please attach the First*	**International**	**National**

Page of Publication)	1. 2.	1. 2.

HUMAN CAPITAL DEVELOPMENT

KPI FOR HUMAN CAPITAL DEVELOPMENT

	PhD Student	Master Student
KPI	**1**	
Achievement	**1**	

Human Capital Development	**Number**				**Others** (please specify)
	On-going		**Graduated**		
Citizen	Malaysian	Non Malaysian	Malaysian	Non Malaysian	
PhD Student	1				1 Research Assistance
Masters Student					
Undergraduate Student			2		
Total	1		2		

Name of Student: Muhamad Hadi Bin Sulaiman
ID Matric No: PKC16012
Faculty: FKKSA
Thesis title: Simulation of Solid Scale Dissolution and Synthesis of Ionic Liquid as Solid Scale Dissolver
Graduation Year: On-Going

Name of Student:
ID Matric No:
Faculty:
Thesis title:
Graduation Year:
*** enter for more space*

INTELECTUAL PROPERTIES

KPI FOR INTELECTUAL PROPERTIES

Patent, Copyright, Trademark,Industrial Design: ____________

Patent, Copyright, Trademark, Industrial Design ect	

OTHERS

KPI FOR OTHERS

Prototype, Technology,Collaborations etc: _____________

Prototype, Technology, Collaborations etc	**VanishIL**

ASSET *(Aset)*

E

Bil	**Peralatan** *(Equipment)*	**Model**	**No Daftar Aset** *(Asset Tagging No)*	**Amount** (RM)	**Lokasi** *(Location)*
1	Center 300 Thermometer, K Type, 1 Channel with TP-K01 Probe	Centre	-	508.00	FKKSA Lab
2	CENTER TPK-04, K-Type Piercing Probe -50~600degC , -58~1122degF	Center	-	282.00	FKKSA Lab

PRODUCT DESCRIPTION FOR UMP R&D DIRECTORY (SHORT & BRIEF) *Only for Final Report*

F

VanishIL is the new formulated solution for dissolution of solid scale in oil & gas well stimulation that targetting, barium sulphate ($BaSO_4$) as well as calcite. This scale dissolver utilised the combination of chelating agent to chelate common scales like carbonate and barium. It is suitable to be used for applications where using other mineral or organic acids is not desirable. Handling of VanishIL is safer compared to organic acid due to the stability of the product similar to water. This product will serve as preliminary blending for future blends that will incorporated newly developed dissolver.

PRODUCT PICTURE FOR UMP R&D DIRECTORY *Only for Final Report*

G

Figure 1: VanishIL solution produce have similar stability as water and colourless

SUMMARY OF RESEARCH FINDINGS (*Ringkasan Penemuan Projek Penyelidikan)*

H

This study involves characterisation of Scale 1 and Scale 2 obtained from Terengganu and Sarawak oilfield respectively. Scale 1 contains a high concentration of barite while Scale 2 contains a high concentration of silica. A trial using two commercial ionic liquid prove that IL containing fluorine can be used as solid scale dissolver. Dissolution of solid scale using raw material solution for synthesis shows that glutamate salt, monosodium glutamate (MSG) can dissolve more solid scale compared to L-glutamic acid thus MSG was chosen to synthesise the glutamic acid based ionic liquid. The synthesis produced monosodium glutamate hydrochloric acid that can dissolve only 8% of calcite and less than 1% barite. Monosodium glutamate hydro fluoroboric performed better in dissolution, dissolving 6.9% calcite and 7.7% barite. Two

	chelating agents, A and B were evaluated for the dissolution of calcite and barite at several different concentration. Chelating agent B is best for the dissolution of barite at concentration 40g/L in alkaline condition. It can be concluded that barite solid scale can be dissolved in alkaline condition. Chelating Agent B was blended with buffer and synergist and produced preliminary blending product named VanishIL. Dissolution study shows VanishIL can dissolve 9.5g/L of barite and 7.83 g/L of calcite at temperature 60 °C in 24 hours' time. Increasing the temperature to 80 °C improved the dissolution to 12.41g/L of barite and 11.94 g/L of Scale 1. Further analysis and characterisation are still needed for VanishIL prototypes such as viscosity and corrosivity to evaluate its viability to be used in well stimulation.
PROBLEMS / CONSTRAINTS IF ANY *(Masalah/ Kekangan sekiranya ada)*	
I	The VanishIL need to be evaluated at high-temperature high-pressure condition however the availability of equipment to conduct such an experiment is unavailable.
Date : *Tarikh*	**Project Leader's Signature:** *Tandatangan Ketua Projek*
COMMENTS, IF ANY/ ENDORSEMENT BY FACULTY *(Komen, sekiranya ada / Pengesahan oleh Fakulti)*	
J	**Recommend / Not Recommend / KIV / Need Ammendment** .... **Name:** *Nama:* **Signature:** *Tandatangan:* **Date:** *Tarikh:* ** Dean/TDR/Director/Deputy Director
COMMENTS, IF ANY/ ENDORSEMENT BY RMC PNI *(Komen, sekiranya ada / Pengesahan oleh RMC PNI)*	

K	**Recommend / Not Recommend / KIV / Need Ammendment** ……… ……… ……… **Name:** *Nama:* **Date:** *Tarikh:*	**Signature:** *Tandatangan:*

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SV PETROLEUM

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SETEGAP VENTURES PETROLEUM

FINAL REPORT

UIC 170801

DEVELOPMENT OF GLUTAMIC AND FLUORINE BASED IONIC LIQUID

PROF. MADYA DR. FATMAWATI BINTI ADAM

Fakulti Kejuruteraan Kimia & Sumber Asli
Universiti Malaysia Pahang

2018

SULIT

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Abstract

This report presents the study of amino acid-based ionic liquid as scale dissolver in well stimulation as well as the blending formulation of solid scale dissolver. Scales have been a major problem in the oil and gas industries. Problems with scales cost the industries millions of dollars in damage and loss of production. Scales usually occur at the wellbore, oil pipelines, and other production facilities. Scales need to be controlled since the effects of the production lost and cost management cost is massive. Precipitation of scales contributes to equipment wear, corrosion and flow restriction which then lead to decreasing in oil and gas production. The aim of this study is to synthesise glutamic acid based ionic liquid incorporated with fluorine as an alternative scale inhibitor and control in well stimulation. The targeted scales are Calcite ($CaCO_3$) and Barite ($BaSO_4$). The second objective is to evaluate the ionic liquid for dissolution test of solid scale and finally to develop a preliminary blending formulation of solid scale dissolver targeting barite scale. In this study, two commercial ionic liquids were used to evaluate the potential of ionic liquid in solid scale dissolution. New amino acid ionic liquid (AAIL) based from glutamic was synthesized and evaluated to determine its ability as a scale dissolver. The dissolution of solid scales was determined by using dissolution test utilizing the gravimetric method and elemental analysis using inductively coupled plasma optical emission spectrometry (ICP-OES).

ABSTRAK

Laporan ini membentangkan kajian cecair ionik berasaskan asid amino sebagai pelarut kerak pepejal dalam stimulasi telaga minyak dan gas serta formulasi bahan untuk pelarut kerak pepejal. Kerak pepejal dalam industri minyak dan gas menyebabkan kehilangan pengeluaran serta kerosakan yang menelan belanja jutaan ringgit. Oleh itu, ianya harus dikawal bagi mengelakkan kerugian yang lebih besar. Pemendakan kerak pepejal boleh menyebakan kehausan peralatan, pengakisan dan sekatan aliran yang menyebabakn kekurangan penghasilan mingay dan gas. Tujuan kajian ini adalah untuk mensistesis cecair ionik berasaskan glutamat yang digabungkan denganh florin sebagai perencat dan pengawal pertumbuhan kerak pepejal. Jenis kerak pepejal yang disasarkan adalah kalsit ($CaCO_3$) dan barit ($BaSO_4$). Objektif kedua adalah untuk menilai cecair ionik dalam pelarutan kerak pepejal dan akhirnya untuk membangunkan formulasi awal pelarut kerak pepejal yang menyasarkan skala jenis barit. Dalam kajian ini, dua cecair ionik yang dikomersialkan digunakan untuk menilai potensi cecair ionik dalam pelarutan kerak pepejal. Cecair ionik asid amino (AAIL) yang berasaskan glutamat telah disintesis dan dinilai untuk menentukan keupayaannya sebagai pelarut nkerak pepejal. Pelarutan kerak pepejal ditentukan dengan menggunakan ujian pelarutan yang menggunakan kaedah gravimetrik dan analisis unsur menggunakan plasma berganding secara aruhan spektrometri pancaran optik (ICP-OES).

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1.0 INTRODUCTION

Aggregation of deposit that cake the production well perforation, casing and tubing as well as valve and other downhole completion equipment will lead to scale formation that will completely block the flow of the liquid stream. Over time, the deposition or crystallisation will grow to form a thick lining on the tubular surface, thereby reduce the flow and eventually completely block it (Crabtree et al., 1999). One of the recorded scale problems is in the North Sea, Miller field where scale causes the production fall from 4770 m^3/d to zero in just 24 hours. Such case shows how severe scale problem can affect oil and gas production (Brown, 1998).

The main source of scale is, without doubt, the reservoir itself. However, the scale will only form if water is produced or injected into the well. Some minerals are readily dissolved in the produced water, full of ions such as Ca^{2+}, Mg^{2+}, Ba^{2+} and Sr^{2+}. Alteration of reservoir formation such as improving permeability will increase the concentration of dissolved minerals until it reaches its saturation limit (Nassivera & Essel, 1979; Read & Ringen, 1982; Vetter, Kandarpa, & Harouaka, 1982). Mechanism and factors contributing to scale formation are various, among others are changed in temperature and pressure (Mackay, 2007; Moghadasi, Müller-Steinhagen, Jamialahmadi, & Sharif, 2007). When changes on this fluid occur either by production or stimulation, such as solubility of one or more components exceeded the saturation limit, the scale will start to form (Crabtree et al., 1999).

Currently, chemical treatment methods to dissolve scale available are acidizing and chelating agent. Chelating agent function to chelate the dissolve metal ions to avoid precipitation. Due to this capability, the chelating agent may be used as an inhibitor by chelating the metal ions in the produced water to avoid precipitation (Frenier, Wilson, Crump, & Jones, 2000; Mahmoud & Abdelgawad, 2015). Even though acid is effective, it will damage the tubular and pipeline wall due to corrosion and reprecipitation of scale might occur (Smith & Hendrickson, 1965). Often, the acid will be mixed with a chelating agent to give optimum result. Currently, the only chemical treatment in well enhancement for dissolving sandstone and silica scale is a hydrofluoric acid-hydrochloric acid matrix or mud acid (Di Lullo & Rae, 1996; Smith & Hendrickson, 1965).

