

Faculty of Science and Engineering

**Operability and Optimum Control of the MEG Bench Scale and
Distillation Plant**

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Doctor of Philosophy
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DECLARATION OF ACADEMIC INTEGRITY

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material, which has been accepted for the award of any other degree or diploma in any university.

(Samer Al-Ajooli)

DEDICATION

*I would like to dedicate my thesis to the memory of my father (peace be upon him),
for his assurance and certitude in me as an educated person*

To my dear mother, for her prayer and wishes

To my divine wife and my children for their greatest support and patience

To my brother, sisters, family, and friends for their prayers and encouragement

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In The Name of Allah, the Most Gracious, the Most Merciful

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Abstract

Monoethylene Glycol (MEG) is a gas hydrate inhibitor that has been commonly used in the oil and gas industry. The inherent properties and characteristic of MEG facilitate the regeneration of the chemical from the solution such that it can be reused in a continuous loop system. Over the past decade, the regeneration process of the MEG has been studied intensively and widely considered as one of the most cost effective processes, through reusing an inhibitor without the need for continuous injection. The design of a MEG regeneration plant is complex in nature and its configuration depends on various factors such as the size of the production site, the extent of water formation, percentage of ions concentration in the brine as well as temperature, pressure and pH value of the reservoir. The MEG regeneration process is typically a closed loop system involving number of chemicals and physical processes. This thesis contains nine chapters including six technical chapters starting from the equipment used in the MEG facility, where full description of each equipment have been illustrated as well as the process flow diagram (PFD) and the piping and instrumentation diagram (P&ID). In chapter four, the design of the MEG pilot plant has been fully covered and examples of how the plant is operated and controlled are given. Clean-up study was the first experiment conducted in the MEG pilot plant. This study focused on the behaviour of the well completion fluids and drilling muds, which are expected during the initial start-up phases, and their effects on inlet separation process. Results showed that when drilling mud present, emulsion was formed in both cases that have been studied. The majority of drilling mud accumulated in the MEG phase before adding the demulsifier. When demulsifier was added, the drilling mud accumulated in the MEG/ condensate interphase of the three phase separator (TPS). The performance of pre-Treatment system in MEG pilot plant during Switch over Corrosion Management Strategies has been thoroughly studied during the transition from pH stabilisation to film foaming corrosion inhibitor for both Janze and Gorgon fields. Results showed that the pH above 8 was required in the MEG pre-treatment vessel (MPV) to precipitate calcium salts. Magnesium salts stayed in solution at this pH level (pH 8) and were not removed in the MPV under those conditions. In addition, a pH of more than 10 resulted in the lean Glycol tank LGT due to the plant upstream alkalinity addition. For Gorgon field, although the same conditions were required to remove the divalent salts, the MDEA downstream the facility was not fully removed because of the high pH coming from

the reboiler and it was estimated that 30 inventory turnover were required in order to remove the MDEA, which will take about 30 days in the current plant configuration and nearly 2 years for the real field. Therefore, the plant design has been modified to tackle this problem. Additional HCl dosing point was added to the reboiler feed to reduce the pH value. It was found that when pH was adjusted to 6, the strategy worked much faster and it took only 10 inventory turnovers rather than 30. In addition, the required low alkalinity (<10 mM) to minimise the risk of scaling in the pipeline has been achieved using the additional dosing point after only 5 inventory turnovers. Lastly, the pH and alkalinity control of lean MEG has been studied for Wheatstone field. Results showed that the resulting lean glycol pH under rich glycol operating conditions will pose a risk of subsea scaling if sudden formation water break through occurs and a rich glycol pH of 7 should be targeted to minimise the hydroxide and carbonate alkalinity produced in the lean glycol product to reduce the risk of scaling. It was also found that MDEA is a strong alternative to KOH for rich glycol pH control in Wheatstone field and it was highly recommended to be used instead of KOH.

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Nomenclatures

General abbreviations

μ_i^o	=	Chemical potential at standard state
f_i^o	=	Fugacity at standard state
a_i	=	Activity of component i
CW	=	Condensed water
DCS	=	Distribution control system
FB	=	Feed blender
FFCI	=	Film forming corrosion inhibitor
g_i	=	Mass of solute (grams)
g_o	=	Mass of solvent (grams)
ISM	=	Intelligent Sensor Management
KH	=	Dissolution equilibrium constant
kPa	=	Kilopascal
Ks	=	Thermodynamic solubility product of salt
K_{sp}	=	Solubility equilibrium constant
LGT	=	Lean MEG tank
m	=	Molality
MDEA	=	Methyldiethanolamine
MEG	=	Mono-ethylene Glycol
MeOH	=	Methanol

m_i	=	Molality of species i
M_i	=	Molecular weight of solute (g/gmol)
MPV	=	MEG pre-treatment vessel
MRU	=	MEG recovery unit
n_i	=	Moles of solute
ppmw	=	Part per million weight
P&ID	=	Pipng and instrumentation diagram
PFD	=	Process flow diagram
PLC	=	Process logic control
RGT	=	Rich MEG tank
sH	=	Structure H
sI	=	Structure I
SI	=	Saturation index
sII	=	Structure II
SR	=	saturation ratio
TDS	=	Total dissolved solids
TPS	=	Three phase separator
V	=	Velocity
VLE	=	vapour liquid equilibrium
WBT	=	Water brine tank
Wt%	=	Weight percent

γ_i	=	Activity coefficient
ΔG	=	Excess gibbs free energy
ΔH	=	Enthalpy change
ΔT	=	Hydrate temperature depression
$\Delta\mu$	=	Change in the chemical potential energy
μ	=	Chemical potential
μ_i	=	Standard chemical potential of component i
ρ	=	density
ν	=	Stoichiometric number

1 Introduction

1.1 Background

Global natural gas demand has significantly increased over the past few decades. Therefore, more development of deep offshore gas wells are required with deeper wells, longer subsea transportation pipelines under higher pressures and lower temperatures. Hydrate is more likely to form under such conditions, which blocks the pipelines and cause plant breakdown. In this case, effective hydrate inhibition is necessity.

MEG (mono ethylene glycol) is one of the most commonly used thermal hydrate inhibitors. It is used in petroleum and gas transportation pipelines where the conditions are ideal to hydrate formation such as high pressure and low temperature.

1.1.1 Mono-Ethylene Glycol (MEG)

Ethylene glycol 1,2-ethanediol, $\text{HOCH}_2\text{CH}_2\text{OH}$, usually called glycol, is the simplest diol. It was first prepared by WURTZ in 1859 [1]; by treatment of 1,2-dibromoethane with silver acetate yielded ethylene glycol diacetate, which was then hydrolysed to ethylene glycol. Ethylene glycol was first used industrially in place of glycerol during World War I as an intermediate for explosives (ethylene glycol dinitrate) [2], it has developed remarkably to one of the important industrial products. The worldwide capacity for the production of ethylene glycol via the hydrolysis of ethylene oxide is estimated to be 7×10^6 t/a. Ethylene glycol is used mainly as an antifreeze in automobile radiators and as a raw material for the manufacture of several polymers such as polyesters, polyurethanes, pharmaceuticals and others [1].

1.1.1.1 MEG Physical properties

Ethylene glycol is a clear, colourless, odourless liquid with a sweet taste [2]. It is hygroscopic and completely miscible with many polar solvents, such as water, alcohols, glycol ethers, and acetone. However, its solubility is low in nonpolar solvents such as benzene, toluene, dichloroethane, and chloroform. Some of the physical properties of ethylene glycol are shown in *Table 1-1* [3]:

Table 1-1 MEG physical properties [3]

Boiling point at 101.3 kPa	197.60 °C	Critical pressure	6515.73 kPa
Freezing point	-13.00 °C	Critical volume	0.186 L/mol
Density at 20°C	1.1135 g/cm ³	Flash point	111°C
Refractive index,	1.4318	Ignition temperature	410°C
Heat of vaporization at 101.3 kPa	52.24 kJ/mol	Lower explosive limit	3.20 vol %
Heat of combustion	19.07 MJ/kg	Upper explosive limit	53 vol %
Critical temperature	372 °C	Viscosity at 20°C	19.83 M Pa.s

Ethylene glycol is difficult to crystallise; when cooled, it forms a highly viscous, supercooled mass that finally solidifies to produce a glasslike substance. The widespread use of ethylene glycol as an antifreeze is based on its ability to lower the freezing point when mixed with water. The physical properties of ethylene glycol – water mixtures are, therefore, extremely important. The freezing points of mixtures of water with mono-ethylene glycol is shown in *Figure 1-1*. The temperature dependencies of *the thermal conductivity*, density, and *viscosity* of ethylene glycol and ethylene glycol – water mixtures are shown in *Figure 1-2*.

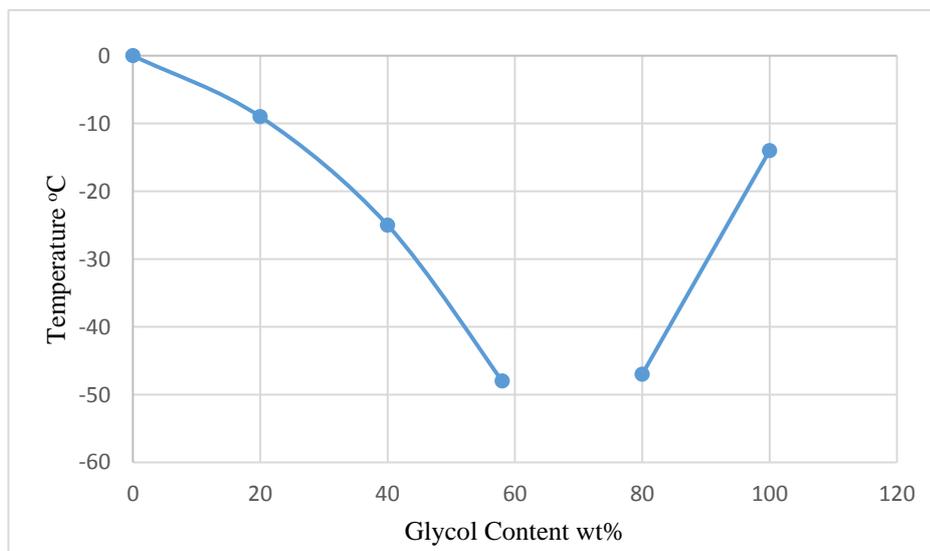


Figure 1-1 Freezing points of MEG- water mixtures [1]

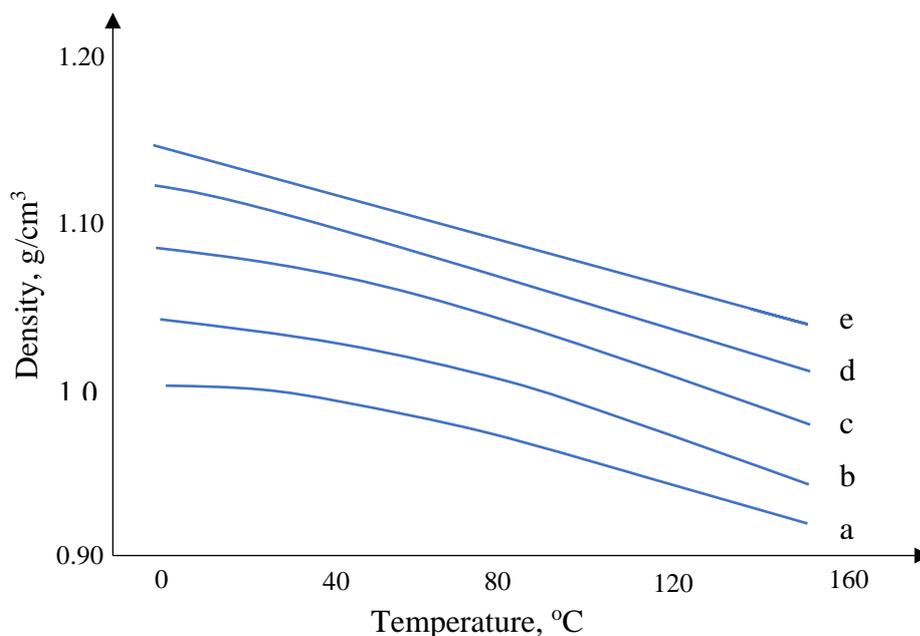


Figure 1-2 Temperature dependency of the density of water-MEG mixture, mole%

a) 0; b) 26.1 c) 50.95; d) 76.9; e) 100 [1]

1.1.1.2 MEG Chemical Properties

The ethylene glycols (commonly called diols) are dihydric alcohols that have an aliphatic carbon chain. The two hydroxyl groups result in high water solubility and hygroscopicity and provide reactive sites. The heavier glycols exhibit some of the properties of ethers because of the ether linkage in their molecular structure such as di, or tri ethelene glycol, and other oligomers. The reaction of the ethylene glycols are similar to those of the monohydric alcohols in which the hydrogen group is replaced by halogens.

1.1.1.3 MEG as Antifreeze Agent

Due to its low freezing point, mono ethylene glycol (MEG) resists freezing. MEG disrupts hydrogen bonding when dissolved in water. Pure ethylene glycol freezes at about $-12\text{ }^{\circ}\text{C}$ ($10.4\text{ }^{\circ}\text{F}$), but when mixed with water molecules forms a solid crystal structure, and therefore the freezing point of the mixture is significantly depressed. The minimum freezing point is observed when the ethylene glycol percent in water is about 70%, as shown in [Table 1-2](#) [1];

Table 1-2 MEG / water mixture freezing points [1]

MEG/ water wt%	Freezing point (°C)	MEG/ water wt%	Freezing point (°C)
0	0	60	-48
10	-4	70	-55
20	-7	80	-45
30	-15	90	-29
40	-23	100	-12
50	-34		

However, the boiling point for aqueous ethylene glycol increases monotonically with increasing ethylene glycol percentage as shown in *Table 1-3*. Thus, the use of ethylene glycol is not only to depress the freezing point, but also elevates the boiling point such that the operating range for the heat transfer fluid is broadened on both ends of the temperature scale. The increase in boiling temperature of the MEG/water mixture is related to the higher boiling point and lower vapour pressure of MEG than pure water. [4].

Table 1-3 boiling points of MEG/ water mixtures [4]

MEG/ water wt%	Boiling point (°C)	MEG/ water wt%	Boiling point (°C)
0	100	60	110
10	102	70	116
20	102	80	124
30	104	90	140
40	104	100	197
50	107		

Although MEG is a relatively stable compound, special care is required when MEG is heated to a high temperature in the presence of an alkaline such as sodium hydroxide. Fragmentation of the molecule begins at temperatures above 250 °C and the decomposition is accompanied by the exothermic evolution of hydrogen ($\Delta H = -90$ to -160 kJ/kg). This leads to build-up of pressure in closed vessels [4].

1.2 Research Objectives:

The main aim of this thesis is firstly to study the optimum operation and control conditions of MEG pre-treatment, regeneration and reclamation units and evaluation of the technical issues of the system and secondly simulating these parameters to Australian deep water conditions.

Consequently, the objectives of this work are:

- 1- Optimising the control system of the MEG benchtop facility to allow detailed studying of MEG and its degeneration, salt removal processes and use production chemical additives.
- 2- Optimise, make the necessary improvements, and do the necessary changes to the control system with shifting scope of work. A complex and advanced control system to be used including Control-loops, safety trips, logical trips, complete mass balance of plant using LabVIEW logic control as the implementations of this software have the advantages of being relatively cheap and flexible.
- 3- Design and operate the MEG bench top pilot plant and simulate all the field conditions for the expected fluids and gases compositions. As a result, the data that will be collected from the MEG plant are applicable to the field conditions.
- 4- Simulate the start-up and clean-up conditions and fluid compositions of both field 1 and field 2 from wells back to the onshore production facility.
- 5- Study the performance of pre-treatment system in MEG pilot plant during switch over corrosion management strategies (pH stabilisation to film forming corrosion inhibitor) for field 1 and field 2.
- 6- Study the performance of pre-treatment system in MEG pilot plant during switch over corrosion management strategies (film forming corrosion inhibitor to pH stabilisation).
- 7- Investigate and understand the practicalities around chemical injection through the process to maintain the target values for pH and strong alkalinity of the lean MEG for field 3.

1.3 Thesis outline and organisation

Mono-ethylene Glycol (MEG) is used regularly in the oil and gas industry to prevent the formation of hydrates and resulting blockages in pipelines and equipment. There is a

requirement for continual injection of MEG for effective operations. To reduce costs and the quantity of wasted MEG, MEG is often regenerated. The MEG is injected on the platform and processed onshore to recover a MEG concentration suitable for recycling back into the pipeline. The purpose of the MEG regeneration unit is to remove water from the MEG, and also to remove the monovalent and divalent salts that are produced as a solid by-product during formation water breakthrough and water removal during regeneration. When produced from a reservoir, natural gas usually contains a large amount of salt water and is typically completely saturated or at the water dew point. This water can cause several problems for downstream processes and equipment. At low temperatures, water may either freeze in piping or, as is more commonly the case, form hydrates with CO₂ and hydrocarbons (mainly methane hydrates). Depending on composition, these hydrates can be formed at relatively high temperatures plugging equipment and piping. Glycol dehydration inhibits the hydrate formation and increases the time of “free flow”, decreases plug formation and inevitable off-line time whilst the plugs are removed and the pipeline brought back on line – a very costly exercise. MEG stream is often also contaminated with inorganic materials such as Ca, Ba salts, and in particular larger amounts of sodium chloride. MEG plant is capable of handling these issues.

The thesis consists of seven chapters outlines below:

Chapter one: Introduction. Gives a brief introduction of the background, general issues encountered, and solutions regarding MEG as a hydrate inhibitor. It also includes the research objectives and the thesis’ structural organisation.

Chapter two: Literature review. Detailed summary and review of the past studies of MEG as thermodynamic hydrate inhibitor, MEG regeneration, and reclamation plant operations, and literature gaps.

Chapter three: MEG bench scale pilot plant equipment. This chapter illustrates in details the equipment used in the pilot plant as well as the description of PFD and P&ID of each section.

Chapter four: Design, operation, and control of MEG plant. Details about the MEG plant sections, the function of each part and a brief description on how each device is being controlled and operated accompanied with with typical results.

Chapter five: MEG bench scale clean up study, operating results using field data, this chapter covers the investigation of the emulsion tendencies of the production fluids in the pre-treatment system during the first commissioning for both field 1 and field 2. The investigation also covers studying the ability of MEG pre-treatment vessel to remove the divalent salts and the effect of some chemicals on the fluid and the system behaviour such as the demulsifier and NaOH.

Chapter six: Study the performance of pre-treatment system in MEG pilot plant during switch over corrosion management strategies (pH stabilisation to film forming corrosion inhibitor). This chapter investigates the performance of the MPV during the switchover procedure.

Chapter seven: Study the performance of pre-treatment system in MEG pilot plant during switch over corrosion management strategies (film forming corrosion inhibitor to pH stabilisation). This chapter covers the performance investigation of the MPV during the switchover procedure.

Chapter eight: pH and Alkalinity Control of Lean MEG for Field 3. This chapter covers the feasibility investigation of the current operational methodology compared to a proposed target of pH value to reduce scaling within the regeneration system.

Chapter nine: Conclusions and Summary of the results obtained in this thesis.

2 Literature review:

2.1 Mono ethylene glycol

Ethylene glycol is produced from ethylene (ethene), via the intermediate ethylene oxide. Ethylene oxide reacts with water to produce ethylene glycol according to the chemical equation



This reaction can be catalysed by either acids or bases, or can occur at neutral pH at elevated temperatures. The highest yields of ethylene glycol occur at acidic or neutral pH in the presence excess of water. Under these conditions, ethylene glycol yields of 90% can be achieved. The major by-products are the oligomers diethylene glycol, triethylene glycol, and tetra-ethylene glycol. The separation of these oligomers and water is energy-intensive. About 6.7 million tonnes are produced annually by this technology [1].

A higher selectivity is achieved by use of Shell's OMEGA process. In the OMEGA process, the ethylene oxide is first converted with carbon dioxide (CO₂) to ethylene carbonate. This ring is then hydrolysed with a base catalyst in a second step to produce mono-ethylene glycol in 98% selectivity [5]. The carbon dioxide is released in this step again and can be fed back into the process circuit. The carbon dioxide comes in part from the ethylene oxide production, where a part of the ethylene is completely oxidized.

Ethylene glycol is also produced from carbon monoxide in countries with large coal reserves and less stringent environmental regulations. The oxidative carbonylation of methanol to dimethyl oxalate provides a promising approach to the production of C₁-based ethylene glycol [6]. Dimethyl oxalate can be converted into ethylene glycol in high yields (94.7%)[7] by hydrogenation with a copper catalyst [8].

2.1.1 Mono-ethylene Glycol historical background

Many sources stated that ethylene glycol was first prepared in 1856 by a French scientist Charles-Adolphe Wurtz (1817-1884) [9]. He first treated "ethylene iodide" (C₂H₄I₂) with silver acetate and then hydrolysed the resultant "ethylene diacetate" with potassium hydroxide. Wurtz named his new compound "glycol" because it shared qualities with both ethyl alcohol (with one hydroxyl group) and glycerine (with three

hydroxyl groups). In 1859, Wurtz prepared ethylene glycol via the hydration of ethylene oxide. There appears to have been no commercial manufacture or application of ethylene glycol prior to World War I, when it was synthesised from ethylene dichloride in Germany and used as a substitute for glycerol in the explosives industry. In the United States, semi commercial production of ethylene glycol via ethylene chlorohydrin started in 1917. The first large-scale commercial glycol plant was erected in 1925 at South Charleston, West Virginia, by Carbide and Carbon Chemicals Co. (now Union Carbide Corp.). By 1929, ethylene glycol was used by almost all dynamite manufacturers. In 1937, Carbide started up the first plant based on Lefort's process for vapour-phase oxidation of ethylene to ethylene oxide. Carbide maintained a monopoly on the direct oxidation process until 1953, when the Scientific Design process was commercialised and offered for licenses.

2.1.2 Ethylene Glycol Uses

2.1.2.1 Coolant and Heat Transfer Agent

The major use of ethylene glycol is as a medium for convective heat transfer such as automobiles and liquid-cooled computers [4]. Ethylene glycol is also commonly used in chilled-water air-conditioning systems that place either the chiller or air handlers outside, or systems that must cool below the freezing temperature of water. In geothermal heating/cooling systems, ethylene glycol is the fluid that transports heat through the use of a geothermal heat pump. The ethylene glycol either gains energy from the source (lake, ocean, water well) or dissipates heat to the sink, depending on whether the system is being used for heating or cooling [10].

2.1.2.2 Antifreeze

Ethylene glycol is used as an antifreeze agent in more than 50 percent of its commercial use because it decreases the water freezing point [1] as seen in *Figure 1-1*. Corrosion inhibitors should be added wherever ethylene glycol is used as an anti-freezing agent such as in motor vehicles, solar energy units, heat pumps, water heating systems, and industrial cooling systems. However, pure ethylene glycol should not be used as an engine coolant or antifreeze in most cases due to the low specific heat capacity and heat transfer efficiency [11]. In the MEG /water mixture, the concentration of MEG has a direct effect on the freezing protection level. For instance, 70 percent glycol

lower the freezing point to $-55\text{ }^{\circ}\text{C}$, which is the ultimate freezing point for glycol-water mixture *Table 1-2*.

2.1.2.3 Hydrate Inhibitor

As the oil and gas industries continue to increase their activity in deep water, the production and transportation of natural gas in long subsea pipelines are challenges when it comes to hydrate prevention, corrosion, and mineral scaling [12]. Calcium carbonate could precipitate in the pipelines when carbon dioxide from the gas is absorbed in the calcium hydroxide present in the water originating from the reservoir, which reduces heat transfer efficiency. Ethylene glycol is commonly used in dehydration and hydrate inhibition of natural gas as it could remove water and inhibit the formation of natural gas hydrates and be reused after purification treatment [13].

2.1.2.4 Other uses

Ethylene glycol is an excellent solvent and has been used in numerous applications, such as humectants for tobacco, media for suspending conductive salts in electrolytic capacitors, stabilizers for soy bean foam used in fire extinguishers and in the manufacture of explosives, plasticizers, elastomers, and synthetic waxes. Separation of aromatic and paraffinic hydrocarbons, detergents for equipment cleaning, and inks for ball-point pens [14].

2.2 Gas Hydrate

Gas hydrates are also known as clathrate hydrates. They were first documented in 1810 by Sir Humphry Davy who found that water was a primary component of what was earlier thought to be solidified chlorine [15]. Gas hydrates are icelike structures in which water molecules, under pressure, form structures composed of polyhedral cages surrounding gas molecule “guests” such as methane and ethane. Rarely encountered in everyday life, they occur in staggering abundance under the sea floor and permafrost environments where pressure and temperature conditions ensure their stability. The natural gas trapped in these deposits represents a potential source of energy many times greater than all known natural gas reserves. Hydrates can form as well in undersea piping and above ground gas pipelines where they pose a major problem for gas/oil producers [16].

Gas hydrates has involved in an enormous amount of scientific researches in the nineteenth century as most of the well-known clathrate hydrates now were prepared

and identified before 1900 except the more complex halogenated hydrocarbons, cyclic ethers and imines [17].

Many researches and studies have focused on the hydrocarbon hydrates in the United states in the mid of 1990s because of their flow assurance effects in natural gas transportation pipelines. In Germany, Gas hydrates properties were studied again during 1940s because of their possible relationship to the storage and transportation of hydrocarbon fuels. In 1960s, gas hydrates refrigeration was studied because of the industrial potential of clathrate hydrate desalination process.

More technological research relating to natural gas pipeline problems have been reviewed thoroughly by Deaton and Forest in 1948 [18]. The discovery of the other two major groups of hydrate inclusion compounds, the alkyl amine hydrates and the quaternary ammonium salt hydrates, have resulted from investigations that aimed to understand more properties of aqueous solutions than advancing the knowledge of the solid state chemistry of water. Pickering discovered the tetra-n-butyl and tetra-iso-amyl ammonium salt hydrates in 1893 [19]. Fowler and his team discovered the tetra-n-butyl and ammonium salt hydrates although they were interested in the thermodynamics of the solutions of these compounds [20].

Jeffrey and McMullan investigated the crystal structures of the quaternary alkyl ammonium salt hydrates after it was induced by the curiosity of Henry Frank, the physical chemist who was mainly interested in the thermodynamics of aqueous solutions[21]. However, there was no basic understanding why crystalline compounds should exist until the discovery of the clathrate phenomenon of molecular association by Powell in 1947[22]. However, in the nineteenth century chemists were not concerned about this question because prior to valence theory [23], the gas hydrates compositions, which were thought at that time to be much simpler, were not yet inconsistent with current fact of chemical composition than any other chemicals.

Powell's research on the quinol-SO₂ clathrate, provided the essential clue. The two clathrate hydrate structures, which include most of the gas hydrates structures, were simultaneously investigated by three chemists few years later [17].

2.2.1 Hydrates Structure

In general, three types of hydrate structures are applicable to the natural gas industry. The first two hydrate structures are known as Mark von Stackelberg's Cubic Structure

I and II [24] and the third hydrate structure called Structure H, which was discovered by Ripmeester [25]. Any of these hydrate structures I, II or H is capable of trapping lightweight hydrocarbons that exist excessively in natural gas [26][27]. Ripmeester mentioned two other hydrate structures but they are not applicable for the gas industry [25].

A basic building block of hydrates -the pentagonal dodecahedron- is found in all three types of gas hydrate structures. The pentagonal dodecahedron has 20 water molecules, which means there are 40 hydrogens and 20 oxygen atoms. For a pentagonal dodecahedron structure, there are 12 pentagonal faces, 20 vertices, and 30 edges. A simplified coding for the pentagonal dodecahedron is 512 where 5 represents the number of sides for each face while 12 represents the number of pentagonal faces [26][17]. The oxygen atoms will act as the vertices for the 512 structure and the hydrogen with hydrogen bonding will make the 30 edges. Since there is an excess of 10 hydrogen atoms, the excess hydrogen atoms will be distributed among the 20 oxygen vertices. These excess hydrogen act as donation sites and vertices that lack a free hydrogen atom act as accepting sites allowing hydrogen bonding to occur between one cage with another [17] [28]. *Figure 2-1* shows the details of a pentagonal dodecahedron structure.

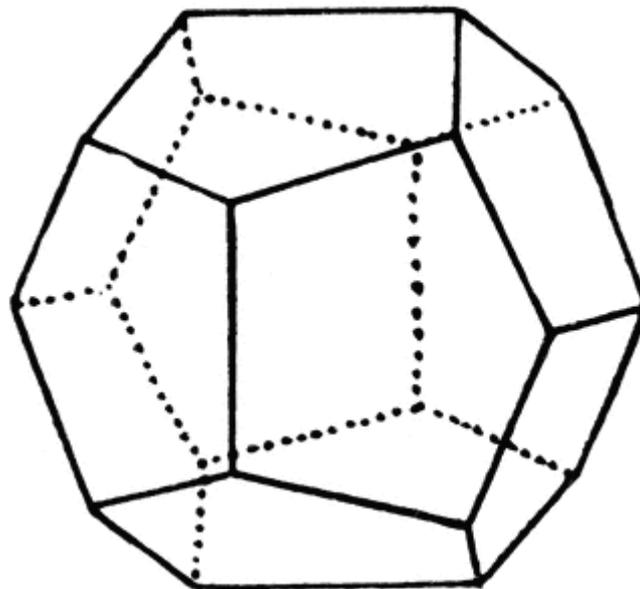


Figure 2-1 Pentagonal dodecahedron structure [29]

2.2.1.1 Gas hydrate structure I

In the natural gas hydrate basic building block, the pentagonal dodecahedron, each having a diameter of 5.1 Angstrom will form a body centred cubic crystal by

connecting other 512 cages at the vertices. This model will cause strains on the hydrogen bonds, therefore, 2 extra hexagonal faces are included to relieve the bond strain, making it a tetra-decahedron. This structure is called sI and it exists naturally outside of the pipeline as methane hydrates [28]. A unit cell of sI consists of 2 small pentagonal dodecahedron (5_{12}) and 6 larger tetra-decahedron cavities ($5_{12}6_2$) and it is formed from a total number of 46 water molecules with a unit length of 12 Angstrom [27]. This type of hydrate structure is able to accommodate up to 8 guest molecules, with a maximum diameter of 5.7 -5.86 Angstrom [24] [26] [28]. The examples of guest molecules that can be accommodated by sI are methane (4.36 Angstrom), ethane (5.5 Angstrom), and carbon dioxide. Any larger molecule, such as propane is unable to fit into the cavities of sI [27]. In addition, a single guest molecule that is smaller than 70-75% of the cavity would not be able to form a stable hydrate structure and a hydrate structure would not form [26] [30]. However, it has to be noted that hydrates are potentially non-stoichiometric clathrate compounds, therefore, not all the cavities in the unit cell will be filled by guest molecules to maintain a stable structure [26] [30]. Although pure methane gas is able to form sI hydrates, it cannot effectively stabilise the $5_{12}6_2$ cage [28]. *Figure 2-2* shows the arrangement of structure.

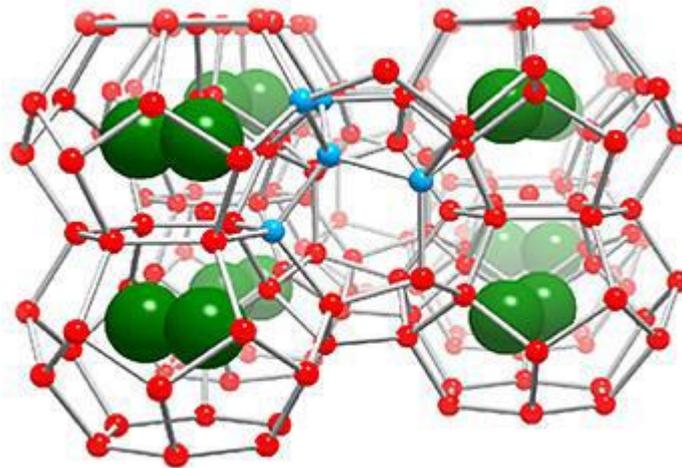


Figure 2-2 Gas hydrate Structure I [31]

2.2.1.2 Gas hydrate Structure II

The second type of gas hydrate is the structure II (sII) in which hydrate is formed from 136 water molecules while having a cubic framework with a unit cell diameter of 17.1 Angstrom. The sII has 16 small pentagonal dodecahedral (5_{12}) and 8 larger hexa-decahedral cavities ($5_{12}6_4$), therefore it can accommodate up to 24 guest molecules with a

maximum free diameter of 6.66 Angstrom [26] [28]. These $5_{12}6_4$ cages can accommodate bigger guest molecules that consists of argon, krypton, oxygen and nitrogen to fill the small and large cavities [27] while propane (6.3 Angstrom), isobutane (6.5 Angstrom), and 2-methylpropane are trapped in the larger cavities, leaving the small cavities empty [26] [27], [28]. The type of hydrate structure formed depends on the size of guest molecules. When larger molecules such as the propane molecules are found in the gas mixture, the structure II will more likely be formed. This is because the propane molecules provide more stability for the $5_{12}6_4$ cages to form. Moreover, propane molecules would not be able to fit into structure I. Therefore, in natural gas production with large gas molecules such as propane and isobutane is common, sII will be dominant, and sI would be hardly present [28]. The hexa-decahedron structure is shown in *Figure 2-3*:

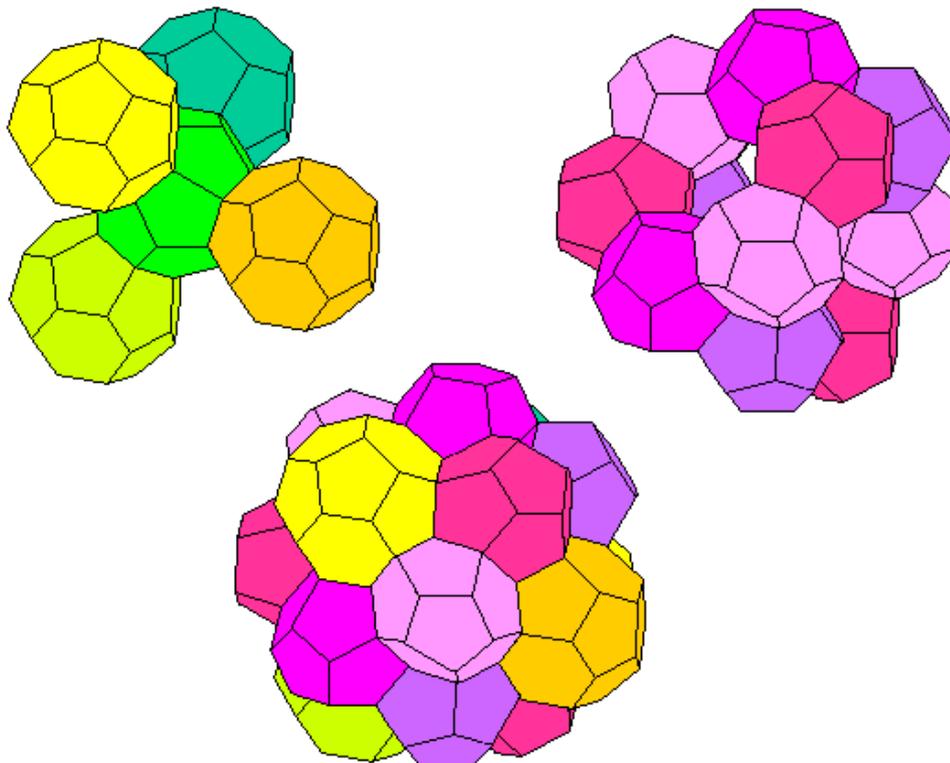


Figure 2-3 Gas hydrate structure II [32]

2.2.1.3 Gas hydrate structure H

Structure H (sH) contains 34 water molecules per unit cell with a hexagonal structure. The unit cell has a length of 12.2 Angstrom and width of 10.1 Angstrom. It consists of 1 icosahedron ($5_{12}6_8$), 2 irregular dodecahedron ($4_35_66_3$) and 3 pentagonal dodecahedron (5_{12}). It can accommodate large guest molecules such as 2, 2- dimethyl

butane in the largest cavity [26]. Structure H has less importance in regard to the oil and gas industry as they are seldom found naturally or artificially occurring, however it is mentioned that the principles being applied to structure I and II can also be applied to structure H [28]. *Figure 2-4* shows the 3D model of structure H.



Figure 2-4 Structure H [28]

2.3 MEG or Methanol?

Generally, there are two main thermodynamic hydrate inhibitors frequently used in the gas industry; Mono Ethylene Glycol (MEG) and Methanol. However, MEG is preferred over methanol despite of being very expensive (900\$/ton) [33]. The disadvantage of using Methanol as a thermodynamic inhibitor in terms of subsequent processing of natural gas is that methanol will accumulate in the Liquefied Petroleum Gas (LPG) stream, which are typically composed of propane, n-butanes, and Iso-butanes. This will produce azeotropes due to the presence of methanol with propane and n-butane, which makes the separation by distillation irrelevant and might increase the cost of reducing the methanol content in LPG streams [34].

Also, the advantage of using MEG over methanol is that MEG can be easily recovered. Although recovering technologies exist for both components, MEG recovery is more favourable due its lower vapour pressure and high boiling point compared to water. On the other hand, Methanol has high vapour pressure and has high potential to be lost in the vapour phase, which increase the complexity of the recovery process [34].

The MEG recovery facility is well developed and widely used. Also, MEG is easily recovered because it has low vapour pressure, higher boiling point than water and does

not form azeotropes with hydro-carbons. Moreover, the regeneration process only requires a short distillation column [33].

In terms of gas loss, the maximum loss of MEG to gas is 0.3 kg per 1 million standard m³ of gas while it is 16 kg per 1 million standard m³ of gas for every wt.% MeOH in aqueous phase [35]. MEG is non-flammable with a flash point of 111°C while methanol is highly flammable and has a flash point of 11°C, which make MEG far safer than methanol. In addition, the cost of using corrosion inhibitors with MEG is less compared with methanol as it has better corrosion resistance properties [33].

2.4 MEG as hydrate Inhibitor

Thermodynamic inhibitors such as MEG inhibit the formation of gas hydrate because they are able to break the hydrogen bonding between the hydrate structures and leads to bond with free water molecules [36]. As a result, the phase equilibria curve will be shifted to the left, resulting in a lower temperature and higher-pressure hydrate formation conditions along an isobaric and isothermal line respectively. A graph explanation of the described phase equilibria shift of methanol injection is shown in *Figure 2-5* [36]. However, the same shifting trend can be seen when MEG injection is used. *Figure 2-5* shows that the hydrate temperature depression (ΔT) is lower than the freezing point depression ($\Delta T'$). Giving the fact that ice is able to form together with hydrates, however deep-sea surface temperature is around 4°C, which will not reach the freezing point of water, and therefore formation of ice is not too much of a concern in natural gas pipeline transportation.

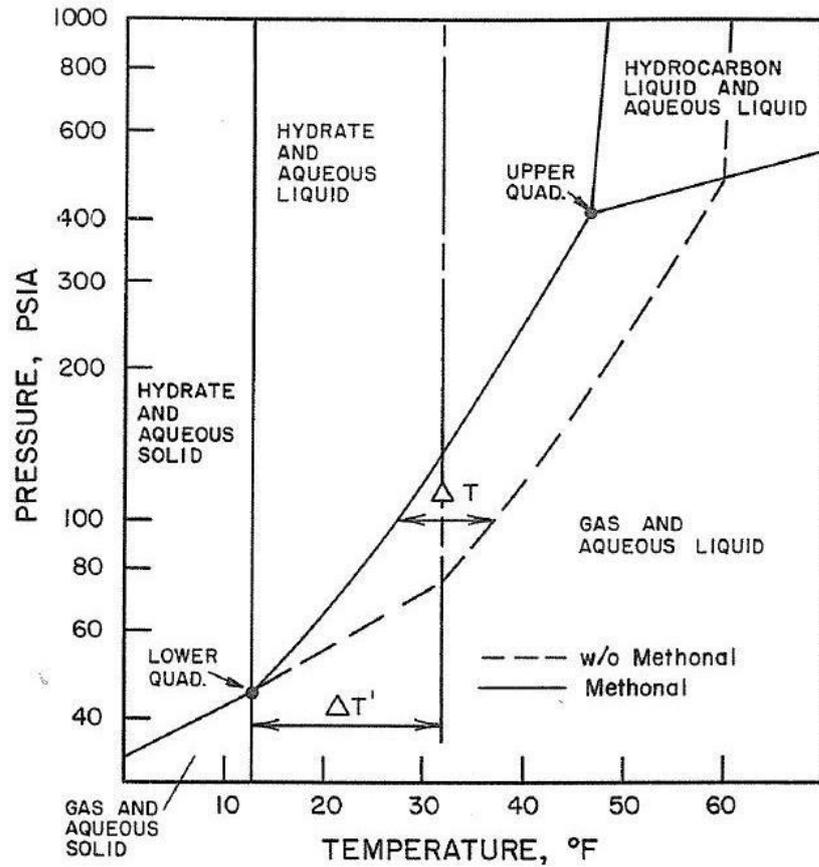


Figure 2-5 Shift of phase equilibria curve with methanol injection [36]

2.5 MEG recovery unit (MRU) configuration

In the modern design of natural gas transport systems, platforms are no longer used. The produced fluid such as gas, condensate, formation water, and condensed water will be transported directly through a series of subsea equipment and multiphase pipeline to reach the onshore facilities. This design leads to reduce the capital of offshore platform construction and maintenance. However, the lack of upstream gas processing in this design results in the onshore receiving facilities having to provide more equipment and perform more work to treat the unprocessed gas [37]. Typical modern onshore receiving facility is shown in [Figure 2-6](#).

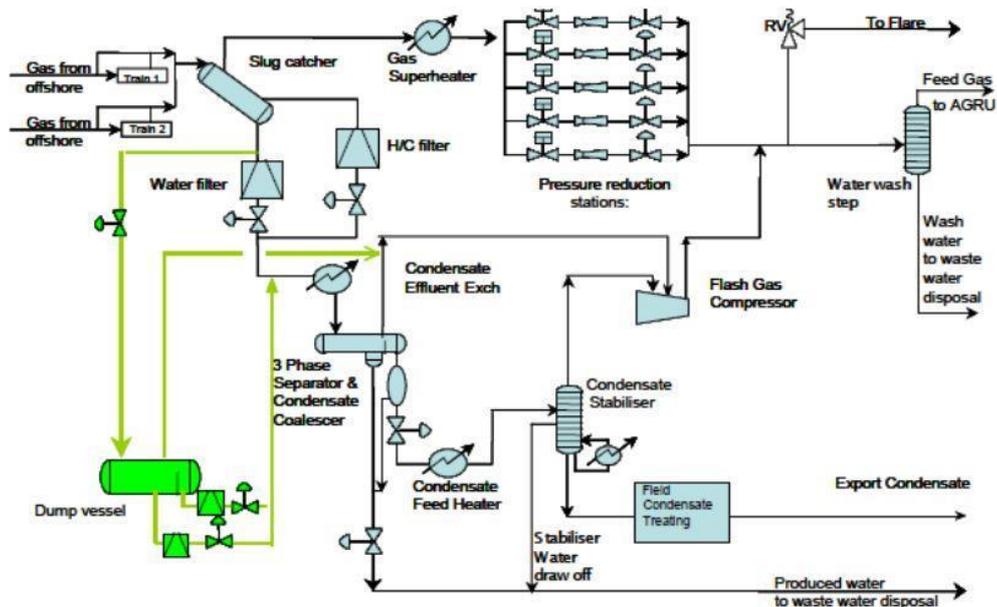


Figure 2-6 Onshore receiving facility (no MRU) [37]

The two main components in the setup shown in *Figure 2-6* are the slug catcher and the 3-phase separator. The slug catcher is used mainly to separate the phases and store liquid surges under pressure temporarily to ensure that the supply of gas to the processing unit is manageable. There are 2 main types of slug catchers, the vessel type and the finger type, the vessel type is often chosen for their compact design, but the finger-type has the advantage of cost and flexibility [37].