This study proposed ionic liquid as one of the alternative chemical solvents for scale dissolution. The simplest way to define ionic liquid is a molten salt or salt in liquid form. It refers to liquid composed of only cations and anions. However, modern chemistry restricts ionic liquid (IL) definition to salt that melts or in liquid form at a temperature below 100ºC. Salt that exists in the liquid phase at room temperature thus called room temperature ionic liquid (RTIL) (Benzagouta, AlNashef, Karnanda, & Al-Khidir, 2013; Brennecke & Maginn, 2004; Castner & Wishart, 2010; Coleman & Gathergood, 2010).

Currently, there is no thorough study on the potential of ionic liquid as solid scale dissolution. Current available study involving the dissolution of the metal ion by the ionic liquid for mining operation (Hoogerstraete, Onghena, & Binnemans, 2013; Vander Hoogerstraete & Binnemans, 2014) and water treatment (Fischer et al., 2011). Study of ionic liquid related to oil and gas is for enhanced oil recovery by dissolution of extra heavy crude oil (Bin-Dahbag et al., 2013; Lago, Francisco, Arce, & Soto, 2013). This study proposed the use of glutamic acid as a base to develop the ionic liquid. As the natural source of the carboxylic group. The carboxylic group available will capture the metal ion and dissolve carbonate and barite sale. Fluorine ion in the ionic liquid is expected to attack difficult solid scales such as silicon dioxide and another scale.

The main objectives of this research are:

1) To synthesise glutamic acid based ionic liquid incorporated with fluorine as an alternative scale inhibitor and control in well stimulation. The targeted scales are Calcite ($CaCO3$) and Barite ($BaSO4$).

2) To evaluate the ionic liquid for dissolution test of solid scale. The scale should undergo characterisation using XRD/XRF and SEM prior to a dissolution test. Ionic liquid after dissolution test will be tested using ICPMS to determine the concentration of solid scale dissolved.

3) To develop a preliminary blending formulation of solid scale dissolver targeting barite solid scale.

Development of ionic liquid for scale dissolution will introduce an alternative solution for scale treatment. Since ionic liquid for scale dissolution is new, this study will add data and knowledge to improve understanding of the potential of ionic liquids for this application. Some publication only focuses on the synthesis and properties of ionic liquid without a proper study on the potential application of the developed ionic liquid. The ionic liquid can be design to fit the desired application and properties. In an extreme environment of oil and plant, using volatile and hazardous chemical can be fatal. Ionic liquid has negligible vapour pressure thus making it safer to operate.

2.0 Literature Review

2.1 Ionic Liquid

The ionic liquid is a molten salt or salt in liquid form. It refers to liquid composed of only cations and anions, not to be confused with salt solutions. It may include salt heated to its melting point until it becomes completely liquid. However, in some context, the terms have been exclusively used to salt that melts or in liquid form at a temperature below 100ºC. Salt that exists in the liquid phase at room temperature thus called room-temperature ionic liquid (RTIL) (Benzagouta et al., 2013; Brennecke & Maginn, 2004; Castner & Wishart, 2010; Coleman & Gathergood, 2010; Earle & Seddon, 2000; Visser et al., 2001). Ionic liquids (ILs) has received much attention in green chemistry as an environmentally friendly solvent for many application albeit not all ILs can be considered green. The unique properties of ILs such as consist of only cation and anion, make it part of the research towards "green" chemistry. However, the vast varieties of ionic liquid reported in the literature and lack of guidance on this new solvent create a barrier for industries application. Different shorthand notation used to describe ILs also adds to the confusing information (Wilkes, 2004).

ILs has been generally described as having a negligible vapour pressure, high thermal conductivity and stability, non-flammable, high density and high heat capacity (Carda-Broch, Berthod, & Armstrong, 2003; Domańska, 2005; Wei et al., 2010). Even so, as there are thousands of ionic liquid reported, produced and currently used as well as potentially synthesised in the future, it is ineffective to just generally describe ILs properties as it cannot provide enough data on how it can be used. However, there are literature summarised properties of ionic liquid from various source. Wilkes (2004) summarised various ILs properties relevant to its usage as a solvent for the catalyst. Even though the summary specified for ILs as a solvent for the catalyst, it can still be a good reference for ionic liquid properties considering the lack of available comprehensive data on ILs properties. Wilkes summarised all important properties usually associated with ILs including density, viscosity, melting points, glass transition, and thermal stability (Wilkes, 2004).

Similarly, Zhang et al. (2006) provide a collection of ILs physical properties cited from various literature. The collection includes 588 available ILs involving 267 kinds of cation and 55 kinds of anion. Zhang et al. presenting the data in tables including several physical properties such as phase transitions temperature, density, viscosity, and surface tension (Zhang, Sun, He, Lu, & Zhang, 2006) Figure 2.2 below show the example of an ionic liquid, ethylammoniumnitrate. Ethylammonium nitrate is believed as the earliest reported example of room temperature ionic liquid (Koel, 2008). Table 2.2 shows some ionic liquid and its potential application.

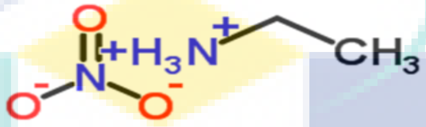


Figure 1: Molecular structure of the first reported an example of room temperature ionic liquid, ethyl ammonium nitrates. Source: Ethylammonium nitrate (ChemSpider, 2017a).

Table 1: Ionic liquid and its potential application.

Ionic Liquid	**Potential Application**	**References**
1-butyl-3-methylimidazolium hexafluorophosphate [BMIM]	Application of ionic liquid polymeric microsphere in oil field scale control process ($CaCO_3$).	(Lakshmi, Senthilmurugan, Drioli, & Figoli, 2013)
Betainium bis-(trifluoromethylsulfonyl) imide, [Hbet][Tf2N]	Homogeneous liquid-liquid extraction of metal ions (Cu^{2+}) with a functionalized ionic liquid	(Hoogerstraete, Onghena, & Binnemans, 2013)
Trihexyl (tetradecyl) phosphonium Chloride	Enhanced Oil Recovery with the Ionic Liquid	(Lago, Francisco, Arce, & Soto, 2013)
1-Butyl-3-methylimidazolium	Anodic dissolution of metals in ionic liquids for	(Abbott, Frisch, Hartley, Karim, &

chloride, [C4mim][Cl]	electroplating application.	Ryder, 2015)

2.2 Amino Acid-Based Ionic Liquid

The twenty essential amino acids are grouped into different categories depending on their chemical structure and properties (Baynes and Dominiczak, 2010). They can be grouped into one having acidic or basic side chains at neutral pH conditions. This group consist of five of the essential amino acids namely, glutamic acid, aspartic acid (acidic) and arginine, histidine and lysine (basic). These acids are utilized in functionalizing some of the ionic liquids (ILs). These ILs are termed as amino acid-based ionic liquids (AAILs) (Mjalli, 2015). The discovery of amino acid-based ionic liquids (AAILs) has generated widespread interest due to their distinctive properties such as unique acid-base characteristics, hydrophobicity, hydrogen bonding ability and strong hydration effects (Dagade, 2014). Several studies had been carried out to determine the ability of the AAILs to dissolve cellulose and lignocelluloses biomass (Swatloski et al., 2002).

The previous study had used 1-ethyl-3-methylimidazolium glycinate (EmimGly) as a liquid solvent for dissolving the preconditioned bamboo biomass (Muhammad et al., 2011). During the dissolution process using EmimGly, the anionic part played an essential role. The anion part of the ionic liquid disrupted the hydrogen bonding among the biomass components (Remsing et al., 2008) whereas the cationic part of the ionic liquid interacted with biomass through the covalent bond (Ebner et al., 2008). In addition, during the process, the IL rapidly broke the intermolecular and intramolecular hydrogen bonds within the bamboo biomass structure and destroyed the original crystalline structure. This had been proven from the change of fibrous form of the bamboo biomass structure into a more homogeneous macrostructure by the characterization of the sample using Scanning Electron Microscopy (SEM). The study proved that the dissolution process of the bamboo biomass in EmimGly ionic liquid (Muhammad, 2011).

2.3 Solid Scales

Scale deposition is one of the production issues in the oil and gas industry which results from the waterflooding process (Time, 2011). In this process, scale deposits may occur due to the water injection to the producing well and also after injection operation in the injector wellbore, near the injection well bottom hole, in the reservoir between the injector and producer, at the skin of producer well, in the producer wellbore, oil well casing, oil pipelines and other production facilities. (Liu et al., 2012; Dickson et al., 2011). Scale deposits are made up of organic, inorganic, and crystal water. (Jiecheng et al., 2011). They start to form when the solubility limit for one or more components is exceeded (Jinling et al., 2009).

The most common oilfield scales are calcium sulphate, $CaSO_4$ (anhydrite, gypsum), barium sulphate, BaSO4 (barite), strontium sulphate, $SrSO_4$ (celestite), calcium carbonate, CaCO3 (calcite), sodium chloride, NaCl (halite), iron sulphides, FeS and silicates, SiO_2 (Kelland, 2009; Bin Merdah, 2008). The impacts of scales can be dramatic and immediate. Scale precipitation can reduce oil production capacity to zero and the cost of the treatment can be massive. Furthermore, scale deposition restricts the flow of fluid through the formation of a thick layer in the wellbore tubular which reduces the diameter of the production tubing and chokes the production from the reservoir. This will result in increasing of pressure drop and thus decreasing in the well productivity. Formation damage in the reservoir, flow loss of blockage on flow lines and equipment, energy leak, accelerate corrosion, and severe accidents are also caused by scale precipitation (El-Said et al., 2009).

2.3.1 Calcium Carbonate Solid Scale

Calcium carbonate scale can be considered as one of the most common scales in oil and gas industries especially in well tubular (O. J. Vetter & Farone, 1987). The saturated calcium carbonate aqueous solution in the well, when mixed with incompatible water from well injection, can cause crystallisation of carbonate and start forming scale (H. A. Nasr-El-Din, Al-Saiari, Al-Ruwaily, & Al-Gamber, 2006). The loss of CO2 in the formation water due to drop of pressure remove carbonate acid that keeps the calcite dissolved (Ramstad, Tydal, Askvik, & Fotland, 2005; O. J. Vetter et al., 1982). This lead to precipitation of calcite from salt-forming ions; in this case calcium ions. At high temperature, calcium carbonate solubility will significantly reduce (Weyl, 1959). This will likely cause the increase in calcite deposit at high temperature.