The 3-phase separator is placed after the slug catcher, its main function is to remove the aqueous phase from condensate before being sent for further processing. If the separator fails to do its job, there will be significant problems for the downstream processing units. If MEG is used as a hydrate inhibitor, then additional facilities and considerations are required to recover and reuse the MEG.

The MEG recovery unit (MRU) is placed in the aqueous phase stream that is downstream the 3-phase separator. *Figure 2-7* shows the process flow system for onshore receiving facilities when MRU is used.

There are a few design considerations that have to be addressed when MRU is in use [37]. These includes:

- Gas Washing
- Separation of MEG and condensate

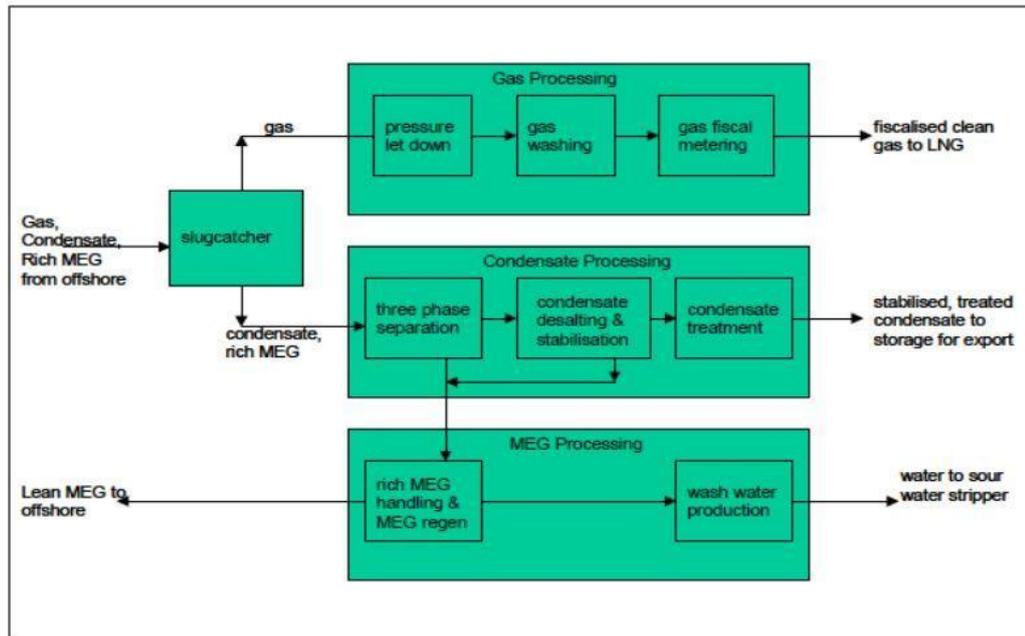


Figure 2-7 Onshore receiving facilities with MRU [37]

- Ensure temperature limit of condensate stabilizer is below the MEG degradation temperature
- Washing of condensate
- Regeneration of MEG
- Ensure pumping pressure is required to pump MEG back to the wellhead
- Building up of salt content in the Lean MEG

For natural gas treating facilities, using chemical inhibitors including MEG will require gas washing to remove them. The presence of such inhibitors will increase downstream operation risk and could affect the quality of the product [37].

The separation of MEG and condensate is to be done in the 3-phase separator. This process is crucial as it will affect the recovery of MEG if separation has not been completely done.

The condensate stabilisers bottom temperature is limited to below the temperature of MEG degradation. The degradation product, which is mainly organic acids, will foul the stabilisers. However, according to Zomermen et al. [37], the degradation of MEG

in stabilisers are not significant as MEG concentration inside the stabiliser is low or the kinetics of degradation is low.

Washing the condensate enable to reduce the chances of fouling in the condensate stabilizer system and the stabilizer overhead compressor. This water wash can also remove MEG and other contaminants in the condensate and improving the quality of product.

The regeneration of MEG will increase the load on the onshore facilities as a reboiler and a distillation column are required. The boiling points of water and MEG are far apart (100°C and 197.6°C) making it easy to separate them. It is usually required to re-concentrate MEG in aqueous phase from around 50wt% (rich MEG) to a concentration of 90wt% (lean MEG) [37].

2.6 MEG Regeneration and reclamation

As discussed before, one of the advantages of using MEG over methanol is that MEG can be recovered after being used. In addition to that, corrosion inhibitors and pH stabilisers can also be recovered in some cases through the same process, providing extra value to the system [38]. Lean MEG, which is the MEG recovery product, may contain some contaminant or could be thermally degraded. Therefore, it is important to study the recovery process in more details. Understanding the recovery of MEG provides a holistic view on using MEG as a flow assurance inhibitor. The recovery process is a complex close loop system containing various physical and chemical processes. According to the water content, the system can be separated into two parts; rich MEG, which is (50 -75 wt. % MEG in water) and lean MEG (more than 75 wt. % MEG in water) [39]. Rich MEG is an aqueous solution of MEG that is rich in other components such as salts, condensate, and drilling mud whereas the lean MEG is the rich MEG that has been stripped off from water and other impurities to meet design specifications so that it is acceptable to be reinjected into the natural gas pipeline for hydrate inhibition [40].

In general, there are three different types of MEG Recovery units; Conventional Regeneration, Slip-Stream Salt Removal, and Full Reclamation.

2.6.1 Conventional Regeneration

Conventional Recovery is the most simplified method where the solutions are to be treated by boiling off the water to leave MEG, salt and non-volatile chemicals in the

solution. The water is removed by sending the process fluid through a distillation column with a reboiler due to the difference in boiling points between MEG and water. This method is suitable for the process fluids, which are predicted to have a very low concentration of salt ions as the downfall of this recovery method is the inability to remove salt ions and solid particles. The removal of divalent salt ions is not completed in this recovery method, instead the ions are allowed to accumulate in the MEG loop. Conventional recovery is not suitable when there is continuous production of formation water as this introduces a large concentration of salt particles into the system which cannot be separated [33].

Brustad [33] stated a number of locations around the globe where the conventional recovery method is used. The Troll Gas plant, for instance, was operated by Statoil/Gassco and started in 1996. This facility experienced some problems such as a significant amount of salt leaving the gas transport pipeline and entering the onshore process plant and also scaling was noticed on inlet heaters, inside distillation columns and on the distillation column reboiler. The conventional regeneration method was also used in the Shell's Mensa field and the same problems were experienced. A larger than expected production rate of condensate into the system leads to increase the concentration of ions to be higher than predicted. On the other hand, the conventional recovery method is unable to remove divalent salt ions from the solution, this leads to scaling, fouling and plugging of the MEG injection system. Therefore, using the conventional recovery method could sometimes lead to operational failure due to salt precipitation and scale formation [33].

2.6.2 Full stream regeneration and reclamation

When salt production rate is high, the full stream regeneration and reclamation method become a necessity. In which the total rich MEG stream is to be send to the reclamation system [41]. This is a proven method that produces a high purity of lean MEG where each section was designed to remove a particular impurity from the system to approach the desired purity of lean MEG [33].

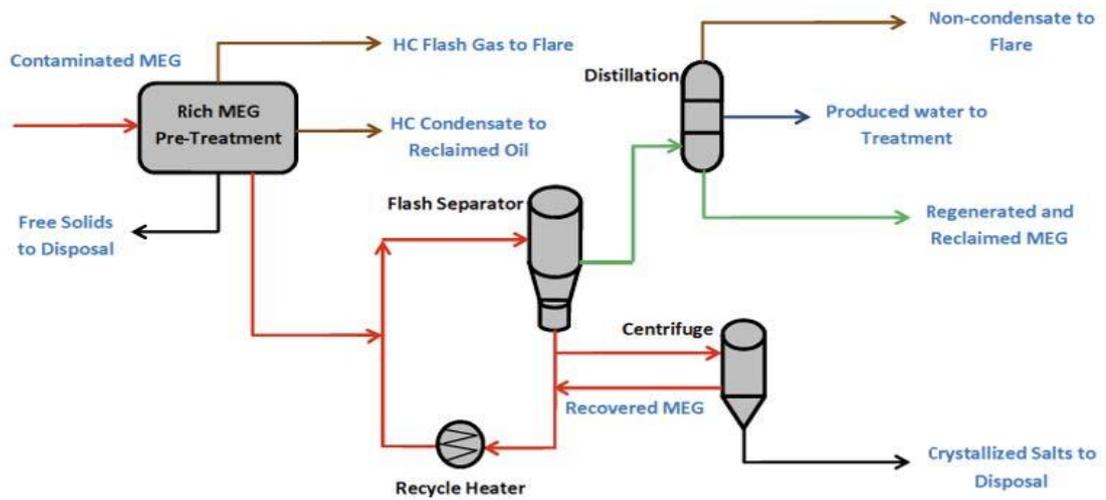


Figure 2-8 Full stream regeneration and reclamation system

2.6.3 Slip stream regeneration and reclamation

Same as the conventional recovery method with an extra option to slip stream a portion of the process fluid through a reclaimer or ion exchanger (see *Figure 2-9*). The rate at which the slip-stream is used depends on the amount of salt impurities in the lean MEG. The advantage of being able to slip-stream through a reclaimer rather than processing the full stream is that inhibitors and pH-stabilisers could be reused rather than being completely separated. This method saves significant amounts of energy as there is no need to heat or cool the entire process fluid during regeneration [33]. Although this method maintains the inhibitors and pH stabilisers in the solution, impurities such as salts could accumulate in the system. While the system could still be functional with the existence of some impurities in the lean MEG, it is more likely to form scale on hot surfaces due to more salts being precipitated as experienced in the conventional recovery method [33]. Slip stream method has been used in some locations around the world such as the Norsk-Hydro Ormen Lange (Norway), Statoil Snøhvit/Hammerfest (Norway), BP Shah Deniz and the Chevron Gorgon MEG recovery processes.

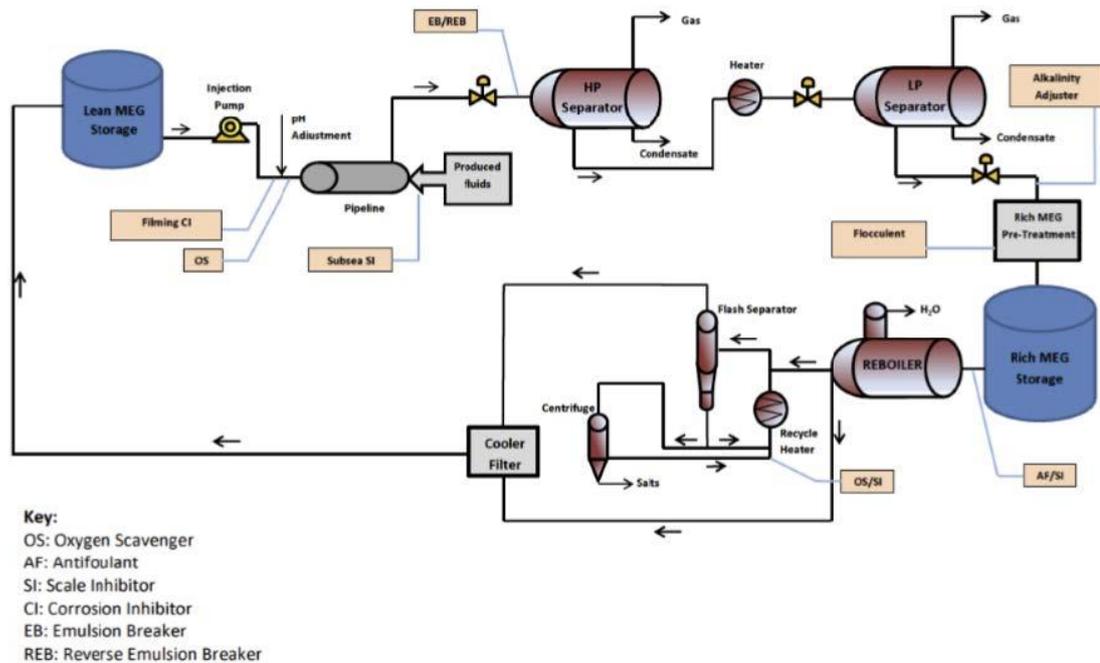


Figure 2-9 Slip stream regeneration and reclamation system [41]

2.6.3.1 MEG Pre-treatment vessel (MPV)

Before MEG undergoes regeneration, it has to be sent to the pre-treatment vessel. It is the first unit in the MRU where the MEG is to be purified from the impurities such as hydrocarbon fluids and divalent salts [33]. The hydrocarbons are removed from the top due to the density difference while the divalent salts precipitate at the bottom of the vessel. It is important to remove the divalent salts at the beginning of the process to reduce the risk of scale formation on the equipment downstream as the distillation column is at higher risk of scale fouling because of the high operating temperatures. Salt precipitation is encouraged in the MPV through manipulating the operating conditions such as temperature, pressure, composition, and pH value.

2.6.3.2 MEG regeneration

MEG regeneration is usually called reconcentration. It uses the boiling points difference between MEG and water to increase the MEG concentration in a distillation tower. The process is typically operated at 120-135 °C and 0-101 kPa [42].

In short, the regeneration system is basically a distillation column that has a feed inlet of rich MEG and separates water from top and lean MEG from bottom.

2.6.3.3 MEG reclamation

The third step in the MEG plant is the reclaimer. It is basically a flash separator that remove the monovalent salts and unwanted suspended particles from the salty lean MEG coming from the regeneration system [43]. The overhead top product will be high purity Lean MEG stream and the bottom product will be a salt slurry stream. The operating conditions for the reclaimer are usually 10-15 kPa [44].

2.6.4 MEG regeneration and reclamation system contaminants

Any substance that can cause an undesired products during the regeneration process is called contaminant and it has to be removed from the system. Different substances cause different problems such as scale precipitation, fouling, and deposition.

2.6.4.1 Salts

According to Latta et al [40], the MEG regeneration unit contains different kinds of salt. These salts may be accompanied with the formation water produced as corrosion product in the pipelines, or injected into the system. However the injected chemicals are not considered as contaminants if they do not react with other contaminants, which could cause some issues such as precipitation or fouling in the heat exchangers, because they are injected to achieve a desired condition and they are recycled in most cases. *Table 2-1* shows the source of different salts that may be present in the MEG regeneration units.

Table 2-1 Source of ions from different salts [40]

Source	Monovalent ons	Divalent ons
Formation water	Na ⁺ , Li ⁺ , K ⁺ Cl ⁻ , B ⁻ , HCO ³⁻ , CH ₃ CO ²⁻ , C ₃ H ₅ O ²⁻	Cations: Ca ²⁺ , Mg ²⁺ , Sr ²⁺ Anions: CO ₃ ²⁻ , SO ₄ ²⁻
Pipeline corrosion		Fe ²⁺ , CO ₃ ²⁺

Due to the high solubility of the monovalent ions salts such as Chloride and Bromide, they do not cause any problem to the system if their concentration did not increase beyond the saturation point. If so, scaling will occur due to the monovalent salts accumulation and that is why they have to be removed from the system using the reclaimer [40]. As the solubility of monovalent salts decrease with decreasing the

temperature, the deduction in temperature after the reboiler is a serious problem in the MEG regeneration system [45]. On the other hand, divalent salts, which are mostly calcium and magnesium salts, have low solubilities that decrease with increasing temperature and could precipitate anywhere inside the MEG regeneration unit causing fouling issues [38]. Therefore, the system will have a high risk of fouling when the MEG stream temperature is increased to 120°C or more [46].

2.6.4.2 Hydrocarbons

Some hydrocarbons such as gas condensates are soluble in the rich MEG (aqueous phase of production fluid). Other hydrocarbons will form emulsion when mixed with the Rich MEG. These hydrocarbons will go through the MEG regeneration system if the separation of the phases is not efficient. Light hydrocarbons which has carbon chains below C17 can contaminate the produced water stream because of their high volatility [47]. Heavy hydrocarbons, on the other hand, with chains above C17, are less volatile and will stay in the MEG stream when being transferred through the MEG recovery unit.

The presence of hydrocarbons in the MEG regeneration system could have negative consequences even if they existed at low concentrations. Light hydrocarbons will flash with the overhead stream and damage the distillation tower when passing through the regeneration system. The consequences could be worse inside the tower with high concentration of hydrocarbons [40]. The best way to reduce the effect of hydrocarbon on the MRU is to increase the efficiency of the upstream hydrocarbon separation.

2.6.4.3 Other contaminants

There are some other chemicals that may be considered as contaminant in the MEG reeration and reclamation system such as suspended solids, organic acids, acid gases, mercury, corrosion inhibitors, oxygen scavenger, de-emulsifiers, wax, and scale inhibitors. Latta et al, [40] studied intensively the origin, consequences, and treatments of these contaminants.

2.7 MEG pre-treatment vessel operating conditions

The MEG regeneration and reclamation unit contains various physical and chemical processes in each section. As such, we will be focusing in this research on the operating conditions of the MEG pre-treatment section. The main function of the MEG pre-treatment vessel (MPV) is to remove the divalent ions salts from the solutions. The

precipitation of divalent ions in the MEG Pre-Treatment Vessel is promoted through adjusting the operating conditions to achieve a supersaturated solution and increasing the rate of precipitation inside the vessel. The divalent salts precipitation is a complex process and it depends on number of variables that must be optimised to achieve the optimum precipitation rate. The temperature and pH are the most influential operating parameter which impact the precipitation in the MPV. In addition to this, the composition of the stream entering the vessel must be considered to ensure it contains a sufficient concentration of anions and cations to allow the precipitation to occur.

2.7.1 MPV temperature

The operating temperature is the most important parameter in the divalent salt separation process that is easily controlled and adjusted throughout the operation. Some of the upstream operating conditions such as pressure and flowrate remain constant with the upstream pipeline.

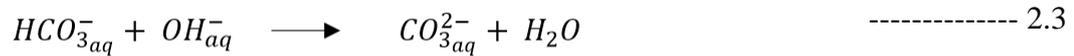
There are number of competing equilibriums and reactions which are affected by temperature such as the solubility of carbon dioxide, dissolution reaction, and interactions with MEG. Due to the complexity of the interaction and considering each effect, the temperature is not a sufficient way to optimise the vessel. The effect of temperature as a whole must be considered to obtain the most accurate results.

2.7.2 pH

The value of pH only affects the precipitation of specific salt compounds that are pH-sensitive. Divalent salts can be classified into two categories, pH-independent and pH-sensitive [48]. Calcium sulfate is a pH independent salts therefore is not a strong function of the solution pH. All carbonate salts are strongly influenced by the pH of solution and cannot precipitate unless specific pH conditions are met [48].

At high pH, the equilibrium will favour the formation of carbonate ions and thus increase the activity of carbonate ions. Due to this, the precipitation of calcium carbonate will reduce the pH of the solution as the carbonate ions are consumed [49]. The continual addition of a base alkaline or carbonate ion injection may be required to ensure sufficient carbonate ions are present in solution to maintain the rate of precipitation.

Temperature and pH are usually linked together due to the relationship between carbon dioxide solubility and the formation of carbonate ions. As the temperature increases the solubility of carbon dioxide in the solution decreases due to the volatility of the gas and this can lead to a lower concentration of carbonate ions [33], [47]. Despite this trend, the temperature is maintained at a high level (generally 80°C) to maintain an ideal equilibrium position for the reactions of carbon dioxide with water and to promote the nucleation and growth of crystals. To combat the low solubility of carbon dioxide at high temperatures, a basic solution can be added to ensure there is a sufficient concentration of carbonate ions in solution. When a base is added to the solution, the following reactions (*equations 2.2 and 2.3*) take place with carbon dioxide and bicarbonate ions to form additional carbonate ions [47]



The desired solution pH is approximately 9.0 for carbonate precipitation to occur but this value can be lowered and still achieve sufficient precipitation [47]. The case at which the pH must be decreased or increased depends on the composition of the production fluid. However, the pH must be increased in some cases due to the presences of organic acids in the formation water. This could be done by injecting NaOH into the MPV [47]. If the precipitating carbonate ions are still efficient then the pH will be kept as low as possible as downstream regeneration equipment requires a lower pH that is normally achieved by injecting an acid. Due to the large costs associated with needing to continuously inject a base (NaOH) and then neutralize with an acid (HCl), the lowest amounts of both chemicals should be injected in order to optimize the operational cost.

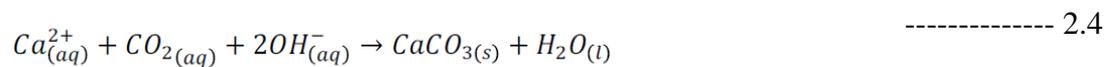
A research completed by Bache [49] investigated the change in pH that occurs during the simultaneous precipitation of calcium carbonate and calcium sulphate during MEG regeneration. This study was completed over a range of MEG concentrations and at two different temperatures and confirmed the expected results that the precipitation of calcium carbonate will lower the pH and the precipitation of calcium sulphate will not change the pH of the solution. This research is significant in being able to identify the

calcium salt which has formed based on the pH of the solution entering and leaving the MPV.

2.7.3 Feed compositions

The operating conditions and required chemical injection rates are affected by the composition of the feed. An important consideration for the composition is the ratio between the concentration/flowrate of the divalent ion and carbon dioxide in the sparging gas. For a production fluid which contains large amounts of divalent ions, a proportionally large amount of carbonate ions are required in the solution.

The optimum amount of carbon dioxide in the MEG solution is the concentration which balances *equation 2.4*:



The concentration of calcium ions cannot be manipulated or changed as they are already present in the formation water. There is minimal carbonate ions produced from the reservoir and the only natural source of carbonate ions is through the dissolution of carbon dioxide. The temperature and pH are controlled during operation to 80°C and 9.0 respectively and the pressure is manipulated to assist in the production of carbonate ions. However, if these conditions do not produce sufficient amount, an injection Na₂CO₃ will be required to introduce more carbonate ions [47]. Sodium hydroxide is recommended as a source for additional alkalinity if require to increase the pH of the system as it has a minimal impact on the downstream reclaimer size when compared to other hydroxide salts such as KOH. This is due to the lower molecular weight which will results in a lower mass of salts being produced [47].

2.7.4 Pressure

According to Anderko [50], Pressure does not begin to influence the solubility of a salt in the solution until the pressure is at a very high level. The advantages in the performance due to the increase in pressure are minimal and do not offset the large amounts of energy and large costs associated with pressurising the MPV. Due to this, the MPV is typically run at atmospheric or low pressures [50]. The MPV at Curtin University facility is operated at atmospheric pressure however in industry it is common to increase the pressure of the vessel as large companies are interested in high

performance for a moderate increase in operational cost [47]. The increase in pressure is advantageous as high pressure will lead to increase the solubility of carbon dioxide in the solutions. This promotes the formation of carbon dioxide ions and increases the pH all of which are advantageous as a low concentration of carbon dioxide will prevent precipitation. An increase in the pressure may reduce the need for injecting a base or additional source of carbonate ions [47].

2.8 Carbon dioxide solubility

The solubility of carbon dioxide in solution depends on the operating temperature of the MPV. The solubility of carbon dioxide in a liquid solution decreases as the temperature increases as gas has a lower volatility [42]. A lower concentration of carbon dioxide in the solution results in a low concentration of carbonate ions and this may prevent carbonate salts from forming. *Figure 2-10* shows the trends of the dissolution equilibrium constant (KH) of carbon dioxide into a solution as a function of temperature (*equation 2-5*).



As the MPV must be operated less than 100°C to prevent boiling of water, the data shows that at lower temperature, larger fraction of CO₂ dissolves in the solution.

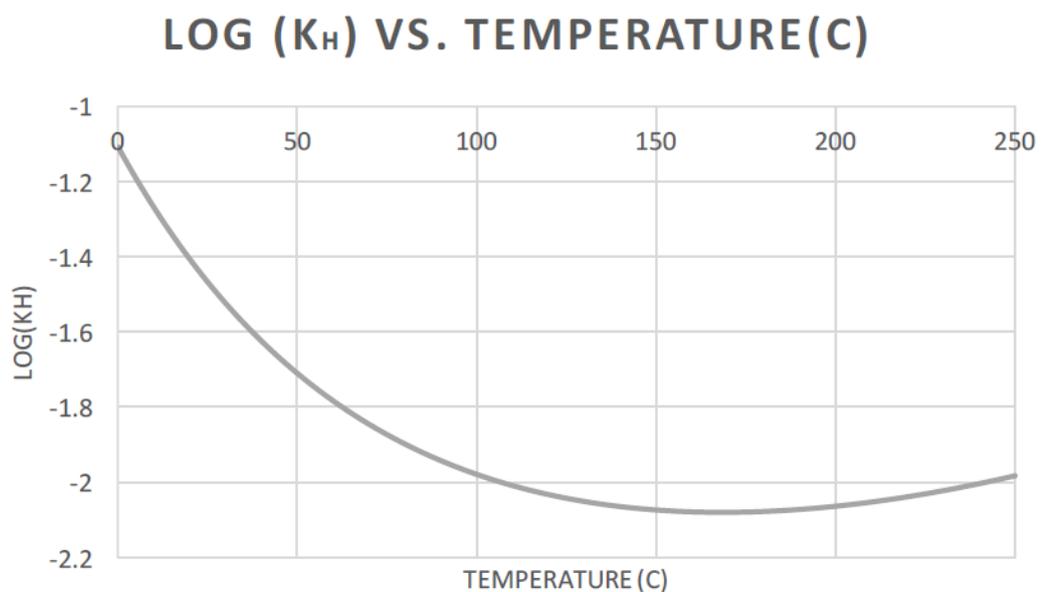


Figure 2-10 The effect of temperature on the CO₂ dissolution equilibrium position [51]

This relationship data was obtained from experimental data for a water/CO₂ system without MEG. The numerical values obtained from *Figure 2-10* are not directly applicable due to this project however the trend is important to be considered. The introduction of a co-solvent MEG will not influence the trend of increasing temperature lowering the solubility of carbon dioxide in the solution. Research has shown that the solubility of carbon dioxide in MEG is larger than in water and this phenomenon has been attributed to the intermolecular forces, which enhances the affinity of carbon dioxide to MEG more than to water [42].

2.9 Emulsion

Emulsion is basically a mixture of liquids that are immiscible with each other. It usually occurs when two different liquids act as two phases called dispersed and continuous. The dispersed phase is simply scattered in the continuous phase to form the emulsion [52]. The boundary layer between the dispersed and continuous phase is called interphase, which looks cloudy because of the scattering phases.

Emulsion may occur in multiple forms; oil in water o/w emulsion where oil is the dispersed phase and water is the continuous phase, water in oil w/o emulsion where water is the dispersed phase and oil is the continuous phase. It is also possible that multiple emulsion form such as water in oil in water w/o/w and oil in water in oil o/w/o emulsions[53].

2.9.1 Demulsifier

Separating water from oil is the most important objective in any oil and gas production facility. The separation process could be very challenging due to the limited residence time. Therefore, demulsifiers (emulsion breakers) are usually used to enhance the separation process. Demulsifiers work by targeting the interface layer between the two phases to enforce the droplets to disperse or form larger ones. As a results, this action changes the density and makes the separation process easier.

Many factors have to be considered when choosing and analysing for the proper type of oilfield demulsifier; the type of emulsion whether it is oil-in-water or water-in-oil, the API gravity of the crude, the rate of water drop, sharpness of oil/water interface, and cleanliness of the water.

The need for demulsifiers is seen anywhere oil and water are in use. For instance, emulsion breaker are used in; chemical processing, petroleum refineries, fuel washing

prior to gas turbines, slop and tramp oil treatment, and more importantly in the processing of crude oil in the oil field, both to treat synthetic mud and to treat the produced hydrocarbons [54].

2.10 MEG degradation

MEG degradation can be defined as MEG that has subjected to chemical changes to form other products. The degradation products formed are mainly glycolic acid and formic acid with a small amount of acetic acid [42]. Glycolic acid and formic acid as main degradation products were reported by Rossiter et al [55]. However, results from AlHarooni et al. has shown significant amount of acetic acid in thermally degraded MEG [56]. The reason for the difference between the results is speculated to be the higher temperature used in AlHarooni et al.'s work (135-185°C). While Psarrou et al. and Rossiter et al. conducted thermal degradation experiments at a lower temperature, 80-140°C and 75-101°C respectively. A visual method to determine thermal degradation of MEG is to observe the colour changes of the thermally exposed MEG. The higher the temperature MEG is exposed to, the darker the solution becomes. *Figure 2-11* shows the degradation level that is assigned with a certain characteristic. Also, as the level of degradation becomes higher, the hydration inhibition effect is lowered [57]. unexpectedly, MEG with the least effective hydrate inhibition was observed for samples that are exposed to 135°C, compared to MEG that were more severely degraded at higher temperature [57].

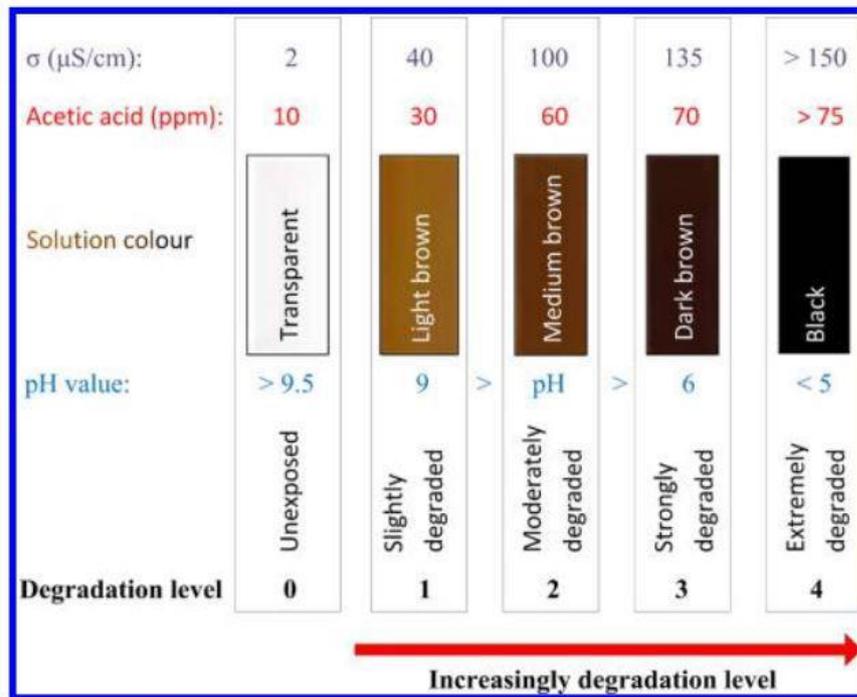


Figure 2-11 The effect of temperature on MEG degradation [57]

However, results from AlHarooni et al. (2015), AlHarooni et al. (2016) and Rossiter et al. (1985) indicated that total degradation products increase with temperature. This has a conflict with Psarrou et al. (2011) results from the trend is attributed to ingress of air into the reactor cell during the experiments. In addition, literatures showed that thermal degradation of MEG occurs above 135°C [57], 162 °C [58] or between 170-195°C [41]. No more investigations have been done on the difference in composition of organic acid components. This is because the focus is given to the total amount of MEG degraded. The chemical equations for glycolic acid and formic acid formation are shown in *equation 2.6* and *equation 2.7*. It is obvious that the degradation process is an oxidation process. The degradation would be more significant if MEG is constantly exposed at high temperature conditions for a long time [42]. This term is called thermal oxidation [55]. Also, MEG may degrade at room temperature when exposed to oxygen [57].



Thermal degradation of MEG is more likely to occur inside areas that have high temperature (>162°C) or at sites of possible air exposure. Precipitated sodium chloride

with carbonates, oxide, and sulphide can cause thermal degradation of MEG. This is because the deposited salt will cause hot spots and fouling, resulting in high skin temperatures at the heat exchanger. Thermal degradation occurs when MEG comes in contact with the hot spots [43]. Also, the fluid within the MEG regeneration and reclamation close loop can reach up to 185°C occasionally [41]. Some metal ions can also promote the degradation of MEG, Copper and Aluminium are two metal ions that promotes degradation of MEG [55].

Xia et al. argues that the effect of degradation is small because the production process of Lean MEG is airtight and should not contain oxygen [59]. Furthermore, oxygen scavengers such as ammonium bisulphite (ABS) are present in the Lean MEG, which decrease the oxygen content in the Lean MEG. However, there can be oxygen leakage into the MEG reclaimer through equipment connections and instrumentations due to the vacuum condition in the flash separator or distillation column [44]. A side effect on the degradation of MEG is that the produced organic acids can lower the pH value of the solution, causing acceleration on the corrosion of metals [55].

To prevent degradation of MEG, the best way is to ensure no ingress of oxygen will come in contact with MEG. In the regenerator, a blanket gas can be used to reduce the contact of MEG with oxygen. Also, using a back flush filter is able to reduce MEG degradation by preventing air diffusing into the system [40].

2.11 Solubility thermodynamics

Understanding the solubility thermodynamics of strong electrolytes in a solution is critical in order to gain an understanding and to optimise the operation of the MPV. Extensive research has been done on the thermodynamics of divalent salt ions solubility in aqueous conditions and accurate solubility models that could be applied to predict the solubility. The solubility of ions in water and MEG solution is less clear and heavily reliant on experimental data rather than correlations [12].

2.11.1 Thermodynamics of solutions

A solution is made from various pure species which are referred to as the components or constituents of the solution [60]. In aqueous solutions, the measure of composition and concentration of each species is through the concept of molality, 'm'. Molality is a measure of the number of moles of the solution in kilogram of solvent, which is slightly different from traditional calculations of concentration that are based on a

volume. This measurement of composition is advantageous in solution thermodynamics as it is independent of temperature and due to this, the density of solution can remain unknown and a mole composition can still be determined. The molality of a species ‘i’ in a solution can be calculated by *equation 2-8* [60].

$$m_i = \frac{1000g_i}{M_i g_o} = \frac{1000n_i}{g_o} \quad \text{-----} \quad 2.8$$

Where:	m_i	Molality of species ‘i’ (mole solute / kg solvent)
	g_i	Mass of solute (grams)
	g_o	Mass of solvent (grams)
	M_i	Molecular Weight of solute (g/gmol)
	n_i	Moles of solute

2.11.2 Thermodynamic of precipitation

The precipitation of divalent salt ions occurs through a precipitation reaction whereby the constituent cation and the anion form a solid ionic salt from an aqueous solution. These reactions are reversible and it is convention to show the dissociation reaction as the forward reaction whereby the salt is dissolving into the constituent ions. The dissociation/precipitation reaction for calcium sulphate can be expressed as per *equation 2-9*.



The equilibrium position of the above reaction is a function of number of variables that can be manipulated to encourage the desired steady state conditions. In the MPV, for instance, the desired equilibrium state is the reverse reaction whereby the solid divalent salt is being formed [60].

2.11.2.1 Solubility equilibrium

For precipitation to occur, the precipitation reaction must be at an equilibrium position, which favours the formation of salt. For equilibrium to occur, two equilibrium

constraints must be met; the phase equilibrium and the reaction/ionic equilibrium [60]. Zemaitis et al. (1986) states phase equilibrium occurs when “the chemical potential of any species i in phase a is equal to the chemical potential of that same species i in phase b ” Consider the aqueous salt A in equilibrium with the solid salt A, the phase equilibrium state can be represented as per [equation 2-10](#) [60]:

$$\mu_{A,AQUEOUS} = \mu_{A,SOLID} \quad \text{-----} \quad 2.10$$

The driving force which causes crystallisation is the change in chemical potential energy between the solution and the solid crystal state [61]. This can be expressed in [equation 2.11](#):

$$\Delta\mu = \mu_{\text{solution}} - \mu_{\text{crystal}} \quad \text{-----} \quad 2.11$$

The second equilibrium state that must be satisfied is the ionic reaction equilibrium for the dissociation reaction of a salt into its anions and cations components [60]. Considering the dissociation reaction of the strong electrolyte salt A into the constituent ions (B and C) in [equation 2.12](#):



The chemical reaction/ionic equilibrium can be described by [equation 2.13](#):

$$\mu_{A,AQUEOUS} = v_c\mu_c + v_b\mu_b \quad \text{-----} \quad 2.13$$

Where, v_b and v_c are the stoichiometric numbers of the anion and cations respectively. The chemical energy of a species in solution is expressed in terms of activity (a_i).

2.11.2.2 Activity and Activity coefficients

The general practice of calculating the chemical potential of a species in a solution is relating the fugacity and activity of each specific species [62].

$$\mu_i(T) - \mu_i^o(T) = RT \ln \left(\frac{f_i}{f_i^o} \right) = RT \ln(a_i) \quad \text{-----} \quad 2.14$$

Where f_i^o and $\mu_i^o(T)$ are the fugacity and chemical potential at a standard/reference state. A species chemical potential at any given time cannot be measured directly and as such the species activity (a_i) is used to relate the current potential energy to a reference state [60]. For an ideal system, the activity of a component is equal to the concentration. However, in reality, there is a slight deviation due to particle

interactions. The concept of activity coefficient (γ_i) is added to adjust for the deviation [63]

$$a_i = m_i \gamma_i \quad \text{-----}2.15$$

Figure 2-12 shows the deviation between molality and activity over a range of molality.

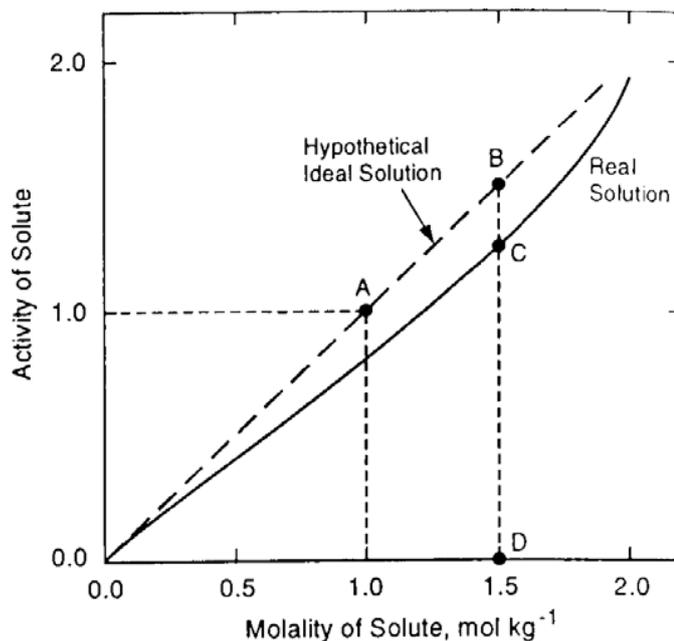


Figure 2-12 Activity and molality deviation [62]

The deviation between the real and ideal activity is due to the interaction between the solute and the solvent. The dotted hypothetical line is the line where $m_i = a_i$ and as can be seen in Figure 2-12, at low molality this tends to be the case [62]. As the molality increases, the deviation away from the hypothetical line becomes more prominent and the activity coefficient can be used to quantify and account for this. With reference to Figure 2-12, at a molality of 1.5 mole/kg, the real activity is approximately 1.3 (pt B) whereas the ideal activity is 1.5 (pt C). Therefore the activity coefficient ($\gamma_i = a_i/m_i$) is $1.3/1.5 = 0.87$. This is an important thermodynamic principle for when a co-solvent, such as MEG, is added to the solution as the interactions between Water-MEG-salt cause an additional deviation between the real and ideal states [62].

The difference between the Gibbs energy of the ideal solution and the real solution is a powerful quantity for determining the solution properties known as “Excess Gibbs

Energy". The equation for the Excess Gibbs Energy of a solution (at the same temperature, composition, and pressure) is as per [equation 2-16](#).

$$\Delta G^E = \Delta G^{Real} - \Delta G^{deal} \quad \text{-----2.16}$$

The standard states for the ideal and real energies are the same and therefore the excess Gibbs energy can be expressed in terms of the activity and activity coefficient as below;

$$\Delta G^E = RT \ln (a_i^{Real} - a_i^{ideal}) \quad \text{-----2.17}$$

$$\Delta G^E = RT \ln (m_i y_i - m_i) \quad \text{----- 2.18}$$

$$\Delta G^E = RT \ln (y_i) \quad \text{-----2.19}$$

This expression can be rearranged for the activity coefficient as per equation 2.20 [62].

$$\gamma_i = \left(\frac{\delta \left(\frac{G^E}{RT} \right)}{\delta n_i} \right)_{T,P,n_i} \quad \text{-----2.20}$$

[Equation 2.20](#) forms the basis for which activity coefficient models have been created from. A number of activity coefficient models have been determined which relate the operating conditions with the activity coefficient for a solute in a solvent [62].

2.11.2.3 Saturation Index

To design, optimise, and control the MPV, process engineers rely on software to predict the extent at which a salts solubility varies with key operating conditions such as temperature, pressure and anion and cation concentration. The Saturation Index (SI) is used to measure the precipitation tendency of a specific salt and is calculated by [equation 2-21](#)

$$SI = \log_{10} \left(\frac{\{Ion Activity Product\}}{K_{sp}(T, P)} \right) \quad \text{----- 2.21}$$

CaCO₃ (Calcite) is a divalent salt which precipitate in the MPV and the Saturation index for this salt compound can be determined by [equation 2-22](#)

$$SI_{calcite} = \log_{10} \left(\frac{a_{Ca^{2+}} \cdot a_{CO_3^{2-}}}{K_{sp,calcite}(T, P)} \right) = \log_{10} \left(\frac{[Ca^{2+}][CO_3^{2-}] \cdot \gamma_{Ca^{2+}}^S \cdot \gamma_{CO_3^{2-}}^S}{K_{sp,calcite}(T, P)} \right) \quad 2.22$$

- Where:
- K_{sp} Solubility product of calcite as a function of temperature and pressure
 - $a_{Ca^{2+}}$ Activity of calcium ions
 - $[Ca^{2+}]$ Molality (mol/kg of H₂O)
 - $\gamma_{Ca^{2+}}^S$ Activity coefficient of calcium (calculated by solubility models)

The Saturation Index describes the extent of super-saturation of a solution with respect to the equilibrium position and thus determines the behaviour of the solution (precipitation or dissolution). The denominator of the saturation index contains the solubility equilibrium constant (K_{sp}) for the specific salt at the given temperature and pressure. The numerator of the saturation index is calculated in the same manner as the solubility equilibrium constant by multiplying the activity of the anion and cation. However, this is not calculated at the equilibrium condition, this is calculated at the specific point in time. If the system is at equilibrium, the numerator and denominator will be the same value and thus the fraction will be equal to one. If the product of the activity of the ions is greater than the equilibrium value (such that the solution is supersaturated), the fraction will be greater than one which suggests that precipitation may occur. Similarly, if the product of the activities is less than equilibrium, the numerator will be less than the equilibrium state and thus the fraction will be less than one suggesting that dissolution is more likely to occur.

The risk of precipitation that may occur can be determined by the value of saturation index as per [Table 2-2](#) [64].

Table 2-2 risk of precipitation [64]

SI range	Risk of precipitation
SI < 0	No risk
0 < SI < 0.5	Low
0.5 < SI < 1.0	Medium
1.0 < SI < 2.5	High

For positive SI values the salt is supersaturated and crystal formation may occur. If the saturation index is only slightly positive (less than one), the formation of crystals may not be observed due to slow kinetics as the system is very close to equilibrium [65]. If the Saturation Index equals zero, the salt is in equilibrium and for negative value of saturation index the salt is under-saturated and additional dissolution will occur if solids are present.

2.11.3 The effect of MEG on salt solubility

The solubility of divalent ions changes significantly with the addition of a co-solvent and the solubility limits and saturation index are much harder to determine. The precipitation of divalent salts in the Pre-Treatment Vessel occurs from a mixed solvent solution that contains rich MEG of approximately (44 wt%) MEG and (56 wt%) water and this is an important factor, which must be considered. MEG has been known to lower the solubility of most salts as MEG interacts with each component to prevent the ability of the ions to dissolve in the solution [62]. The activity of water decreases with an increasing concentration of MEG. The Pitzer model is very accurate at calculating the activity coefficients for aqueous solutions however it is unable to calculate the activity coefficients for a MEG and water mixed solvent.

Divalent ions become less soluble with the addition of MEG as a co-solvent due to the additional interactions between molecules [62]. This phenomenon can be seen in [Figure 2-13](#) where the solubility of calcium sulphate is varying with different MEG concentrations.

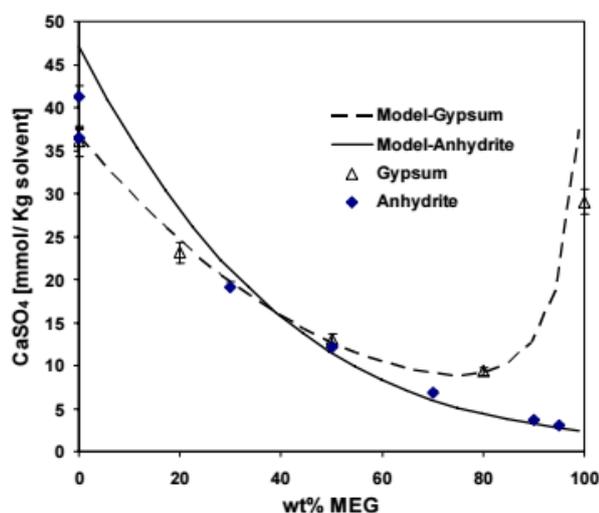


Figure 2-13 Calcium sulphate in MEG Solution [62]

The solubility of anhydrite continues to decrease with the increasing fraction of co-solvent MEG in solution. For instance, the solubility of gypsum continues to decrease with MEG concentration until approximately 80% wt. MEG where the solubility increases [62]. In the MEG regeneration plant, the target concentration of lean MEG is 80% wt. and therefore any concentration greater than this value will not be experienced in the MEG plant. Thus, this trend for concentrations greater than 80% wt. can be neglected.

2.12 Scale

Common impurities in water may lead to scale or sludge deposits in boilers and cooling towers. Four easily identifiable impurities are Hardness, Alkalinity, Silica, and Iron.

- Hardness: Calcium and Magnesium salts in the water.
- Alkalinity: Can be combined with hardness forming scale.
- Silica: Can form tenacious deposits on heat transfer equipment and power generation equipment.
- Iron: Can form very dense deposits on heat transfer equipment.

As only pure water is evaporated from cooling water and steam boiler systems, impurities remain and concentrate, increasing the potential for scale formation and sludge deposits. Scale and sludge deposits in boilers and cooling towers impede heat transfer, which leads to higher energy costs and can cause a loss of equipment operation and premature failure. The reason water is treated for scale and sludge control is to extract all of the beneficial characteristics of water, while neutralizing the negative effects of impurities in the water [66].

2.12.1 Scale prediction

In most oil and natural gas fields, scale prediction and inhibition could be very challenging especially at high temperatures above (150°C) and pressure (1000 bar) and the total dissolved solids (TDS) is greater than (300 000mg/L). In order to easily predict scale and even the corrosion tendency, it is necessary to predict the brine chemistry, the pH level, and the scaling tendency of the production system. However, some systems are complicated and therefore scale prediction is not an easy process [48]. The following points has to be addressed to predict the scale formation within complex systems:

- The theoretical background of scale prediction and reliability
- The effect of brine salinities, composition, and temperatures on pH, scale, and corrosion
- The effect of organic acids on scale formation and;
- The impact of hydrate inhibitors on scale formation and prediction

In general, two types of scale could be found in the oil and gas production fields; pH-dependent and pH-independent. For example; the carbonate and sulphide scales are soluble in acids and therefore their scaling tendencies are highly affected by the solution pH. The scale prediction for this case is more complicated as the component that control the brine pH are also affect the scaling tendency giving the fact that at constant temperature, the solubility of all mineral scales and divalent ions decreases when pressure decreases. On the other hand, the scaling tendency of sulphates and halites are pH-independent as they are not affected by the brine pH [48]. Sandengen [12] has developed a model to predict the scale tendency in MEG/ water solutions that contain different minerals including pH-dependent and pH-independent salts.

2.13 Process Control

It is usually very difficult to achieve consistent, economic, and safe production level by only human manual control, automatic process control is highly recommended in continuous production processes. It is a combination of control and chemical engineering used in many industrial fields such as oil refining, pulp and paper manufacturing, chemical processing and power generating plants [67].

The automatic process control helps few operators to manage the industrial plants at a high level of consistency despite the size, type and the complexity of the plant. Therefore, the development of large automatic control systems allows to design processes with high volume production rates and complexity that is economically and safely operated [67]. The process control application vary from controlling level and temperature in a single vessel to a whole processing plant that contain large number of control loops.

2.13.1 Historical background

One of the first control system applications came along as water control device created by Ktesibios of Alexandria who invented a float valves to regulate water level in water clocks in the 3rd Century BC. Heron of Alexandria invented a float valve similar to the

fill valve used in modern toilets in the 1st Century AD. However, The physics principal did not involve in process control application until the 16th century when Cornelis Drebbel built a bimetallic thermostat to control a furnace temperature followed by the discovery of the vessel pressure that could be regulated by placing weights on top of the vessel by Denis Papin in 1681. Later, the fantail used to enhance the windmill efficiency was created by Edmund Lee in 1745. It was used to keep the windmill directly facing the incoming wind [67].

More automatic control processes were invented with the dawn of the industrial revolution to replace manual operation with automatized processes. Oliver Evans invented a water powered flourmill, which is operated by buckets and screw conveyors in 1784. In 1910, the same idea was applied by Henry Ford who created an assembly line to reduce operator interventions in car production processes [67].

However, the formal control method (PID control) that is used for the continuous process control was not developed until 1922. When the Russian American Engineer (Nicolas Minorsky) used theoretical analysis to design a full automatic ship steering for the US navy. He noted that his observations of the helmsman drove the ship based on the current and the past course error as well as the current rate of change [68]. Then, he developed a mathematical analysis as he was aiming to stabilize the ship not only general control [69]. Although proportional control provides the stability required for small disturbances, dealing with steady control need to include the integral term as the proportional control is insufficient. Lastly, the term derivative was added to enhance the process stability and control [69].

2.13.2 Process control development

The development of the process control operation of large industrial plants has gone through many stages. First, process plants were controlled by local panels. This operation required large number of operators to attend these distributed panels to watch and modify the operation if necessary. In addition, there was no process overall view at that stage. The next stage of development was to move all the plant measurements to a central control room. This method was effective in terms of localising all the plant panels into a centralized room and also to reduce the manpower resources and provide a decent overview of the whole process. However, this method was inflexible because every single control loop has its own controller hardware. As such, the operators

needed to continuously move within the room to watch different parts of the process[69].

Lastly, the distributed control system (DCS) was created after the electronic processors and graphic displays became available. This method replaced the old discrete controllers with computer based algorithm that connected to a network of input-output racks along with their own control processors. These racks are to be distributed around the large industrial plants and communicate with the control rooms through graphs display[69].

The DCS method simplified the plant control interconnection and reconfiguration such as cascade loops and interlocks. It also interfaces easily with other production computer systems. With the DCS method, there is no more need to physically record events logging such as charts as it is all automatically recorded. Finally, it provides high level overview and production of the plant (*Figure 2-14*) [70].



Figure 2-14 Modern Control room [71]

2.13.3 Control system component

A simplified control loop in any process should contain the following four elements [71]:

- *Field devices.* A sensor (or transmitter) measures some variable in the process, such as temperature, liquid level, pressure, or flow rate, and converts that measurement to a signal (usually 4 to 20 mA) for transmission to the controller or control system.

- *Control algorithm.* A mathematical algorithm inside the control system is executed at some time period (typically, every second or faster) to calculate the output signal to be transmitted to the final control element.
- *Final control element.* A valve, airflow damper, motor speed controller, or other device receives the signal from the controller and manipulates the process, typically by changing the flow rate of some material.

Process. The process responds to the change in the manipulated variable, with a resulting change in the measured variable.

2.14 Corrosion control strategies in MEG plant

The corrosion of the MEG Regeneration plant is an important design consideration must be considered and developed during the design of the processing plant. Execution of the corrosion control plan during operation is equally important to the design prior to process plant construction. The corrosion mitigation plan is designed to combat the corrosion rate in order to maintain it below an acceptable rate for the entire life of the reservoir production. There are a number of factors which impact the selection of corrosion mitigation plan such as the expected production rate, gas composition and expected rate of water production [72]. For wet sour gas fields, it is required to use both hydrate inhibitors (MEG) and corrosion inhibitors. However, the interaction between these two chemicals can lead to counterproductive effects such as emulsification, the promotion of corrosion and hydrates and foaming. The type of corrosion mitigation and the rate of injection impacts the performance of divalent salts in the pre-treatment vessel as it can impact the solubility of ions through altering the pH and the way it interacts with each ion species.

Acid gases (CO_2 and H_2S) have a significant impact on the rate of corrosion of the MEG system. When these gases are present with brine and at a high temperature and flow rates, the corrosion of pipelines is more likely to occur. In order to prevent the corrosion of pipelines there are two types of inhibitors which are used; Film Formation Corrosion Inhibitors (FFCI) and pH Stabilisers [38].

2.14.1 pH control strategy

The pH corrosion control method is a very effective corrosion prevention strategy and this is the most commonly used technique in industry. The principles of this method is to basically raise the pH through injecting a chemical that increases the concentration

of carbonate ions and encourage any Fe^{2+} ions to form an iron carbonate (FeCO_3) film layer. The main disadvantage of this technique in the MEG Regeneration system is that the pH stabiliser can encourage the precipitation of calcium carbonate through the increase in pH. This elevated pH may cause scale formation in pipelines rather than the vessel [38]. [38]. Thus, when formation water is produced it is recommended that pH-stabilisers are not used, instead, a pH-neutral stabilisers should be used.

Any basic solution can be used for this method however there are generally two types of pH controllers that could be used, salt based or amine based.

2.14.1.1 Salts based pH controllers

Salt based pH-controllers is the most simplistic and efficient method of manipulating the pH. Salt based controllers introduces hydroxide or carbonate anions accompanied by sodium or potassium cations into the solution to raise the pH [39]. Due to the high solubility of these monovalent salts they are unlikely to precipitate and form scale in the system. If large amount of CO_2 is present, it is inefficient to use salt pH controllers as large volumes will be required. There is a significant downfall for this method as the large quantities directly leads to high pH, salt formation, and saturation of the process fluid with respect to other divalent ions [39]. Extensive research needed if this process is to be used to ensure that there is no unexpected precipitation occurring through the MEG regeneration plant and not in the MPV.

2.14.1.2 Amine based pH controllers

Amine based pH controllers behave in a very similar way to salt based controllers. The most commonly used amine based pH controllers is Methyl di-ethanolamine (MDEA) which is a strong base and undergoes the reaction shown in [equation 2.23](#) with carbon dioxide [57]:



MDEA is generally favoured over salt based controllers as it is more thermally stable and it has the ability to be regenerated to reduce the operational cost of needing additional controller [41]. Moreover, MDEA does not add additional salts into the solution, which lowers the potential for scale formation. MDEA does share a number of the same flaws at the pH-controllers in that large volumes may be required for efficient inhibition and this increases the risk of scale formation. However, similar to the previous method, extensive research should be done to ensure that precipitation

does not occur throughout the MEG regeneration plant downstream the MPV. A temperature increase in the regeneration plant, either at the regeneration distillation column or in a heater will cause a significant risk of precipitation. Increases in temperature will induce a reverse reaction to *equation 2-23*. This will cause the evolution of carbon dioxide gas and acidify the solutions [39]. Another important consideration for the MDEA pH controller is the significant increase in boiling point that may occur once MDEA is added. This must be considered in all MEG regeneration equipment such as the MPV, the distillation column and the reclamation flask [39].

2.14.2 Film Forming Corrosion Inhibitors (FFCI) strategy

Film forming corrosion inhibitors are cationic species however there are many different types and the specific composition and chemistry related to each mixture tends to be confidential to operating companies [73]. It is suggested that the most widely used FFCI is a phosphate ester. However, it is predicted that FFCI can contain as many as 32 unique components which confirms the complex nature of these inhibitors [57].

Film forming corrosion inhibitors are the most effective and most suited corrosion inhibitor for large productions of formation water. FFCI are introduced at very small concentrations (at ppm level) and this leads to efficient inhibition [39]. Unlike pH-controllers, the pH is not increased dramatically and the risk of scale formation is lowered [39]. Despite being an effective and well-known corrosion inhibitor method, the exact nature and chemistry surrounding the performance of these corrosion inhibitors remain unknown as they are not published and remain confidential to operating companies.

2.14.3 Switch-over between the corrosion strategies

A common strategy implemented for corrosion control in MEG regeneration plants is the initial use of a pH-controller and then shifting to a Film Forming Corrosion Inhibitor once formation water is produced [39]. This is to prevent the high pH solution in the presence of salt ions to avoid the precipitation of salts in undesirable locations throughout the MEG plant. The removal of a salt pH controller is to be done through passing the fluid through the MEG reclaimer. For safety reasons, the MEG reclaimer should be designed such that it is able to remove the salts from the predicted

formation water and the salt pH-controller if unexpected formation water is produced [39]. To remove the amine pH-controller a distillation column is required or an acid can be introduced to convert the MDEA to salt to be removed in the MEG reclaimer [47].

3 MEG Pilot Plant Equipment

3.1 Introduction

The MEG Bench Scale Pilot plant has been constructed at Curtin University for a maximum of four years' research program. The closed loop bench top scale project was sponsored by an industrial company with an estimated budget of \$1.8 million to cover the equipment, operation cost and the chemicals needed for testing. It was designed to simulate the field operating conditions to pre-determine what will happen during the real operation and reduce/ cut-off the cost of unwanted or unexpected issues that may occur. Therefore, some fluids were used such as condensate, formation water, pure MEG, and gas mixtures. However, some dangerous fluids were not used such as H₂S gas and high flammable hydrocarbons to ensure the safety of operators and the surrounded areas.

3.2 Process Flow Diagram (PFD)

The MEG bench top closed loop process consists of; a) MEG pre-treatment system, where the desired feed composition is achieved and the low solubility salts are separated. b) MEG regeneration system, where MEG- water are separated through a conventional distillation column. c) MEG reclamation system where MEG is flashed in a flash separator and recovered free of salts *Figure 3-1*.

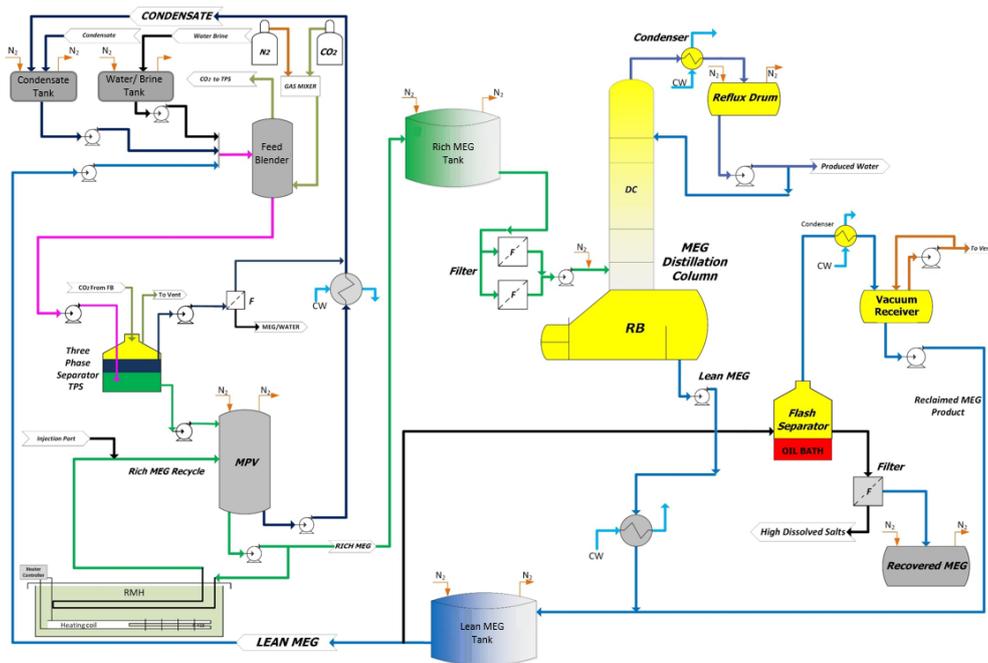


Figure 3-1 Process Flow Diagram PFD

3.3 Piping and Instrumentation Diagram (P&ID)

This research is focused on the pre-treatment system of the MEG bench scale pilot plant. As such, a detailed description of only this system will be discussed here.

The pre-treatment system consists of two sections; 1) feed blending, and 2) pre-treatment area.

3.3.1 Feed blending area

The function of feed preparation and blending system is to supply a constant feed flow stream of the desired composition to the MEG pre-treatment vessel. Also, the role of this system is to replicate liquid compositions and conditions (e.g. shear stress) commonly encountered during the transportation and transfer of production fluids to an onshore facility. The system consists of the following units:

- a) Condensate Tank (*Figure 3-2*, [a])
- b) Water/ Brine Tank (*Figure 3-2*, [b])
- c) Feed Blender (*Figure 3-2*, [c])
- d) Peristaltic pumps (Brine Pump, Condensate Pump, and Lean-MEG Pump).
- e) Constant flow – Pressure Pumps
- f) 3 phase separator (*Figure 3-2*, [d])
- g) Injection/ sampling points

In this configuration, a desired volume of brine, condensate and lean MEG are drawn from their individual storage tanks using dosage pumps into the feed blender. In feed blender, the two phase fluid is mixed thoroughly using an agitator (Ultra Turrax) in order to apply a defined shear stress. The agitator speed (shear stress) can be altered accordingly to simulate the systematic drop in pressures that are experienced in the field conditions. Sampling ports have been allocated at the inlet and outlet streams of the feed blender to monitor the composition and quality of the feed to the pre-treatment vessel. CO₂ and N₂ are mixed using mass flow meters to ensure correct CO₂ concentration and resulting alkalinity. The feed blender can also act as sparging vessel to saturate the liquid with CO₂.



Figure 3-2 Feed Blending Area

Table 3-1 shows the sensors connected to the feed blender with their locations and functions;

Table 3-1 Feed blending system analysers

	<i>Probes / Analyser</i>	<i>Location</i>
O1	Oxygen Probe	Feed Blender 1
pH.1	pH Probe	Feed Blender 1
Con.1	Conductivity Probe	Feed Blender 1
Mass-flow	Mass flowmeters, density and temperature probs	Brine tank, condensate tank,

The mixed fluid enters a glass vessel functioning as a 3-phase separator to separate condensate from rich MEG. By adjusting the shear rate in the feed blender, emulsions

of varying stability can be created to a) simulate condensate carryover into the pre-treatment vessel, and/or b) to test the efficiency of demulsifying additives. The 3-phase separator has been designed as a glass vessel to allow the operators to observe and record the amount of emulsion occurring, and also to get the knowledge of how much condensate is carried over so they can manually adjust the feed tube height inside the glass vessel and ensure no condensate is transferred to the MEG pre-treatment vessel

Figure 3-3.



Figure 3-3 Glass vessel separator (3-phase separator)

The Piping and instrumentation Diagram (P&ID) of the Feed blending area is shown in *Figure 3-4*;

3.3.2 Pre-treatment system

The function of pre-treatment system is to precipitate out the lower solubility salts present in the feed. This system consists of the following:

- a) Pre-treatment vessel (Three-phase separator). (Figure 3-5,[a])
- b) Recycle Pump, *Figure 3-5*, [b]).
- c) Condensate Recycle pump
- d) Recycle Heater. (*Figure 3-5*,[c])
- e) Rich-MEG tank.
- f) Injection/sampling Point



Figure 3-5 Pre-treatment system

In The MEG pre-treatment system, a constant stream of rich MEG is fed into the MEG pre-treatment vessel operating at a pressure of 122 kPa (a). Rich MEG is heated to 80°C using an immersion heater placed in a recycle loop fed by a recycle pump. The vessel has injection points through which alkalinity of the process fluid can be

increased. With the increase in the alkalinity and temperature the low soluble salts, essentially carbonates of iron, calcium, barium, and strontium precipitate out. The precipitated salts are separated out using the rich MEG Storage tank. In addition, a provision for a bypass to the rich MEG tank has been incorporated. The Pre-treatment vessel has been designed to achieve effective separation of the two phases (MEG and condensate) with a retention time of up to 60 min. The stainless steel vessel also has a glass viewing strip with an appropriate light source for visual observation, video capture, emulsion studies, and also to observe crystal growth mechanisms.

The pre-treatment system is able to address and analyse the following issues;

- a) Condensate/MEG-water separation.
- b) MEG chemistry and divalent salts precipitation.
- c) Emulsion and foaming tendencies of the multiphase fluids.
- d) Fouling of rich MEG filter.
- e) Scaling issues.

The pre-treatment vessel has been incorporated with various sensors and probes to monitor and data log various parameters (*Table 3-2*).

Table 3-2 MEG pre-treatment system analysers

	<i>Probes / Analyser</i>	<i>Location</i>
O.3	Oxygen Probe	Pre-treatment vessel (Gas Phase)
Con.3	Conductivity Probe	Pre-treatment vessel- MEG/Brine Phase
pH.3	pH Probe	Pre-treatment vessel- MEG/Brine Phase

The Piping and instrumentation Diagram (P&ID) of the pre-treatment area are shown in *Figure 3-6*;

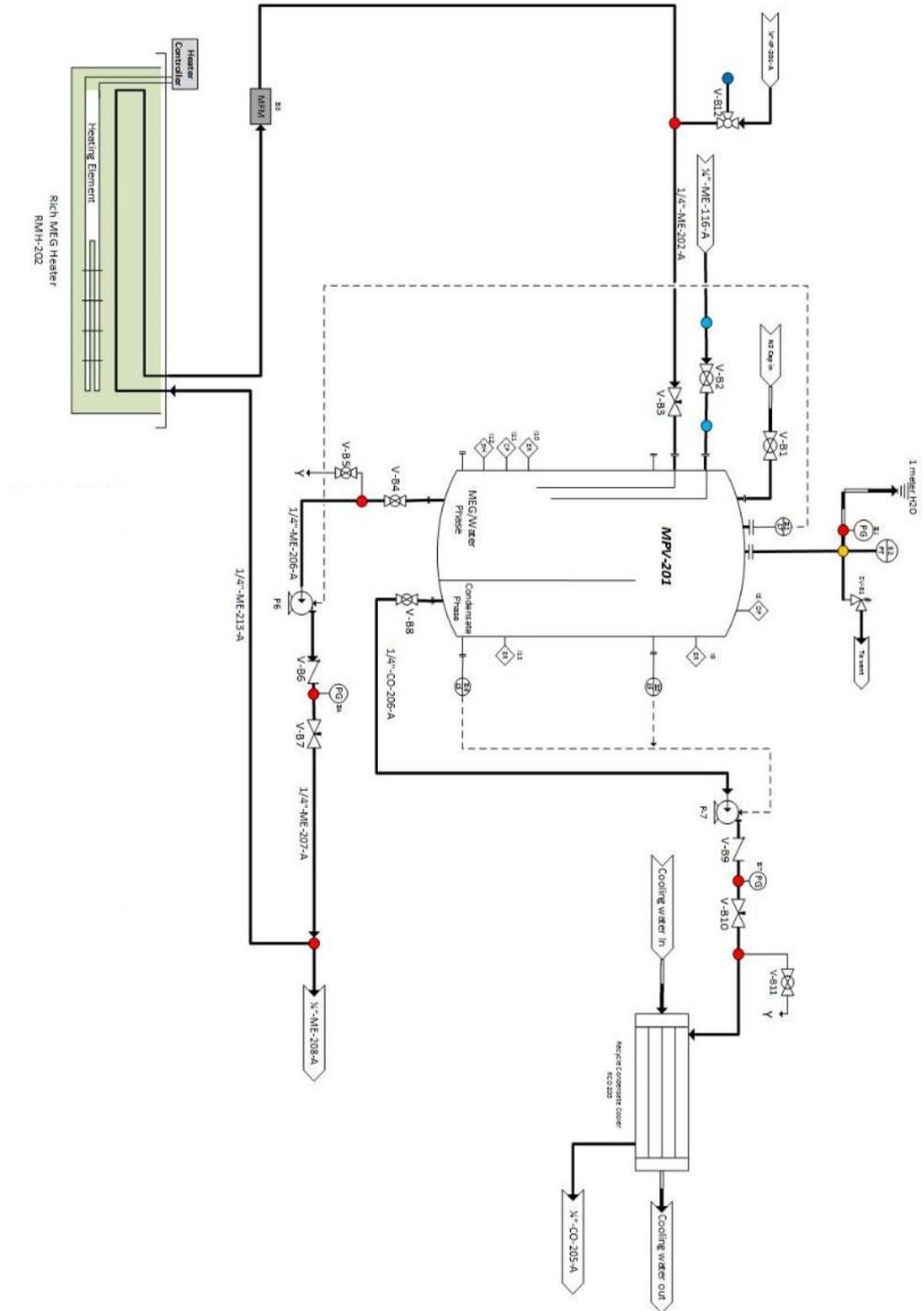


Figure 3-6 Piping and instrumentation Diagram (P&ID) of the pre-treatment area

3.4 Equipment layout (plot plan)

The MEG bench top scale has been constructed in building B614 in the Technology Park at Curtin University. This location has been chosen as the best available space to build the pilot plant. The area is well ventilated as it is located at the backyard of the building with a decent size to allow flexible operation where all the necessary apparatus and equipment can be fitted. A 4-meter distillation column has been easily installed next a powerful chiller that can provide chilled water to the heat exchangers throughout the operation.

The plot plan is shown in *Figure 3-7, and Figure 3-8.*

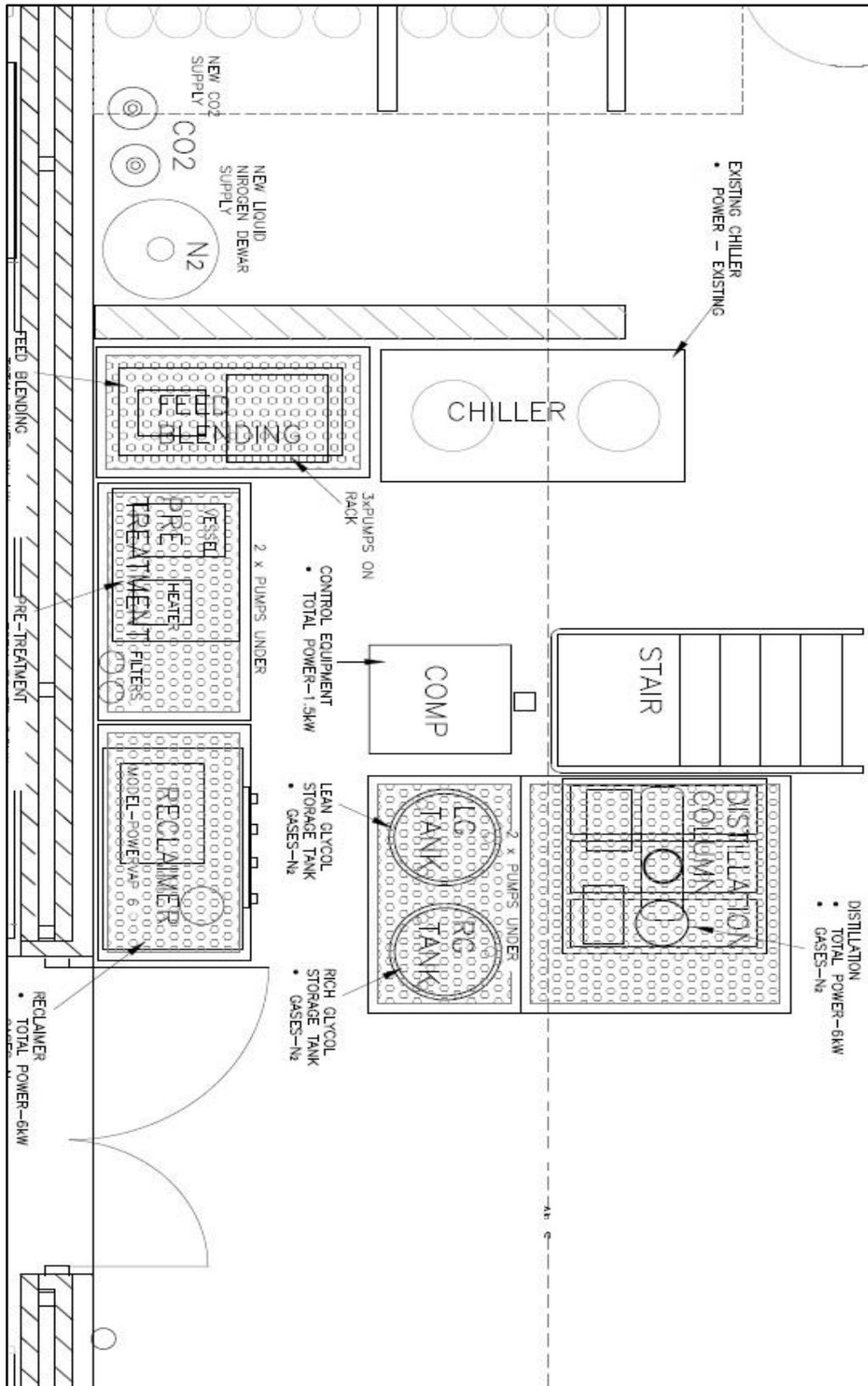


Figure 3-7 MEG Process General Installation Service

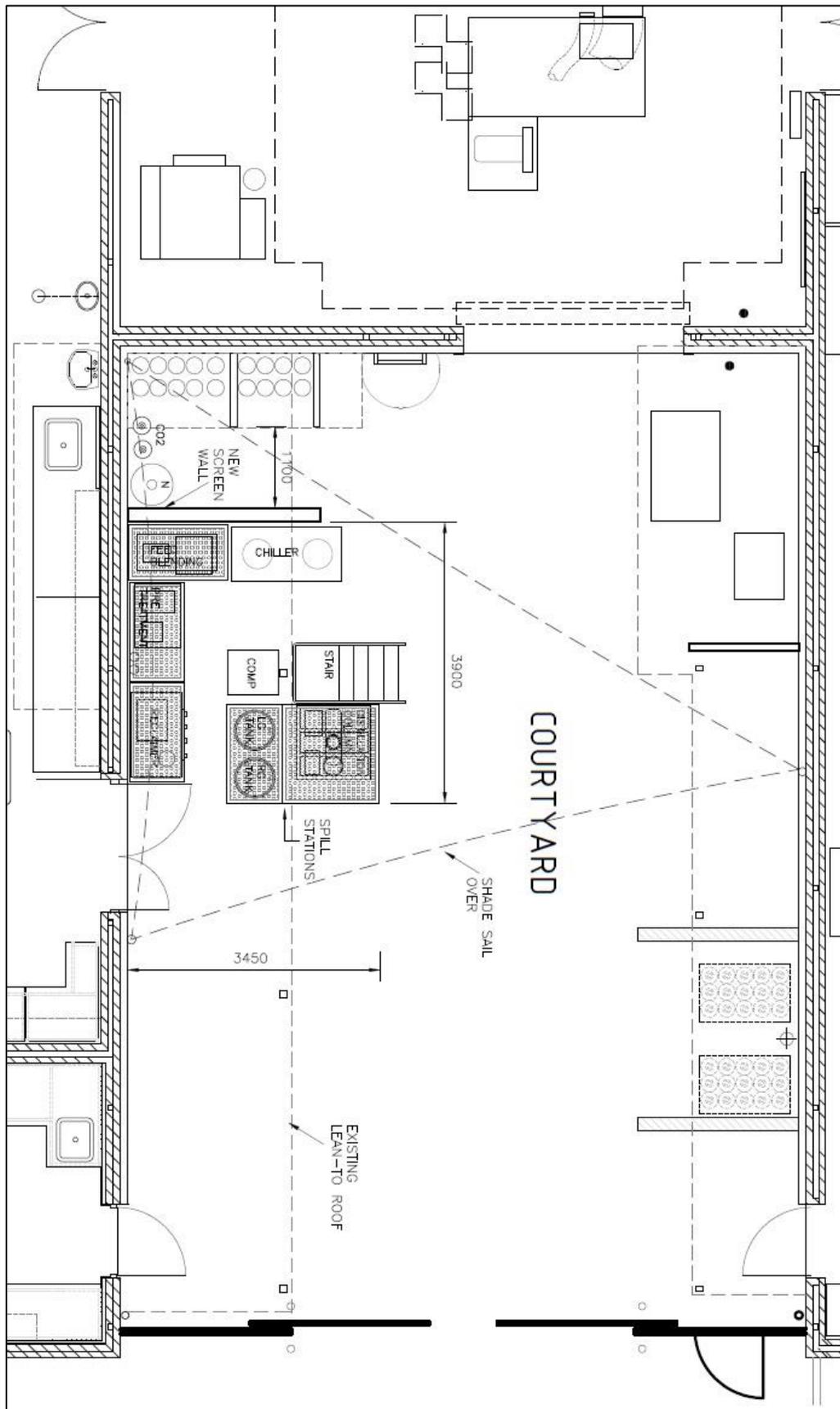


Figure 3-8 MEG Process Installation Plan

3.5 Sensors and Meters

3.5.1 pH and Temperature Electrodes

The type of pH and temperature electrodes used in MEG Pilot Plant system was *METTLER TOLEDO InPro 4800 (i)*, which is the top-of-the-line combined pH and temperature electrode family designed to handle high-temperature and high-pressure for dirty chemical applications. The strong resistance to oxidizing media, solvents, acid, and alkali solutions makes it suitable for highly demanding industrial applications including chemical processing, chlor-alkali, pulp and paper, dyes and pigments, and sugar processing. It is also available with an intelligent Sensor Management (ISM) for “Plug and Measure” and Advanced Diagnostics. pH electrodes with integrated ISM functionality allowing “Plug and Measure” and Advanced Diagnostics. ISM simplifies the installation, handling, and maintenance of measurement equipment [74].



Figure 3-9 InPro 4800 pH and Temperature Electrode [74]

3.5.1.1 Features Overview

- High pressure / high temperature rating 12 bar @ 130 °C (174 psig @ 266 °F)
- Very long diffusion path using two electrolyte chambers
- PTFE annular junction repels dirt

- Resistant to strong oxidizing agents, solvents, acids and alkali, and to poisoning substances
- Watertight connector (IP 68), integral temperature sensor
- InPro 4801 SG features flat pH membrane suited for fibres and high solids samples
- ATEX and FM certified for hazardous areas

The specifications of the pH and temperature electrodes are shown in [Table 3-3](#) below.

Table 3-3 pH electrodes specifications

pH range	1 – 14 pH InPro 4800 (i)
Temperature	– 5 to 130 °C (23 to 266 °F)
Plug head (IP 68)	ISM: K8S; Analog: VP, Pg 13.5 thread
Reference system	Ag / AgCl system, pressure-compensated double gel-electrolyte chambers (patented)
Reference electrolyte	Gel
Lengths	120 mm, 225 mm, 425 mm
Shaft diameter	12 mm
Temperature sensor	ISM: Digital; Analog: Pt 100 or Pt 1000
Solution ground	Platinum
Glass membrane	InPro 4801 SG: Flat, low impedance quality glass

3.5.2 Dissolved Oxygen Sensors

The *METTLER TOLEDO InPro 6800* dissolved oxygen sensor was used in the MEG pilot plant to provide maximum accuracy and ultimate cleanability for vessels with limited space or in containers with smaller volumes. The sensor was provided by *METTLER TOLEDO* with the state-of-the-art VP connector or T-82 connector in

straight or angled versions. A durable 316 L stainless steel construction allows for CIP, steam sterilization or autoclaving in place, and the high sensor finish virtually eliminates contamination of the process. Ingold's PTFE / silicone membranes have been designed with an internal steel mesh that makes the membrane more rugged and dramatically increases membrane life. InPro 6850 sensors with integrated ISM functionality allow "Plug and Measure" and Advanced Diagnostics. ISM simplified the installation, handling, and maintenance of measurement equipment [75].



Figure 3-10 Dissolved Oxygen Sensor [75]

3.5.2.1 Features Overview

- Small 12 or 25 mm diameter saves valuable space
- Pg 13.5 threads for interface into housings
- Comes with either watertight VP connector (IP 68) or T-82 connector
- Ingold 25 mm sensor design recognised as a standard in the industry
- Cap nut allows for easy interface to Ingold ports

The specifications of the dissolved oxygen sensor are shown in [Table 3-4](#);

Table 3-4 Dissolved Oxygen Sensor Specifications

Performance	
Operating range	6 ppb to saturation
Accuracy	$\leq \pm [1 \% + 6 \text{ ppb}]$
Response time at 25 °C (77 °F)	98 % of final value in < 90 s
Sensor signal in air 25 °C (77 °F)	50 to 110 mA
Residual signal in oxygen-free medium	< 0.1 % of the signal in ambient air
Construction	
Measuring principle	Polarographic Clark electrode
Cable connection	Analog VarioPin (IP 68) Digital K8S (IP 68)
Connector design	Straight or angled
Sensor body	316 L stainless steel
Membrane material	PTFE / Silicone / PTFE (reinforced with steel mesh)
Surface roughness of wetted parts	N5 / Ra16 (Ra = 0.4 μm / 16 μin)
O-ring material	Silicone (FDA and USP Class VI positive listed)
Sensor diameter	12 mm / 25 mm
Working Conditions	
Temperature compensation	Automatic
Measuring temperature range	0 to 80 °C (32 to 176 °F)
Environmental temperature range	- 5 to 140 °C (23 to 284 °F)
Measuring pressure resistance	0.2 to 6 bar (2.9 to 87 psi absolute)
Mechanical pressure resistance	Maximum 12 bar (174 psi absolute)

3.5.3 Conductivity Sensors

The *InPro 7100* from *Mettler Toledo* conductivity sensor was used in the MEG pilot plant. This type is particularly suited for applications in the Chemical and Pharmaceutical industries, Food & Beverages and Pulp and paper. The fast response time allows quick detection of process changes, leading to better process control. The PEEK shaft material offers high resistivity against aggressive solutions and is particularly suitable in process with frequent CIP / SIP cycles [76].



Figure 3-11 Conductivity sensor [76]

3.5.3.1 Features overview

- Wide measurement range (0.02 – 500 mS / cm, depending on the transmitter)
- High resistance against aggressive chemicals
- Compatible with a variety of process connections of Mettler Toledo InFit 761 series
- Digital connector
- “Plug and Measure” functionality
- Can be used with the transmitters M300 SM, M400, M800 and M400 2-wire

Table 3-5 shows the specification of 7100 conductivity sensor;

Table 3-5 7100 conductivity sensor specification

Performance	
Cell constant nominal	0.31 cm ⁻¹
System accuracy	± 5 % or better
Operation range	0 to 20 bar at 135 °C (0 to 290 psi at 275 °F) 0 to 10 bar at 150 °C (0 to 145 psi at 302 °F)
Temperature range (sterilisation)	(sterilisable) – 20 to 150 °C (– 4 to 302 °F)
Temperature accuracy at 25°C (77 °F)	± 0.1 °C (± 0.1 °F)
Construction	
Measuring principle	4-electrode sensor
Electrode material	SS 316 L / 1.4435 Hastelloy C22
Body material	PEEK
Sensor diameter	12 mm
Sensor length	120 mm (4.72"), 425 mm (16.73")

3.5.4 M800 Transmitter

The M800 transmitter series features premium Intelligent Sensor Management (ISM) technology measuring pH / ORP, optical DO, aerometric oxygen (DO as well as O₂ gas), dissolved carbon dioxide, turbidity, and conductivity. The multi-parameter transmitter accepts any compatible combination of ISM sensors. Up to four channels of process measurement provide immediate Plug and Measure installation and operation, predictive sensor maintenance and dynamic lifetime status. The color

touchscreen ensures intuitive operation, with user selectable control and alarm management [77].

3.5.4.1 Features overview and highlights

- Colour touchscreen
- Intuitive operation
- Premium ISM functionality
- Multi-parameter measurement
- 1- / 2- / 4-channel versions
- iMonitor
- 8 current outputs
- 8 output relays
- Traffic light coded sensor information
- IP 66 rated
- 2 PID process controllers



Figure 3-12 M800 Transmitter [77]

Table 3-6 below the specification of M800 transmitter

Table 3-6 M800 Transmitter specifications

General Specification	
Measurement parameters	pH / ORP, aerometric and optical oxygen, conductivity, dissolved carbon dioxide, turbid ty and temperature
ISM	Plug and Measure, Advanced Diagnostics (Dynamic Lifetime indicator, Adaptive Calibration Timer, CIP / SIP counter etc.), Monitor
Power supply	100 to 240 VAC, or 20 to 30 VDC, 12 VA
AC frequency	50 to 60 Hz
Current (analog) outputs	8 x 0/4 to 20 mA, 22 mA alarm
User interface	Colour touchscreen 5.7", resolution 320 x 240 px, 256 colours
Languages	10 (English, German, French, talian, Spanish, Portuguese, Russian, Japanese, Korean and Chinese)
Ambient temperature	– 10 to 50 °C (14 to 122 °F)
Relative humidity	0 to 95 %, non-condensing
Rating	IP 66 (when back cover is attached)
PID process controller	2
Hold input	Yes
Control input	Yes
Analog input	Yes
Alarm contact	Yes (alarm delay 0 to 999 s)
Measuring range	Parameter and sensor depending
Measuring accuracy	± 1 digit (sensor depending)
Measuring repeatability	± 1 digit (sensor depending)

3.6 Pumps

Various types of pumps were used in the MEG pilot plant to comply with the various areas that have different fluids, which need to be transferred through the plant and also the different chemicals required to be dosed into some vessels.

3.6.1 Peristaltic Dosing Pumps

The variable flowrate metering pump purchased from *SEKO* was mainly used to pump the carryover contaminated condensate from the 3-phase separator to a residual container. This type of pumps has a speed controller easily and quickly adjusted depending on the condensate level inside the glass vessel (3-phase separator) [78].



Figure 3-13 Peristaltic dosing pump [78]

3.6.2 Solenoid Dosing Pumps

The *TeknaEVO* TPG Solenoid dosing pumps were used in different locations in the MEG pilot Plant. For example, they were used to:

- pump the fluids from the feed blender to the MEG pre-treatment vessel,
- dose NaCl into the pre-treatment vessel
- dose HCl into the Rich MEG Tanks and Lean MEG Tank
- Dose FFCI into the Lean MEG tanks or into the stream line from Lean MEG tank to the Feed Blender.



Figure 3-14 Solenoid dosing pump [78]

The flow rate of this digital dosing pump can be; constant flowrate manually adjustable, proportional flow rate according to an external analog signal (4-20 mA) or digital pulse signal such as from flowmeter [78].

3.6.3 Magnetic Drive Gear Pumps

The magnetic drive gear pumps from *MICROPUMP* have been widely used through the MEG pilot plant as they can provide a precise pulseless flowrates from as low as 10 ml/min and system pressures to 5000 psi [79].



Figure 3-15 Magnetic drive gear pumps [79]

3.7 Vessel Fabrication

The vessels of the MEG pilot plant were designed using Hysis simulation to complete all the data sheets related to these equipment. The material acquisitions were then placed with a reliable fabricator (Rathman) who was following the vessel engineering standards in his shop facility. Many coordination meetings were organised with the shop representatives to purchase the required plate material for the vessel fabrications and to finalise all the welding procedures.