Formation of calcite scale likely occurs follows chemical equation below:

$Ca^{+2} + CO_3^{-2} \rightarrow CaCO_3$ 2.1

Commonly hydrochloric acid at 5-15% concentration is used to dissolve calcite in well under most conditions (Connell, 1983). The dissolution mechanism represented by following chemical equation:

$CaCO_3 + 2HCl \rightarrow H_2O + CO_2 + CaCl_2$ 2.2

2.3.2 Barium Sulphate Solid Scale

Barium sulphate is the most insoluble scale that can be precipitated from oilfield waters. It forms a hard scale which is extremely difficult to remove (O. J. G. Vetter, 1975). The solubility of barium sulphate goes up with increasing temperature, pressure and salt content of the brine (Crabtree et al., 1999; O. J. Vetter et al., 1982). Barium sulphate scale is among the toughest scales to remove, whether mechanically or chemically (Crabtree et al., 1999; Dunn & Yen, 1999). However, chemicals based on EDTA are now available which have had some success in dissolving barium sulphate (Dunn & Yen, 1999). Equation 2.3 shows the chemical equation of barium sulphate formation(A. B. Merdhah & Yassin, 2007). Most of barium ions and sulphate originated from the formation water itself. Mixing of incompatible brine solution often causes the deposition of $BaSO_4$ (Crabtree et al., 1999).

$Ba^{2+} + SO4^{2+} \rightarrow BaSO_4$ 2.3

2.4 Dissolution of Solid Scales

Before dealing with scale dissolution, it is essential to understand the factors of scale deposition. There are there factors that can be identified which are supersaturation, nucleation, and precipitation. Out of the three factors, supersaturation is the primary cause of scale deposition. It occurs when a solution contains dissolved materials at higher concentrations than its equilibrium concentration. A solution can be supersaturated when there are changes in conditions such as temperature, pressure, and pH. Next factor is nucleation. It is initial information of precipitation and usually caused by the presence of foreign crystalline material on sites such as the wall of pipes, vessels, welds or downhole formation rock. Finally, precipitation can then occur to produce a scale deposit (Clemmit et al., 1985). There are several factors that must be considered to study the dissolution of solid scales. Below are the factors that affect scale dissolution (Clemmit et al., 1985):

a) pH:

The lower the pH, the less likely is scale precipitation to occur and the rate of dissolution increases (Moghadasi et al., 2007).

b) The concentration of scale dissolver:

The rate of scale dissolution increases when the concentration of scale dissolver increases (Clemmit et al., 1985).

c) Effect of stoichiometry

Changes in the stoichiometric ratio of scale and scale dissolver can increase the rate of scale dissolution (Clemmit et al., 1985).

d) Effect of temperature

As the temperature increases, the more likely the scale precipitation to occur as the scales become less soluble at a higher temperature. Hence, the rate of dissolution decreases (Moghadasi et al., 2007).

e) Effect of agitation

Stirring of the scale dissolver can dramatically increase the quantity of scales dissolved (Clemmit et al., 1985).

Dissolution mechanism of solid scales can be divided into three types which are the acid transport by diffusion and advection to the solid surface, the chemical reaction at the surface, and the product transport away from the surface (Martinez et al., 2004). Since amino acid-based ionic liquid (AAIL) will be used in this study, the rate of dissolution will be influenced predominantly due to the reaction between the AAIL and scales. In this case, the rate of dissolution is enhanced at low pH as a result of the combined influence of hydrogen ion attack. As the number of hydrogen ions associated with the AAIL increases, the rate of scale dissolution will also increase (Moghadasi et al., 2007). This is because the anionic part of the AAIL has high hydrogen bond basicity which can be helpful in making hydrogen bonding with scale during the dissolution process (Muhammad, 2011).

3.0 Methodology

3.1 Sample Characterization Using SEM

In this experiment, Scanning Electron Microscopy (SEM) was used to study and analyse the surface morphology of real solid scale obtained from Setegap Ventures Petroleum Sdn. Bhd. SEM imaged the surface of each sample by scanning it with electron beams. The solid scale morphology was studied before and after dissolution using two commercialised ionic liquid. The samples were dried in the oven prior to analysis.

3.2 Dissolution Test

To evaluate the dissolution capability, the dissolution test was conducted. In this test 1g-2g of the solid scale was placed in the centrifuge tube and 40mL dissolver solution was added in the centrifuge tubes were then put in an oven at a temperature of 60 ºC for 24 hours. After that, the solution in each centrifuge tube was filtered and the remaining scale was weighted to determine the final mass after drying for at least 24 hours. The filtrate samples were transferred into different vials for samples characterization using Inductively Coupled Plasma Optical Emission Spectroscopy.

3.3 Basic Experimental Set-up for Synthesis

Basic experimental set up was used in this study consisting of reaction flask submerge in heating oil place on a hot plate. The reaction flask having two necks; first for connection with a condenser and second for reactant inlet or temperature measurement. When not in use, the second side neck will be a plug with a hollow glass stopper. The condenser was used to allow reflux. The condenser is necessary for providing continuous heat to the reaction without causing the massive loose of the reactant through evaporation. Commonly, room temperature water from laboratory tab water will use for cooling in the condenser. However, when temperature lower than room temperature is needed, the chiller system will be used. Figure 12 shows the basic experimental set-up for the synthesis of the ionic liquid.

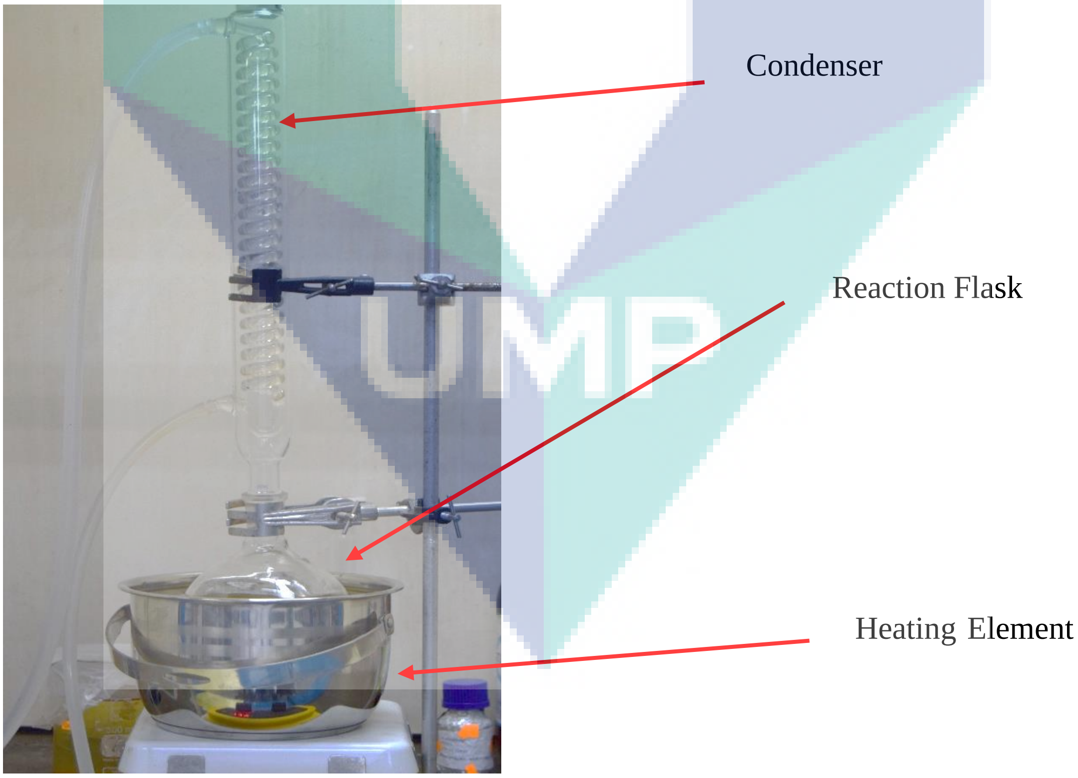


Figure 2: Experimental set-up for synthesis ionic liquid.

3.4 Simple Acidification

Simple acidification involves the reaction of a strong acid with an amino acid. The acid is targeted to attack the amine group in the amino acid forming cation on the nitrogen and anion from the acid (Cl^- or $BF4^-$). This route will produce a new type of salt however the product is usually solid as strong hydrogen bond in amino acid. Figure 14 shows two simple acidification of monosodium glutamate using HCl and HBF_4. The product then filtered and dried for analysis using FTIR.

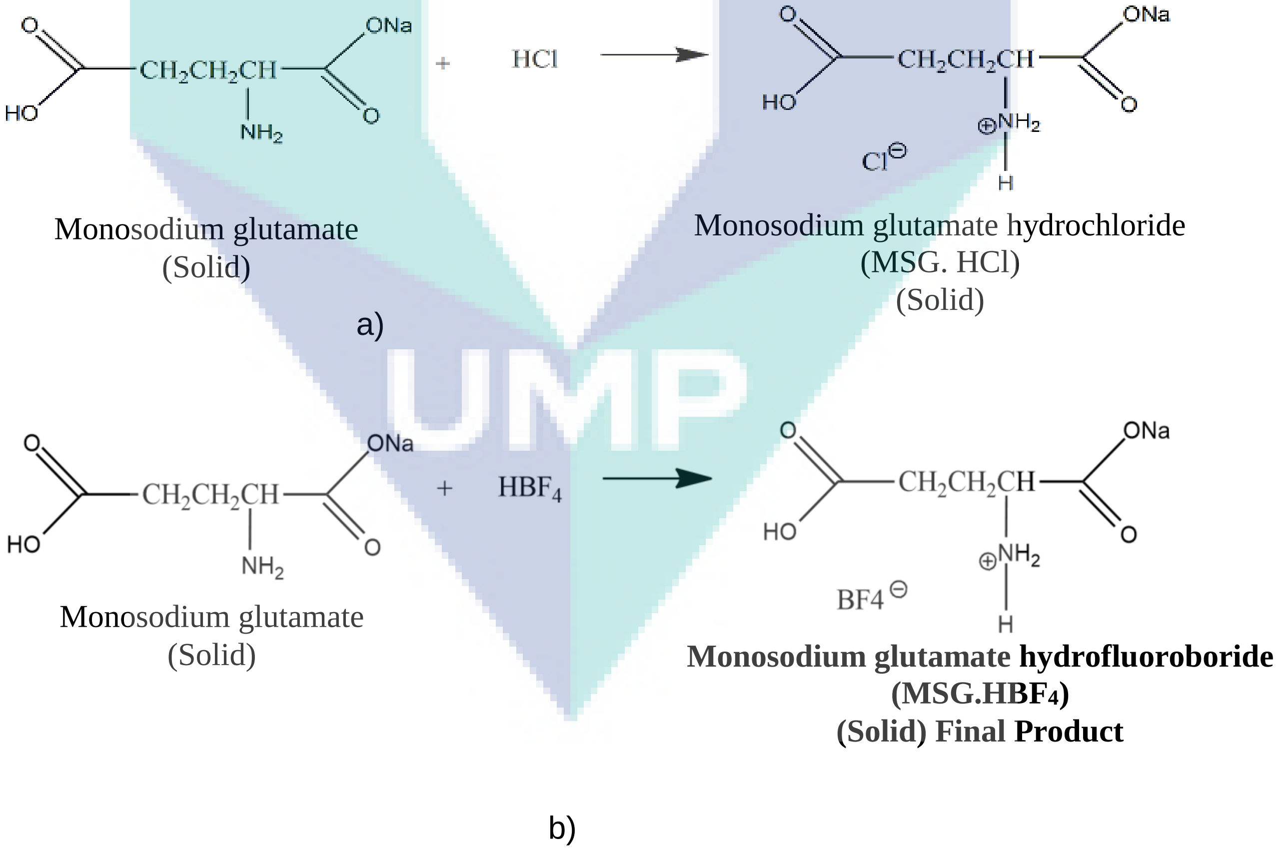


Figure 3: Simple acidification of monosodium glutamate using a) hydrochloric acid and b) hydrofluoroboric acid.

3.5 Alkylation and Metathesis.

One of the methods proposed at the earlier stage of this project is the alkylation and metathesis. The function of alkylation is to expand the chain of the amino acid thus reducing the hydrogen bond at the final product so it will remain liquid. Metathesis is a reaction in which two compounds exchange ions. This step is necessary when the existing anion from alkylation need to be replaced with a targeted anion. Figure 13 shows the synthesis route using alkylation (stage 1) and metathesis (stage 2).

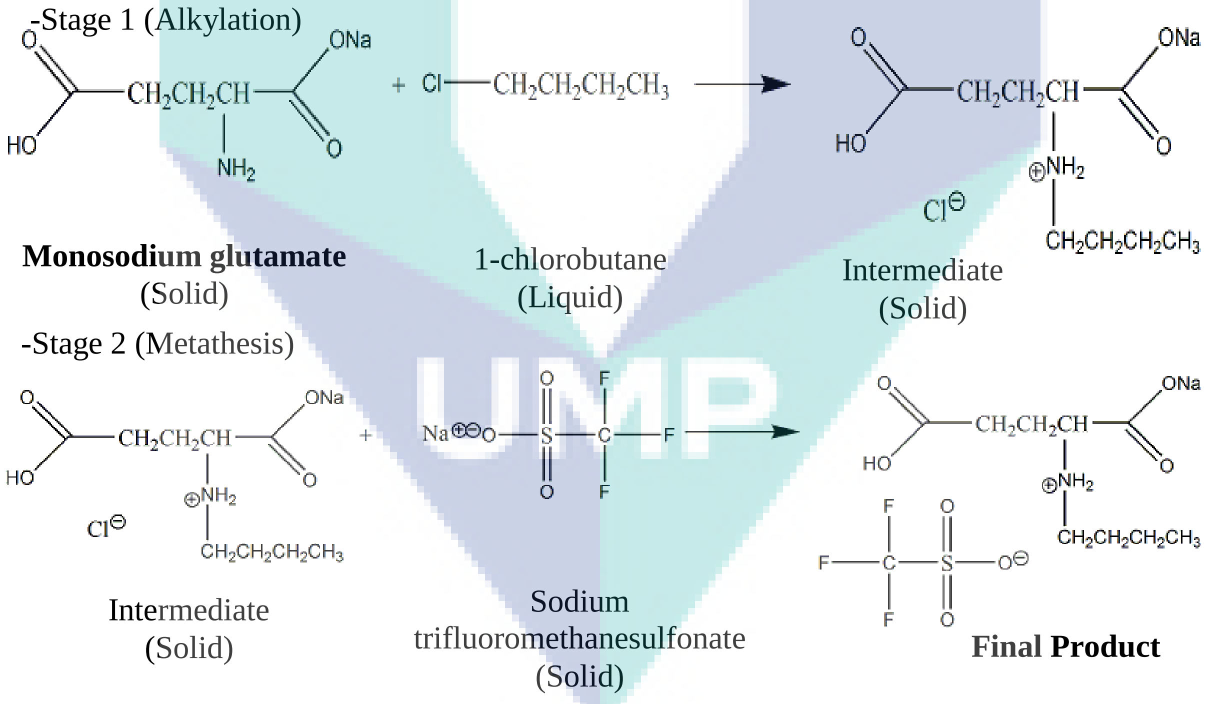


Figure 4: Synthesis route involve alkylation of monosodium glutamate followed by metathesis using sodium trifluoro-methane sulfonate.

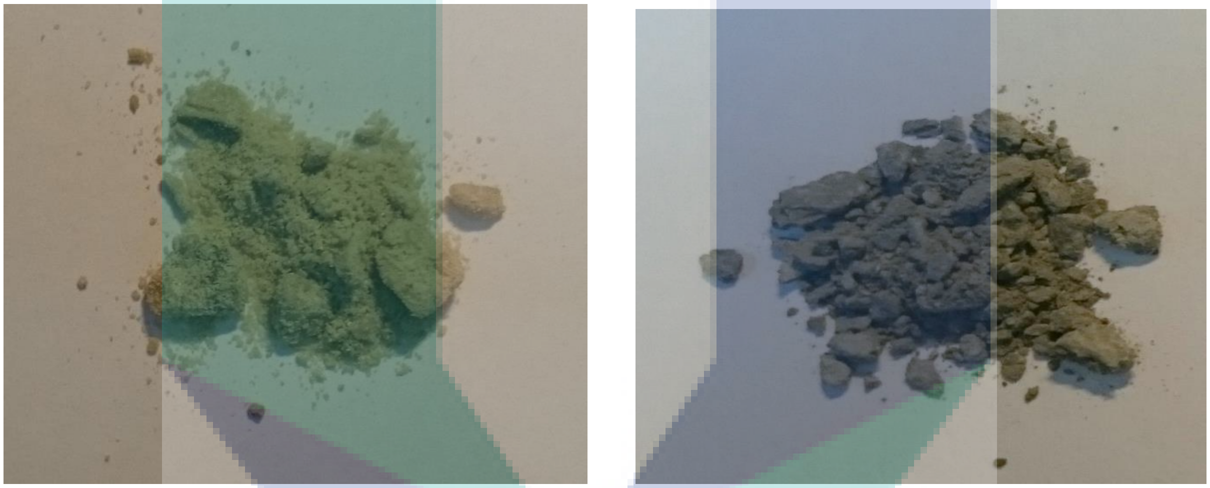
3.6 Blending Formulation

In preparation of preliminary blending, two chelating agents was chosen namely chelating agent A and B. Both of this chelating agents are an amino poly-carboxylic compound with different numbers of carboxylic group present. The effectiveness of these two chelating agents in dissolving solid scale was evaluated at acidic at pH <3 and alkaline at pH> 10. The concentration of chelating agents were varied at 20g/L, 40g/L and 60g/L. The best concentration of chelating agent was selected focusing on barite scale for further addition of synergist and the final blending will be called VanishIL.

4.0 Result and Discussion

4..1 Surface morphology of Solid Scale

Two solid scales have been obtained from Setegap Ventures Petroleum originated from Terengganu oilfield and Sarawak oilfield later referred to as SCALE 1 and SCALE 2 respectively. Both scales have been crushed and analysed under a Scanning Electron Microscope to observe the surface morphology of the scale. Figure 5 below shows the image of a) SCALE 1 and b) SCALE 2. SCALE 1 have yellowish colour while SCALE 2 has dark greyish colour.



(a) **(b)**

Figure 5: a) SCALE 1 solid scale and b) SCALE 2 solid scale.

Table 2 and Table 3 below shows the composition of SCALE 1 and SCALE 2 solid scale respectively. Based on the composition, SCALE 1 solid scale contains a high amount of barium (Ba) at 53.62% while SCALE 2 contains a high number of silica (Si) at 24.77%. Both solid scales are mixed type scale however SCALE 1 are mainly barium type scale such as barium sulphate ($BaSO_4$), and celestite ($SrSO_4$). The composition of SCALE 2 is more varies with quartz (SiO_2) as a major component bonded with other metals such as aluminium and magnesium. The composition will reflect the surface morphology of the scale examined using a scanning electron microscope.

Table 2: Composition of SCALE 1 solid scale

Elements	Percentage (%)	Possible Compounds
Ba	53.62	Barium Sulphate, celestite
O	26.03	
S	12.50	
Sr	1.82	

Table 3: Composition of SCALE 2 solid scale

Elements	Percentage (%)	Possible Compounds
Si	24.77	Quartz, Muscovite, Calcite, Lepidolite Kaolinite
O	42.8	
Al	10.94	
Fe	2.97	
K	2.97	
Ca	2.58	
Mg	1.03	

Figure 6 shows the SEM image of SCALE 1 solid scale at different magnification. Based on the XRD and XRF analysis, SCALE 1 contains a high amount of barium, probably barium lead sulphate and barium sulphate. Barium sulphate can form a crystalline structure that will eventually growth becoming solid scale. SEM image at 1000x magnification of SCALE 1 solid scale shows it having crystalline structure probably form from the main component present, barium sulphate. At some point, this structure can be very strong and difficult to break. There is various way crystal can growth. One of the growth called Terrace Ledge Kink model (TLK), which is also referred to as the Terrace Step Kink model (TSK), describes the thermodynamics of crystal surface formation and transformation, as well as the energetics of surface defect formation. This result in terrace-like surface of the crystal. However, because barium sulphate is not the only component presence, the structure contains flaws, microcrack and porous space allowing absorption of chemical solvent and speed up dissolution.