During vessel fabrications, many inspection visits were made to the fabricator's shop to make sure matching of the sizes, testing of welds nozzles orientation and whether sizing were correctly matching the design drawings and data sheets.

Upon completion of fabrication, hydrostatic testing was performed by the fabricator and witnessed by a representative from the MEG pilot plant. This test included pressurising and testing the vessels up to twice the operating pressures. The vessels fabricator then issued the certificates for these vessels confirming conformity with the MEG team engineering specifications and the engineering standards.

Full documentation for the welding procedures and shop fabrication drawings were issued and all certificates were submitted to the project engineer. The vessels were then transported to the pilot plant site and located according to the location on the plot plan of the MEG pilot plant.

3.8 Operational Hazop

Similar to the real plants, the operators in the MEG pilot plant followed the same safety procedures and had to comply with the operational hazop in case of emergency. A sample of the operational hazop is shown in *Table 3-7* ;

Table 3-7 Feed Blending Section operational Hazop

Feed Blending Area							
Description: From Condensate tank to Feed blending vessel							
Item N°	Deviation	Causes	Consequences	Inherent Risk			Safeguards
				Con	Li	Risk	
1.1	Fire	Human Error, ignition of condensate fumes, high temperature in condensate vessel. Extreme weather (Heat wave).	Shut down, personal injury, damage of equipment.	Major	Possible	High Risk	Deploy CO ₂ fire extinguishers or Dry powder extinguisher or foam extinguishers . Fire blanket, High temperature alarm, Smoke detectors, water shower, and visible warning signs. Avoid operating during extreme weather
1.2	Power failure	Power failure from main power grid, Overconsumption of power limit in building 614, Electrical fault. Extreme weather conditions.	Loss of control and operation, Deviation from normal operating conditions.	Moderate	Unlikely	Medium risk	Monitor consumption of power in the building, Have back up power for emergency shut down operations. Implement safe guard to avoid power surges. Avoid operating during extreme weather conditions. (such as heavy rain, strong winds, storm and heatwave conditions)

1.3	Electrical short	Overload power supply, wet condition, human mistake, exposed live wires	Short circuit, personal injury due to electrification.	Moderate	Unlikely	Medium risk	Surge protectors, fuses, circuit breakers. Follow Curtin's policy and procedures for electrical safety issues.
1.4	Utility failure	Failure of Utilities pumps, Failure of utilities valves and control system, empty N ₂ gas cylinders.	Abnormal operating conditions, Loss of Blanketing gas, Loss of feed.	Minor	Unlikely	Low risk	Safety and redundancy barriers to be implemented for all utilities and associated equipment
1.5	Equipment failure	Faulty equipment, Human error, Abnormal operating conditions	Fire risk, personal injury, chemical spill, shut down	Moderate	Unlikely	Medium risk	Develop safe work procedure, Emergency shutdown button. Only trained personnel to operate equipment. Annual inspection and certification.
1.6	Leak-gas (Condensate Vapour, CO ₂ ,N ₂)	Loose piping component. Human mistake, equipment failure, faulty pressure relief valves	Fire risk, personal injury due to inhalation of leaked gas.	Moderate	Unlikely	Medium risk	leak detection system, HC Detector ,Pressure and gas leak test to be carried out
1.7	Spillage-liquid	Overfill the tank, broken drain valve, leakage in piping component, human mistake	Chemical hazard, Fire risk, Risk to personnel health depending on degree of exposure to chemicals.	Moderate	Unlikely	Medium risk	High level alarm, personal protective equipment. Spillage containment strategies- Strategic use of individual equipment crates to contain spillage.
1.8	Overpressure	Overfed of N ₂ due to faulty valve V-A4, V-	System overpressure and causes	Moderate	Unlikely	Medium	Pressure safety valve PSV-A1

		A5 and pressure transmitter PT-A2	abnormal operation				releases at 2.5 bar
		Overfed of N ₂ due to faulty valve V-A9, V-A10 and pressure transmitter PT-A27		Moderate	Unlikely	Medium	Pressure safety valve PSV-A2 releases at 2.5 bar
		Overfed of N ₂ due to faulty valve V-A14, V-A15 and pressure transmitter PT-A28		Moderate	Unlikely	Medium	Pressure safety valve PSV-A3 releases at 2.5 bar
		Overfed of CO ₂ due to faulty valve V-A33, and manifold		Moderate	Unlikely	Medium	Pressure safety valve PSV-A4 on BOC gas cylinder
1.9	High temperature	Extreme weather conditions (Heat wave), Off spec Lean MEG temperature.	Fire risk due to condensate fume, Deviation from normal operating conditions personal injury.	Minor	Unlikely	Low risk	Temperature sensors and gauges to be installed at condensate line and lean MEG line. Do not operate during extreme weather conditions(heat wave),
2.0	Area emergency	Emergency situation such as fire, gas leaks, chemical spill , natural disaster (bush fire), surrounding equipment failure such as gas cylinder used by other labs	Shut down, Personal injury, Damage to equipment.	Moderate	Possible	Significant risk	Fire extinguisher, Personal protective equipment
2.1	Operator risk	Human Error, equipment failure, tripping hazard, chemical spill, gas leak	Personal injury	Moderate	Unlikely	Medium risk	Personal protective equipment, hazard notification and symbols
2.2	Pumps	Failure of pump , Cavitation, Operator error:	Pump failure	Minor	Possible	Medium risk	Safe work procedures, safety

		Pump not turn off after the experiment, suction valve closed to the pump					barriers, and regular inspections.
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4 Design, operation and control of MEG plant

4.1 Introduction

Monoethylene glycol (MEG) regeneration pilot plant has been designed at Curtin University to simulate the real field conditions in a smaller scale. As such, the data and the results that will be obtained from the MEG bench scale will be highly useful in a larger industrial size plant. This chapter focuses on design and operating conditions of the pilot plant. It explains in detail the design and the function of each section. It also mentions the operation method and gives example about how the control system works depending on the collected data.

Mono-ethylene glycol (MEG) is a gas hydrate inhibitor widely used in the oil and gas industry. MEG favourable properties allow the chemical to be easily regenerated from the solution and re-used in a continuous loop. The regeneration process for MEG has become a popular area of study due to the financial benefits associated with re-using an inhibitor without requiring a continuous injection. The MEG Regeneration Pilot Plant at Curtin University allows for research to be completed in this field with high confidence as the results obtained are accurate and applicable to real-life MEG Regeneration Plants used in the industrial field.

The configuration and design of a MEG regeneration plant varies greatly depending on the size of the production site, the extent at which formation water is being produced, the concentration of ions in the brine and the temperature and pressure of the reservoir. The precipitation of salts such as calcium carbonate (CaCO_3) and calcium sulphate (CaSO_4) is a widespread problem in the natural gas industry and the presence of MEG as a co-solvent enhances this problem. The production of formation water (brine) introduces divalent ions into the production facility, which unless planned for and processed correctly, can lead to scaling and precipitation in pipelines and on hot surfaces. This phenomenon has significant consequences in the operation and control of the MEG Regeneration Plant and thus removal of divalent salts is of the utmost importance.

A vital aspect of flow assurance is preventing the formation of gas hydrates in subsea pipelines. The formation of gas hydrates is a common issue in the offshore gas production facilities due to the presence of both natural gas and water, under high pressure and at low temperature conditions, which occurs during subsea transportation. Gas hydrate formation have severe consequences such as reduction in the gas production rates,

blockage of pipes and valves, contribution to explosions and loss of containment of hydrocarbons to the environment. The prevention of gas hydrates is of utmost importance to ensure the safety of workers and to protect the surrounding environment. Monoethylene glycol (MEG) is an important chemical used extensively in subsea gas production facilities as a hydrate inhibitor. MEG is injected into production wells and gas pipelines prior to long distance subsea transport to prevent the formation of gas hydrates [33].

MEG is preferred over Methanol for usage as a flow assurance inhibitor for several reasons including; MEG is recoverable and recyclable, whereas Methanol is usually used in once-through systems and in some cases only partially recovered. Methanol poses greater safety risks in handling and storage compared with MEG; the flash point of Methanol is 11°C and 111°C for MEG, also MEG provides a greater degree of corrosion protection than methanol. The solubility loss of MEG into the sales gas is negligible and its losses into the liquid hydrocarbon phase is low whilst the solubility loss of Methanol into sales gas can be high and the losses to the liquid hydrocarbon are higher than MEG, which may cause problems for the refineries and gas processing plants downstream [33].

A closed loop MEG system is complex and involves a number of chemical and physical processes, hence, operational challenges. Consequently, it is important to utilize a closed loop MEG system from a holistic point of view. The consequences of neglecting this will, in many cases, cause severe operational problems leading to plant downtime and losses of income. [33]

Øi [81] developed a model for the most used glycol regeneration processes using HYSYS simulation based on Peng-Robinson equation of state. The models can be implemented into other process simulation programs and with other vapour/liquid equilibrium models. Parameters in the models have been adjusted to simulate actual regeneration plant performance. The models have been used to evaluate alternative regeneration processes.

A concise description of the MEG regeneration and reclamation system has been provided by Condilis et al, [81] where Gas, hydro- carbon condensate and rich MEG -MEG associated with formation water and condensed water- is delivered via a pipeline to the gas processing plant, where the three phases are separated. The rich MEG- typically having a concentration of less than 75% wt. - is routed to the MEG regeneration unit. At the MEG regeneration unit, residual hydrocarbons are separated and skimmed off from the rich MEG. Subsequently, water is removed in the reconcentration process and salts are

removed in the reclamation section. The regenerated MEG -typically having a concentration of 80 to 90wt. %- is returned to the gas field in a separate pipeline for re-injection into the gas flow lines at or near the well head.

The pressure of the rich MEG collected from a slug catcher is reduced and the phases are separated. Furthermore, in some cases, pre-treatment operations include controlled precipitation and removal of the low soluble divalent salts prior to reconcentration and reclamation to avoid/reduce scaling issues. The controlled separation of the low solubility salts from the rich MEG at an early stage in the regeneration process provides an elegant engineering solution to the problem of unwanted settling of carbonate precipitation or scaling in downstream processes [81]. When pre-treatment is used, the function of the downstream reclaimer is reduced to primarily remove highly soluble salts (monovalent salts such as chlorides).

Several research facilities have simulated the MEG recovery systems, however, the MEG bench-scale facility at Curtin Corrosion Engineering Industry Centre, Curtin University is a unique unit in the world to the best of our knowledge as it simulates all the MEG regeneration/ reclamation processes in a closed loop system at a bench-scale level. In general, a MEG bench scale closed loop facility consists of a MEG pre-treatment system, MEG regeneration system and MEG reclamation system.

4.2 Background

MEG recovering process is known as MEG regeneration. Typically, there are three different configurations for the MEG close loop system, which are most commonly used. These methods are Conventional Regeneration, Slip-Stream Salt Removal, and Full Reclamation. The selection of which method to be used depends on the composition of the process fluid, the predicted concentration of salt ions and the required MEG composition leaving the regeneration plant [33].

4.2.1 Conventional Regeneration

This method is based on boiling off the water from the solution, while MEG, salts, and non-volatile chemicals remain and accumulate in the closed loop system. The removal of water is done by passing the process fluid through a distillation column system, which includes a reboiler, and is based on the difference in volatility between MEG and water. This method is suitable for process fluids which are predicted to have a very low concentration of salt ions as the downfall of this recovery method is the inability to remove salt ions and solid

particles. The removal of divalent salt ions is not completed in this recovery method, instead the ions are allowed to accumulate in the MEG loop. Conventional recovery is not suitable when there is continuous production of formation water as this introduces a large concentration of salt particles into the system which cannot be removed [82] .

4.2.2 Slip-Stream Salt Removal

The Slip-Stream Salt Removal method is based on the conventional recovery method with additional option to slip-stream a portion of the process fluid fed to a reclaimer. The rate at which the slip-stream is used depends on the amount of the salt impurities in the lean MEG. The advantage of being able to slip-stream through a reclaimer rather than processing the full stream is that inhibitors and pH-stabilisers are reused rather than being completely separated. This method makes significant savings through avoiding the need to heat or cool the entire process fluid during regeneration. While it is advantageous to maintain the inhibitors and pH-stabilisers in the solution, the main disadvantage of this method is that impurities accumulate in the system. The increasing concentration of salt impurities is likely to lead to salt precipitation and the formation of scale on hot surfaces as experienced in the conventional recovery method [83][33].

4.2.3 Full Reclamation

The Full Reclamation MEG Regeneration method is the most reliable and commonly used method when higher production rates of water and condensate are anticipated. This processing facility includes a Pre-Treatment Vessel, a regeneration section (distillation column), and a reclamation section which removes the water, salts, and all other impurities from the solution. The full reclamation process is a proven method which has had great success in processing rich MEG into lean MEG at a specified purity. Each specific section of this method is designed to remove a particular impurity from the system in order to achieve the final high purity lean MEG [41].

The MEG Benchtop facility has been designed as a MEG regeneration and reclamation closed loop system having a design capacity of 4 kg/hr of lean MEG. The facility includes a feed blender, a MEG pre-treatment section, regeneration system, the reclamation unit, and corresponding lean and rich MEG storage tanks, in addition to the brine and condensate reservoirs.

Some of the capabilities of the MEG Benchtop facility include:

1. Simulating the effects of well clean-ups;

2. Simulating the effects of condensate carryover into the MEG pre-treatment vessel;
3. Verifying production chemical additive compatibility;
4. Simulating the effects of corrosion management strategy switch over.
5. Providing input into methods for optimising salt removal.
6. Improving plant operational costs and reducing down-time; in-situ cleaning process development for scale removal.

4.3 MEG pre-treatment system

The pre-treatment section is the first step in the MEG bench scale closed loop system. It is used to remove hydrocarbons from the rich MEG and precipitate the divalent ions upon heating before transferring the rich MEG to the re-concentration and reclamation units. The pre-treatment system contains the following equipment (*Figure 4-1* & *Figure 4-2*):

Condensate tank	MEG pre-treatment vessel
Brine tank	Recycle Pump and Peristaltic pumps
Lean Glycol Tank	Rich MEG recycle Heater
Feed blender	filters
3-phase separator	Rich MEG Tank

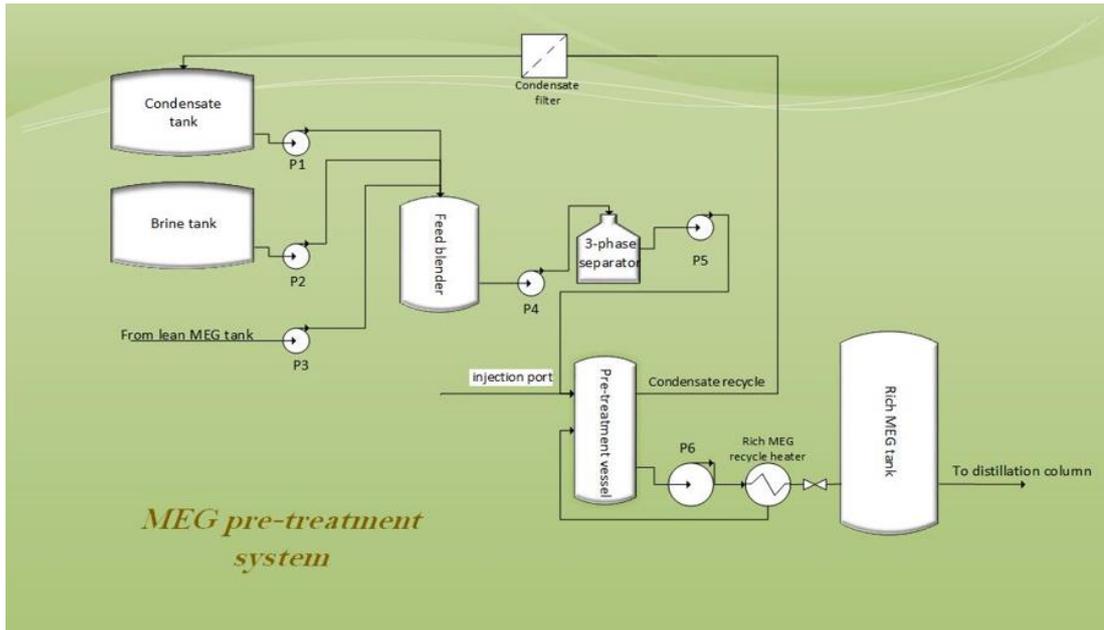


Figure 4-1 MEG pre-treatment system



Figure 4-2 MEG pre-treatment system

The brine is prepared using a specified recipe that simulates the fluid field compositions. The solutions from the brine tank and condensate tank are pumped to the feed blender using dosing pumps controlled by mass flowmeters. And the lean MEG (75%-85% pure MEG) from the lean MEG tank is pumped to the feed blender using a micro pump controlled by a mass flowmeter.

4.3.1 Condensate Tank

The condensate tank is used to store the condensate phase (if applicable). Stainless steel 316 was used of a total volume of 31 litres and a working volume of 19 litres.

The tanks was designed to work at 45°C and 1.8 bar.

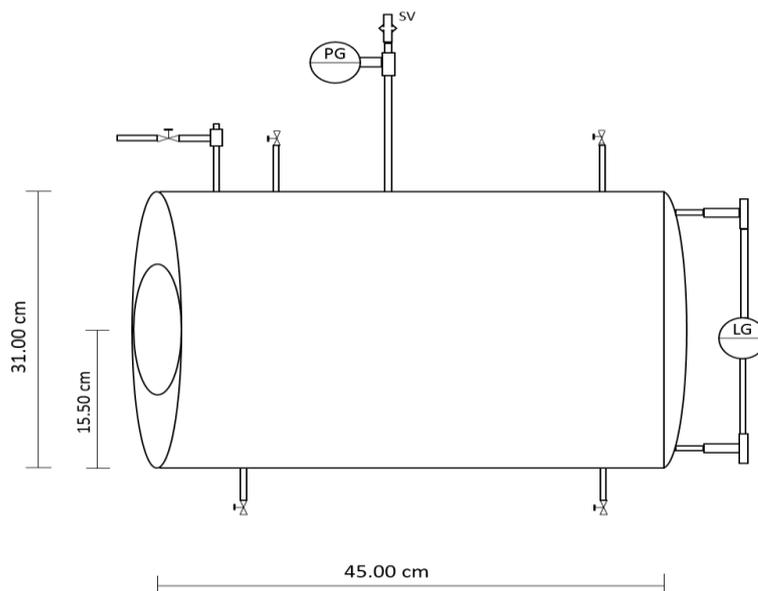


Figure 4-3 Condensate tank

The condensate composition is shown in [Table 4-1](#);

Table 4-1 Condensate Composition

Component	FEED COMPSITIONS (Mole Fraction)	Component	FEED COMPSITIONS (Mole Fraction)
i-C4	0.0007	C12	0.2574
n-C4	0.0082	CO₂	0
i-C5	0.0202	H₂O	0
n-C5	0.0183	N₂	0
C6	0.0689	MEG	0
C7	0.108	Benzene	0.0105
C8	0.1003	Toluene	0.0469
C9	0.1428	m-Xylene	0.0504
C10	0.0927	E-Benzene	0.0054
C11	0.0693		
Total		1	

4.3.2 Brine Tank:

Before starting any experiment, the brine was prepared and stored in the water brine tank (WBT). It was manufactured from 10mm PVC with a total operating capacity of 100L. The translucent window on the side of the tank allowed us to monitor the level inside.

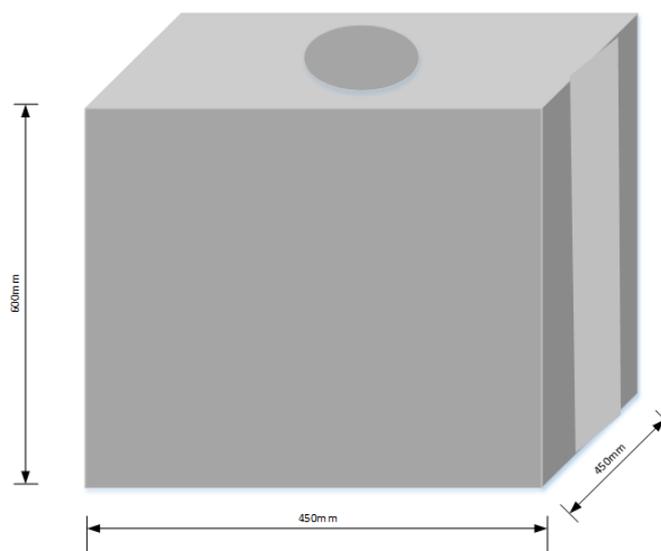


Figure 4-4 Water brine tank (WBT)

Typical composition of the brine are shown in [Table 4-2](#);

Table 4-2: Typical Brine Tank Composition

Component	Concentration (g) /Kg water	Component	Concentration (g) /Kg water
NaCl	11.097	NaHCO₃	0.068
KCl	1.140	Na₂SO₄	0.015
CaCl₂.4H₂O	0.009	acetic acid	0.352
MgCl₂.6H₂O	0.202	Butanoic acid	0.029
FeCl₂.4H₂O	0.790	propionic acid	0.015
SrCl₂.6H₂O	0.109	Pentanoic acid	0.205
BaCl₂.2H₂O	0.001	phenol	2.560
LiCl	0.046	MEG	0

4.3.3 Lean Glycol Tank (LGT)

The lean glycol tank (LGT) is pre-filled with lean glycol before starting the experiment. It is also used to store the produced lean MEG after the regeneration process. LGT is made from stainless steel 316 mounted vertically with a maximum working capacity of 120 litres.

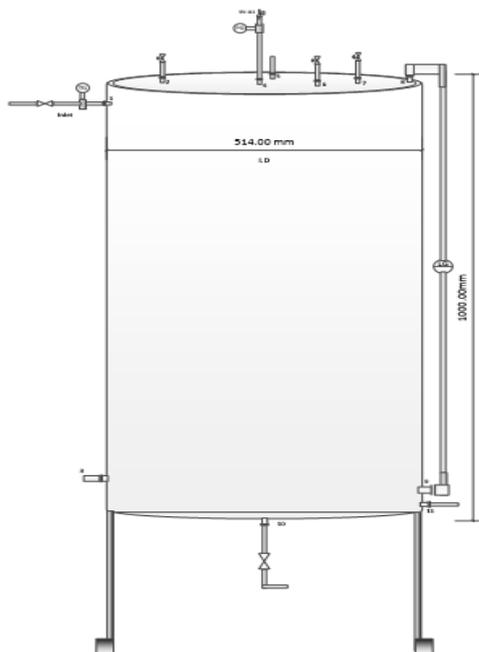


Figure 4-5 Lean MEG Tank

Typical concentrations of the salts in LGT are shown in [Table 4-3](#)

Table 4-3 LGT Typical Concentration

Component	Concentration (g) /Kg water	Component	Concentration (g) /Kg water
NaCl	8.638	NaHCO ₃	0.011
KCl	0.827	Na ₂ SO ₄	0.007
CaCl ₂ .4H ₂ O	0.007	acetic acid	0.827
MgCl ₂ .6H ₂ O	0.147	Butanoic acid	0.007
FeCl ₂ .4H ₂ O	0.023	propionic acid	0.363
SrCl ₂ .6H ₂ O	0.042	Pentanoic acid	0.040
BaCl ₂ .2H ₂ O	0.001	phenol	0.003
LiCl	0.015	MEG	80%

4.3.4 Feed Blender

Brine, lean MEG, and condensate are transferred to the feed blender, where all the fluids are mixed and homogenised using a high shear blender. The feed blender is a vertical cylindrical vessel made from stainless steel having a maximum working volume of 15 litres.

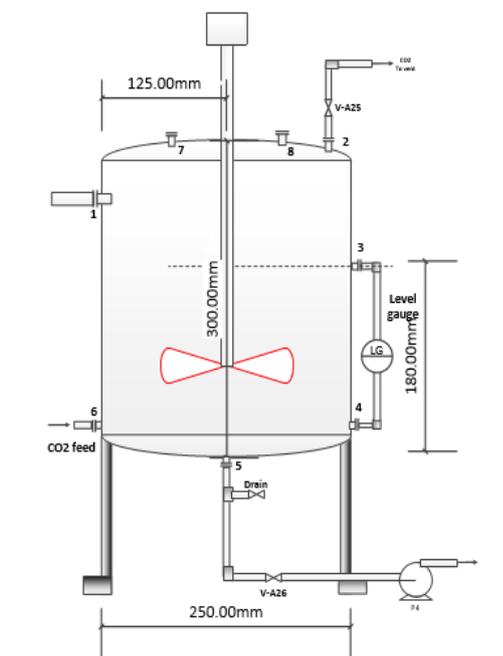


Figure 4-6 Feed Blender

Table 4-4 shows typical operating conditions of the feed blender;

Table 4-4 Feed blender operating conditions

Operating data	Input	output
Max operating temperature(°C)	30	30
Max Operating Pressure(bar)	1.2	1.2
Mass Flow Rate(Kg/hr)	10	5
Density(Kg/m ³)	1.004	1.055
Design Temperature(°C)	45	
Design Pressure(bar)	1.8	

4.3.5 MEG Pre-Treatment System

The next step is pumping all the fluids from the feed blender to the MEG pre-treatment vessel, where the temperature and the pH can be adjusted. MPV has been designed to allow the injection of alkalinity in order to control and maintain the pH value. It also has a vertical weir installed inside to separate the condensate from the mixture relying on the density differences. The MPV is a vertical vessel made from stainless steel 316 with a maximum working volume of 18 litres *Figure 4-2*. A glass viewing strip in the front has been added to the design of the MPV vessel to allow the operators to observe and monitor the level inside, estimate the quantity of condensate / drilling mud carried over, and check if there is any emulsion happening *Figure 4-7*.

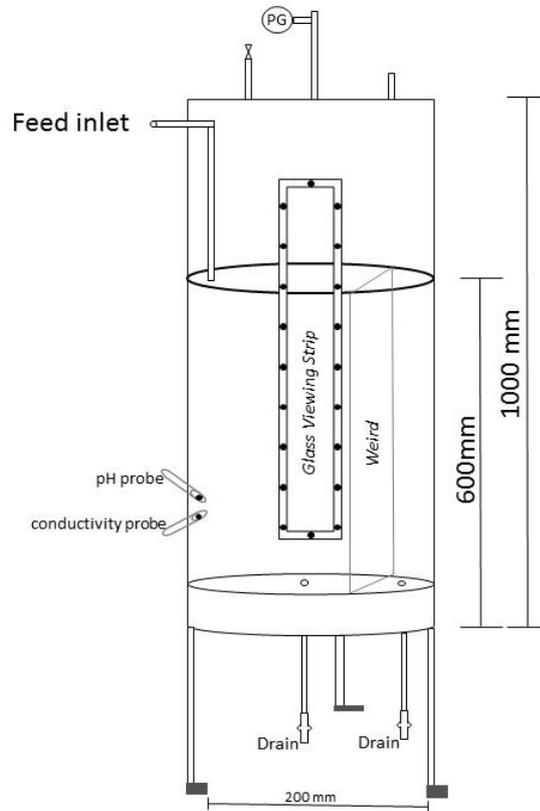


Figure 4-7 MEG Pre-Treatment System

For sizing of 3-phase separator, Brown- Saunders equation was used based on calculating the allowable vapour velocity given in the formula below:

$$Va = K [(\rho_l - \rho_v) / \rho_v]^{1/2} \quad , ft/sec \quad \dots\dots\dots 4-1$$

ρ_l = density of the light liquid phase lb/ft³

ρ^v = density of the vapour phase lb/ft³

K = 0.2 for vertical drum without a wire mesh

Also, for liquid- liquid separation, Stokes equation was used based on free settling velocity for the droplet of the heavy liquid (MEG and water + dissolved salts) from the light condensate phase using the formula;

$$V_{\text{settling}} = k_s \frac{\rho_h - \rho_l}{\mu_c} \quad \text{ft/ sec} \quad \dots\dots\dots 4-2$$

ρ_h = density of heavy liquid phase lb/ ft

ρ_l = density of light liquid phase lb/ ft

μ_c = viscosity of the continuous phase cp

k_s is usually selected 0.333

The settling design should comply with the requirement that for each continuous liquid phase the residence time is larger than the settling time needed by the droplets of the dispersed liquid to settle out.

The main function of MPV is to remove the divalent on salts from solutions. Specific conditions, such as pH and temperature, is required to be maintained inside the vessel to approach sufficient salt removal. *Figure 4-8* shows the efficiency of MPV in terms of Calcium ons removal. The upper curve represents the feed input that comes from the feed blender, while the bottom curve shows the output feed that goes to the regeneration system. It can be seen that after reaching the desired conditions (approximately 60 hours) the MPV was able to separate out most of the calcium salts.

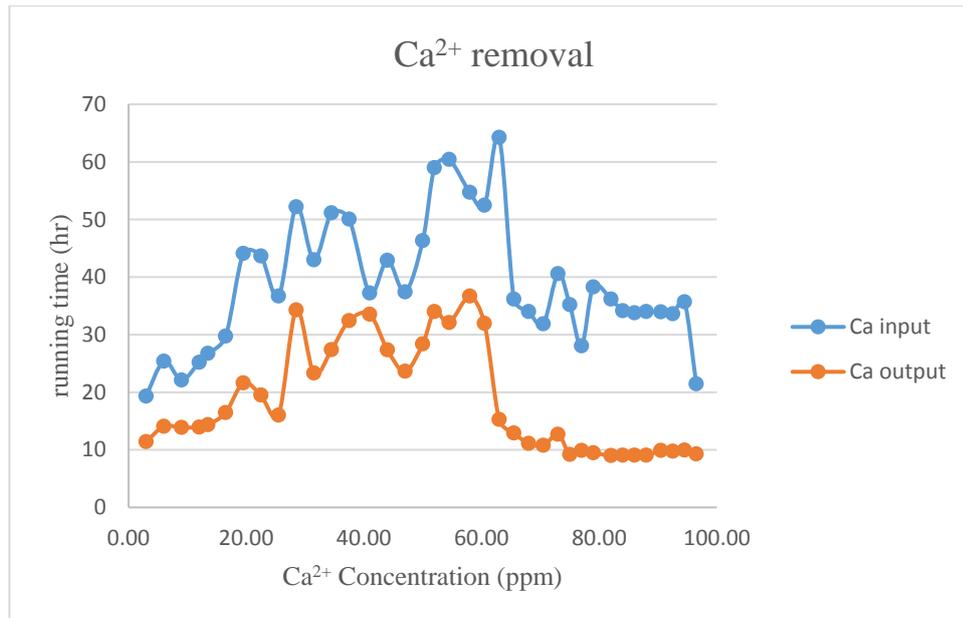


Figure 4-8 Calcium ion removal in MPV

4.3.5.1 MPV control

To maintain or change the desired operating conditions, the MEG pre-treatment vessel is controlled continuously during operation by different type of instruments and control systems, each instrument is responsible for a specified parameter that transmits a reading to the PLC (process logic control), which runs under LabVIEW software installed on a close by computer.

4.3.5.1.1 pH Control

One of the most important parameters in MPV is the pH value. Low pH can reduce the carbonate ion concentration, lower the precipitation rate, and increase the risk of corrosion. Therefore, a pH probe was installed inside the MPV to transmit the reading to the PLC. The PLC will then compare the pH value with the pre-set value in the system. A signal will then be transmitted to a dosing pump downstream the alkalinity source to start dosing the alkalinity. Once the desired pH is achieved, the dosing pump will stop and start again automatically if the pH value goes down below the pre-set value.

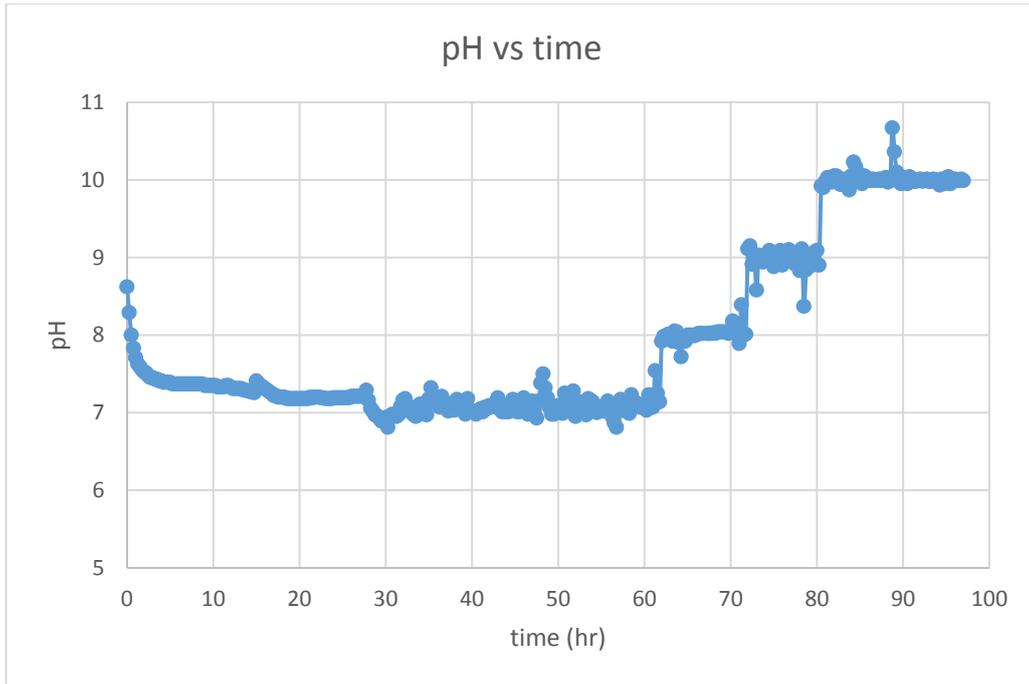


Figure 4-9 pH control in MPV

Figure 4-9 shows the pH value over 97 hours of operation period. Over the first 28 hours, the pH was constant. Once it went down, the dosing pump started to dose alkalinity such as NaOH to bring the pH to the desired level. The set point was 7.2 at that stage and it was changed after 62 hours of operation to 8.0, then to 9 after 72 hours and then to 10 at 80 hours. The reason for increasing the set point of pH was to investigate the effect of pH on the divalent salts precipitation, which will be explained in details later in this thesis.

4.3.5.1.2 Level Control

It is important to maintain a safe operating level inside the pre-treatment vessel and make sure that the MPV does not overflow. Also maintaining a constant level leading to constant precipitation rate of divalent salts. A level sensor was installed at the top of the vessel to send the signal back to the PLC. A control valve was installed downstream the MPV to respond to the open / close signal depending on the operator pre-set value, which is normally around 20-26% by volume of MPV *Figure 4-10*.

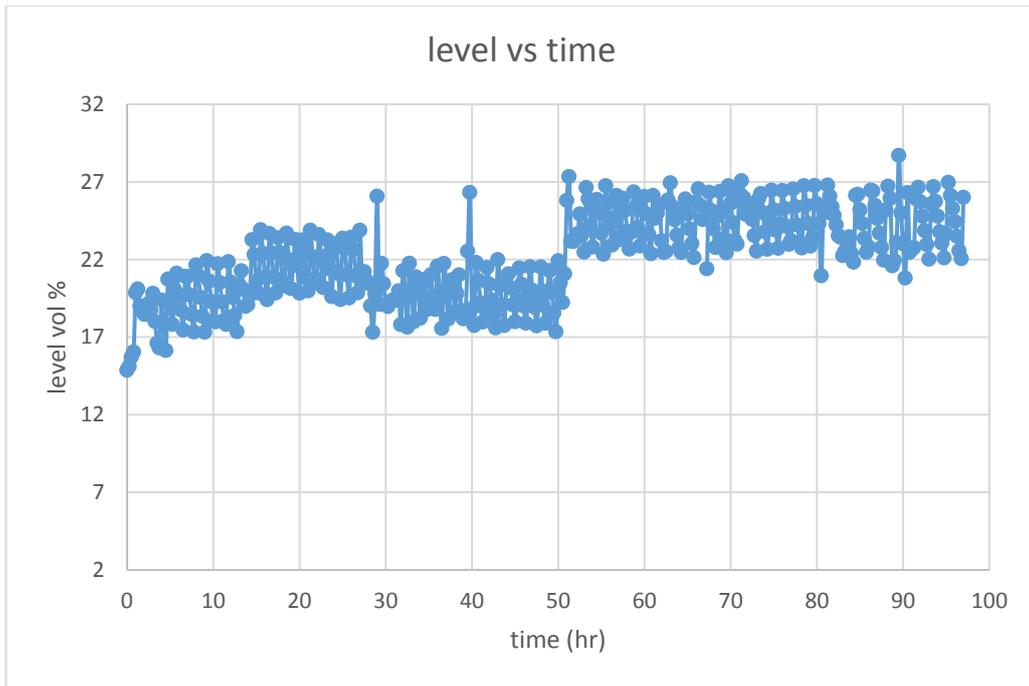


Figure 4-10 MPV Level Control

4.3.6 Rich Glycol Tank RGT

The rich MEG tank is acting as a settlement tank to ensure the liquids are free of suspended materials before transferring them to the regeneration section. A 2M filter was installed on the tubing just after the RGT to remove any particles in the fluid. RGT is made from stainless steel 316 vertically mounted with a maximum working capacity of 120 litres *Figure 4-11*.

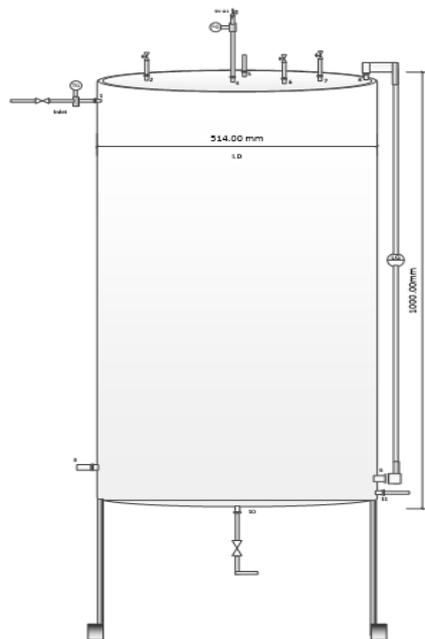


Figure 4-11 Rich Glycol Tank (RGT)

A typical rich MEG composition is shown in *Table 4-5*

Table 4-5 Rich MEG composition

Component	Concentration (g/Kg Water)	Component	Concentration(g/ Kg Water)
NaCl	8.936	SrCl₂.6H₂O	0.024
KCl	0.162	BaCl₂.2H₂O	0.027
CaCl₂.4H₂O	0.242	LiCl	0.012
MgCl₂.6H₂O	0.059	NaHCO₃	0.918
FeCl₂.4H₂O	0.001	Na₂SO₄	0.007

4.4 MEG regeneration system

In the MEG plant, the regeneration system is the next step after the pre-treatment section, which mainly consists of a distillation column, reboiler, peristaltic pumps heat exchanger and reflux drum *Figure 4-12* [85].

4.4.1 The distillation column

The distillation column was designed with two individual packing sections of 2 meters height in total. The diameter of the structured packing is 80mm fitted inside the column [85].

4.4.2 The reboiler

The reboiler is located at the bottom of distillation column heated by a 5 kW immersion heater. The heater is connected to the control system PLC (programmable logical control) to maintain the temperature at the desired value. The products are to be pumped out constantly from the bottom of the reboiler using a peristaltic pump, which is connected to the PLC and MFM (mass flow meter) to control the flow rate [84].

4.4.3 The Heat Exchanger

After reaching steady-state conditions, the liquids pass through a plate heat exchanger, which is cooled by water at 15°C that was supplied from an external chiller.

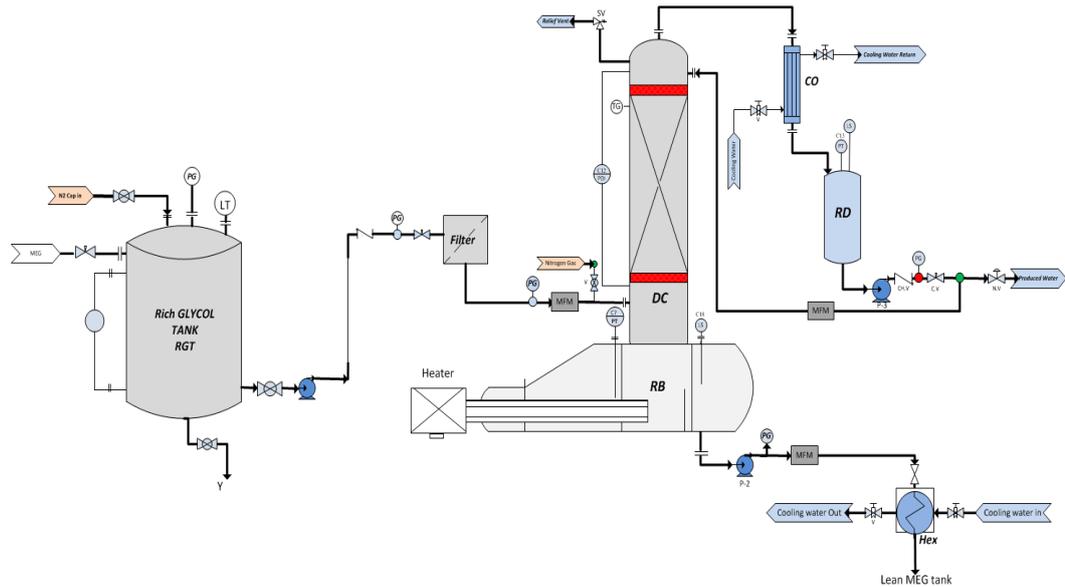


Figure 4-12 MEG Regeneration system [8]

4.4.4 The reflux Drum

The boiled water from the reboiler passes through a condenser where it is cooled down using counter current chilled water from the external water chiller and collected in the reflux drum. The reflux drum is a glass vessel connected to the distillation column used to ensure that the distillation column has reached the steady state condition at the start-up of the run and to maintain the VLE (vapour liquid equilibrium) during the operation.

4.5 MEG reclamation system

The reclamation system is the last step in the MEG pilot plant. It consists of a reclaimer that operates under vacuum pressure to reduce the processing temperature and avoid the degradation of MEG. The reclaimer operation temperature is around 140-165°C and 100 mbar pressure. The oil path uses silicon oil to heat the solution inside the rotation flask. The main function of the reclaimer is to separate the salts from the solution and produce a high quality MEG, which feeds back to the LGT (lean glycol tank) to be reused again *Figure 4-13*.

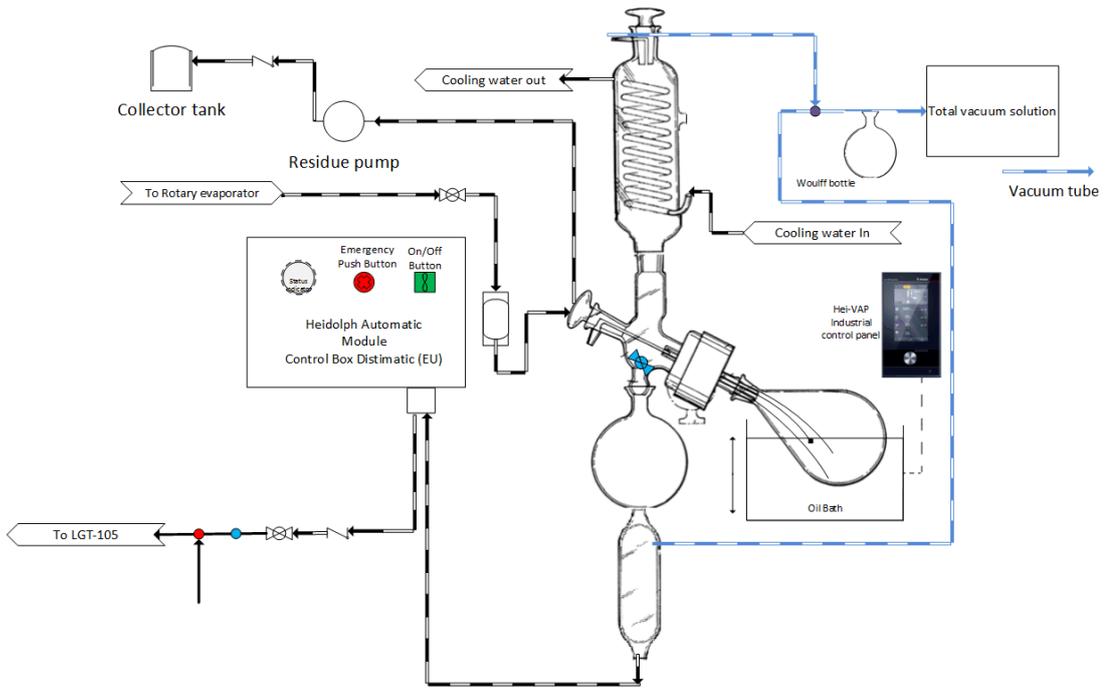


Figure 4-13 MEG Reclamation System

Figure 4-14 shows that the reclaimers has the ability to remove over 95% of the sodium salt after applying deal conditions in the reclaimers. The top blue curve represents the Sodium concentration entering the reclamation unit, which is fluctuating around 5000 ppm, while the bottom orange curve represents the output concentration of Sodium. This data has been extracted out from one of the corrosion management tests carried out within the MEG bench top scale.

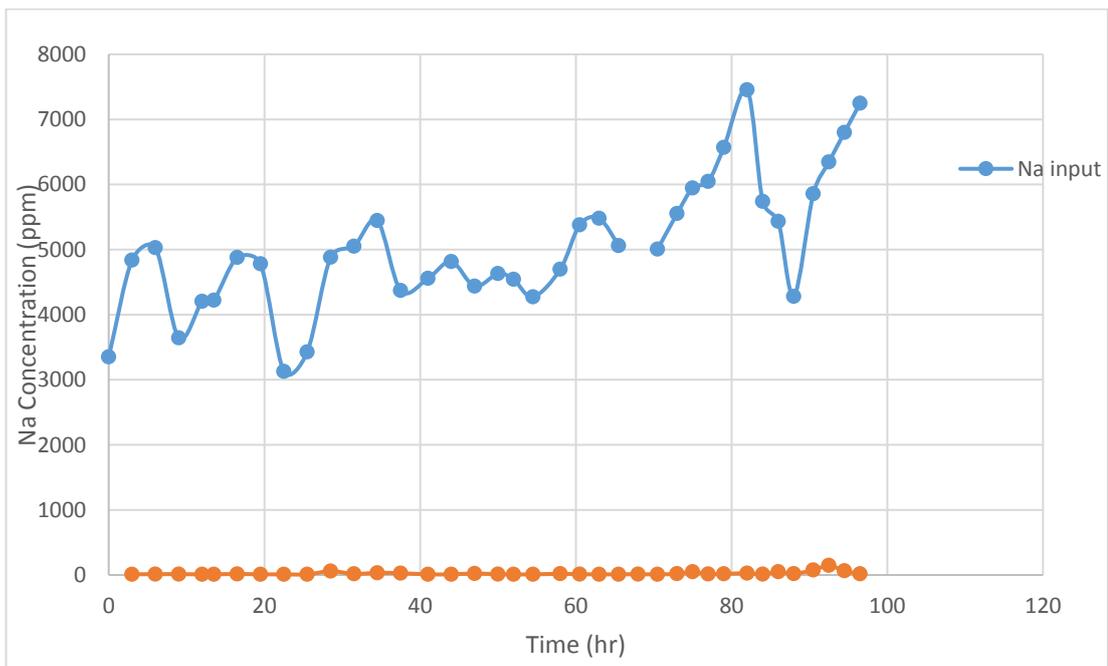


Figure 4-14 The efficiency of the reclaimers in terms of Na salt removal

4.6 Conclusions

The MEG bench scale pilot plant was successfully designed, constructed, and operated to serve the actual field conditions. The Benchtop facility was used to simulate different scenarios that could possibly occur during the operation of certain gas wells back to the onshore production facility, such as clean up to host study, switchover between different corrosion management strategies, oxygen scavenger evaluation, pH-Alkalinity control and scale tendency evaluation. It is proposed to use realistic simulated production fluids, such as condensate mixtures and simulated formation water/brines.

The bench-top scale closed loop MEG regeneration/reclamation system can minimize the gap between individual laboratory scale tests and the comprehensive testing protocol, which will enable laboratory scale testing to be correlated to field conditions.

5 Mono-ethylene Glycol bench scale clean up study, operating results using field data

5.1 Introduction

Mono-ethylene Glycol (MEG) Benchtop facility was used to simulate the start-up and clean-up of the gas wells fields back to the onshore production facility. Drilling muds and well completion fluids contain high concentrations of divalent cations, particulates as well as various production chemicals, which could result in various system upsets of the onshore plant. The behaviour of the well completion fluids and drilling muds expected during the initial start-up phase, and their effect on the inlet separation train and the downstream MEG system, has been investigated.

The MEG Benchtop facility is designed as a MEG regeneration and reclamation closed loop system with a production capacity up to four kilograms per hour of lean MEG. The use of the MEG facility and its realistic simulated production fluids such as condensate mixture and simulated formation water will improve the laboratory scale experiments to be correlated to the field conditions and create better understanding of the results.

MEG is one of the well-known flow assurance hydrate inhibitors often used in natural wet gas pipelines to prevent hydrate formation during production and transportation of fluids from the subsea wells [85].

MEG closed loop system is a complex system containing various chemical and physical processes utilised to regenerate and reclaim MEG for re-injection at or near the well head [86]. A better understanding of these processes on the individual process units can be useful to plant operation world-wide.

The analysis of MEG and its degradation products poses continuous challenges to the industry, therefore, analytical capabilities that are transferable from the laboratory into the field have been developed, giving operators better tools to monitor the state of its MEG systems process equipment.

Although the MEG regeneration and reclamation close loop system is very complex and presents a number of operational difficulties, it is still known as the best reliable and cheapest method in terms of hydrate prevention in many gas/ oil fields and transportation processes [33].

Several models have been developed by Øi [80] to be used for all MEG regeneration processes. These models are applicable to other process simulation and vapour-liquid equilibrium programs.

The MEG regeneration and reclamation system has been briefly described by Condilis [81]. Rich MEG (75% concentration), condensate (hydrocarbon base), and brine are transferred through the pipelines to the processing plant for separation. The rich MEG is then sent to the regeneration process where the remaining condensate is separated from the solution. Thereafter, the water is removed in the distillation stage and the salts are removed in the reclaimer. The produced lean MEG (85% wt. MEG concentration) or the regenerated MEG is then sent back to the field to be reused again.

Rich MEG obtained from the slug catcher (represented by the feed blender in the MEG facility) has to encounter pre-treatment before the regeneration process. In the pre-treatment section, the pressure of the rich MEG is reduced and the phases are separated. In many situations, the divalent salts that have low solubilities are to be precipitated out and separated from rich MEG in the MEG pre-treatment vessel (MPV) before transferring the rich MEG to the reconcentration and reclamation unit. As a result, the main function of the reclaimer will be to remove the monovalent salts, which have lower solubilities such as Chlorides. This method reduces the risk of Carbonate precipitation and scaling in the downstream equipment [81].

Although many studies have illustrated the MEG regeneration system, the MEG bench-scale facility at Curtin Corrosion Engineering Industry Centre (CCEIC), Curtin University has some outstanding features as it simulates all the MEG regeneration/reclamation processes in a closed loop system. In general, a MEG bench scale closed loop facility consists of a MEG pre-treatment system, MEG regeneration system and reclamation system [38].

5.2 Objective

The analysis of MEG and its degradation products present ongoing challenges to the oil and gas industry. To assist in understanding some of these issues, a MEG Benchtop facility that emulates the functionality of typical MEG facilities has been constructed at Curtin University. Research conducted at the MEG Benchtop facility will help to provide early insights into solving some of the operational challenges that arise locally within the industry.

The MEG Benchtop facility has been used to simulate the start-up and clean-up of the specific feed from wells back to the onshore production facility. Drilling muds are normally oil-based and contain excessive amounts of calcium in terms of an internal calcium chloride in the brine phase plus calcium carbonate and calcium hydroxide solids. The suspension fluid contains sodium and potassium chlorides in the MEG-water brine (80/20 MEG/water), whereas the gravel pack carrier fluid is sodium or potassium chloride brine without MEG. The gravel pack carrier fluid also contains a gel consisting of acetic acid, caustic soda, potassium chloride, sodium bromide and some other components.

This study has been focused on the behaviour of the well completion fluids and drilling muds (between 0.4 to 1.2% based on condensate) that may be expected during the initial start-up phases, and their effects on inlet separation process. Drilling muds and well completion fluids contain high concentrations of divalent cations, which could result in various system upsets of the onshore plant. The experimental work studied the partitioning of the drilling muds into the condensate and MEG phases in the inlet separation unit. It also investigated the emulsion formation tendency and the effectiveness of production chemicals to break emulsions. Furthermore, the efficiency of the pre-treatment system in terms of removing the divalent cations that have originated from the well completion fluids was investigated by adding excess alkalinity to the fluid to aid precipitation and separate the particles from the liquid phase.

5.3 Process Description

The pre-treatment section is the first step in the MEG bench scale closed loop system. It is used to remove the drilling mud from the fluid mixture, separate the condensate phase from the rich MEG, and precipitate the divalent Ions upon heating before transferring the rich MEG to the regeneration and reclamation units. The Pre-treatment system is shown in *Figure 5-1*;

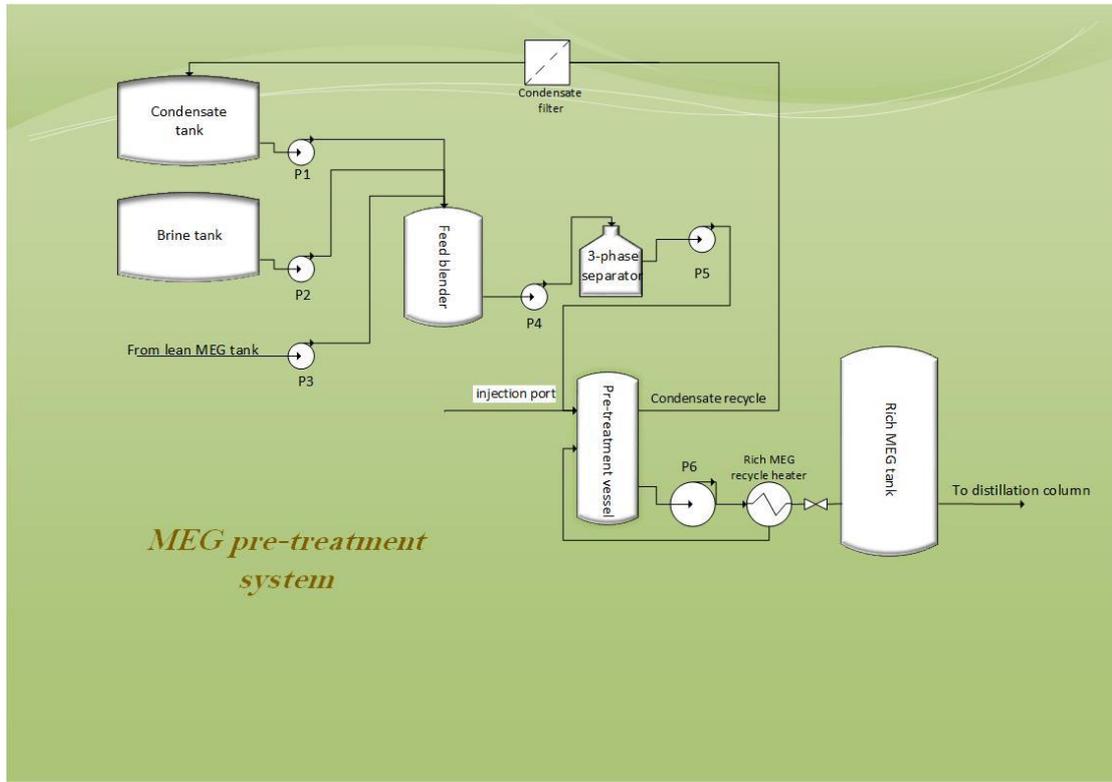


Figure 5-1: MEG pre-treatment system

The oxygen, pH and conductivity probes are installed in the feed blender and MEG pre-treatment vessel in order to get better understanding of the behaviour of fluids inside the system. Condensate, brine and lean MEG are transferred together to the feed blender using the peristaltic pumps at the required flow rates. In the feed blender, the fluids are mixed thoroughly using an installed mixer to form the desired shear stress in the feed blender. In the MEG pre-treatment vessel, rich MEG is heated to 80°C and the pH maintained around 8.5 to precipitate the divalent Ions out of rich MEG. MEG pre-treatment vessel provides sufficient residence time to separate the liquid hydrocarbons, which are returned back to the condensate tank after filtration.

5.4 Salts Removal

Rich MEG (MEG with more than 25wt% Brine) normally contains a high amount of dissolved salts and Iron resulting from the corrosion of the natural gas transportation pipelines that have to be removed. In order to remove these chemicals, a precipitation process is essential.

In the MEG bench scale, salts are removed in two stages; the divalent ion salts having low solubilities such as Ca^{2+} and Fe^{2+} are precipitated out of the solution in the MEG pre-

treatment vessel. While the high soluble salts are separated in the reclamation section as a slurry.

The saturation ratio (SR) represents the capability of salts to precipitate out of the solution and can be defined by the following equation:

$$SR = \frac{a_{salt}}{K_s} \quad \dots\dots 5-3$$

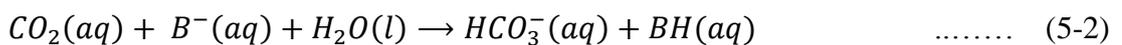
Where a_{salt} is the activity of the salt and K_s is the thermodynamic solubility product of salt.

The solution is called supersaturated when SR is more than 1 and the salts can be precipitated out. This can happen by increasing the concentration of the dissolved salts, decreasing the solubility product or both. [87]

Heating leads to increase the solubility of monovalent ions salts such as (NaCl and KCl) because the dissolution reaction is endothermic, which leads to increasing the K_s . whereas K_s will decrease with increasing the temperature for divalent ion salts such as $CaCO_3$ as the dissolution reaction is exothermic.

It can be noticed from above that the best way to remove the salts of monovalent ions out from rich MEG is to increase the concentration of the salts beyond the supersaturation level to increase the SR in the reconcentration section. While the majority of divalent ions such as Ca^{2+} and Fe^{2+} can be removed from the rich MEG upon heating in the pre-treatment section.

The pre-treatment vessel (MPV) is designed to allow injection of alkalinity to the rich MEG, which can be carbonate, bicarbonate, or hydroxide. The amount of the alkalinity injected to the pre-treatment vessel is controlled by maintaining the pH value at 8.5. The alkalinity in the regeneration and reclamation field can be divided into strong alkalinity and weak alkalinity; The strong alkalinity reacts with the CO_2 and gives a high concentration of HCO_3^- while the weak alkalinity is formed by carboxylate and weak bases. [86]



In order to simulate real field start-up conditions, it is necessary to react realistic production fluids by adding drilling mud and other types of chemicals such as film forming corrosion inhibitor (FFCI), demulsifier and oxygen scavenger.

This study is focused on; the behaviour of the drilling mud and the well completion fluids in the initial start-up phase, the behaviour of drilling mud in the MEG/condensate interphase with and without adding the demulsifier, the emulsion formation tendency and the effect of demulsifier to break emulsions, the efficiency of the pre-treatment system in removing the divalent cations.

5.5 Operating Procedure

In the MEG bench top facility, the lean MEG is mixed with a brine solution to form a rich MEG that can be transferred to the feed blender. In this study, the drilling mud was mixed with the condensate at the desired concentration in a separate vessel containing a magnetic stirrer to keep the mud in suspension while a peristaltic pump was used for feeding at constant flow rate of the mixture to the feed blending vessel.

The total inlet feed rate to the feed blender was 10 kg/hr (5kg/hr for rich MEG and 5kg/hr for condensate-drilling mud mixture). The required shear mixing was used to mix all the fluids inside the feed blender before transferring the mixture to the three phase separator where the rich-MEG was separated from the bottom of the vessel and pumped at a flow rate of 5kg/hr to the MEG pre-treatment vessel (MPV).

5.5.1 Phase 1 (field 1)

In order to simulate field 1 conditions and provide the correct amount of CO_2 and HCO_3^- , CO_2 gas percentage in MEG bench top facility was adjusted using ALIKAT mass flow meters as follows: 6.2 mole%, 5.8 mole%, and 3.5 mole% for the feedblending vessel, the 3-phase separator and the MEG pre-treatment vessel, respectively.

In the MPV the rich-MEG was heated to 80°C via a recycle heater where a heat exchanger was installed and the alkalinity injected to the MPV using 0.45M NaOH solution and a dosing pump (*Figure 5-1*). The dosing rate was adjusted manually depending on the pH reading from the pH probe located inside the MPV. The rich-MEG was then transferred to the rich MEG tank (RMT) after achieving the required fill height and a temperature of 80°C .

The following cases have been simulated in the MEG Benchtop facility:

a) Clean (Baseline):

This case was simulated by running the equipment using first fills (clean fluids for commissioning, no salts added, low shear applied).

b) Start-up MEG + drilling mud, no emulsion:

This case was done to simulate that condensate, drilling mud, and rich MEG (74.5% MEG) containing the dissolved salts are effectively separated in the 3-phase separator prior to entering the MEG system.

c) Start-up MEG + drilling mud, + emulsion:

To simulate that condensate, drilling mud, and rich MEG (74.5wt% MEG) containing the dissolved salts are not effectively separated (in the form of an emulsion) in the 3-phase separator prior to entering the MEG system, thus additional condensate/rich MEG separation was needed to take place in the pre-treatment vessel.

d) Start-up MEG + drilling mud + emulsion:

To simulate that condensate, drilling mud, and rich MEG (74.5wt% MEG) containing the dissolved salts are effectively separated by the addition of a demulsifier prior to entering the 3-phase separator located upstream the MEG system.

Table 5-1 shows the matrix of the experiments for phase 1 that were carried out:

Table 5-1 The experimental matrix of phase 1

experiment	Description	Rich MEG: Condensate	Drilling Mud in Condensate	Demulsifier
1	Clean (Baseline)	50:50	0	0
2	Rich MEG + drilling, no emulsion	50:50	1.2%	0
3a.	Rich MEG + drilling mud + emulsion	50:50	0.6%	0
3b.	Rich MEG + drilling mud + emulsion	50:50	1.2%	0
4a.	As 3a. + Demulsifier	50:50	0.6%	2000 ppm
4b.	As 3b. + Demulsifier	50:50	1.2%	2000 ppm

The rich MEG composition is shown in *Table 5-2*:

Table 5-2 Rich MEG composition for phase 1

NaCl	1.6%(wt)
KCl	0.5%(wt)
Water	24.5%(wt)
MEG	73.4%(wt)
Oxygen Scavenger	25 ppm
MDEA	6.4 mmol/kg
Acetic Acid	60 ppm

5.5.2 Phase 2 (field 2)

The composition of the CO₂ sparge gas was adjusted to 100 mole%, 100 mole%, and 76 mole% in the feed blending vessel, 3-phase separator, and MEG pre-treatment vessel respectively. However, the amount of dissolved CO₂ in the liquid phase of the first two vessels could be lower than expected in the real plant because the vessels could not be pressurised above the atmospheric pressure, which impacted some of the results (e.g., pH and alkalinity).

In the pre-treatment vessel (MPV), the rich MEG was heated via the circulation heating loop to 80 °C and the alkalinity was raised using 1 M NaOH solution via a dosing pump to maintain the pH at the required value (*Figure 5-2*). The dosing rate was adjusted automatically based on the pH readings from the in-line pH probe that has been installed downstream the MPV in the circulation loop to prevent fouling of the probe with the drilling mud. Once the temperature of 80°C was reached in the MPV at the required level, rich MEG was transferred to the rich Glycol tank via a level controlled valve to maintain a constant fill height in the MPV.

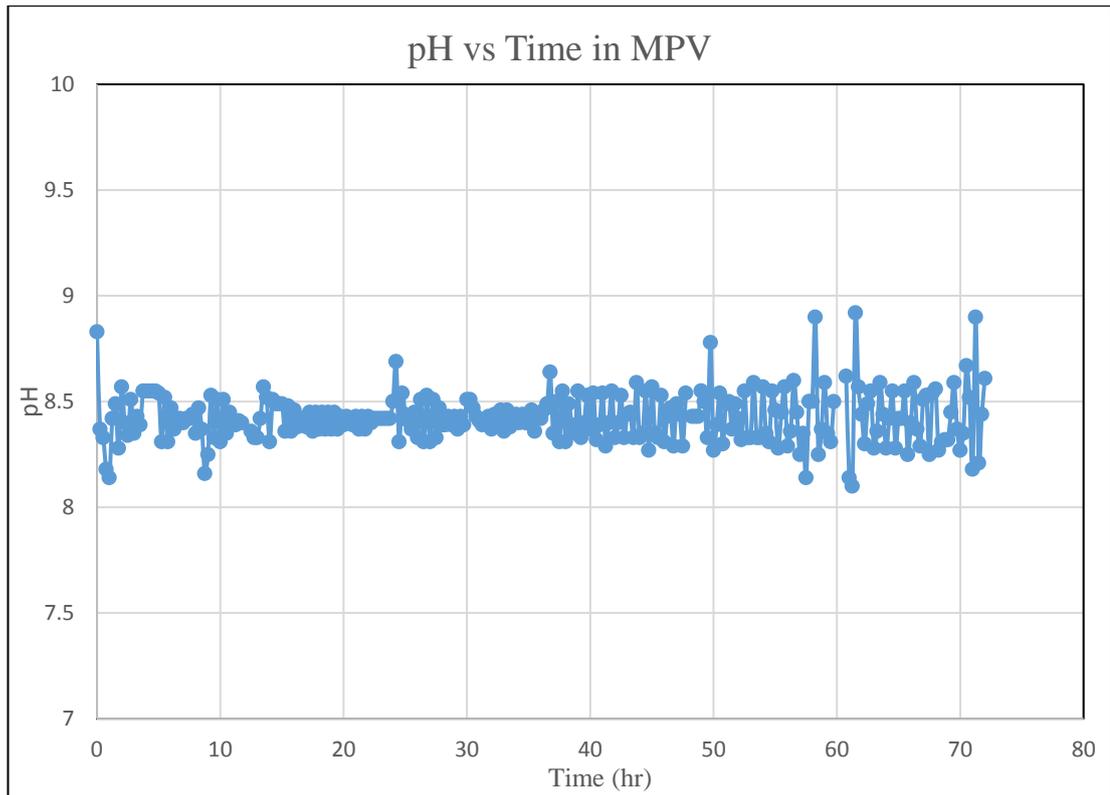


Figure 5-2 Response of NaOH dosing pump in MPV

The following cases have been simulated in the MEG Benchtop facility:

a) Start-up MEG + drilling mud + emulsion

Condensate, drilling mud, and salt laden rich MEG were not effectively separated (in the form of an emulsion) in the 3-phase separator prior to entering the MEG system, thus additional condensate/rich MEG separation was needed to take place in the pre-treatment vessel

b) Start-up MEG + drilling mud + emulsion

Condensate, drilling mud, and salt laden rich MEG were effectively separated by the addition of a demulsifier prior to entering the 3-phase separator located upstream the MEG system.

c) Start-up MEG + drilling mud (reduced concentration), no emulsion.

Condensate, drilling mud, and salt laden rich MEG are effectively separated in the 3-phase separator prior to entering the MEG system, and condensate carryover to pre-treatment vessel was very small.

The matrix of the carried out experiments is listed in *Table 5-3*:

Table 5-3 The experimental matrix of phase 2

experiment	Description	Rich MEG:	Drilling Mud in Condensate	Demulsifier
1	Rich MEG + drilling mud, with emulsion	50:50	0.6 %	0
2	As 1 + Demulsifier	50:50	0.6%	400ppm
3	Rich MEG + drilling mud, no emulsion	50:50	0.4%	0

The rich MEG composition used in this phase is listed in [Table 5-4](#):

Table 5-4 Rich MEG composition for phase 2

NaBr or other salts	0
Water	30%(wt)
MEG	70%(wt)
MDEA	2 mmol/kg
Film Forming Corrosion Inhibitor (FFCI)	1500 ppm
Acetic Acid	60 pm

5.6 Experimental results and Discussion

5.6.1 Phase 1 (field 1)

A laboratory pre-test experiment was carried out using emulsion test procedure to investigate the fluids behaviour and settlement time of the drilling mud in different test solutions as shown in [Table 5-5](#).

Table 5-5 Pre-tests for investigating the drilling mud behaviour

Test solution	Rich MEG Composition	Rich MEG : Condensate (Wt. %)	Drilling mud in condensate	Demulsifier (Based on total liquid vol.)
Blank sample Case 3a	As per <i>Table 5-2</i>	50:50	0.6 %	0 ppm
Case 4a – 1		50:50	0.6 %	1000 ppm
Case 4a – 2		50:50	0.6 %	2000 ppm
Blank sample Case 3b		50:50	1.2 %	0 ppm
Case 4b – 1		50:50	1.2 %	1000 ppm
Case 4b – 2		50:50	1.2 %	2000 ppm

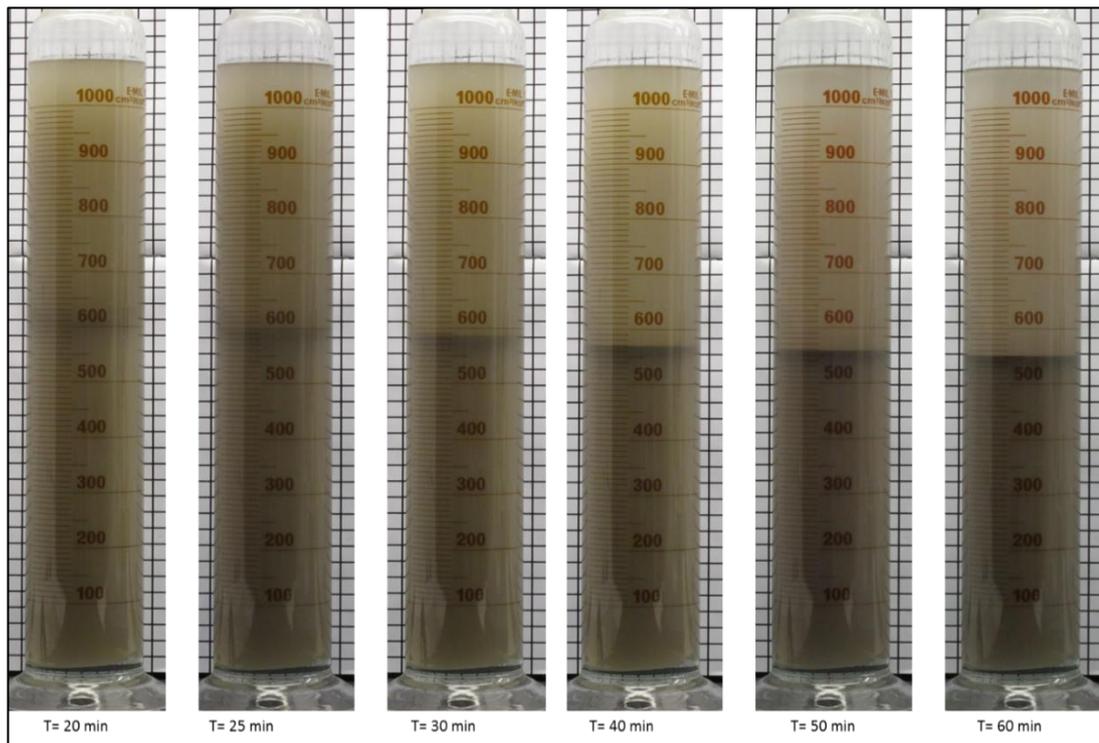


Figure 5-3 Case 3b: 1.2% drilling mud with no demulsifier

The results illustrate that in the presence of the drilling mud, emulsions are present that do not fully separate even after a period of 60 minutes at room temperature (Cases 3a and 3b). There is also an effect on the concentration of drilling mud observed. While in Case 3a solution, the emulsion started to break after 2 minutes and it took over 5 minutes for the Case 3b solution to start separating. In both cases, MEG and condensate phases remained cloudy, indicating that the drilling mud had no clear tendency to partition into the MEG phase (the images for Case 3b are shown in [Figure 5-3](#)).

Adding the demulsifier to the test solutions resulted in a more rapid breakdown of the emulsion and the concentration of the drilling mud at the MEG/Condensate interface. It was also noticed that for a drilling mud concentration of 1.2% wt. in the condensate, 2000 ppm of demulsifier was needed to break the emulsion within 30 minutes at room temperature. However, this also resulted in the accumulation of the bulk of the drilling mud at the MEG/Condensate interface (*Figure 5-4*).

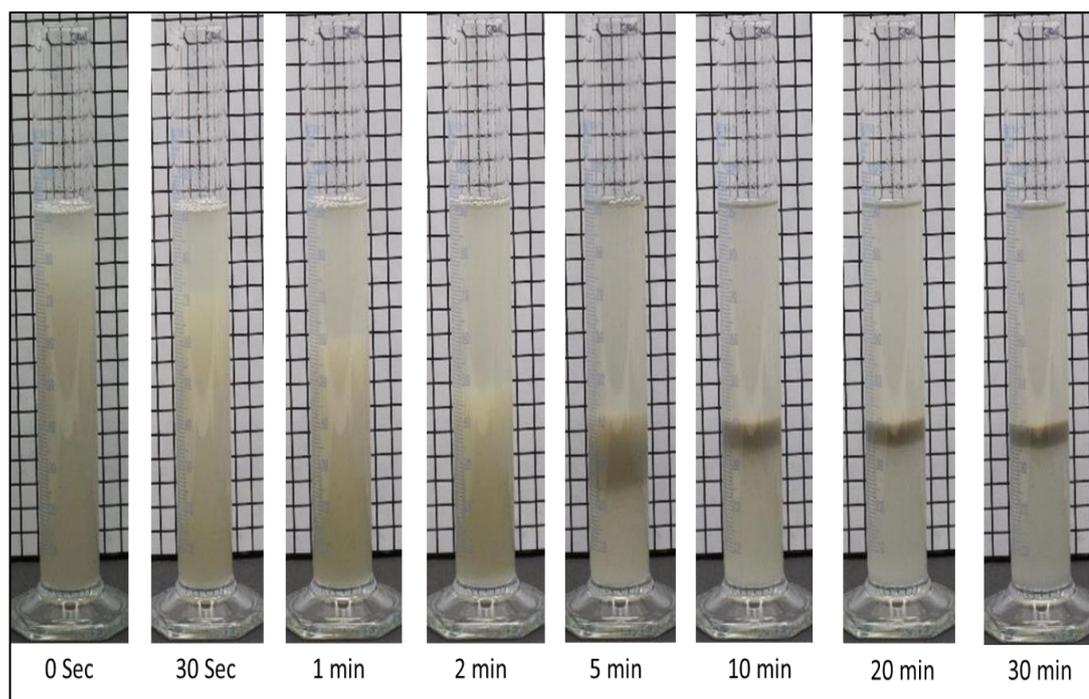


Figure 5-4 Case 4b-rich MEG + 1.2 % drilling fluid + 2000 ppm demulsifier

5.6.1.1 Three-phase separator

MEG pilot plant was designed to simulate field operation conditions as indicated previously. During the initial operation, drilling mud was added to the condensate phase by 0.6 and 1.2 wt. %. In addition, the well completion fluids with high divalent cations concentration were added to the brine tank. The separation efficiency and the effect of the various additives were investigated and examined thoroughly during the operation. The initial results indicated that the drilling mud stays at the MEG phase of the 3-phase separator by forming an emulsion. It was also observed that when adding a specific amount of the demulsifier, the drilling mud remained at the interphase layer between MEG and condensate in the 3-phase separator at ambient temperature (*Figure 5-5*). It was noticed that the drilling mud settled at the bottom of the condensate phase, therefore, it is possible to separate the mud from the condensate easily if the contaminated condensate is stored for

approximately one day in a separate container to give the mud enough time for settling down. The drilling mud separates partially into the MEG phase, while after addition of 2000 ppm demulsifier (Cases 4a and 4b), the condensate phase became less translucent, indicating better separation of the drilling mud. However, the majority of the drilling mud accumulates at the MEG/Condensate interphase.



Case 1: clean fluids



Case 2: Rich MEG + 1.2 % drilling mud (no emulsion)



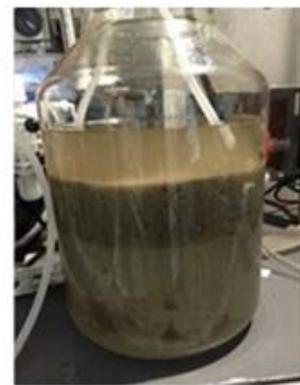
Case 3a: rich MEG + 0.6% drilling Mud, (emulsion)



Case 3b: Rich MEG + 1.2% drilling mud with emulsion



Case 4a: Rich MEG + 0.6% drilling mud emulsion with demulsifier



Case 4b: Rich MEG + 1.2% drilling mud, emulsion with demulsifier

Figure 5-5 Three phase separator (TPS) in all cases

5.6.1.2 MEG pre-treatment vessel

After the 3-phase separator, the Rich MEG (from the bottom of the TPS, which still contains some mud in the emulsion form) was pumped to the MPV, where it was heated to 80°C. Inside the MPV, the high temperature leads to breaking down the emulsion. It was noticed that the drilling mud accumulated at the interface layer between the rich MEG and the condensate phases in all cases where the drilling mud was used. In the presence of the demulsifier, the condensate phase is transparent while it is opaque if no demulsifier is added. Moreover, the experiment showed that the emulsion form in the presence of drilling mud even with low shear mix applied (< 3000rpm).

Case 2: Rich MEG + 1.2% drilling mud + NO emulsion	Case 3a: Rich MEG + 0.6% drilling mud + emulsion	Case 3b: Rich MEG + 1.2% drilling mud + emulsion	Case 4a: As 3a + demulsifier	Case 4a: As 3b + demulsifier
				
15% condensate carryover @ 3000 rpm	10% condensate carryover @ 7000 rpm	15% condensate carryover @ 6000 rpm	2.5% condensate carryover @ 7000 rpm	5% condensate carryover @ 7000 rpm

Figure 5-6 Pre-treatment vessel after 240 min of operation

It can be seen that despite applying a low shear stress during the feed blending process, a particular amount of condensate was carried over into the MPV for case 2. Increasing the shear stress (Case 3a&b) resulted in much higher condensate carryover. Adding the demulsifier (Case 4a&b) leads to significant reduction of condensate carry over into the MPV.

All the experiments were run at atmospheric pressure and the CO₂ concentration of the sparging gas was adjusted to 6.2 mole%, 5.8 mole% and 3.5 mole% for the feed blending vessel, 3-phase separator and MEG pre-treatment vessel respectively to simulate the comparable CO₂ partial pressure to the field conditions. During the experiment, it was

observed that the dissolved oxygen level fluctuated, thus it was assumed that full saturation with CO₂ at the required concentration was not achieved during the whole experiment period, as the dissolved oxygen was not replaced fully by the sparging gas mixture.

In the MPV, it is necessary to remove the Calcium ions as these ions came from the drilling mud and were partitioned in the MEG phase in the 3-phase separator vessel. The alkalinity was raised using 1M NaOH solution to facilitate precipitation of calcium carbonate. The removal efficiency data in the MEG pre-treatment system are shown in *Table 5-6*.

Table 5-6 Efficiency of the MEG pre-treatment process

	[Ca ²⁺] before MPV	[Ca ²⁺] after MPV	% Ca ²⁺ removal efficiency	pH inside MPV
Case 2	180	29	84	8.7
Case 3a	180	5.4	97	8.3
Case 3b	450	72	84	8
Case 4a	180	17	91	8.1
Case 4b	397	190	52	8.3

The Calcium ions were not successfully removed in most cases, it could be because the solution was not fully saturated with the right gas mixture (6.5 mole% CO₂ in N₂), which have caused an insufficient carbonate ion concentration (Case 3b). In addition, the accumulation of drilling mud in the MPV resulted in fouling of the pH electrode, which made dosing of NaOH to increase the alkalinity difficult. Thus the resulting pH readings could not be trusted. Therefore, modifications to the pH measurement (probe location) and dosing pump (implementing pH controlled dosing) were done as well as modifying the gas sparging system to improve saturation of the feed as it can be seen in phase 2.

5.6.2 Phase 2 (field 2)

In order to gain the knowledge of how the fluids will behave and to estimate the settlement time of the drilling mud. The experimental matrix in *Table 5-3* were tested

in the laboratory using the standard test protocol for emulsion stability before applying the experiment to the MEG plant. It is important to determine which concentration of drilling mud should be used, therefore, two different concentrations of mud (0.4% and 0.6%) were tested as shown in *Table 5-7*.

Table 5-7 pre-tests for investigating the drilling mud behaviour of phase 2

Test solution	Rich MEG Composition	Rich MEG : Condensate (Wt. %)	Drilling mud in condensate	Demulsifier (Based on total liquid vol.)
Case 1	As per Table 4	50:50	0.6 %	0 ppm
Case 2		50:50	0.6 %	400 ppm
Case 3		50:50	0.4 %	0 ppm

The results demonstrate that in the presence of the drilling mud of 0.6% in condensate, emulsions are present and the phases did not fully separated even after rest times of 80 minutes at room temperature (Case 1) (*Figure 5-7*). Thus, using 0.6% drilling mud was chosen as the worst case scenario for this study.

At a concentration of 0.4% of drilling mud (Case 3), no stable emulsion was formed and the phases separated within 25 minutes (*Figure 5-8*). It can be noted that the majority of the drilling mud settles in the rich MEG phase. Thus, 0.4% drilling mud in condensate has been chosen as a non-emulsion case for this study.

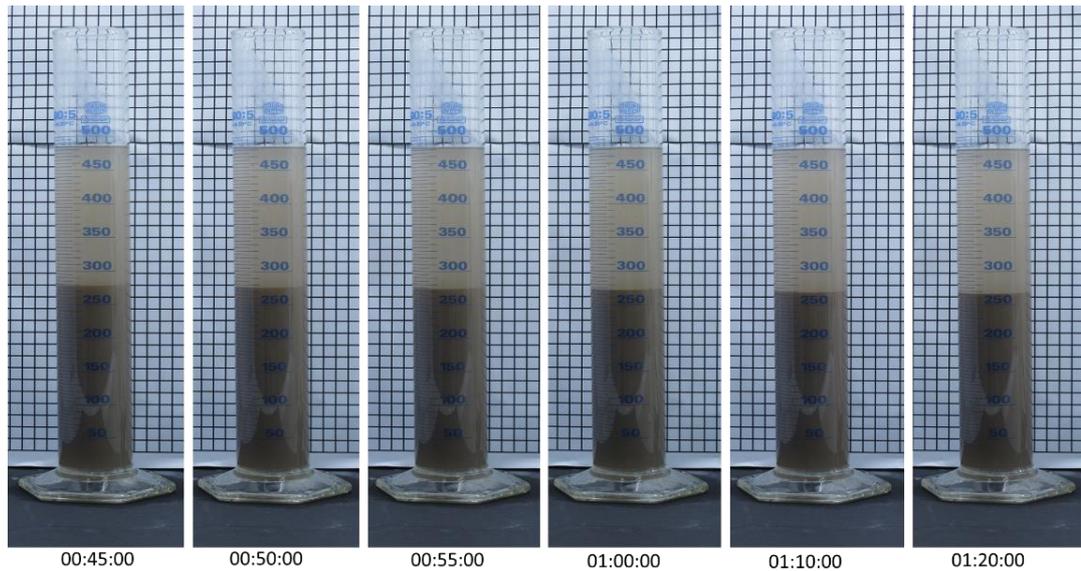


Figure 5-7 Case 1 (0.6% drilling mud) after 45 to 80 minutes of settlement time

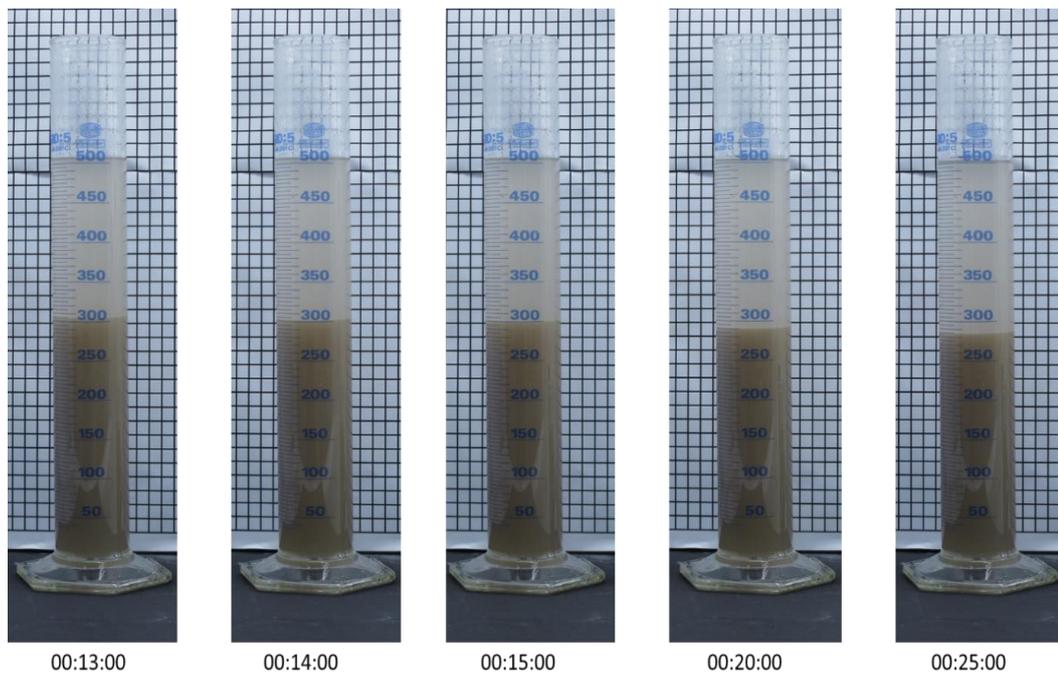


Figure 5-8 Case 3 (0.4% drilling mud) after 13 to 25 minutes of settlement time

5.6.2.1 Three-phase separator

In this phase, drilling mud was added to the condensate at 0.4 and 0.6wt % and the well completion fluids were added to the brine tanks as in phase 1. The results showed that the drilling mud separates partially into the MEG phase. However, after addition of 400 ppm demulsifier (Case 2), the condensate phase became less translucent, indicating better

partitioning of the drilling mud compared to Case 1. In sum, the majority of the drilling mud accumulates at the MEG/Condensate interface or drops down with time to the bottom of the TPS.