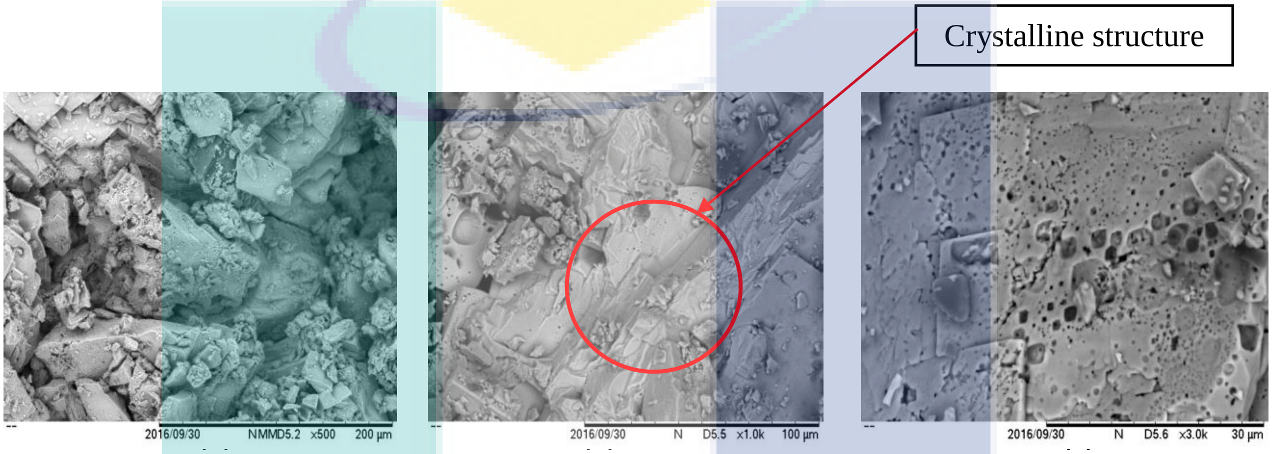
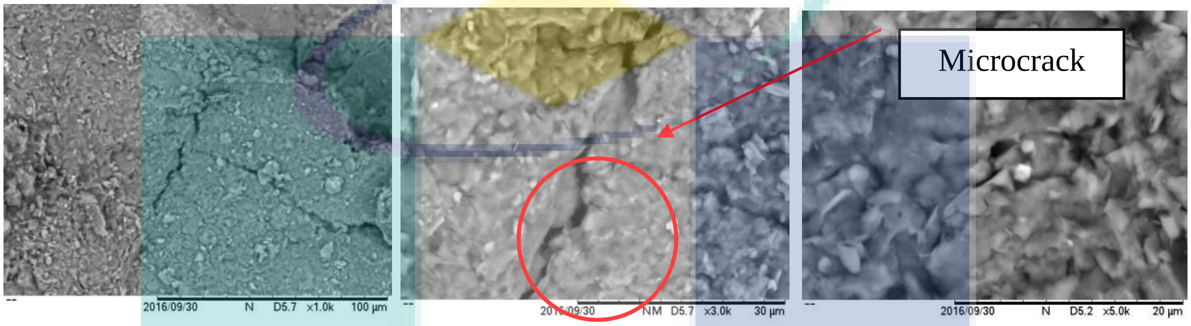


Figure 6: SEM image of SCALE 1 solid scale at a)500x magnification, b) 1000x magnification and c) 3000x magnification.

Figure 7 shows the SEM image of SCALE 2 solid scale at various magnification. Based on the XRD and XRF analysis SCALE 2 scale contains a high amount of silica and aluminium. The first assumption, the scale structure will have similarities with quartz or amorphous silicon dioxide. However, SEM image shows a slightly rough surface with microcrack without typical crystal structure expected like quartz. Silica or sand particles itself do not easily dissolve, however, dissolve silica if present, usually in alkaline condition, can form silicate scale (Arensdorf, Hoster, Mcdougall, & Yuan, 2010; Arensdorf, Kerr, Miner, Incorporated, & Ellis-toddington, 2011; Sazali, Sorbie, & Boak, 2015).

It is still poorly understood on the mechanism of this silicate scale formation. The mechanism likely starts with the dissolution of silica (SiO_2) during matrix acidizing or alkaline flood. When this dissolved silica meets neutral pH water, it will start to form colloidal silica. The presence of metals such as magnesium will bond this colloidal silica and from the amorphous structure eventually grow to become silicate scale (Arensdorf et al., 2010). Silicate scale is very difficult to remove from oil wells and traditionally has required mechanical removal.

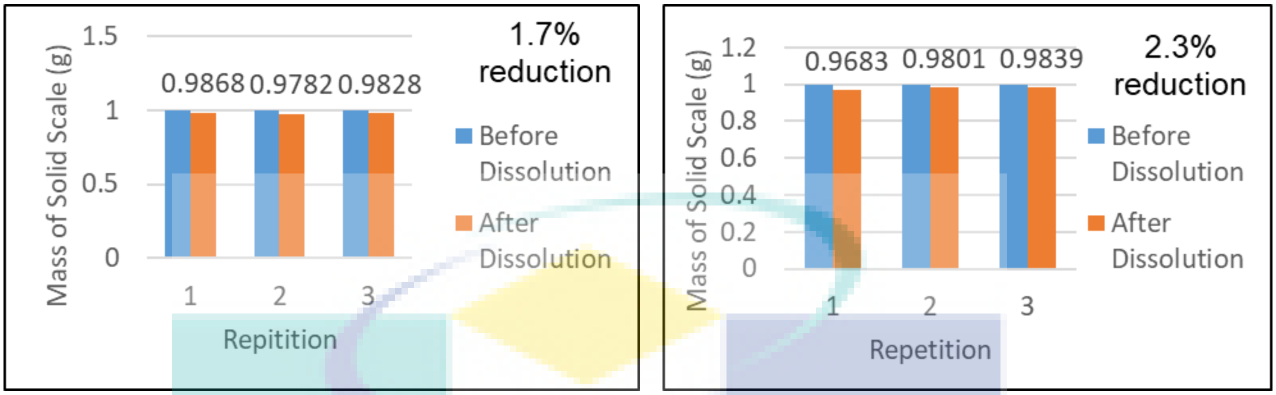


(a) **(b)** **(c)**

Figure 7: SEM image of SCALE 2 solid scale at a) 500x magnification, b) 1000x magnification and c) 3000x magnification.

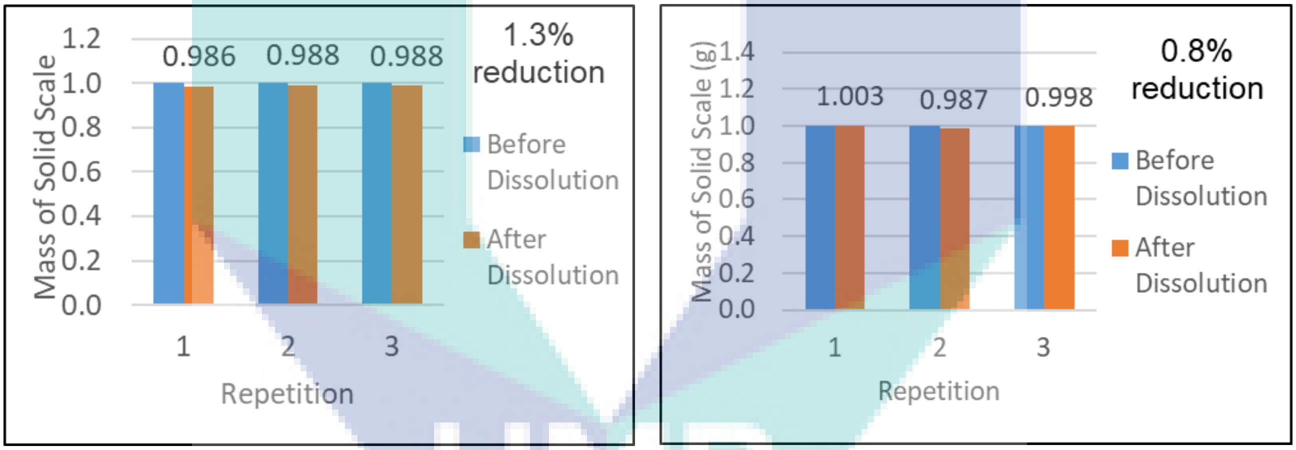
4.2 Dissolution of Solid Scale using Commercial Ionic Liquid

Part of this study involves the dissolution of solid scale using commercialised ionic liquid. This dissolution is to investigate the potential of the ionic liquid is dissolving solid scale. Figure 8 shows the dissolution result of SCALE 2 scale and SCALE 1 scale in 1-butyl-3-methylimidazolium hexafluorophosphate aqueous solution in acetone (4% v/v). The dissolution result shows a small reduction in mass after dissolution at only 2.3% and 1.7 % reduction for SCALE 2 scale and SCALE 1 scale respectively. A similar result can be observed for tetrabutylammonium nonafluoro-butane sulfonate in Figure 11. Only 0.8% SCALE 2 scale was dissolve and 1.3% for SCALE 1 scale.



(a) (b)

Figure 8: Dissolution results solid scale a) SCALE 1 and b) SCALE 2 in 1-Butyl-3-Methylimidazolium hexafluorophosphate (4% in Acetone)



(a) (b)

Figure 9: Dissolution result solid scale a) SCALE 1 and b) SCALE 2 in Tetrabutyl ammonium nonafluoro-butanesulfonate (4% in Acetone)

The ionic liquid solvent used in dissolution was then tested using ICPMS to determine the concentration of scale ion that might exist. It should be noted that SCALE 2 scale is silica based scale while SCALE 1 scale is barium based scale. Therefore only reading for silica and barium was provided for SCALE 2 and SCALE 1 respectively. Table 1 shows the ICPMS result of the ionic liquid solution after the dissolution. Even though percentage dissolution using gravimetric method show a small reduction, ICPMS result shows significant silica concentration in the solution. The result shows 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid can dissolve 1622.3 ppm of silica while tetrabutylammonium nonafluoro butane sulfonate ionic liquid can dissolve up to 2754.5 ppm of silica. Barium, however, was not detected in both ionic liquid solution. As a comparison GLDA can dissolve more than 10 000 ppm depends on the pH (Mahmoud et al., 2011). In order for the ionic liquid to be used as solid scale dissolver, similar dissolution capability should be achieved.

Table 4: ICPMS result for silica and barium concentration in ionic liquid solution after dissolution.

Dissolution	Metal Ions Detected	Concentration of Metal Ions (ppm)	% Reduction
1-Butyl-3-Methylimidazolium hexafluorophosphate Ionic Liquid in Acetone + SCALE 2	Si	1622.3	2.3
1-Butyl-3-Methylimidazolium hexafluorophosphate Ionic Liquid in Acetone+ SCALE 1	Ba	Not Detected	1.7
Tetrabutylammonium nonafluorobutanesulfonate Ionic Liquid in Acetone + SCALE 2	Si	2754.5	0.8
Tetrabutylammonium nonafluorobutanesulfonate Ionic Liquid in Acetone + SCALE 1	Ba	Not Detected	1.3

Hypothesis on the mechanism of dissolution; the ionic properties (cation and anion) plays the main role in the dissolution of solid scale having silica, calcium, iron and barium. This result shows that ionic liquid has the potential to be used as solid scale dissolver. Future work on the synthesized ionic liquid attacks mechanism on the solid scale i.e; chelating, should be further conducted. It was proposed to incorporate carboxylic and an amine group in ionic liquid as well as utilizing ionic properties to dissolve scale.

4.3 Evaluation of L-Glutamic acid and Monosodium Glutamate as Calcite Scale Dissolver

Two glutamic acid were selected for preliminary studies in determining the potential solid scale dissolver. In this study, L-Glutamic acid and its sodium salt, monosodium glutamate (MSG) were used in dissolution test of calcite. Figure 10 and 11 shows the dissolution of calcite in L-Glutamic acid solution and MSG solution respectively. In average, MSG gives better dissolution at 15% solid scale reduction compare to L-Glutamic acid at just 6.8% reduction. Thus for the synthesis of amino acid ionic liquid (AAIL), MSG will be selected ad the main material good solubility of calcite. Other considerations include high solubility of MSG as well as the cost of material.

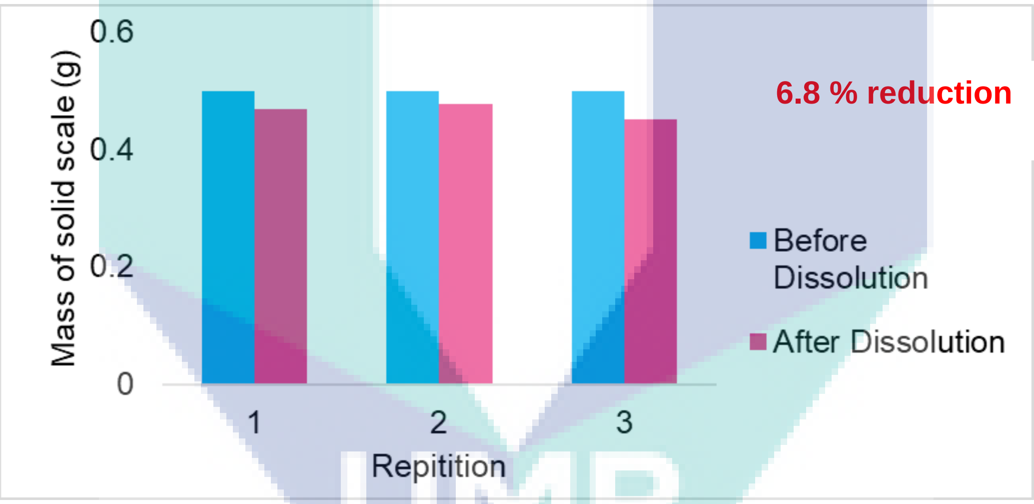


Figure 10: Dissolution of calcite in L-Glutamic acid solution

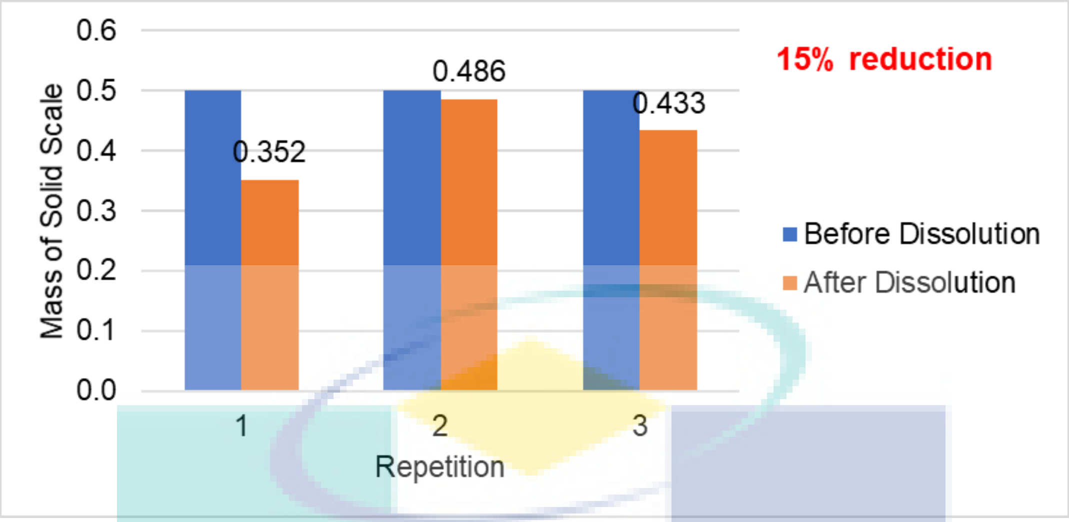


Figure 11: Dissolution of calcite in monosodium glutamate solution

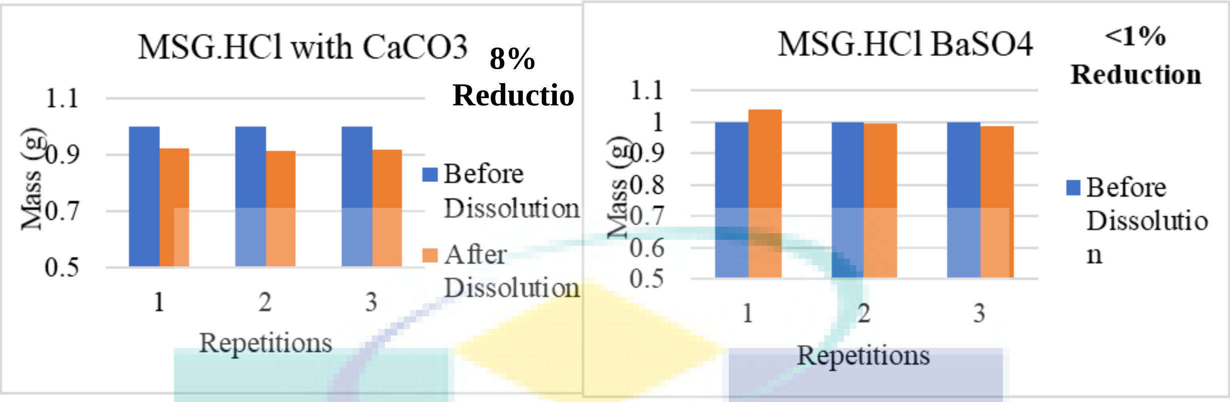
4.4 Synthesis of new dissolver based on MSG

4.4.1 Simple Acidification

Simple acidification of MSG using hydrochloric acid and hydro-fluoroboric acid produce white precipitate named as monosodium glutamate hydrochloric and monosodium glutamate hydro-fluoroboric. However, it was found that the solubility of these two products in water is very low at 4.75 % w/v and 7.6 %w/v for monosodium glutamate hydrochloride (MSG.HCl) and monosodium glutamate hydrofluoroboride ($MSG.HBF_4$) respectively producing a solution of pH 1.5.

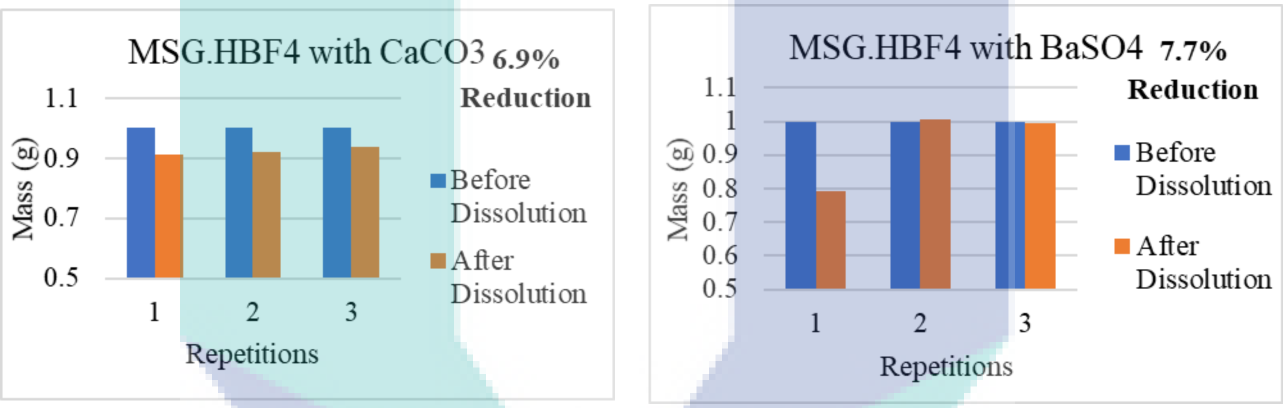
4.4.2 Dissolution using a product from simple acidification

Figure 12 shows the dissolution result of calcium carbonate ($CaCO_3$) and barium sulphate ($BaSO_4$) in MSG.HCl aqueous solution. Only 6.9% of CaCO3 can be dissolved while 7.7% BaSO4 can be dissolved. The reduction of mass after dissolution is small however it should be noted the concentration of the MSG.HCl is just at 4.75% w/v. Figure 13 shows the dissolution of $CaCO_3$ and $BaSO_4$ with MSH.HBF4. At a concentration of just 7.6 %w/v and pH 1.5, the solution can only dissolve 6.9% and 7.7% of $CaCO_3$ and $BaSO_4$ respectively. In order for the full capability of the new compound produce to be evaluated, a higher concentration should be prepared.



(a) (b)

Figure 12: Dissolution of a) $CaCO_3$ and b) $BaSO_4$ in MSG.HCl solution.



(a) **(b)**

Figure 13: Dissolution of a) $CaCO_3$ and b) $BaSO_4$ in MSG.HBF_4

4.4.3 Acidification and Metathesis

Metathesis can be used to further incorporating functional group through exchanging ion. The product from simple acidification can undergo metathesis to add more complicated anions. Figure 14 and Figure 15 show the synthesis route for acidification metathesis of MSG.HCl using sodium tetrafluoroborate ($NaBF_4$) and FTIR analysis of the final compound produce. Sodium tetrafluoroborate can incorporate fluorine into the new salt produce. FTIR analysis shows the successful reaction and new product has been produced however it does not dissolve in water. This makes it unable to be evaluated for solid scale dissolution.

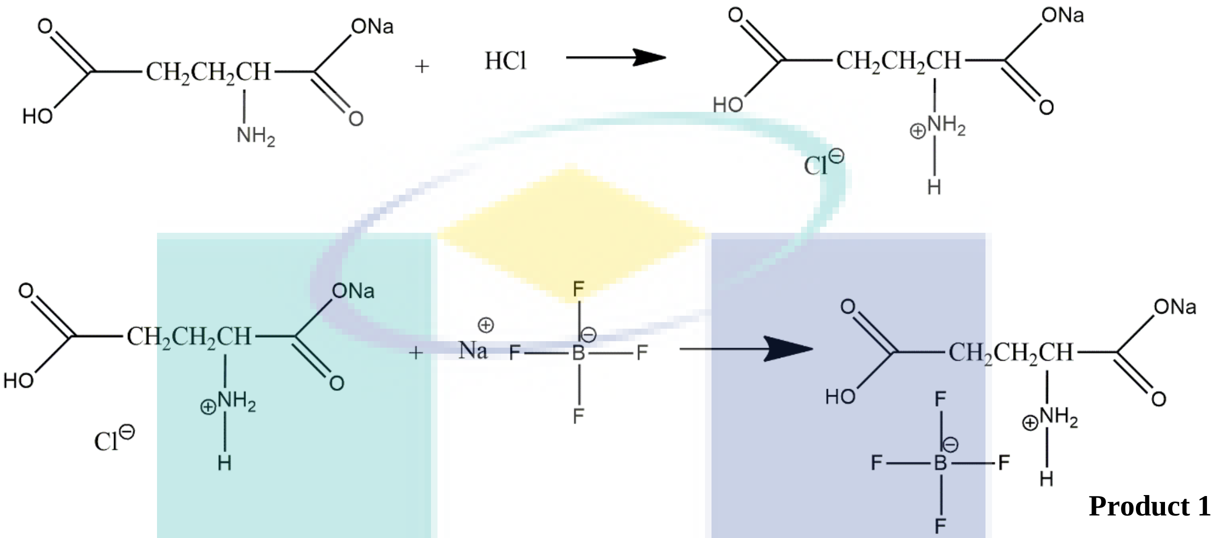


Figure 14: Synthesis route of acidification and metathesis of MSG using HCl and $NaBF_4$