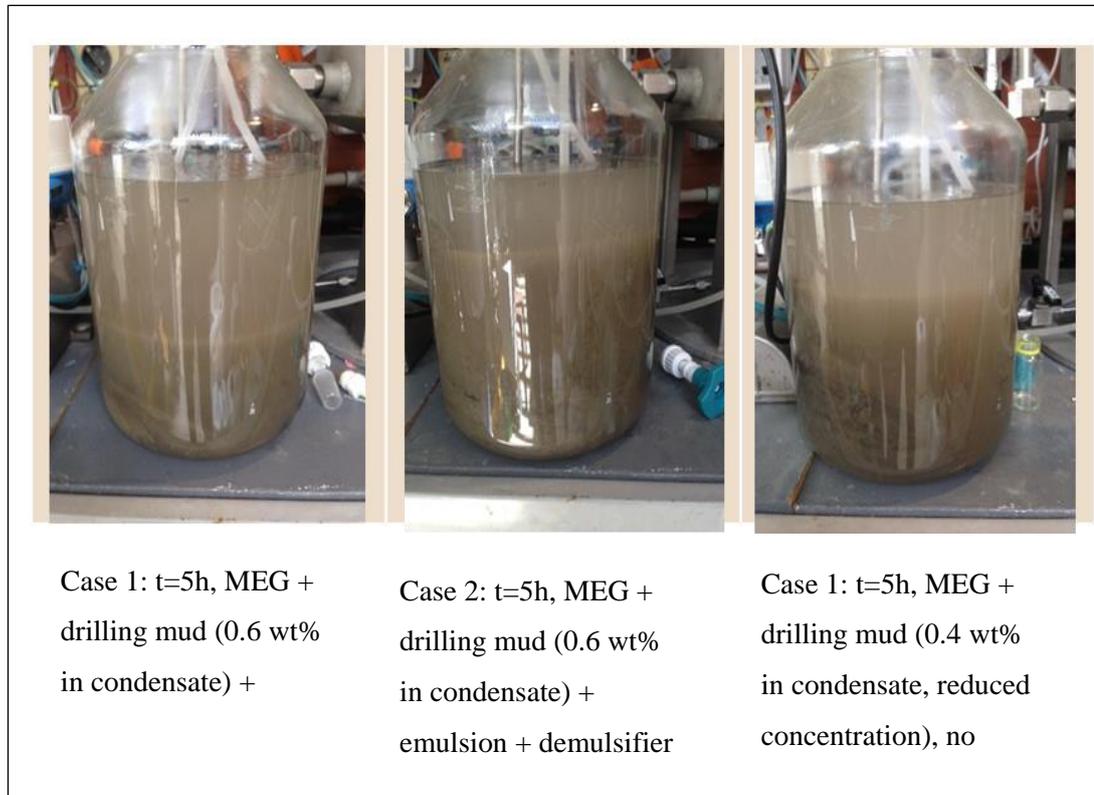


Figure 5-9 Three phase separator in all cases

5.6.2.2 Pre-treatment vessel MPV

From the TPS, the rich MEG phase is pumped into the pre-treatment vessel, where it is heated to 80 °C (*Figure 5-10*). The high temperature (80 °C) inside the pre-treatment vessel (MPV) aids emulsion breakdown/separation of the oil that wets the drilling mud particles. It was observed that the mud accumulated at the interface between rich MEG and condensate. Adding demulsifier resulted in a clear condensate phase in the MPV, whilst without the demulsifier, the condensate phase remained opaque.

The experiments indicate that emulsions form if the drilling mud concentration exceeds 0.4% wt. in condensate and most of the solid particles remain initially inside the MPV but with time, the drilling mud particles are transported to the rich glycol tank (RGT).

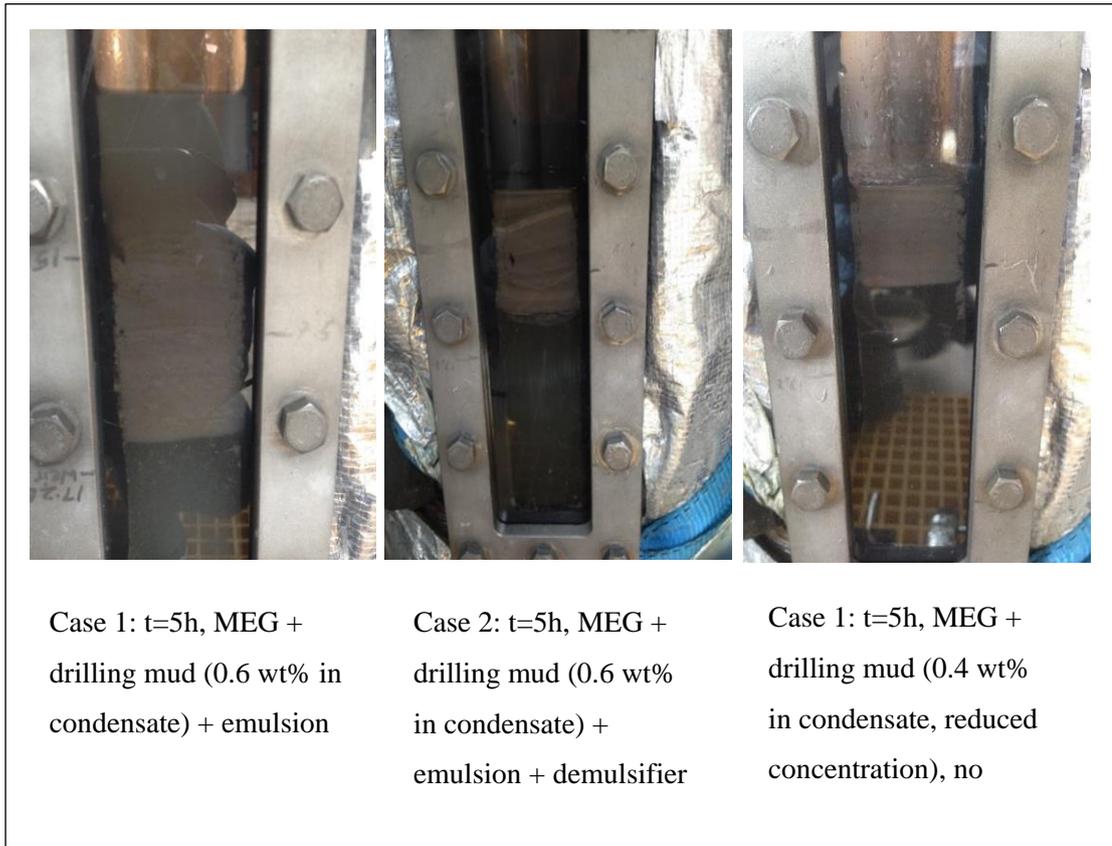


Figure 5-10 Pre-treatment vessel (MPV) in all cases

Table 5-8 below shows the MPV efficiency in terms of removing the calcium ions from the rich MEG. The precipitation process was successful with a removal rate of 96-98% wt.

Table 5-8 Efficiency of the MEG pre-treatment process

	[Ca ²⁺] before MPV	[Ca ²⁺] after MPV	% Ca ²⁺ removal efficiency	pH inside MPV
Case 1	110	4	96	8.3
Case 2	111	4	96	8.2
Case 3	241	7	97	8.3

5.7 Conclusions

The presence of drilling mud facilitates and increases the emulsion formation tendency in both phases. It was observed that a significant amount of the drilling mud partitions into the MEG phase in all cases, and that addition of the demulsifier resulted in accumulation of the drilling mud at the MEG/condensate interface in the bench-top facility TPS. Without the demulsifier addition, the majority of the drilling mud partitions via emulsion formation into the MEG phase and is carried over into the MPV. However, a significant amount of the drilling mud remains in the condensate phase. Adding the demulsifier results in the accumulation of the drilling mud at the MEG/condensate interface inside the TPS. The resulting drilling mud carryover into the MPV is greatly reduced. Most of the drilling mud that is carried over into the MPV is not discharged with the rich MEG leaving the vessel and it accumulates within the vessel at the condensate/rich MEG interface. Visual observations indicate the mud accumulates at the MEG/condensate interface in both phases.

Calcium ions were removed in the MPV only after raising the alkalinity with 1 mole/L NaOH solution to adjust the pH above 8.

6 Study the Performance of Pre-Treatment System in MEG Pilot Plant during Switch over Corrosion Management Strategies (pH Stabilisation to Film Forming Corrosion Inhibitor)

6.1 Introduction

MEG (mono-ethylene glycol) is known as an effective thermodynamic hydrate inhibitor usually used in transportation pipelines of oil and gas from the subsea wells [38]. pH stabilisation method is often used as a corrosion control method when MEG is used as a hydrate preventer, this method is cheap, effective and environmental friendly [88]. pH stabilisation method aids to form a protective corrosion product film by achieving suitable conditions after increasing the pH value significantly. Under these conditions, the corrosion rate tends to be very low (0.1mm/ year). A high corrosion rate can occur when the corrosion products are not precipitated on the internal pipes surfaces. This can be basically reduced in the present of iron Carbonate (FeCO_3) as it can deposit on the surface and form the protective corrosion product film. It is much easier to happen when H_2S and CO_2 are present at high pH values because the protective film of iron Sulphide (FeS) will be formed rather than FeCO_3 film especially at a lower temperature [89]. Miskovic and Hrvatske [90] proved that the protective film with better protective properties forms when the fluoride concentration is low and the value of pH is high in a specific solution, and the corrosion rate was increased by 52% when the pH value was decreased from 6.5 to 4.5 at the same fluoride concentration. Jevermovic et al [91] injected the corrosion inhibitor within a foam matrix, the injected inhibitor liquids are carried with the foam slug along the line with the gas flow, the foam carrier provided a homogeneous delivery of the inhibitor through the pipe. Which then formed a protective film all over the internal pipe surface.

The pH stabilisation technique is a relevance method when no or a very small amount of formation water is present during fluids transportation in pipelines. Increasing pH value of the water phase above 6 will lead to precipitation of the iron carbonate to form the protective corrosion product films on the surface at sweet conditions when CO_2 is present with H_2S absence [92].

This method is only applicable to conditions with condensed water with no Calcium ions. If calcium ions is present with the formation water, then scaling will start to occur

immediately [93]. This technique is very useful in the systems where glycol is used as a hydrate inhibitor. However, it cannot be used in the pipelines transporting a large amount of formation water due to the risk of scale formation from the precipitation of calcium carbonate near the pipelines inlet, which is most likely to happen at a pH of more than 6 [94]. MEG bench top facility constructed at Curtin University was used to simulate the procedure for switching between pH stabilisation corrosion management strategy to film forming corrosion inhibitor.

6.2 Design and operation

MEG pilot plant has been designed as a MEG regeneration and reclamation system, which include three sections; MEG pre-treatment, regeneration and reclamation section. This study is focused on the performance of the pre-treatment section in terms of removing the divalent ions salts and the optimum conditions required to remove these salts. MEG pre-treatment section as shown in *Figure 6-1* consist of:

Brine tank	Rich-MEG recycle heater
Lean MEG tank	Peristaltic pumps
Feed blender	Filters
MEG pre-treatment vessel	Rich MEG tank

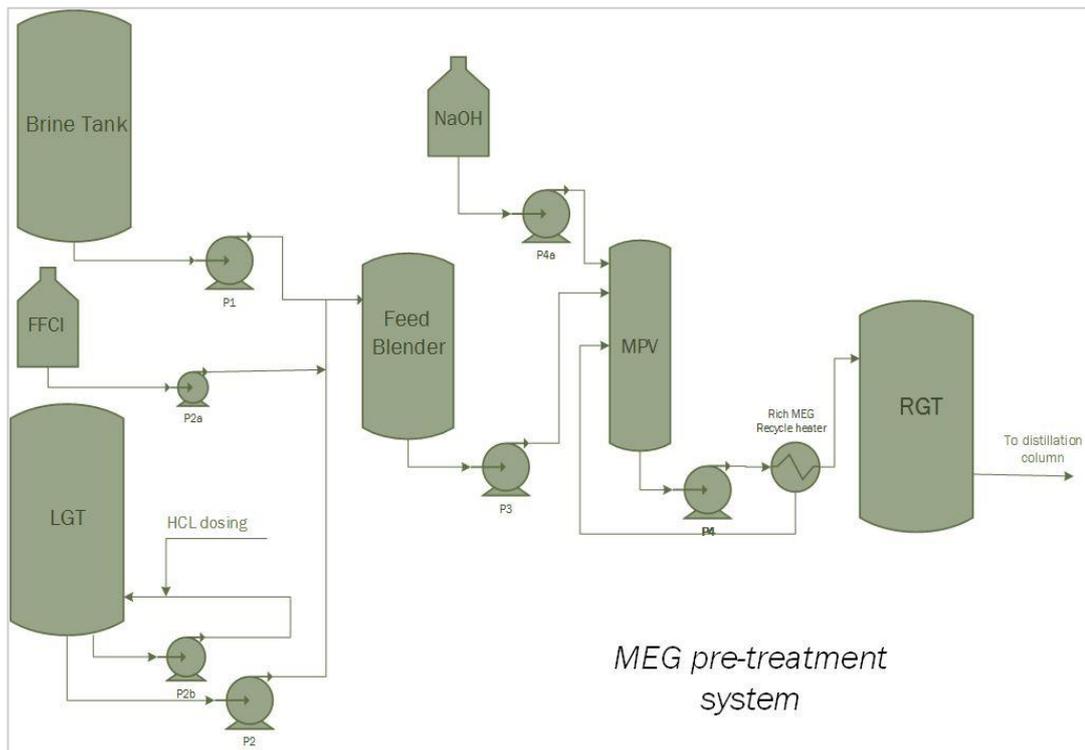


Figure 6-1 MEG pre-treatment section

During operation, the pre-prepared formation water from the brine tank was mixed with the lean MEG (typically 80% MEG) from the lean MEG tank in the feed blender under sheer mix to form rich MEG at the required concentration (normally between 40 and 60 %). Then, the solution was transferred to the pre-treatment vessel, which was operated at 80°C, a rich MEG recycle heater was used to raise the temperature and also to keep the suspended particles in motion during operation. NaOH solution was injected into the pre-treatment vessel to increase and keep the pH value at a certain level using a dosing pump automatically operated depending on the pH sensor reading inside the vessel. A control valve was installed in the tubing between the pre-treatment vessel and the rich MEG tank to control the level inside the pre-treatment vessel. After that, the solution was pumped to the rich MEG tank, which behaved as a settling tank where most of the suspended solids were precipitated at the bottom of the tank before entering the regeneration section.

6.3 Objective

The main method for corrosion control is pH stabilisation where MEDA (Methyl diethanolamine) is added to the solution to increase the pH and decrease the corrosion

rate subsequently when the protective layer of FeCO_3 is formed on the internal pipeline walls. This method is very effective but only before the formation water breakthrough because formation water with high salts concentration will increase the risk of scaling in the subsea transportation pipelines, as a result, FFCI (Film Forming Corrosion inhibitor) as a corrosion management strategy, must be applied. FFCI tends to form a protective film on the internal pipeline walls, which prevents the corrosion. However, FFCI corrosion strategy has to be applied for a limited period only as it increases the risk of emulsions, under deposit corrosion, top of the line corrosion and also fouling of the inlet filters.

In the presence of MDEA and the formation water, the scale will form due to the precipitation of divalent salts such as Calcium carbonate. Therefore, MDEA has to be neutralised. HCl is injected into the lean glycol tank (LGT) to neutralise MDEA using a dosing pump controlled by the pH sensor located in the pipeline of the circulating pump (*Figure 6-1*). The circulating pump has been installed to ensure that there is proper mixing inside the tank. pH was decreased gradually inside LGT to observe the changes to the behaviour of the facility downstream the lean glycol tank (LGT), while some alkalinity need to be dosed into the MPV to increase the pH value if it went down below the required limit to help the divalent on salts to precipitate out from the solution. in MEG benchtop facility, there are some other contributing factors that affect the alkalinity and pH such as dissolved carbon dioxide, carbonate and bicarbonate ions and organic acids.

During the neutralisation process of MDEA, FFCI was injected into the system continuously to maintain its concentration as constant as possible. The dosing point was located in the tubing between the LGT and FB (feed blender). Samples were taken from LGT and FB every hour during operation in order to adjust the dosing rate and keep the FFCI concentration within the optimum range (*Figure 6-2*).

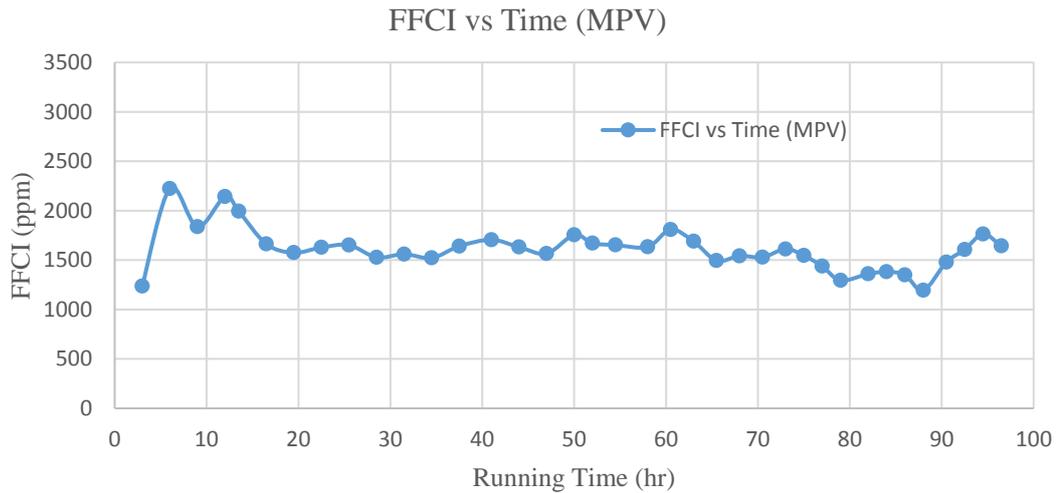


Figure 6-2 FFCI concentration in MPV

To remove the divalent salts from rich MEG, MPV was heated to 80°C using the recycle heater as shown in *Figure 6-1*. Raising the temperature to 80°C or above leads to increase the saturation ratio (*SR*) and help the salts to precipitate after supersaturate the solution [87].

$$SR = \frac{a_{salt}}{K_s} \quad \dots 6-1$$

a_{salt} = the activity of the salt, K_s = thermodynamic solubility constant

knowing that the dissolution reaction for the divalent salts is exothermic [88], increasing the temperature decreases K_s and increases *SR*. therefore, the solution becomes supersaturated and the divalent salts will be removed.

6.4 Results and discussions

The suggested experimental matrix for transition from pH to FFCI stabilisation method is provided in

Table 6-1. Each experiment was performed twice to ensure repeatability of the results. It is anticipated that each experiment will have to be conducted over several days. The time to run one experiment takes into account retention time for the various vessels, concentration of chemicals and pumping capacities of various pumps.

Table 6-1 Experimental matrix for transition from pH to FFCI stabilisation method

Test no.	Description	Initial state		End state	
		FFCI in lean MEG	MDEA in lean MEG	FFCI in lean MEG	MDEA in lean MEG
1	field 1 MDEA to FFCI	0 ppm	100 mM	3000 ppm	Minimum
2	field 2 MDEA to FFCI	0 ppm	580 mM	3000 ppm	Minimum

6.4.1 Phase 1 (field 1)

Test 1 represents the field 1 MEG system in operation after formation water breakthrough. After a period of formation water production in the pH stabilisation mode, the transition back to FFCI mode will take place in the field. The condensed and formation water production and salinities have been assumed to be in accordance with field 1 MEG Unit Basis of Design. Some of the salts are removed by the reclaimers (assumed to be operating at maximum capacity to control the salt build-up). This yielded the concentrations outlined in [Table 6-2](#).

Table 6-2 Field 1 fluid compositions at start of experiment 1

Salt ions	Brine	Rich MEG	Lean MEG
Na ⁺ (ppmw)	4679	4679	3398
K ⁺ (ppmw)	106	106	77
Ca ²⁺ (ppmw)	173	70	5
Mg ²⁺ (ppmw)	13	9	5
Fe ³⁺ (ppmw)	0.31	0.31	0.22
Sr ²⁺ (ppmw)	15	10	5
Ba ²⁺ (ppmw)	38	19	5
Li ⁺ (ppmw)	2.5	2.5	1.8
Cl ⁻ (ppmw)	7217	7216	5242

HCO ₃ ⁻ (ppmw)	828	828	601
SO ₄ ²⁻ (ppmw)	6.2	6.2	4.5
Acetic acid (ppmw)	500	500	363
Propanoic acid (ppmw)	55	55	40
Butanoic acid (ppmw)	4.6	4.6	3.4
Pentanoic acid (ppmw)	2.3	2.3	1.7
Phenol * (ppmw)	32	32	23
Total organic acids (ppmw)	594	594	432
MEG (wt%)	0	57	80

Continue next page

The pH reduction inside lean glycol tank (LGT) went through 8 steps between 9.5 and 5.5 to monitor the effects and the behaviour of the solutions in each vessel of the facility (*Figure 6-3*).

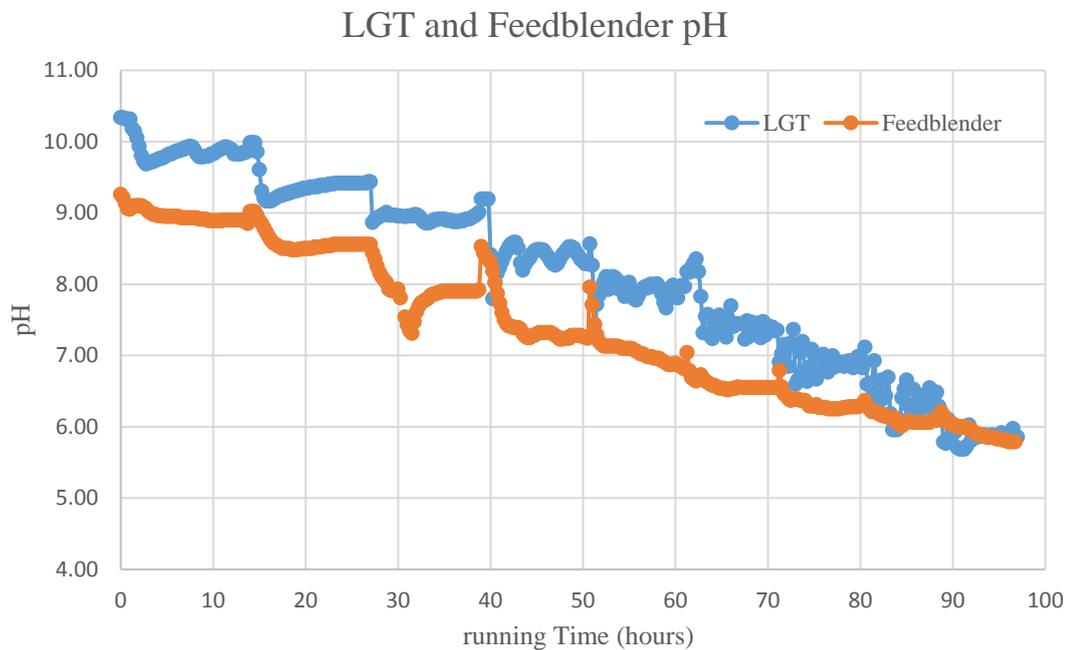


Figure 6-3 pH in lean MEG tank and feed blender

It can be noticed that the pH inside the feed blender is approximately 1 step behind the lean glycol tank and this is due to the sparging gas composition of the feed blender, which contain 6.2 mole% CO₂ in nitrogen. It was noticed that this difference started to

decrease gradually until pH 6, where there was no difference in the feed blender compared to lean glycol tank.

Figure 6-4 shows how the MDEA concentration decreased slowly during the operation time due to it being removed in the reclaimer at a later stage of MEG facility, and it was expected to reach 10 mM after approximately 250 hours of operation. NaOH was dosed into the MPV to keep the alkalinity concentration high and maintain the pH value above 8.2 to remove the divalent salts. The FFCI was kept around the required value (1500ppm) in the rich MEG to simulate the real field data. The dosing rate was adjusted by taking samples from lean MEG tank every 1 hour of the operation and measure the difference between them, for instance; FFCI concentration was 1000 ppm in lean glycol tank and the required level of the rich MEG was 1500ppm, that means only 500 ppm was needed to be dosed at that time and this illustrates why the FFCI concentration is fluctuating around 1500ppm as shown in *Figure 6-2*. FFCI concentration in feed blender was only measured to ensure that the right amount of FFCI was passing through the system.

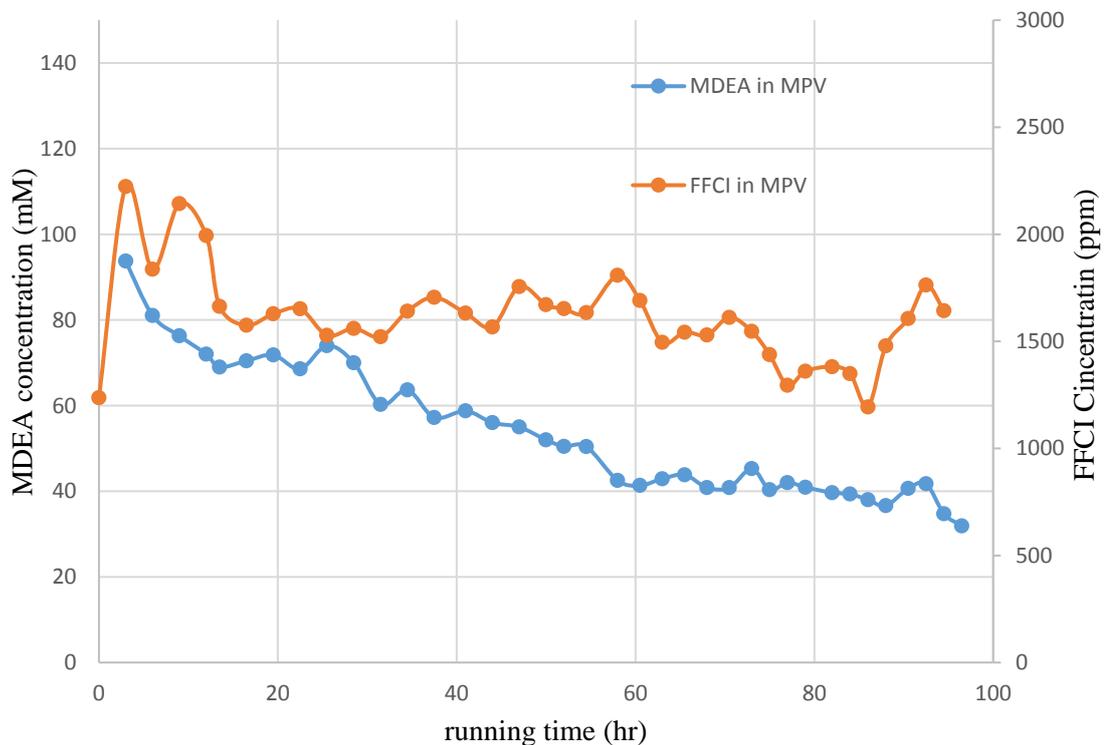


Figure 6-4 MDEA and FFCI concentration in MPV

The main function of the pre-treatment section was to simulate realistic fluid reaching the MEG facility in the feed blending area after applying the optimum shear mix to the

solutions inside the feed blender and also to help the precipitation of divalent salts in the pre-treatment vessel (MPV).

Results indicated that the divalent salts can only be removed if the pH is above 8.2 as shown in *Figure 6-5*.

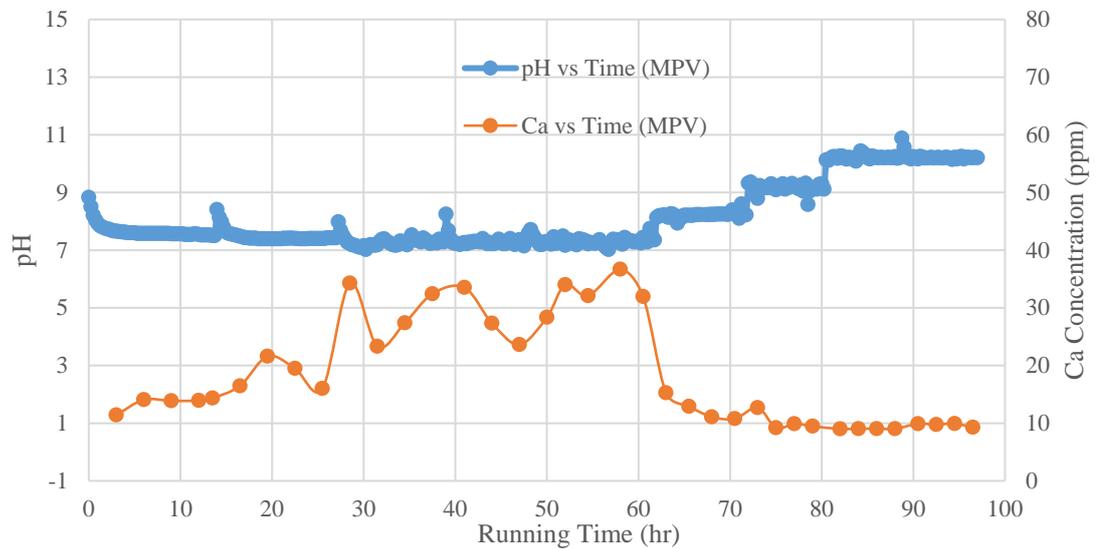


Figure 6-5 pH value and Calcium ions concentration in MPV

Figure 6-5 above shows that any pH below 8.2 could result in accumulation of calcium salts in the system during the long operational hours, but at pH of 8.2, the Calcium concentration after the MPV starts to reduce, which means the majority of the Calcium salts has been precipitated at the bottom of the MPV.

6.4.2 Phase 2 (field 2)

Switchover from pH stabilisation to FFCI mode may be required if field-wide formation water production is unmanageable through alternative means such as production reallocation or scale inhibitor injection. The decision to switchover may also be driven by unfavourable conditions caused by operation in pH stabilisation mode. The condensed and formation water production and salinities have been prepared in accordance with field 2 MEG Unit Basis of Design. Some of the salts are removed by the reclaimers (assumed to be operating at maximum capacity to control salt build-up). These assumptions led to the concentrations outlined in *Table 6-3* below.

Table 6-3 field 2 fluid compositions at start of switchover experiment (MDEA to FFCI)

	Brine	Rich MEG	Lean MEG
Na ⁺ (ppmw)	266	994	1601
K ⁺ (ppmw)	3.5	13	21
Ca ²⁺ (ppmw)	3.4	4	5
Mg ²⁺ (ppmw)	0.32	1.2	1.9
Fe ³⁺ (ppmw)	0.033	0.12	0.20
Sr ²⁺ (ppmw)	0.09	0.34	0.55
Ba ²⁺ (ppmw)	0.64	2.4	3.9
Li ⁺ (ppmw)	0.070	0.26	0.42
Cl ⁻ (ppmw)	361	1348	2172
HCO ₃ ⁻ (ppmw)	118	440	709
SO ₄ ²⁻ (ppmw)	1.1	4.0	6.4
Acetic acid (ppmw)	193	721	1162
Propanoic acid (ppmw)	17	63	102
Butanoic acid (ppmw)	4.1	15	24
Pentanoic acid (ppmw)	5.8	22	35
Phenol (ppmw)	79	293	472
Total organic acids (ppmw)	299	1114	1795
MEG (wt%)	0	44	80

In order to reduce the alkalinity that leads to scale formation, the MDEA will need to be neutralised and removed in the reclamation process in order to avoid the build-up

of highly soluble MDEA salts in the system. In theory, the neutralisation of MDEA will follow a well-defined neutralisation – pH curve as shown in *Figure 6-6*.

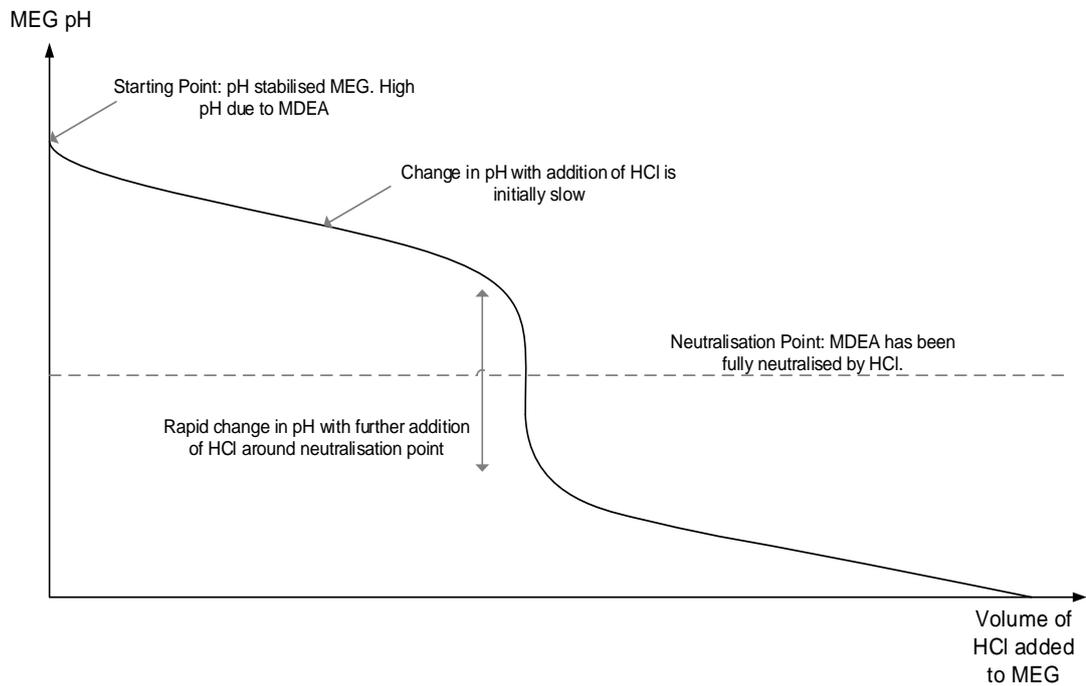


Figure 6-6 Typical MEG pH diagram for neutralisation of MDEA

However, in reality, there are other contributing factors that influence the alkalinity and pH, such as dissolved carbon dioxide, carbonate/ bicarbonate ions, and organic acids. A MEG pH diagram obtained from rich MEG after the MEG pre-treatment vessel is shown in *Figure 6-7*. This may be used as an advantage, since the presence of these components provide some buffer capacity and reduce the influence of acid addition near the neutralisation point, which in turn makes the system less prone to overdosing of HCl, which might result in a low pH that might cause corrosion in the MEG facility.

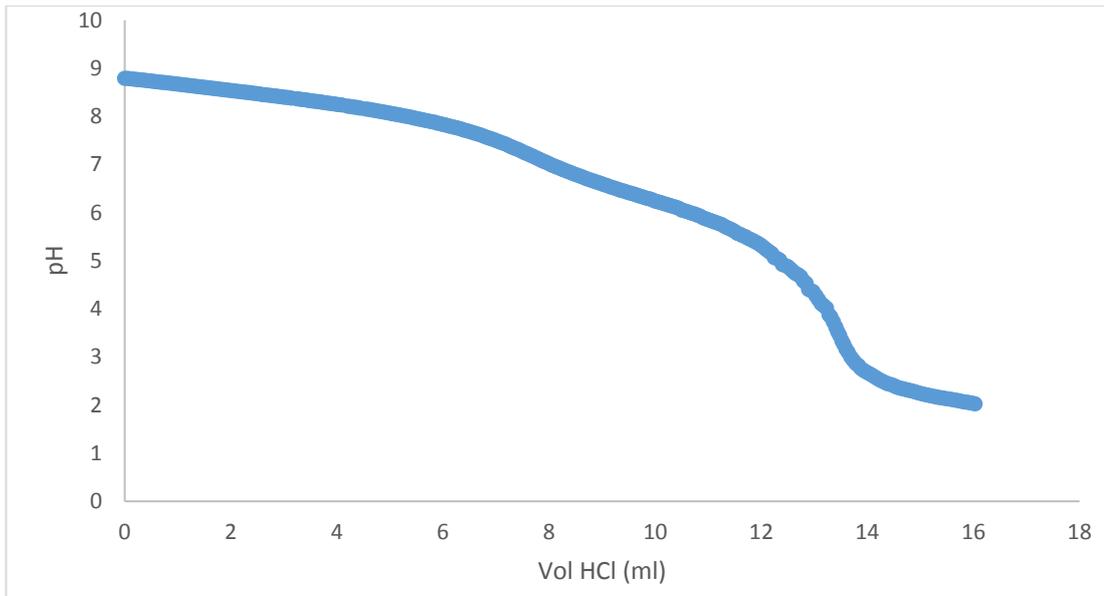


Figure 6-7 Rich MEG pH diagram for neutralisation of MDEA

The complex relationship between pH in the MPV, total alkalinity and the removal of calcium ions from the rich MEG is shown in *Figure 6-8*. MEG was circulated in a closed loop but the volume of the overall inventory is considerable. In the MEG Benchtop facility, one inventory turnover takes around 10 hours to complete. *Figure 6-8* shows the accumulation of calcium ions in the MPV results in an increase in the concentration of calcium in the rich MEG returning from the feed blender in the next inventory turnover (approximately 10 hours later).

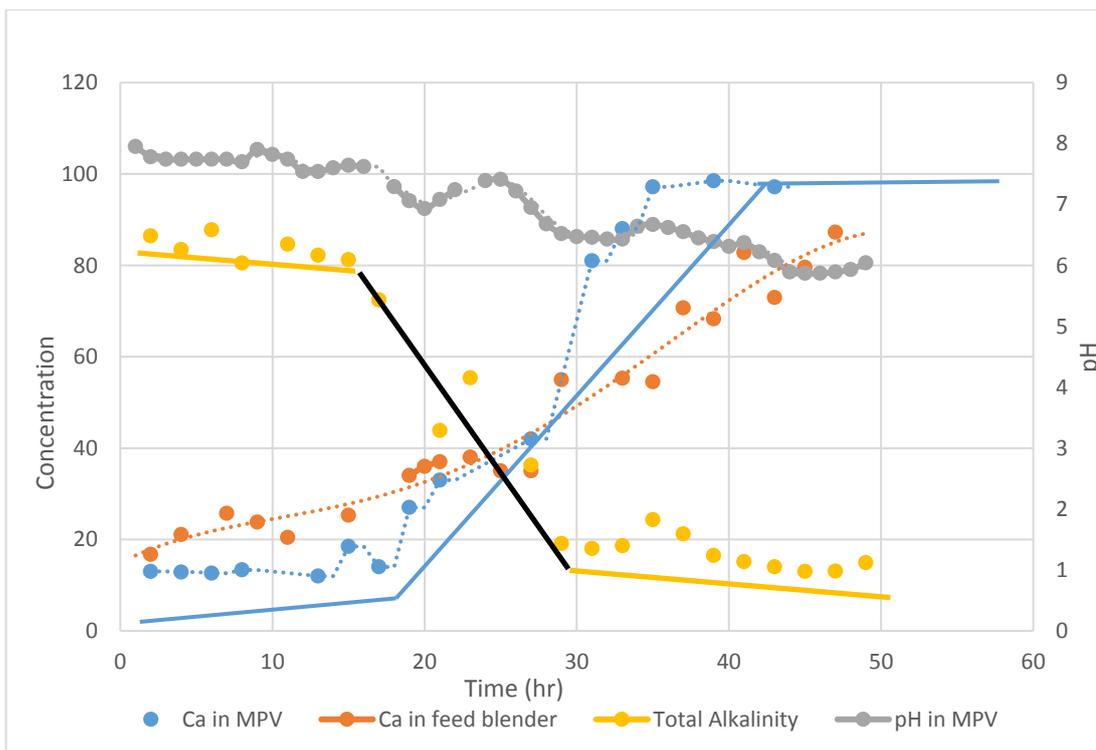


Figure 6-8 Concentrations of calcium ions in the inlet to the facility (Feed blender), MPV, pH (MPV) and total alkalinity as a function of time

Considering all the above, the results for field 2 switchover from pH stabilisation to FFCI are discussed further for each stage of the MEG feed blending and pre-treatment areas. For this experiment the plant was operated for 10 days with a total of 12 inventory turnovers.

6.4.2.1 Feed blending area

MDEA was neutralised by injecting hydrochloric acid into the lean glycol tank in discrete steps for each inventory turnover (one day of operation) using target pH as: 9.5, 9, 8.5, 8, 7.5 and 7. *Figure 6-9* shows the pH adjustment as a function of operation time for both the lean glycol tank (LGT) and the feed blender (FB).

In the feed blender, the initial pH under pH stabilisation was just below pH 8 as shown in *Figure 6-9*. In the field, it is expected that the pH will be substantially lower. As the MEG facility at Curtin cannot operate under pressure in the feed blending unit, the partial pressure of carbon dioxide was limited to 1 bar. In the real pipeline, which operates at around 100bar, the partial pressure of CO₂ will be much higher at around 14bar (field 2 gas contains 14 mol% carbon dioxide).

With increasing operation time, the MDEA concentration reduced to 50 mM after 10 operation days (12 inventory turn overs) and the pH in the feed blender vessel dropped to about pH5.6.

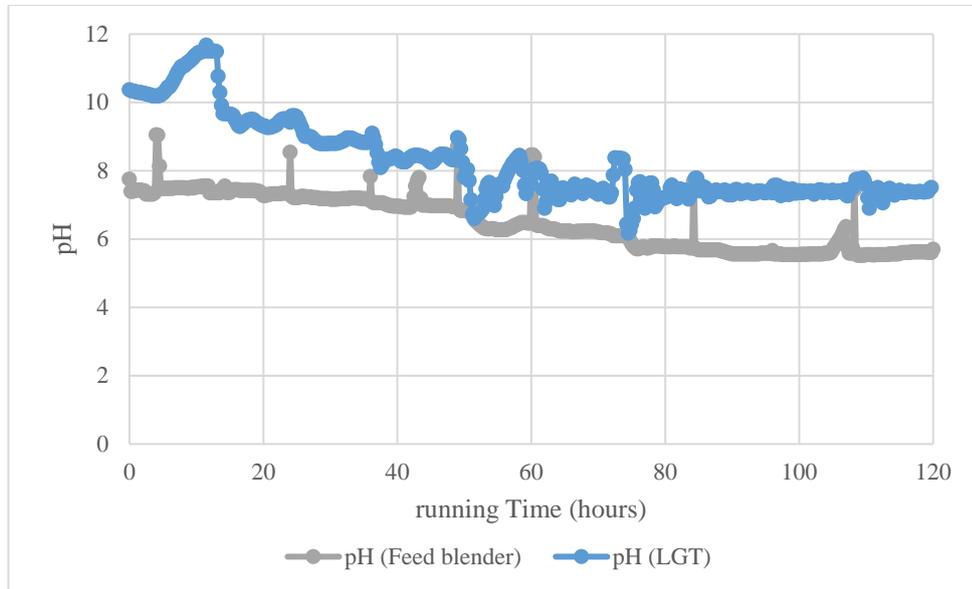


Figure 6-9 pH in the lean glycol tank and feed blender

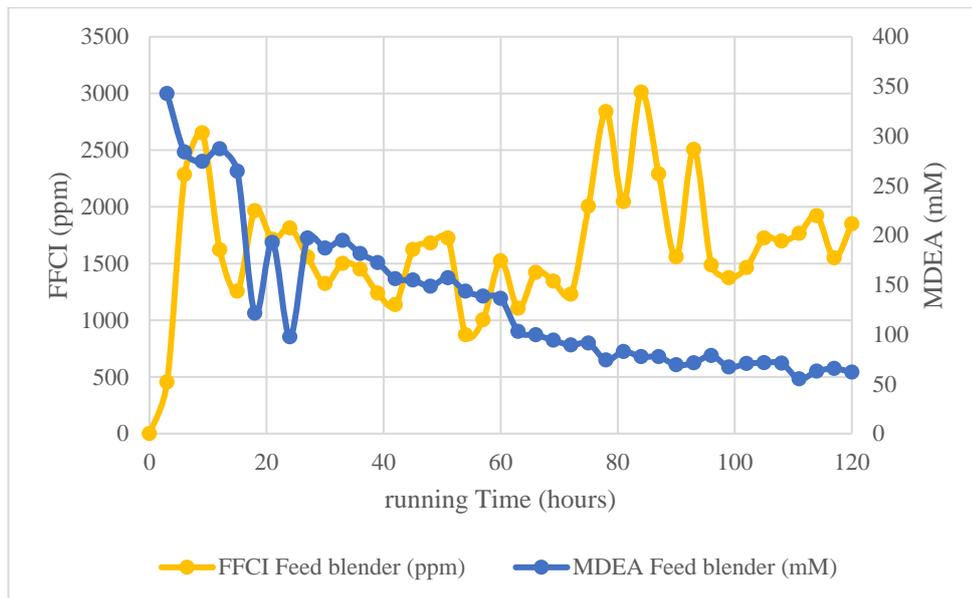


Figure 6-10 FFCI and MDEA concentrations in the feed blending unit

It can be seen from *Figure 6-10* that the dosing of the FFCI to the lean glycol was not easy to achieve in the current plant configuration, which has been rectified for future experiments. The reduction in MDEA concentration in the feed followed an

exponential trend with an R^2 value of 0.87. Extrapolation of the trend predicts that the facility would have to be operated for another 20 days (or 20 inventory turnovers) before only traces of MDEA would remain in the system.