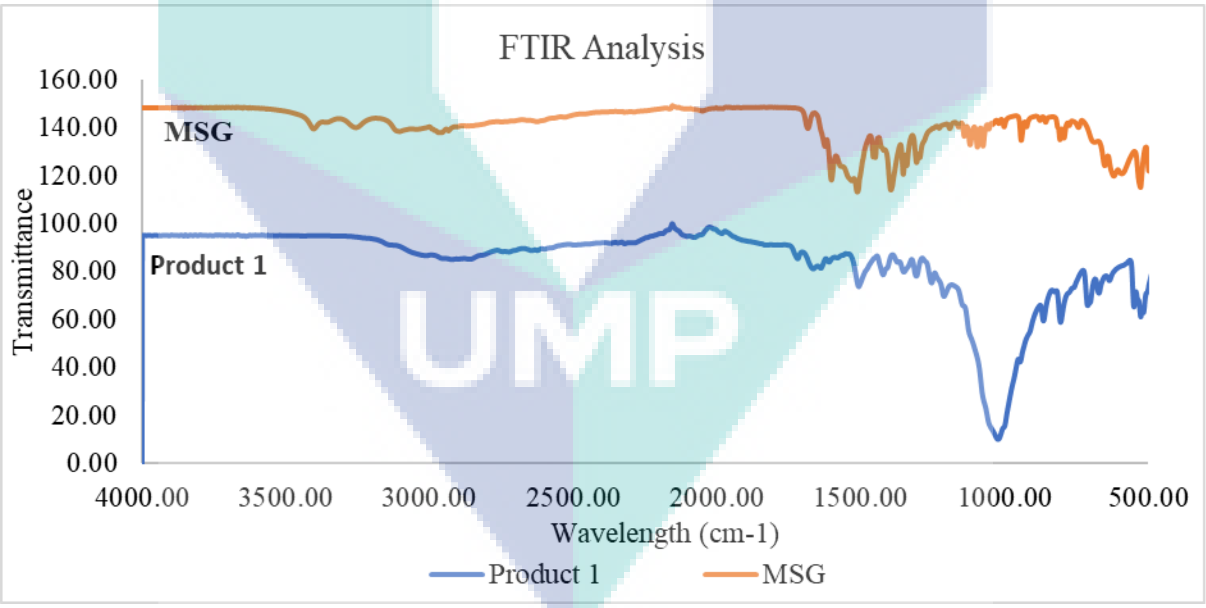


Figure 15: FTIR analysis of the product from acidification and metathesis of MSG using HCl and $NaBF_4$

Another sodium salt can be used is sodium fluorophosphate ($NaFPO_3$) to incorporate both fluorine and phosphate into the new salt. Figure 16 shows the synthesis route for acidizing and metathesis of MSG using HCl and $NaFPO_3$ while Figure 17 shows the FTIR analysis of the final product. FTIR analysis cannot provide a strong indication if the reaction has been successfully carried out. However, the final product does not dissolve and water making evaluation for solid scale dissolution unable to be conducted.

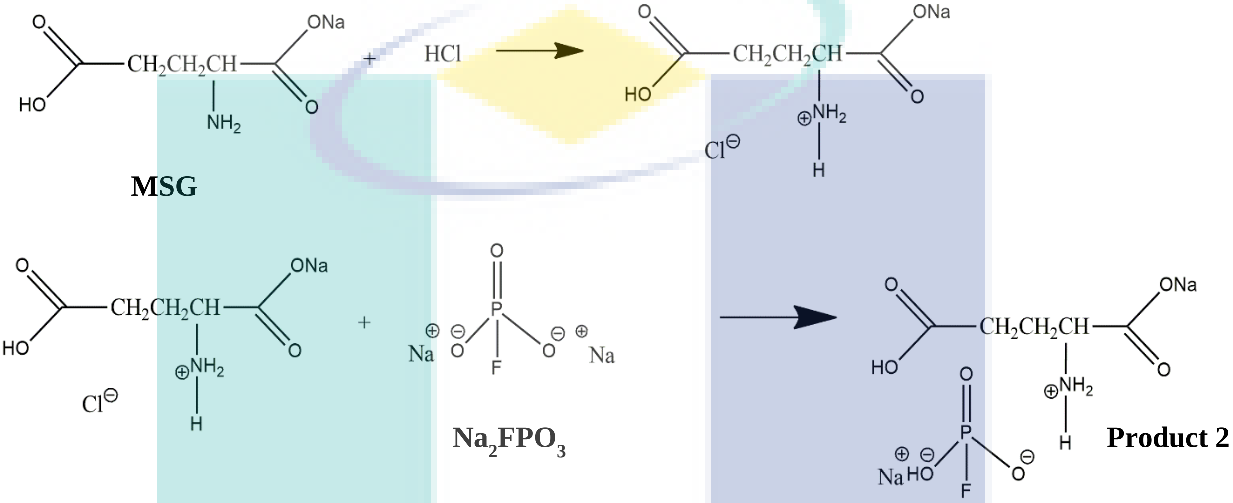


Figure 16: Synthesis route of acidification and metathesis of MSG using HCl and Na FPO_3

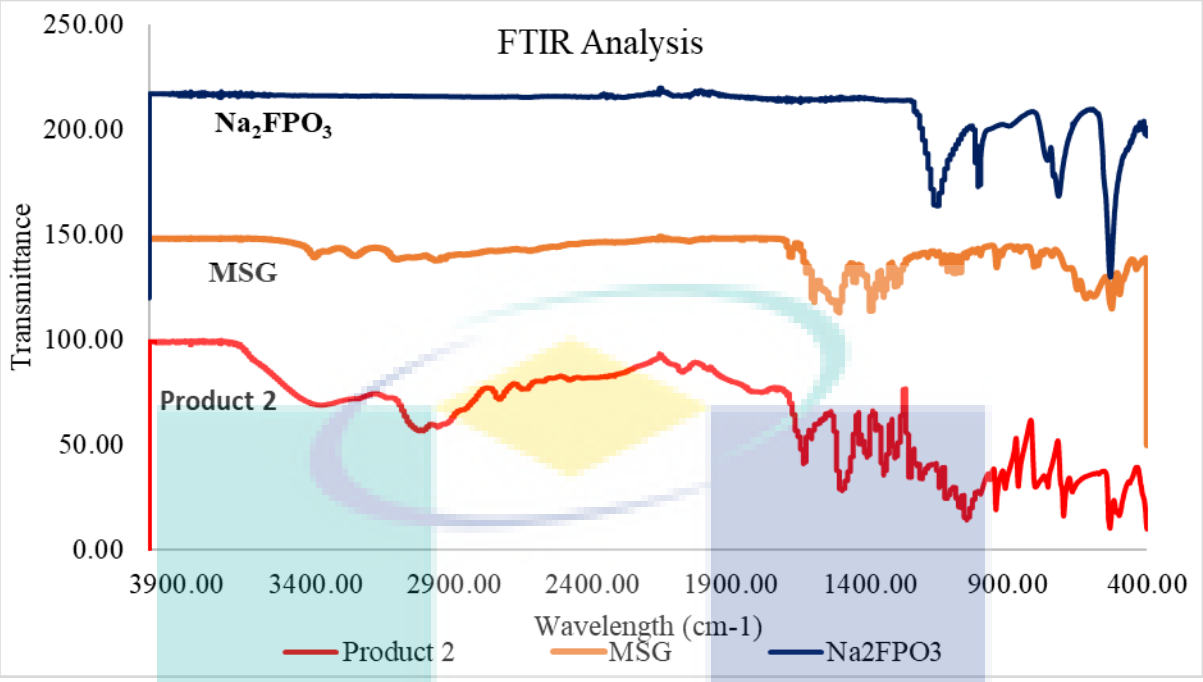


Figure 17: FTIR analysis of final product from acidification and metathesis of MSG using HCl and Na FPO_3

4.5 Blending Formulation for Solid Scale Dissolver

In preparation of preliminary blending, two chelating agents was chosen namely chelating agent A and B. Both of these chelating agents are amino poly-carboxylic compound with different numbers of carboxylic group present. The effectiveness of these two chelating agents in dissolving solid scale was evaluated at the alkaline and acidic condition in three concentrations. Figure 18 shows the dissolution of calcite and barite in chelating agent A and B at the alkaline condition. At alkaline condition, the optimum concentration of Chelating Agent A for dissolution of $CaCO_3$, and $BaSO_4$ is 40g/L giving 9.9%, 17.63% and 1.99% of dissolution respectively. At alkaline condition, the optimum concentration of Chelating Agent B for dissolution of CaCO3, is 60g/L giving 10.9% dissolution, 40g/L for $BaSO_4$ giving 14.6% dissolution. No optimum condition for FeS. Proposed blending for targeting $BaSO_4$ is 40g/L Chelating Agent Aand 40g/L Chelating Agent B

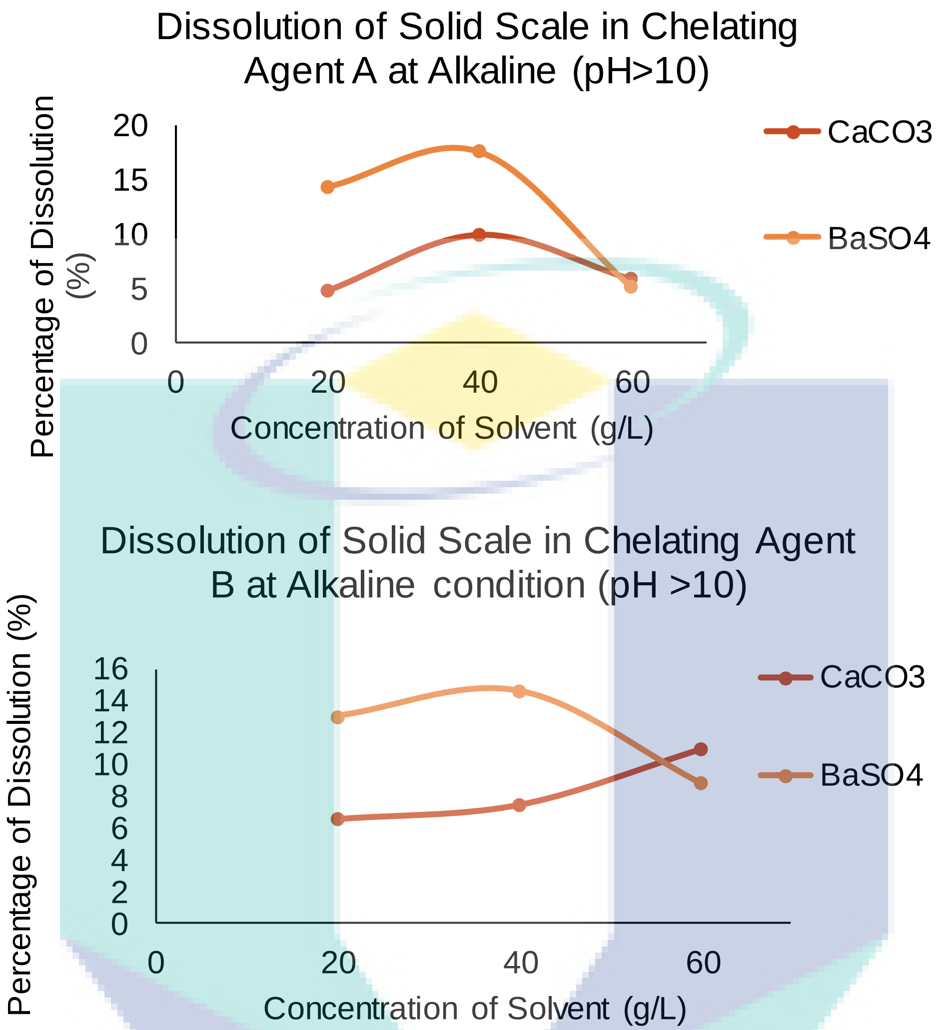


Figure 18: Dissolution of calcite and barite in EDTA salt and DTPA salt at alkaline condition

Figure 19 shows the dissolution of calcite and barite in Chelating Agent A and B in acidic condition. $CaCO_3$ show the highest dissolution in acidic condition. At 20g/L Chelating Agent A and B, more than 50% of calcite dissolved and reached more than 90% at a concentration of chelating agent 60g/L. Chelating Agent B can dissolve more calcite at acidic condition compare to Chelating Agent A. $BaSO_4$ does not shows significant dissolution in both Chelating Agent A and Chelating Agent B.

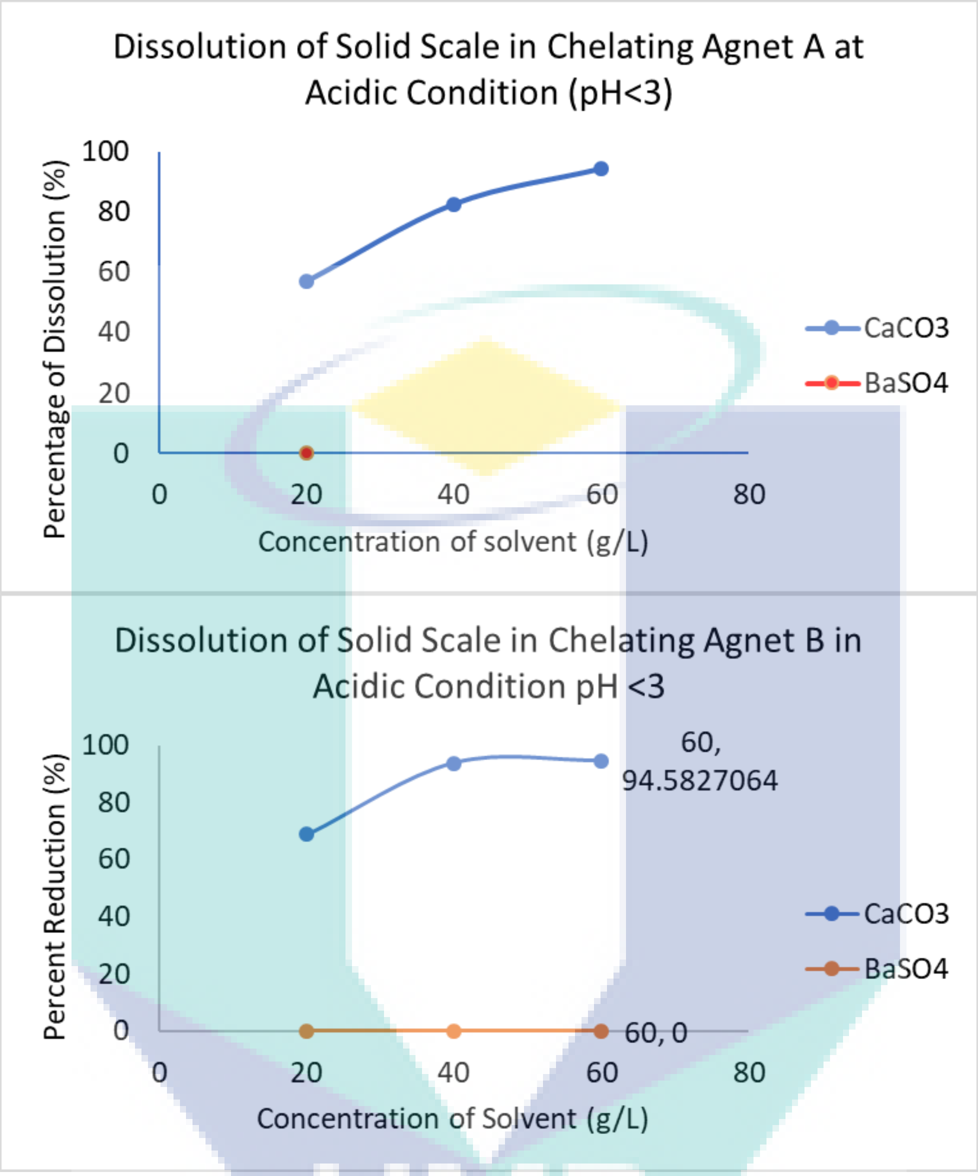


Figure 19: Dissolution of calcite and barite in the Chelating Agent A and Chelating Agent B at acidic condition

Based on the result in Figure 18 and Figure 19, the best concentration of the chelating agent to targeting barite is 40g/L of Chelating Agent B at the alkaline condition. The final blending, VanishIL will include Chelating Agent B, buffer for alkalinity and synergist to improve dissolution of barite. Figure 20 shows the dissolution of calcite, barite and Scale 1 at two different temperature. As VanishIL is developed to focus mainly on barite solid scale, the test at 80 °C only done for barite and Scale 1. For reference Scale 1 containing a high number of barite. The result shows that VanishIL can dissolve 9.5g/L of barite and 7.83

g/L of calcite at temperature 60 °C in 24 hours' time. Increasing the temperature to 80 °C improve the dissolution to 12.41g/L of barite and 11.94 g/L of Scale 1. The data collected from this blending process will be a guide for future improvement and addition to the formulation.

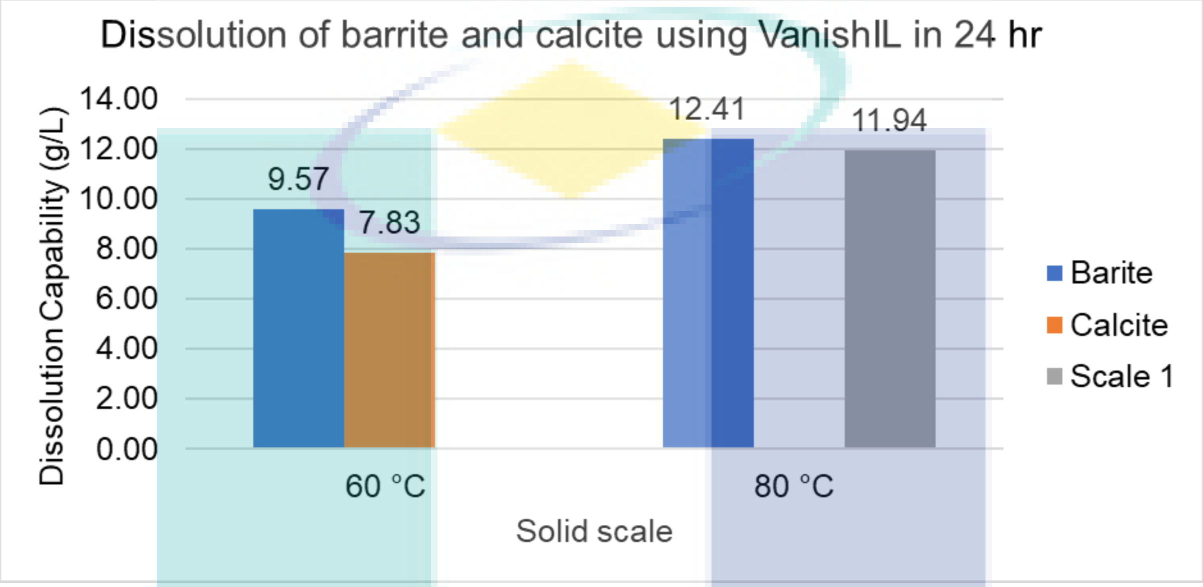


Figure 20: Dissolution of solid scale in VanishIL at 60 °C and 80 °C

5.0 Conclusion

This study involved the characterisation of Scale 1 and Scale 2 obtained from Terengganu and Sarawak oilfield respectively. Scale 1 contains a high number of barite while Scale 2 contains a high number of silica. A trial using two commercialised ionic liquid prove that IL with fluorine can be used as solid scale dissolver. Evaluation of raw material for synthesis shows that glutamate salt, monosodium glutamate (MSG) can dissolve more solid scale compare to L-glutamic acid thus MSG was chosen in the synthesis of the glutamic acid based ionic liquid. Synthesis produces monosodium glutamate hydrochloric acid that can dissolve only 8% of calcite and less than 1% barite. Monosodium glutamate hydro fluoroboric performed better in dissolution, dissolving 6.9% calcite and 7.7 barites. Two chelating agents, A and B were evaluated for dissolution of calcite and barite at several different concertations. Chelating agent B is found to has the best dissolution for barite at concentration 40g/L in alkaline condition. It can be concluded that barite solid scale can be dissolved in alkaline condition. Chelating Agent B was blended with buffer and synergist producing preliminary blending product named VanishIL. Dissolution study shows VanishIL can dissolve 9.5g/L of barite and 7.83 g/L of calcite at temperature 60 °C in 24 hours' time. Increasing the temperature to 80 °C improve the dissolution to 12.41g/L of barite and 11.94 g/L of Scale 1. Further analysis and characterisation are still needed for VanishIL such as viscosity and corrosivity to evaluate its viability to be used in well stimulation.

Achievement & Publication

1) Creation, Innovation, Technology & Research Exposition (CITREX) 2018 Award: Silver Medal,
Title: VanishIL-Solid Scale Dissolver

2) 4th National Conference on Knowledge Transfer (NCKT'17) (11th –12th December 2017)
Conference Proceeding: Incorporation of Ionic Liquid (ILs) In Commercial Solvent Agents for
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