6.4.2.2 MEG pre-treatment (MPV) and rich glycol tank (RGT)

The pH in the MPV was adjusted automatically to a value of 8.0 to 8.2 in order to facilitate the precipitation of calcium and other divalent cations. However, magnesium did not precipitate out as magnesium carbonate or hydroxide as it needed higher pH values [95] (*Figure 6-11*), despite the high surplus of total alkalinity (*Figure 6-12*).

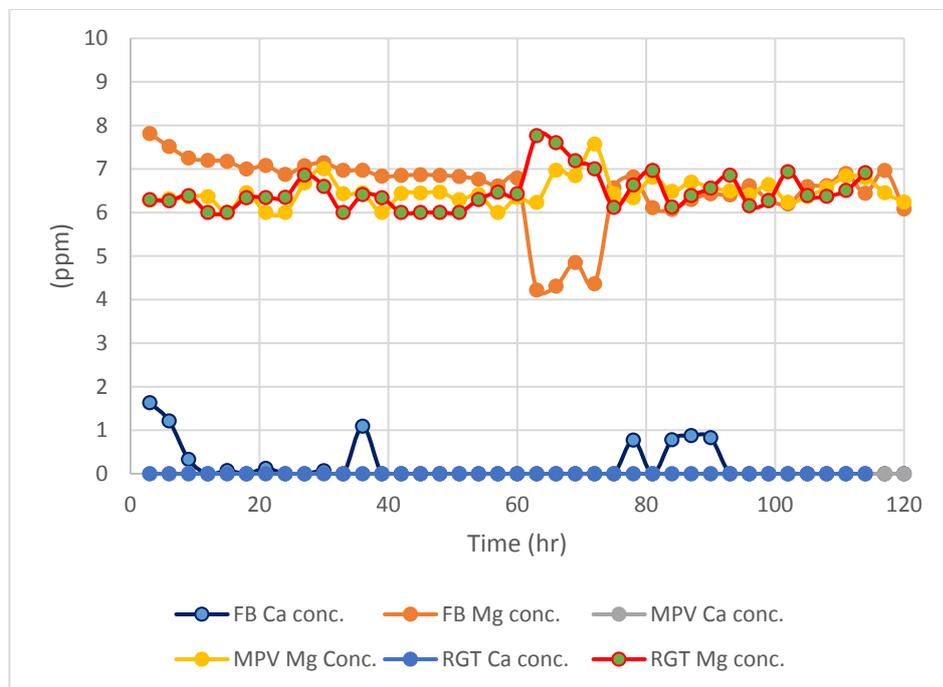


Figure 6-11 Calcium and magnesium concentrations in the feed blender (FB), MEG pre-treatment vessel (MPV) and rich glycol tank (RGT).

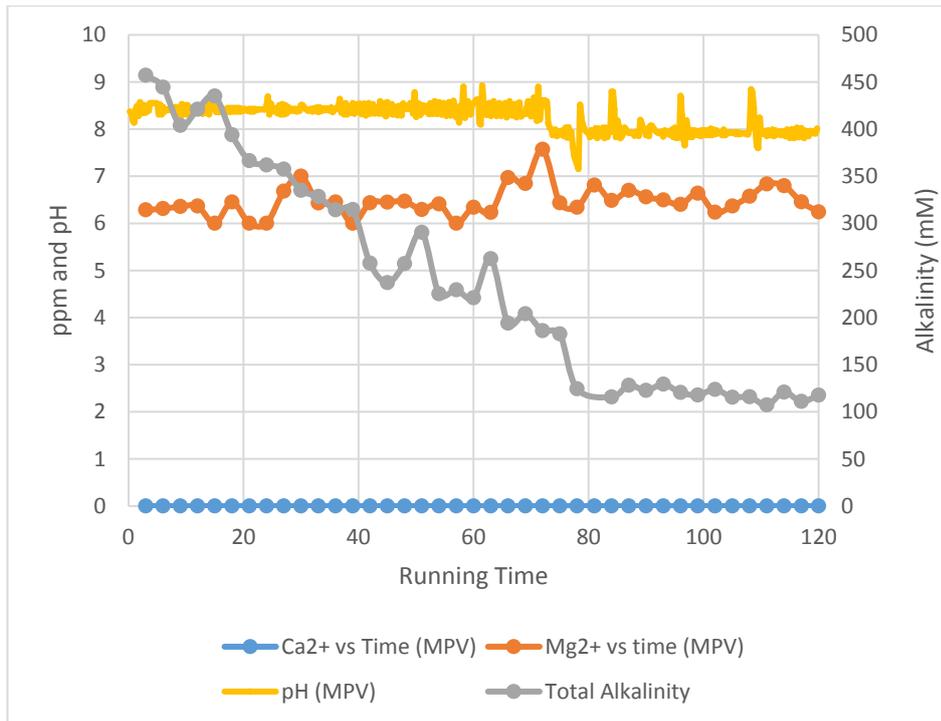


Figure 6-12 Calcium and magnesium ions concentration as well as total alkalinity and pH in the MPV

7 The performance of Pre-treatment System during switchover experiment (from FFCI to pH and follow up vice versa using a modified HCl dosing point)

7.1 Introduction

As discussed in Chapter 6, pH stabilization method is very effective for controlling internal corrosion and reducing the production of corrosion products from the flowlines, which have a tendency to foul downstream the equipment. However, pH stabilisation method cannot be used for pipelines carrying large quantities of formation water due to increasing the risk of scaling in the subsea architectures, particularly in the choke module and well jumpers, and cannot be used once formation water breakthrough occurs, or initially when remnant completion fluids may pose a scaling risk [92].

FFCI method represents an alternative corrosion control method, used when pH stabilisation is not feasible due to scale formation risk (for example, this may occur early in the field life when wells have not been cleaned up during first operation). Under these circumstances, drilling muds may be returned through the pipeline back to shore. FFCIs are organic molecules added in ppm levels to form internal surface layers that help to prevent or reduce the corrosion reactions on the steel [94]. Risks associated with the use of FFCI are; increased risk of emulsions, under deposit corrosion, top of line corrosion, fouling of inlet liquid filters and separators of the rich MEG processing unit.

In the field, FFCI method will be used during the first 6 to 18 months of production. The transition to pH stabilization method will occur once all wells have unloaded the majority of leftover completion fluids and formation water, the rich MEG chemistry has been stabilized and risk of scaling is reduced.

7.2 Objective

The objective was to start up with FFCI mode and achieve steady state operation, once steady state was achieved, the injection of MDEA into the lean MEG was started. Simultaneously, the introduction of FFCI was halted and the FFCI concentration reduced through degradation and losses to the reclamation unit. It was planned to perform the

switchover in a series of discrete steps, with MEG chemistry reviewed/stabilised after each step. Within each step, the dosage of each chemical was sequentially increased/decreased. An example of the theoretical changes in chemical dosage throughout the switchover is shown in *Figure 7-1*.

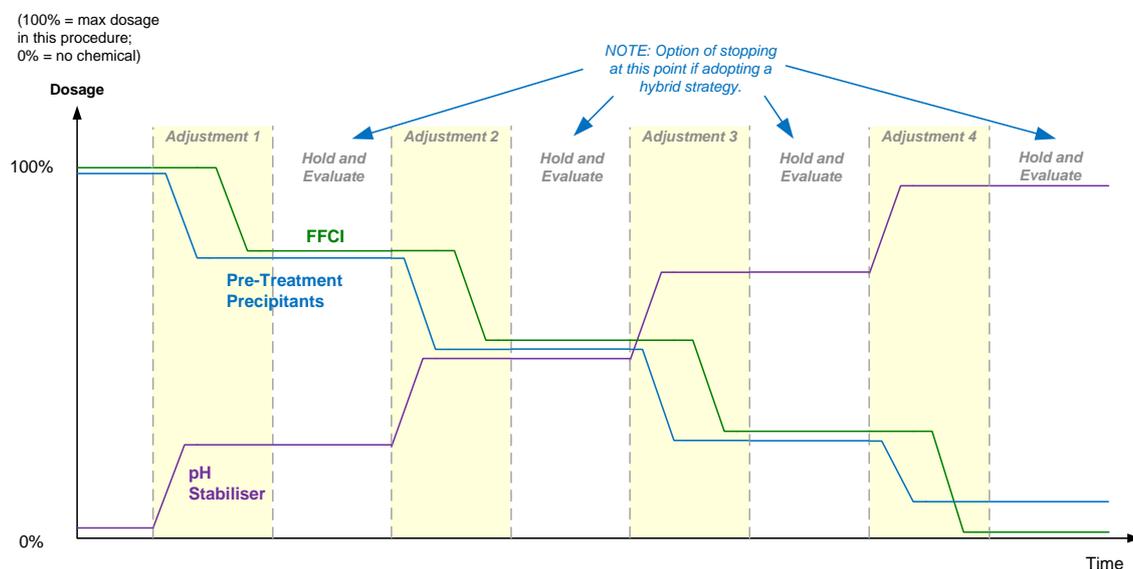


Figure 7-1 Typical switchover scheme

After a period of initial operation under FFCI mode with no evidence of formation water production, the transition to pH stabilisation mode took place. In accordance with field 2 MEG Unit Basis of Design. Field 2 condensation water is assumed to be pure water and contain no dissolved solids. However, it contains organic acids. Some of the organic acids are removed by the reclaimer (assumed to be operating at maximum capacity to control organic acid build-up). This yielded the concentrations outlined in *Table 7-1*. In addition, 50 ppm of Fe^{2+} from pipeline corrosion has been assumed to be present in the rich MEG.

Table 7-1 Field 2 fluid compositions at start of experiment

Component (ppmw)	Brine	Rich MEG	Lean MEG
Fe^{2+}	100	50	5
HCO_3^-	109	55	5.5
Acetic acid	180	715	1198
Propanoic acid	16	64	106
Butanoic acid	4	16	27

Pentanoic acid	6	24	40
Phenol	83	330	552
Total organic acids	289	1148	1923
MEG (wt%)	0	44	80

The sparging gas composition is as per [Table 7-2](#) below:

Table 7-2 Field 2 Sparging gas compositions

	Feed Blender	Pre-treatment vessel
mol% CO ₂ @ 1 bar	100%	76%
mol% N ₂ @ 1 bar	0%	24%

7.3 Results and discussion

7.3.1 Field 2 Switchover from FFCI to pH Stabilisation

Addition of MDEA into lean glycol tank was commenced during the first operation day (the facility was set up to operate under FFCI control). It can be observed that only a small addition of MDEA resulted in a large pH increase as illustrated in [Figure 7-2](#).

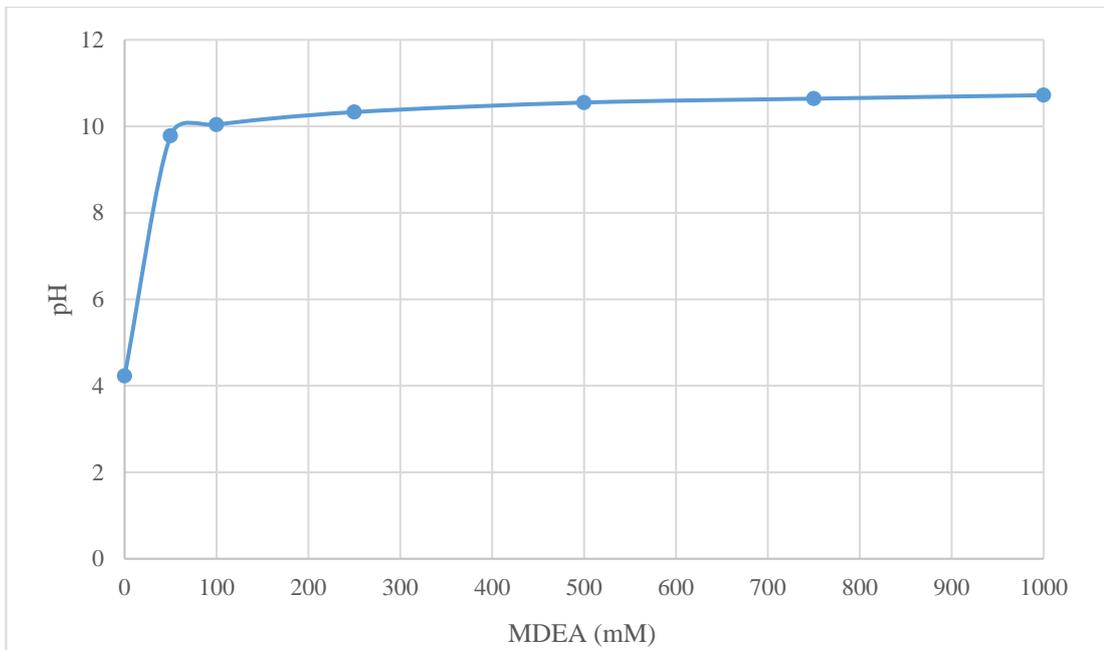


Figure 7-2 pH of field 2 lean MEG as function of MDEA concentration (mM)

It was not practical to follow the dosage of MDEA via monitoring the pH in the solutions. Instead, the amount of MDEA theoretically required to reach the target concentration of 580mM was divided into four and each quantity dosed into the LGT during each operational day (1 inventory turn-over per day), refer to [Figure 7-3](#).

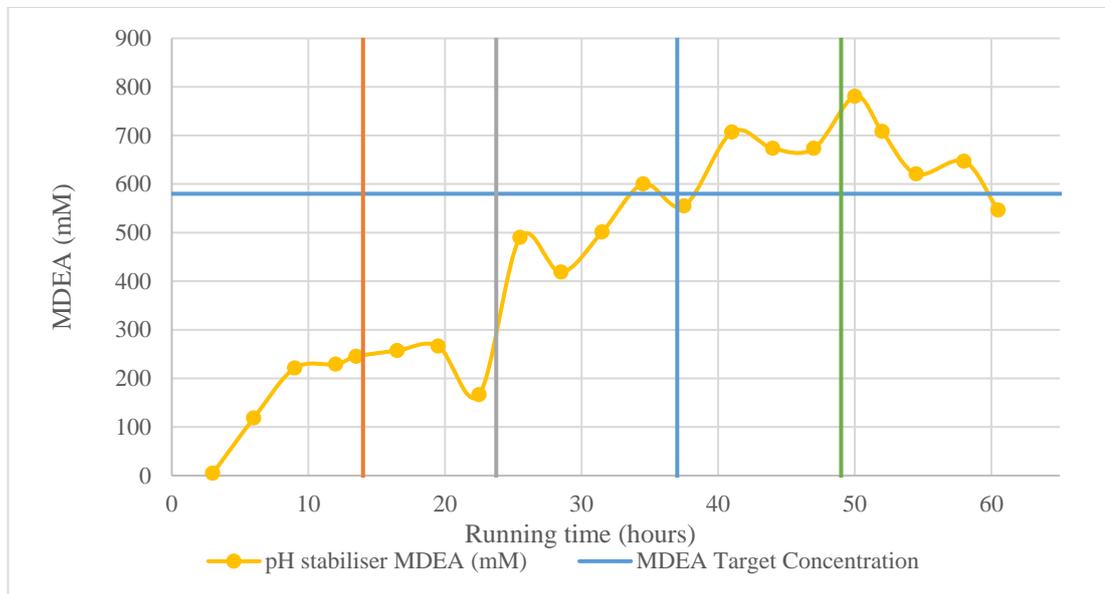


Figure 7-3 MDEA concentration in LGT as result of MDEA dosing directly into the LGT

It was noticed that the concentration of MDEA exceeded the 580mM in the LGT on operation day 4, since the added amount was calculated for the overall inventory. Thus on day 5, when no further MDEA was added, the concentration of MDEA in the LGT reduced towards the target value of 580mM.

The feed blender in the MEG facility was used to blend lean MEG with brine (and condensate, if required) and to saturate the resulting rich MEG with carbon dioxide at the required concentration (see [Table 7-2](#)). The mass flow into and out of the feed blender was monitored. [Figure 7-4](#) shows the change in pH (due to addition of MDEA to LGT) and the FFCI concentration as function of operation time. The decrease of the FFCI concentration is a result of removing the FFCI effectively in the reclamation unit.

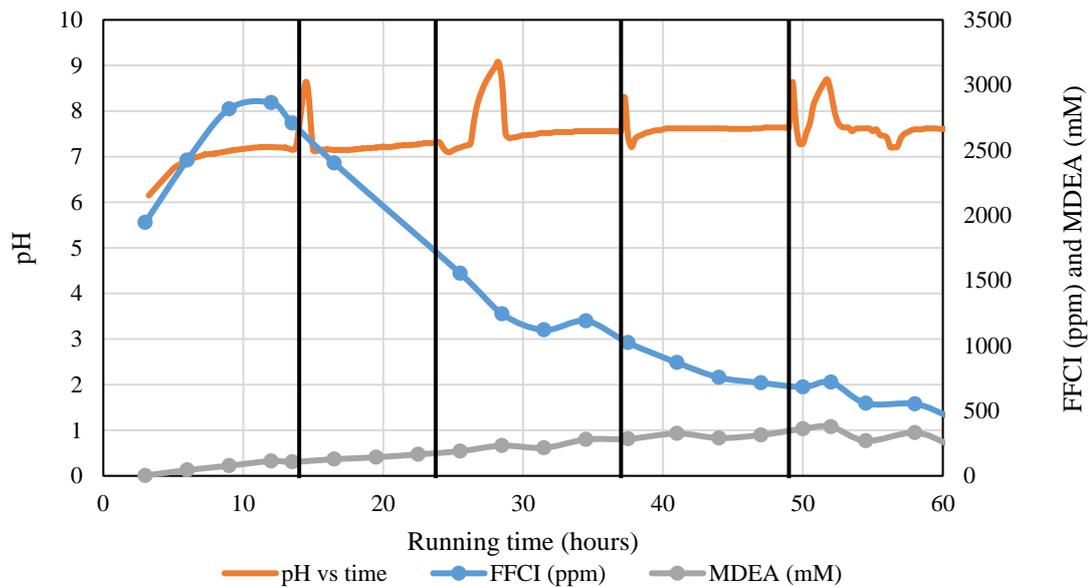


Figure 7-4 pH, FFCI and MDEA concentration measured in the feed blender (rich MEG).

The rich MEG from the feed blender was pumped into the MEG pre-treatment vessel (MPV), which was operated at 80°C. In addition, the partial pressure of CO₂ was reduced from 1 bar to 0.76 bar in the MPV. At this temperature, most of the dissolved carbon dioxide boils out of the solution, which results in a small pH increase (*Figure 7-5*). It can be noted that stopping and starting the MEG facility at the end/beginning of each day resulted in spikes in the pH values measured, which can be attributed to reduction of CO₂ sparging overnight.

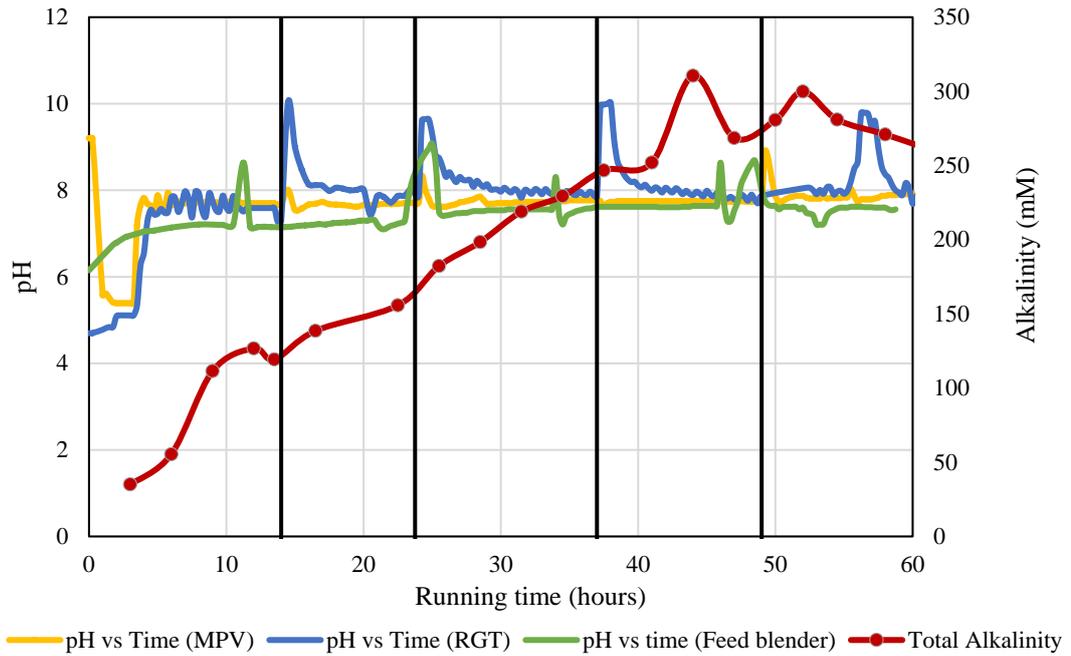


Figure 7-5 pH in feed blender, MPV, RGT and total alkalinity in MPV as function of time

The pH inside the MPV was measured to be between pH 7.6 to 7.8 (near the neutralisation point) without additional NaOH injection as a result of the MDEA addition. This was thought to be sufficient for removal of calcium/iron ions as this experiment was performed first. However, it was noticed that this pH cascades through the plant resulting in high MDEA losses in the reclamation unit downstream the regeneration unit. All other experiments used a target pH of 8.3 in the MPV, which resulted in lower MDEA losses during the reclamation process.

7.3.2 Field 2 Switchover from pH Stabilisation to FFCI using a Modified HCl Dosing Point

Based on the prior experimental results in Chapter 6, follow up research on pH stabilisation to FFCI switchover experiments have been conducted with an additional HCl dosing point installed within the RGT. The aim of this experiment was to verify if reducing the pH of the feed to the reboiler will allow organic acids to boil over into the produced water for removal. The current pH stabilisation to FFCI operational philosophy does not efficiently remove organic acids leading to accumulation within the system. Hence, if not otherwise removed, corrosion issues may arise due to the presence of the accumulating organic acids.

Simultaneously due to a rise in lean MEG pH during the regeneration process, a sufficiently high pH of the regenerated MEG may be achieved to facilitate the removal of MDEA during reclamation whilst also achieving a suitable lean MEG pH without requiring further pH adjustment in the LGT tank. Fast and efficient removal of the MDEA is important during the switch over process as the pH needs to be increased for divalent ion removal in the MPV only to be reduced before re-injection. The longer MDEA is present in the recycled MEG, the longer additional alkalinity and acid will need to be dosed to achieve the desired target pH values, since the excess MDEA will need to be protonated (pH increase for MPV) and neutralised in the LGT. Therefore, by installing an additional dosing point, MDEA and organic acids will be removed more effectively during the reverse switchover process compared to the current procedure.

In contrast to the experiment conducted simulating the current plant configuration (as in Chapter 6), the pH of the lean MEG was not adjusted in the LGT. Instead, the pH of the rich MEG feed to the regeneration column was adjusted using HCl to pH 5.7-5.8 within the RGT. The resulting pH change in the LGT and FB are shown in *Figure 7-6* and the total alkalinity results are presented in *Figure 7-7*. The results demonstrate that it is possible to achieve a pH of 7 in the LGT through this method and to reach the target alkalinity of <10mM within 5 inventory turnovers.

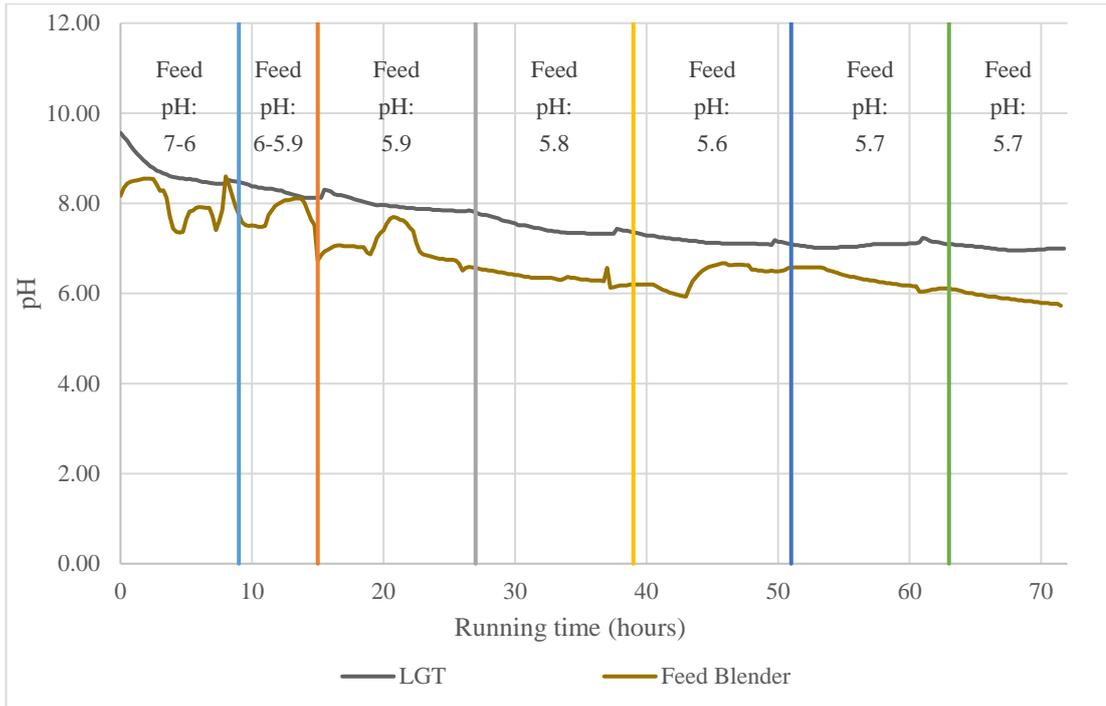


Figure 7-6 The pH in the LGT and FB as result of HCL injection to the rich MEG feed to the Regeneration column. The box indicates the target pH for the lean MEG tank ($\text{pH } 7 \pm 0.5$).

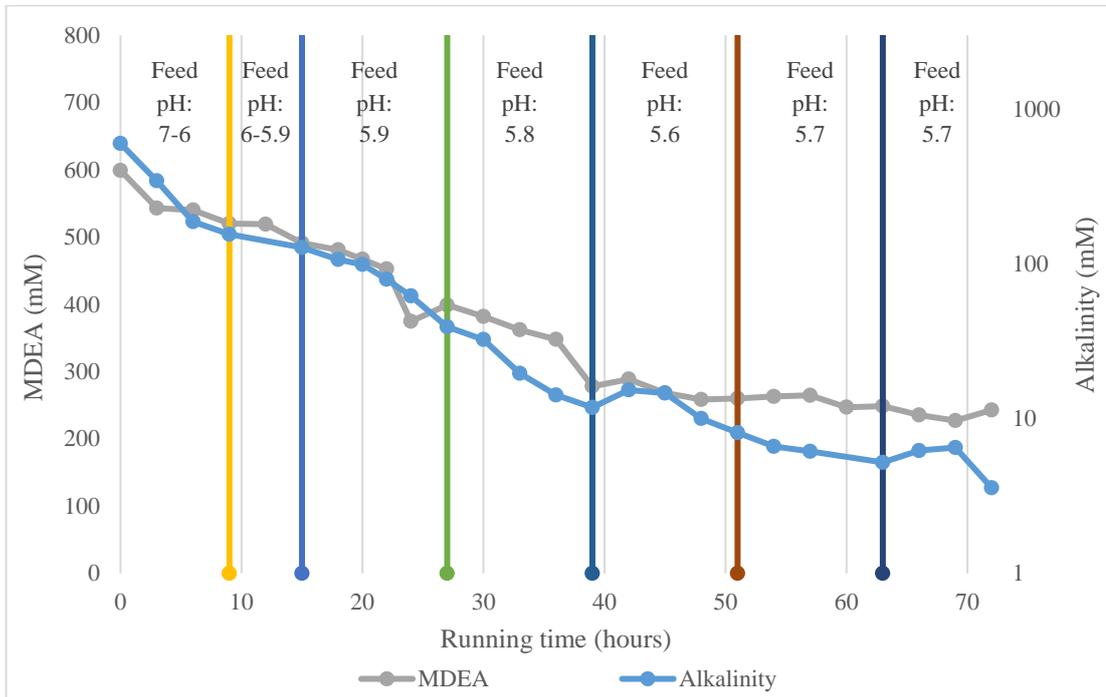


Figure 7-7 Alkalinity and MDEA concentration in the LGT. Each day presents one plant inventory turnover. After 5 inventory turn-overs, the alkalinity in the LGT reached <10 ppm

As discussed previously, a pH of 8.0 to 8.3 is required in the MPV to successfully remove calcium ions from the rich MEG, as shown in [Figure 7-9](#). who calculated that at 50mM CO₂ content, a pH of just above 8.0 is required to form carbonate from bicarbonate as well as dissolved CO₂. Although the pH is not only influenced by alkalinity but also dissolved organic acids, as long as the system operates in the steady state, the pH measurement is a good measure to ensure that the target alkalinity is reached to precipitate calcium and other divalent salts. From an operational point of view, keeping the pH in the MPV as low as possible (pH between 8.3 to 8.5), reduces the amount of alkalinity that needs to be added to achieve the desired divalent ion concentration, since this alkalinity will need to be neutralised before re-injection to reduce the risk of scaling (and resulting under-deposit corrosion) in the pipeline.

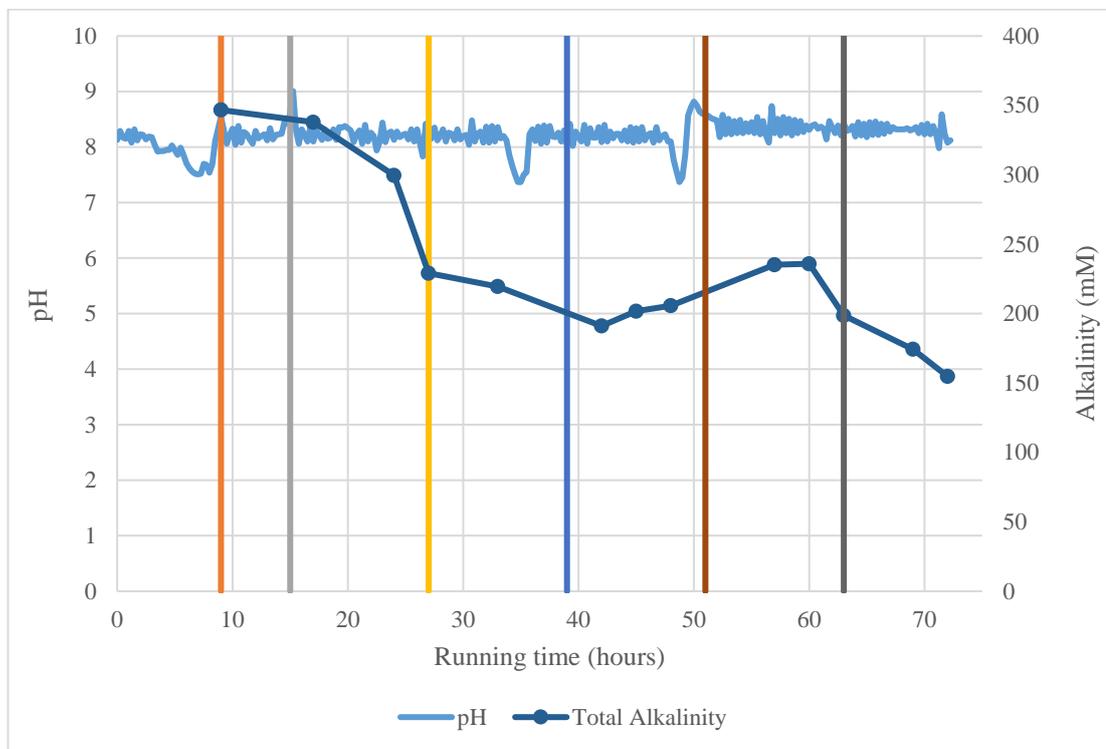


Figure 7-8 pH and total alkalinity in MPV

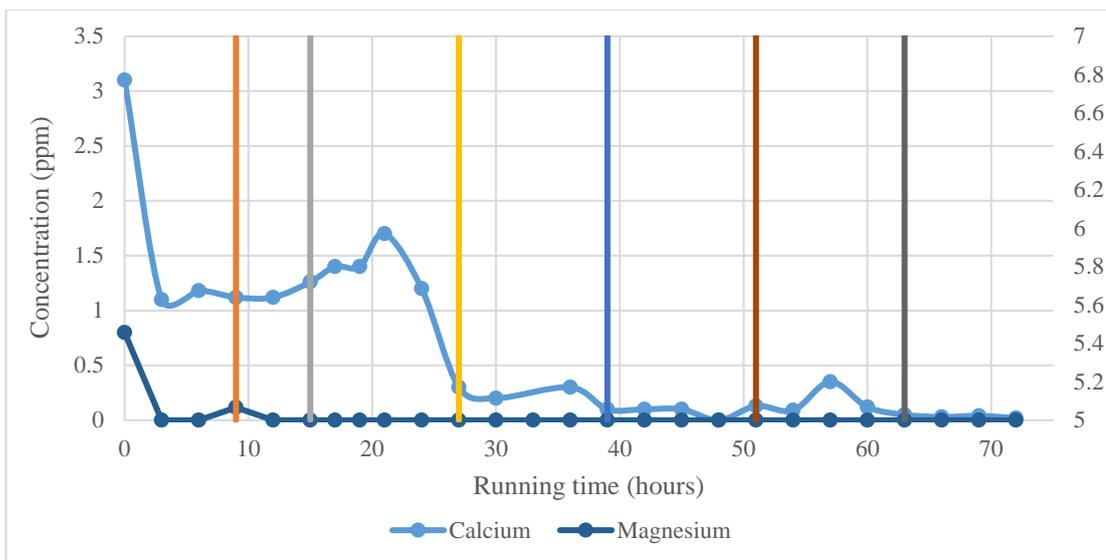


Figure 7-9 Calcium and magnesium ion concentrations in MPV

7.4 Conclusions

The experimental work undertaken in the MEG benchtop facility has demonstrated the switchover from FFCI to MDEA is feasible with the current operating procedure. Care needs to be taken for controlling the alkalinity in the MPV, as dosage rates for sodium hydroxide will change rapidly once MDEA is dosed to the system and returns to the MEG regeneration and reclamation facility. Results indicate that the slipstream that is reclaimed will lose about 50% of its MDEA content, which will have to be replenished under the experimental conditions used in this simulation, if the pH in the MPV is not maintained just above 8 as minimum.

In terms of the switchover strategy using the modified HCl dosing points, it was found that this strategy would work much faster and more efficient if an additional HCl dosing point is installed in the feed to the reboiler and the feed is adjusted to pH 6. This is of particular importance for the operational costs during the switchover period. Under normal operation the results from the benchtop facility indicate that it would take for field 2 about 30 inventory turnovers to remove the MDEA concentration to levels <10 mM. Whilst with the additional dosing point, the same could be expected in about 10 inventory turnovers. Furthermore, the required low alkalinity (<10 mM) to minimise the risk of scaling in the pipeline has been achieved using the additional dosing point after only 5 inventory turnovers.

8 pH and Alkalinity Control of Lean MEG (Field 3)

8.1 Introduction

Due to the presence of organic acids within the condensed water phase produced at (field 3), the addition of potassium hydroxide (KOH) is necessary to mitigate the risk of corrosion to the rich glycol tank (RGT) and other carbon steel sections of the MEG regeneration system. To neutralise incoming organic acids, KOH is injected into the RGT's recirculation loop to target either a neutral pH or a pH of 10.8. Under field 3 current operating philosophy the resulting lean MEG pH should be above 9 but below 11.2 to reduce the risk of subsea scaling if sudden formation water breakthrough occurs. Excessive accumulation of alkalinity (carbonate and hydroxide) during the regeneration process will pose a scaling risk through reactions with divalent cations included calcium and magnesium.

Under the current operational methodology of Field 3 (RGT target pH of 10.8) significant production of both hydroxide and carbonate alkalinity was observed within the produced lean glycol (98.5 and 68.09 mmol/L respectively). In comparison, the proposed operational methodology with a target RGT pH of 7 produced a far lesser amount of both hydroxide and carbonate alkalinity (11.21 and 1.96 mmol/L respectively). As such, the proposed target RGT pH of 7 will reduce the potential of scaling within the regeneration system. However, under both operational methodologies the produced lean glycol pH exceeded the maximum lean glycol pH (11.2) identified in the current MEG operating philosophy to prevent sub-sea scaling in case of sudden formation water breakthrough. The current operating philosophy should therefore be revised to account for the greater lean glycol pH produced during the regeneration process. Alternatively, the produced lean glycol pH and alkalinity can be reduced in several ways including:

- Dosing of hydrochloric acid within the lean glycol tank to reduce lean glycol pH
- Target a lower rich glycol pH (potential corrosion risk in RGT below a pH of 7)
- Reduce the concentration change occurring within the reboiler

Furthermore, the presence of oxygen scavenger (OS) within the regeneration system introduced via the lean glycol stream increased the total KOH required to maintain the

target pH within the RGT. Over a span of five regeneration cycles, approximately 1.4-1.5 times more KOH was required to maintain the desired RGT pH when oxygen scavenger (OS) was present. Additionally, the presence of OS within the regeneration system did not have a significant impact upon the oxygen level measured within the LGT. Due to the limited residence time of OS within the LGT, coupled with the continuous introduction of oxygen via sparging complete oxygen removal was unable to be achieved.

Lastly, testing conducted using MDEA to maintain a pH of 7 within the RGT demonstrated a potential alternative to KOH to control lean glycol pH and alkalinity. Rich glycol maintained at a pH of 7 by MDEA produced a final lean glycol product of pH 9.2 with system wide pH stabilisation occurring within one to two regeneration cycles. Furthermore, the use of MDEA produced little to no carbonate alkalinity within the lean glycol product as a sufficiently high rich glycol pH within the feed blender was unable to be reached to facilitate the formation of bicarbonate. Overall, MDEA presents a strong alternative pH control method resulting in lower lean glycol pH and carbonate/hydroxide alkalinity compared to KOH and hence a reduced scaling risk, however, at the cost of a greater dosage requirement.

The incoming rich MEG may have a pH value as low as 3.8 during production of condensed water only. Due to production of organic acids from some reservoirs. To mitigate against the risk of corrosion in the rich MEG storage tank and other carbon steel sections and to enhance the performance of oxygen scavenger (OS), KOH (or alternatively MDEA) will be injected into the rich MEG, specifically in the recirculation loop of the rich MEG tank.

8.2 Objectives

The key objectives for this work will be to understand the practicalities around chemical injection through the process to maintain the target values for pH and strong alkalinity of the lean MEG. This will be used to develop guidelines and procedures, and if required, modifications for operation of industrial facilities. The primary operational goal will be to target a pH of 7 within the rich glycol tank and to observe the effects upon system wide pH and alkalinity with particular focus on the properties of the produced lean MEG. Furthermore, to simulate a potential overdose of KOH in to the rich glycol, an individual test will be performed where a pH of 10.8 will be

maintained within the rich glycol tank (RGT). This test will evaluate the negative impacts of potential KOH overdosing and the industrial current operational methodology for the field 3 MEG regeneration system. Other operational aspects of particular interest include:

- Effect of the presence of oxygen scavenger (OS) on KOH dosage requirements
- Effect of oxygen scavenger (OS) on oxygen levels within MEG regeneration system whilst sparging with 3% oxygen is applied within the rich and lean glycol tanks
- Effectiveness of MDEA as an alternative method to regulate pH and alkalinity of lean MEG

8.3 Methodology

The evaluation of pH and alkalinity control of lean MEG will be conducted by performing five individual tests as per the experimental matrix defined in *Table 8-1*. The baseline testing involved the injection of KOH solution into the RGT system to achieve a neutral pH of 7.0 with no additional process chemicals (i.e. OS) involved. In addition to the baseline test, tests were conducted to simulate potential overdosing of the rich MEG to pH 10.8 to assess potential resultant issues within the regeneration system. Furthermore, to evaluate the effect of process chemicals such as OS upon system pH and KOH dosing requirements, Experiments 1 and 2 were re-performed with 500ppm OS continuously injected into the lean MEG. Additional testing was also conducted using MDEA as a potential alternative to KOH for pH and alkalinity control. The modified MEG pilot plant configuration illustrated in *Figure 8-1* was used to simulate the operation of field 3 MEG regeneration facilities.

To assess the capability of the produced lean MEG to successfully neutralise the incoming organic acids from the well, the brine composition defined in *Table 8-2* was utilised to simulate the potential brine composition experienced at field 3 during condensed water production only. The theoretical capability of the produced lean MEG to neutralise incoming organic acids was measured by determining the alkalinity of the resultant lean MEG solution. The alkalinity of the lean MEG will be influenced by a combination of the conversion of carbon dioxide to carbonate species within the feed blender and introduction of hydroxide as KOH dosage. To prevent excess production of carbonate alkalinity (a potential scaling risk) a degasser was installed between the

feed blender and rich glycol tank to drive out dissolved carbon dioxide using the sparge gas composition as per

Table 8-3. In addition, an investigation was performed to evaluate the performance of OS within the MEG regeneration facility. Due to the high pH of the lean glycol expected within the reboiler, accumulation of organic acids is anticipated within the MEG regeneration loop under the current field 3 plant configuration (no reclamation). Therefore, to assess the suitability of OS under the current plant operational methodology, the rich and lean glycol tanks were sparged using the gas composition outlined in

Table 8-3 to simulate oxygen contamination. OS was injected at the recommended rate (500ppm) into the lean glycol stream and oxygen levels within the system compared to the baseline testing was measured.

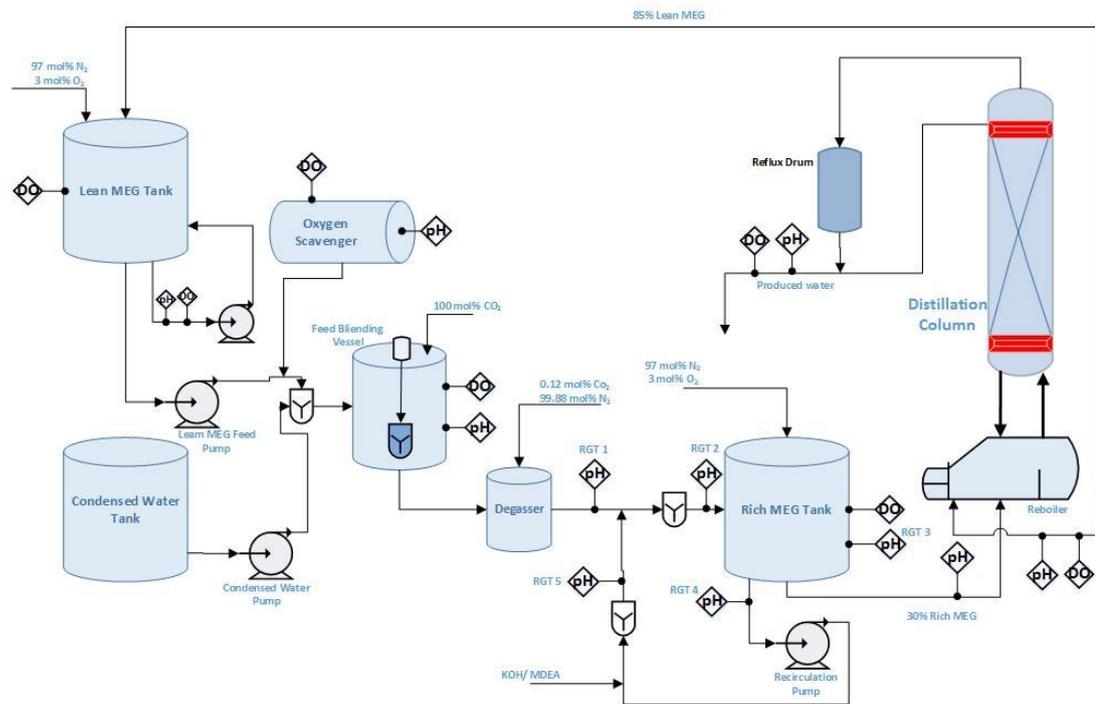


Figure 8-1: pH and Alkalinity Control of lean MEG pilot plant configuration

Table 8-1 Experimental Matrix of pH and Alkalinity Control of Lean MEG
Experimental Matrix

Test no.	Description	MEG [wt. %]	Initial pH	Base	Target RM pH	Resulting LM pH	OS
1	CW only, neutral pH			45% KOH	7	>9	N
2	CW only, elevated pH			45% KOH	10.8	>9	N
3	Same as 1, with OS	30	3.8	45% KOH	7	>9	Y
4	Same as 3, with OS			45% KOH	10.8	>9	Y
5	CW only, neutral pH			MDEA	7	>9	N

Table 8-2 Fluid compositions at start of experiment

	Brine	Rich MEG	Lean MEG
Formic acid (mg/L)	0.06		
Acetic acid (mg/L)	60.96		
Propanoic acid (mg/L)	4.24		
Butanoic acid (mg/L)	17.11	Determined by brine composition	0
Total organic acids (mg/L)	82.37		
MEG (wt%)	0	30	85

Table 8-3 Sparge gas compositions

	Feed Blender	Pre-treatment vessel (MUS Degasser)	Rich and Lean MEG Tank
mole% CO ₂ @ 1 bar	100	0.12	0
mole% N ₂ @ 1 bar	0	99.88	97
mole% O ₂ @ 1 bar	0	0	3

8.4 Results and Discussion

8.4.1 Neutral Rich Glycol pH (KOH)

The pH within the system is illustrated in *Figure 8-2* over a period of five MEG regeneration cycles. From an initial rich glycol pH of 7.0, the pH in the reboiler

increased as the regeneration process occurred. Thus, the pH value of the produced lean glycol was increased to approximately 11.9. The resulting pH of the lean glycol is therefore above the desired maximum lean glycol pH of 11.2 and may pose a risk of subsea scaling in the case of sudden formation water breakthrough. To minimise the pH rise across the reboiler during the regeneration process, either a lower rich glycol pH is required (corrosion risk in RGT) or a lesser concentration increase of the MEG is needed. The final lean glycol pH was confirmed by two independent pH probes within the pilot plant as well as the pH probes used during lean glycol titration analysis. Stabilisation of pH levels within the system was achieved within approximately 1-1.5 regeneration cycles with no deviation occurring during proceeding cycles. The pH of the incoming rich glycol to the rich glycol tank (from degasser) was found to stabilise at approximately 6.2-6.3. This pH may pose a corrosion risk to the rich glycol tank and associated piping if KOH dosage is not maintained within the recirculation loop to achieve the desired pH of 7. Due to the intermittent dosing of KOH within the recirculation loop, sporadic spikes in pH within the recirculation loop were detected by RGT 1 and 3 pH probes as illustrated in *Figure 8-3*. Furthermore, a pH rise across the degasser vessel was measured indicating effective removal of CO₂ from the CO₂ saturated rich MEG product from the feed blender.

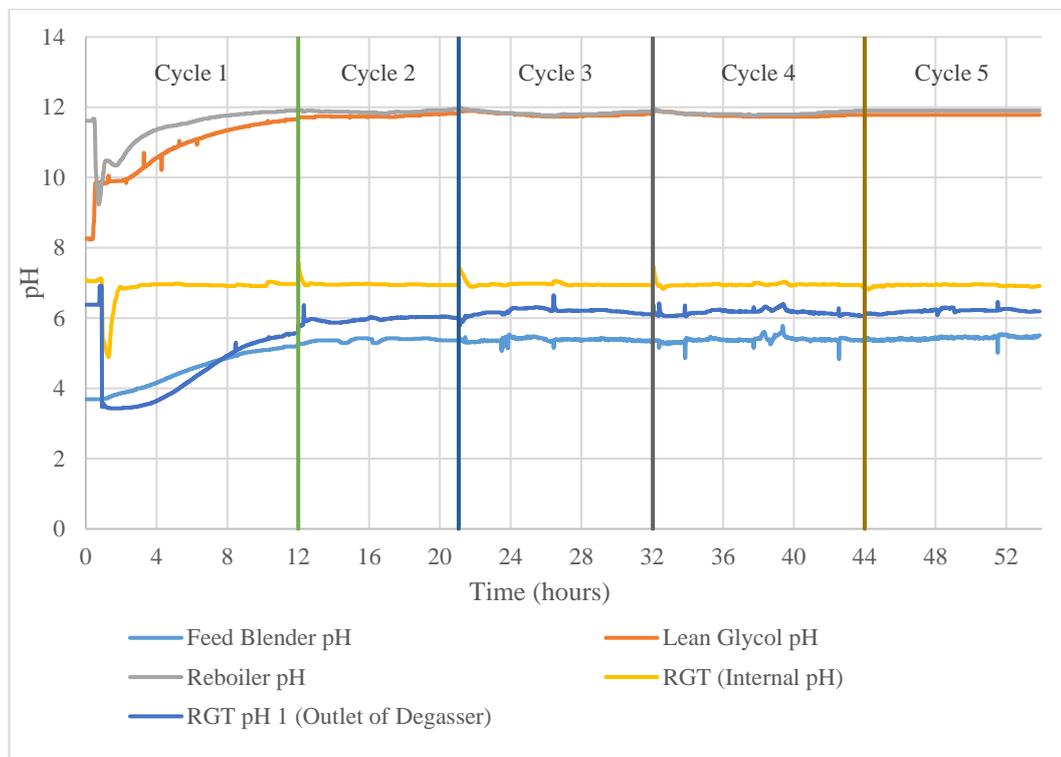


Figure 8-2 MEG regeneration system pH levels (RGT pH 7)

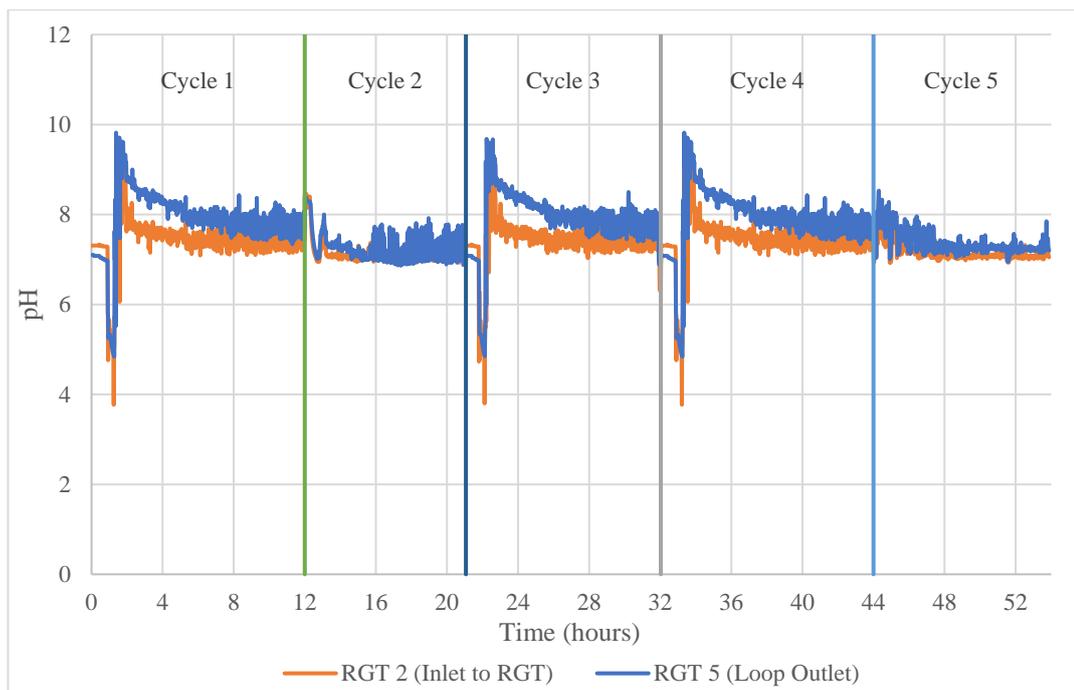


Figure 8-3 – Fluctuation of rich glycol pH within RGT recirculation loop

Furthermore, the change in alkalinity of the lean glycol in 3-hour intervals is illustrated in [Figure 8-4](#) in terms of the total, hydroxide, carbonate and carboxylic (organic acid) alkalinities. It was observed that little to no formation of carbonate and hydroxide alkalinity was formed within the first half of the initial regeneration cycle, as the sufficient pH value that required to form them has not been achieved yet in the lean glycol tank. Once a pH above 10 was reached within the LGT the hydroxide and carbonate alkalinity quickly rose reaching their respective maximums within approximately 1.5 cycles (in-line with pH stabilisation). The high lean glycol pH facilitated a small amount of CO₂ conversion within the feed blender to bicarbonate and subsequently carbonate that could not be removed within the degasser. The total hard alkalinity (hydroxide and carbonate) within the lean glycol reached a maximum of approximately 12-13 mMole/L with hydroxide representing the primary form of the hard alkalinity.

The carboxylic acids was observed to continuously increase with each regeneration cycle demonstrating the accumulation of organic acids within the regeneration loop. Additionally, no organic acids were detected within the reflux drum over all five cycles via on chromatography confirming their accumulation within the regeneration system. The accumulation of organic acids such as acetate may contribute to Top of the Line Corrosion (TLC) within carbon steel systems in the presence of carbon dioxide.

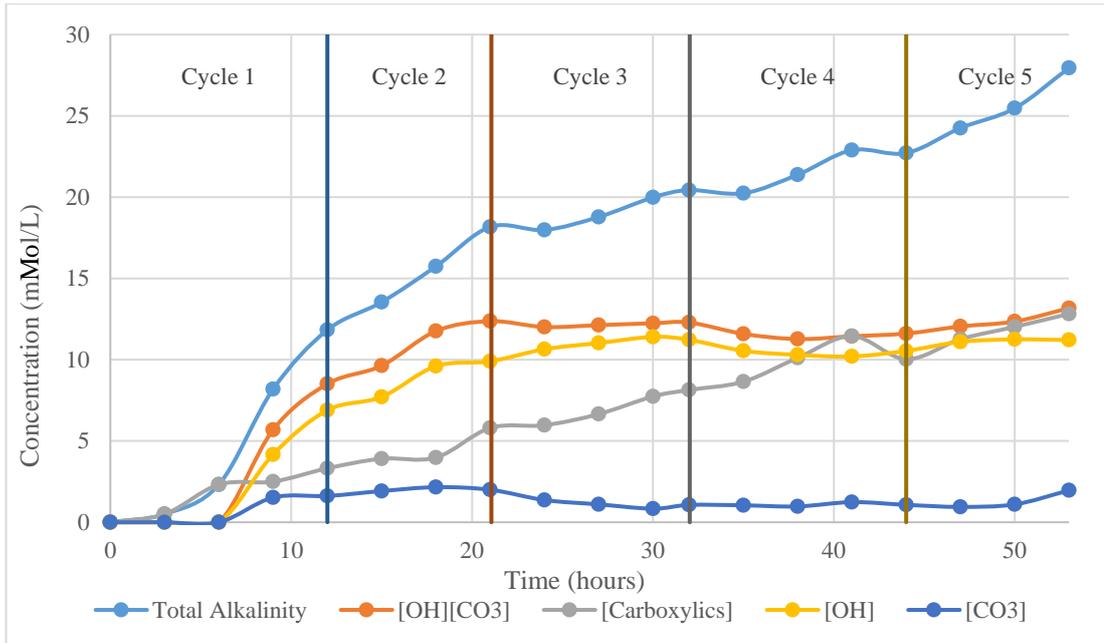


Figure 8-4 - Lean glycol alkalinity (RGT pH 7)

8.4.2 Elevated Rich Glycol pH (KOH Overdosing)

The high initial pH within the RGT (10.8) due to ‘KOH over dosing’ rapidly produced a lean glycol product from the reboiler with an extremely high pH as illustrated in *Figure 8-5*. However, unlike the first experiment (RGT pH 7), the pH of the lean glycol did not stabilise instead undergoing a rapid increase in pH within the first cycle followed by a gradual increase in the proceeding cycles. The resultant lean glycol pH reached a maximum pH of 12.8-12.9 during the fifth cycle with the high pH exacerbating the risk of subsea scaling upon formation water breakthrough. Furthermore, a gradual increase in pH of the rich MEG within the feed blender and degasser was observed as a result of the increasing lean glycol pH. Due to the large pH difference between the rich MEG within the degasser and RGT further pH increase within the system should be expected as more KOH is continuously added with stabilisation of the pH potentially taking upwards of 10 cycles with lean glycol pH in excess of 13.

Similar fluctuations in pH within the RGT recirculation loop were experienced as per Experiment 1 (RGT pH 7) but to a lesser extent due to the higher pH more readily neutralising incoming organic acids. However, to continuously increase the pH of the rich MEG from the degasser to a pH of 10.8, an extremely large amount of KOH in

comparison to Experiment 1 was required. The large dosage rate of KOH required therefore lead to a significant accumulation of both potassium and hydroxide in the form of alkalinity.

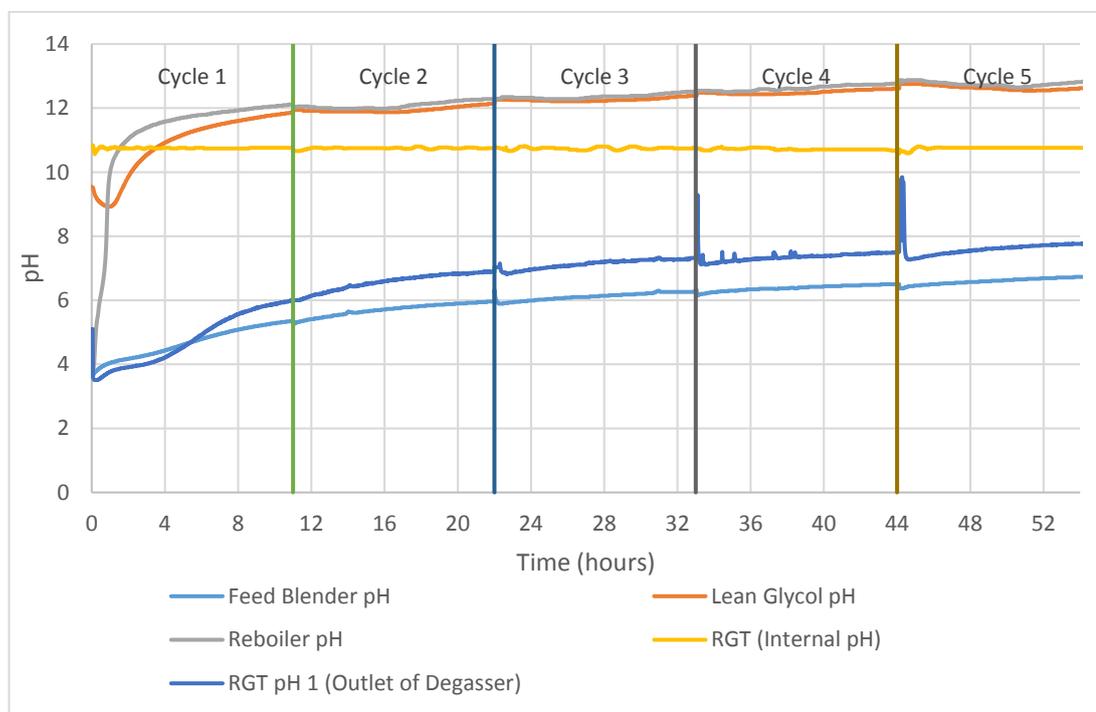


Figure 8-5 MEG regeneration system pH levels (RGT pH 10.8)

The lean glycol alkalinity produced during experiment 2 is illustrated in *Figure 8-6* demonstrating a significant production of both carbonate and hydroxide alkalinity within the produced lean MEG. In comparison to Experiment 1, the production of hydroxide alkalinity is far greater due to the larger KOH dosage required to achieve a pH of 10.8 within the RGT. Furthermore, it was observed that in a similar manner to the lean glycol pH, the hydroxide alkalinity did not stabilise within five regeneration cycles instead increasing consistently. This is again due to the large difference in rich MEG pH within the degasser compared to the RGT requiring a large continuous dosage of KOH to reach 10.8 hence introducing a large amount of hydroxide.

A large increase in carbonate alkalinity within the produced lean MEG was also observed when compared to Experiment 1. During Experiment 1 very minimal carbonate alkalinity was produced, however, due to the far greater pH produced within the feed blender during Experiment 2 (6.7 compared to 5.5), a larger portion of the dissolved CO₂ was converted to bicarbonate. The conversion of dissolved CO₂ to bicarbonate within the feed blender consequently inhibited its removal within the degasser. The high pH within the RGT then facilitated the conversion of bicarbonate

to carbonate leading to the accumulation of carbonate alkalinity within the produced lean glycol. The resulting carbonate and hydroxide alkalinity produced when a pH of 10.8 is maintained in the RGT will pose a major scaling risk upon the onset of sudden formation water production and should be avoided.

Table 8-4 Comparison of alkalinity produced during MEG regeneration

Number of Regeneration Cycles: 5		
Rich Glycol Target pH	7	10.8
Total Alkalinity (mMol/L)	27.95	248.67
Hydroxide (mMol/L)	11.21	98.5
Carbonate (mMol/L)	1.96	68.09

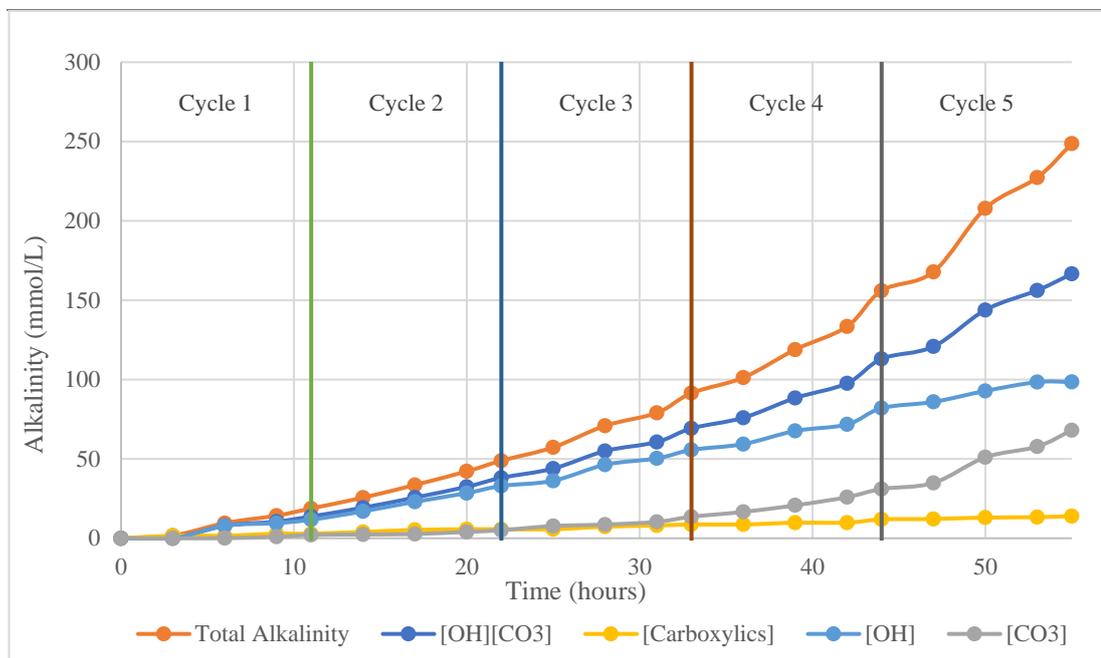


Figure 8-6 Lean glycol alkalinity (RGT pH 10.8)

8.4.3 Neutral Rich Glycol pH with Oxygen Scavenger

The stabilisation of system wide pH whilst OS was present within the system occurred in a similar manner to the corresponding RGT pH 7 testing (*Figure 8-7*). However, in contrast an additional cycle was required to achieve full system wide stabilisation of pH levels. The delayed stabilisation of pH occurred due to the addition of OS inline between the LGT and feed blender requiring an entire regeneration cycle before OS was introduced into the LGT. Furthermore, it was observed that the presence of OS did not have a significant impact on the final lean glycol pH reached in comparison to

the oxygen scavenger free test. The presence of OS within the system did however lead to an increased KOH dosage rate (*Section 8.4.6*) and subsequently a greater accumulation of potassium within the system.

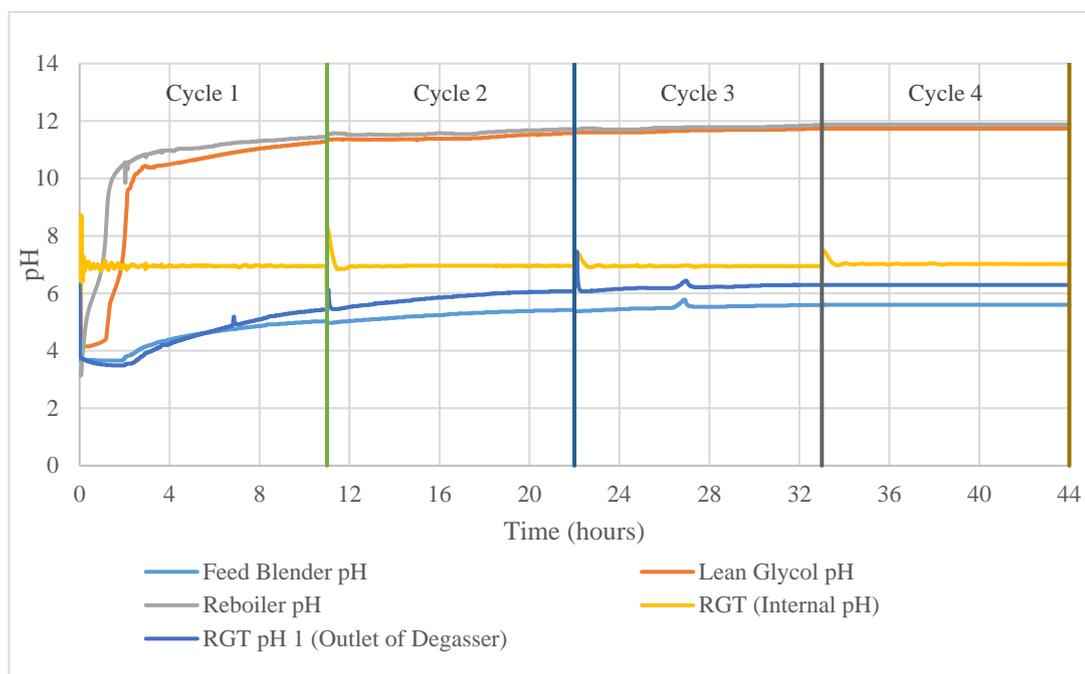


Figure 8-7 MEG regeneration system pH levels (RGT pH 7 with OS)

Stabilisation of both carbonate and hydroxide alkalinity was also found to occur later than the corresponding RGT pH 7 test where OS was not present as illustrated in *Figure 8-8*. This result is in-line with the observed stabilisation of the system wide pH occurring approximately one regeneration cycle later. Although stabilisation of both carbonate and hydroxide alkalinity was delayed, the final hydroxide alkalinity reached within the lean glycol product was consistent with Experiment 1 (RGT pH 7 in the absence of OS).

However, due to the potential for the active oxygen scavenging component of OS (SO_3) to act as an acid-base conjugate pair (*equation 8-1*) interaction of the oxygen scavenger with HCl and NaOH during the titration procedure occurred. As such, the presence of OS within the lean glycol product introduced a source error into the alkalinity calculation procedure within the pH range where conversion from carbonate to bicarbonate occurs. The resulting titration overestimated the total carbonate alkalinity within the lean glycol in comparison to the corresponding test with no oxygen

scavenger present. However, due to the accurate carbonate alkalinity calculated during Experiment 1 and only slight increase calculated during Experiment 3 the carbonate alkalinity produced could be considered minimal.

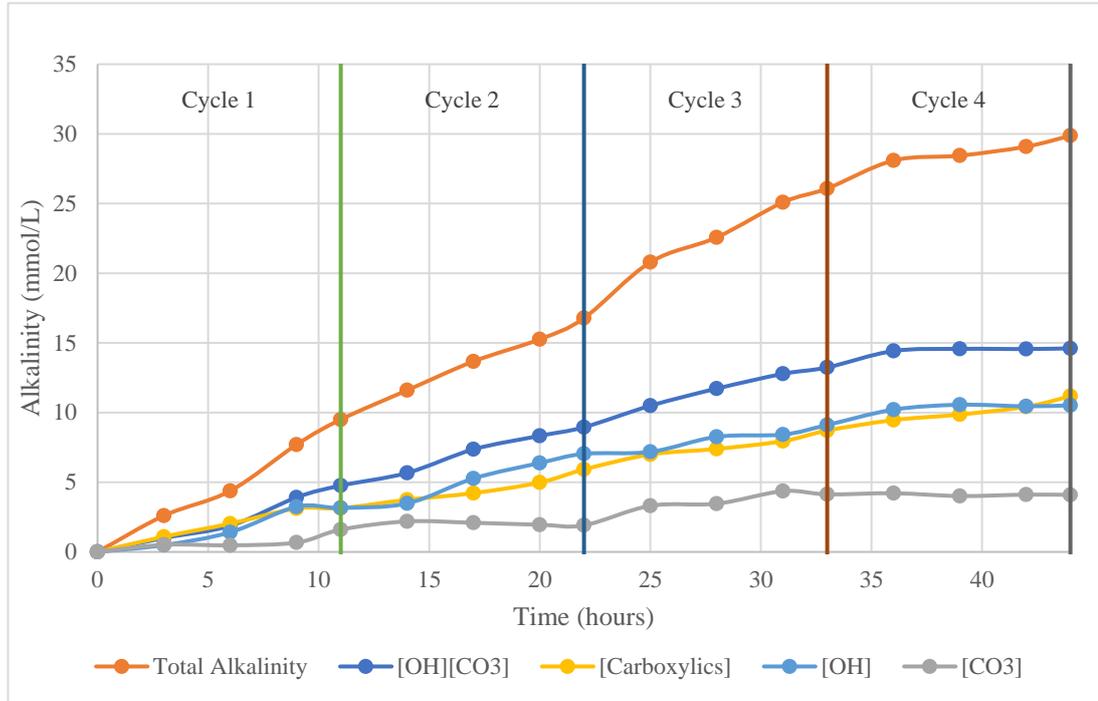


Figure 8-8 - Lean glycol alkalinity (RGT pH 7, with OS)

8.4.4 Elevated Rich Glycol pH with Oxygen Scavenger (KOH Overdosing)

The behaviour of the MEG regeneration system under KOH overdosing (RGT pH 10.8) exhibited no major differences whilst OS was dosed into the system in comparison to oxygen scavenger free testing. The change in system wide pH and lean glycol alkalinity are illustrated by *Figure 8-9* and *Figure 8-10* respectively. The final lean glycol pH reached after five regeneration cycles matched closely to Experiment 2 with a continual increase in pH again experienced within the feed blender leading to the production of significant amounts of carbonate alkalinity. In a similar manner to Experiment 2, the accumulation of carbonate alkalinity increased significantly during cycles four and five as the conversion of carbon dioxide to bicarbonate is facilitated by the increasing feed blender pH and can be expected to further increase during proceeding cycles.

Overall, the presence of OS during the regeneration process did not appear to have a significant impact upon the system in terms of both final lean glycol pH or alkalinity production at both RGT pH 7 and 10.8. However, continuous dosing of OS due to its acidic nature directly lead to an increase in KOH dosing required to maintain the desired pH with a comparison of KOH dosage between each experiment given in [section 8.4.6](#).

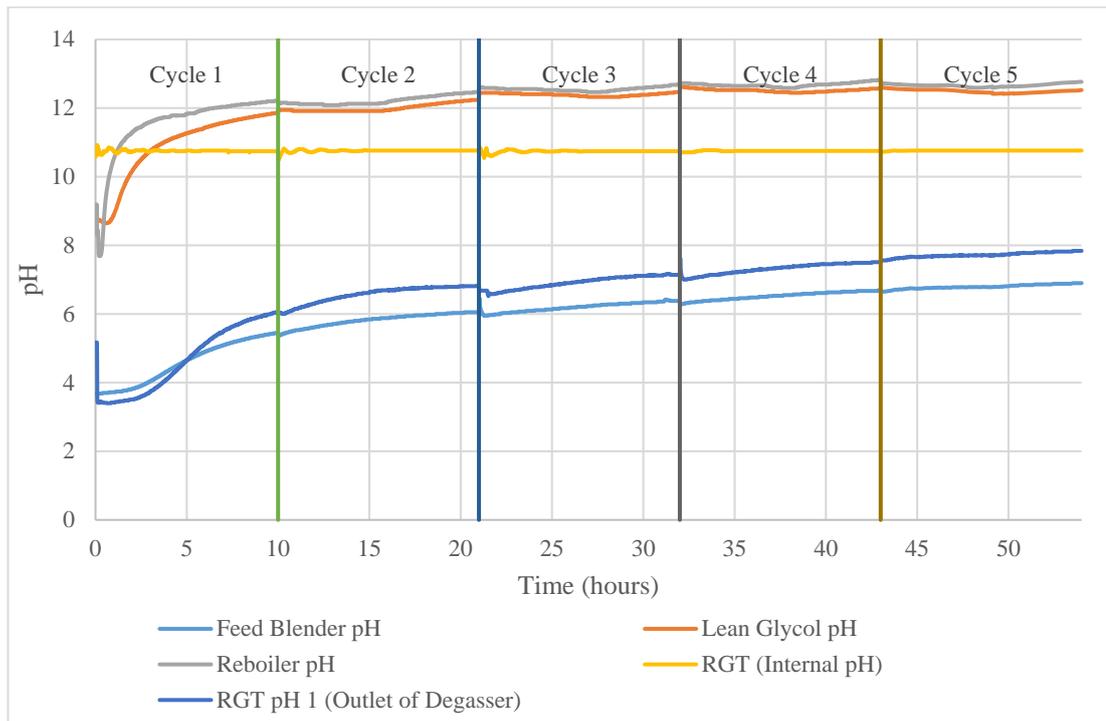


Figure 8-9 MEG regeneration system pH levels (RGT pH 10.8 with OS)

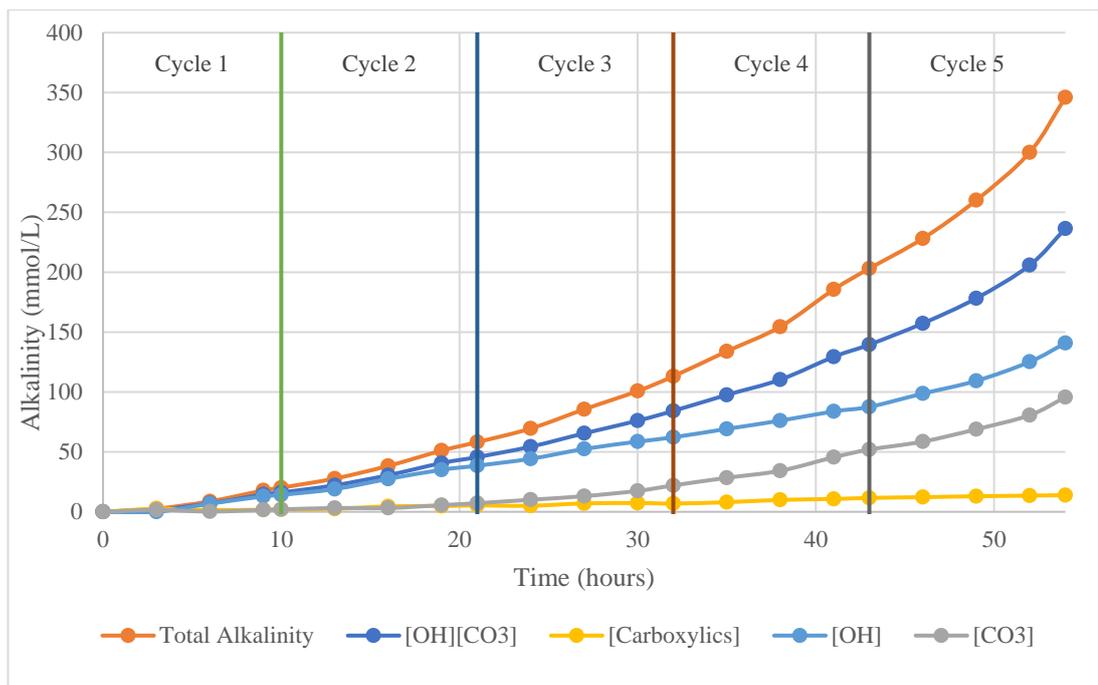


Figure 8-10 Lean glycol alkalinity (RGT pH 10.8, with OS)

8.4.5 Neutral Rich Glycol pH (MDEA)

The control of rich glycol pH using MDEA produced a final lean glycol product of approximately 9.1-9.2 within the reboiler and LGT (*Figure 8-11*) with stabilisation of the system wide pH occurring within two regeneration cycles. The resulting lean glycol pH is therefore within the desired pH range specified by the operator's current operational methodology (9-11.2) and poses a significantly reduced scaling risk following sudden formation water breakthrough compared to the corresponding KOH testing. Furthermore, the MDEA present within the lean glycol provided sufficient buffer capacity to neutralise incoming organic acids within the brine without requiring to increase the lean glycol pH. It was also observed that in comparison to KOH (*Figure 8-3*) the pH fluctuations experienced within the rich glycol recirculation loop were significantly lower (*Figure 8-12*).

In a similar manner to Experiment 1 (RGT pH 7, KOH) the dosage rate of MDEA required to maintain pH 7 within the RGT gradually decreased with time (*Figure 8-13*) with the total MDEA used over three regeneration cycles listed in. As the rich glycol produced within the feed blender increased in pH, only a small dosage of MDEA was required in the RGT to achieve the desired pH (≈ 6.42 to 7). Furthermore, the reducing MDEA dosage rate indicates that little to no conversion of carbon dioxide to

bicarbonate is occurring within the feed blender. However, a significant problem was experienced when a pH of 10.8 was targeted.

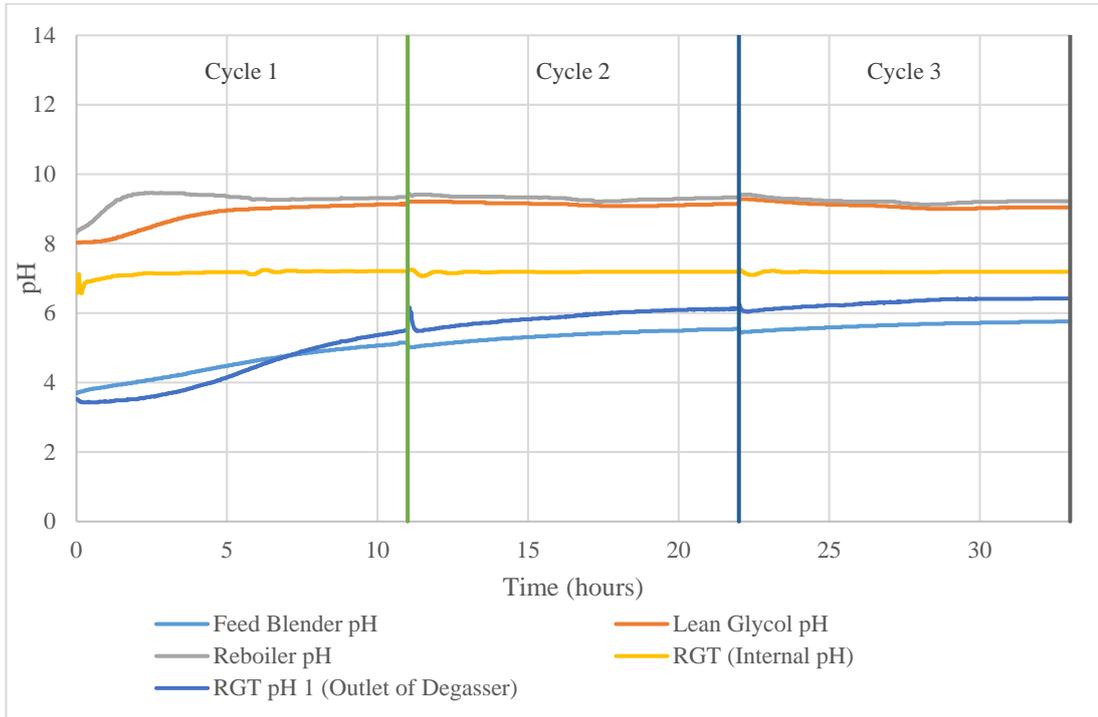


Figure 8-11 MEG regeneration system pH levels (RGT pH 7 MDEA)

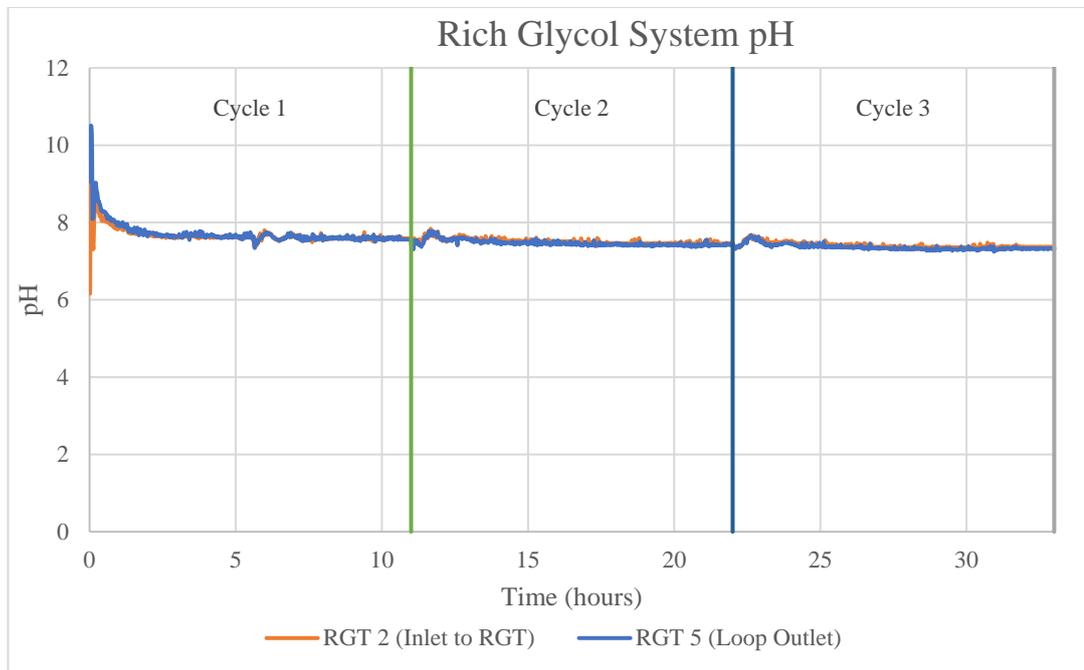


Figure 8-12 - Fluctuation of rich glycol pH within RGT recirculation loop

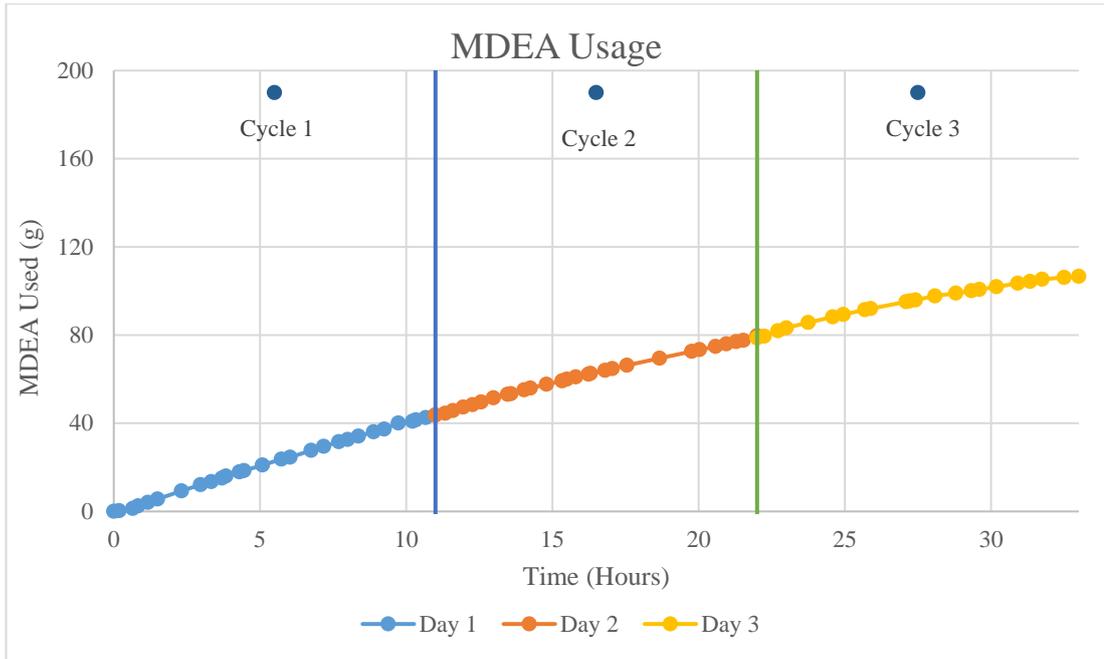


Figure 8-13 MDEA usage during operation (RGT pH 7)

The accumulation of alkalinity and MDEA during MDEA pH control is illustrated in *Figure 8-14* and *Figure 8-15*, with the primary form of alkalinity measured occurring due to the presence of MDEA and organic acids. As a pH of below 6 was maintained within the feed blender, limited conversion of carbon dioxide to bicarbonate occurred leading to minimal formation of carbonate alkalinity. Furthermore, as the pH of the final lean glycol product reached a maximum of approximately 9.2, the formation of hydroxide alkalinity was avoided. Overall, the use of MDEA to control lean glycol pH and alkalinity represents a strong alternative to KOH due to the lower final lean glycol pH and carbonate/hydroxide alkalinity produced. Both of these factors ultimately reduce the scaling risk associated with the produced lean glycol in the event of sudden formation water breakthrough whilst successfully maintaining a corrosion friendly pH within the RGT.

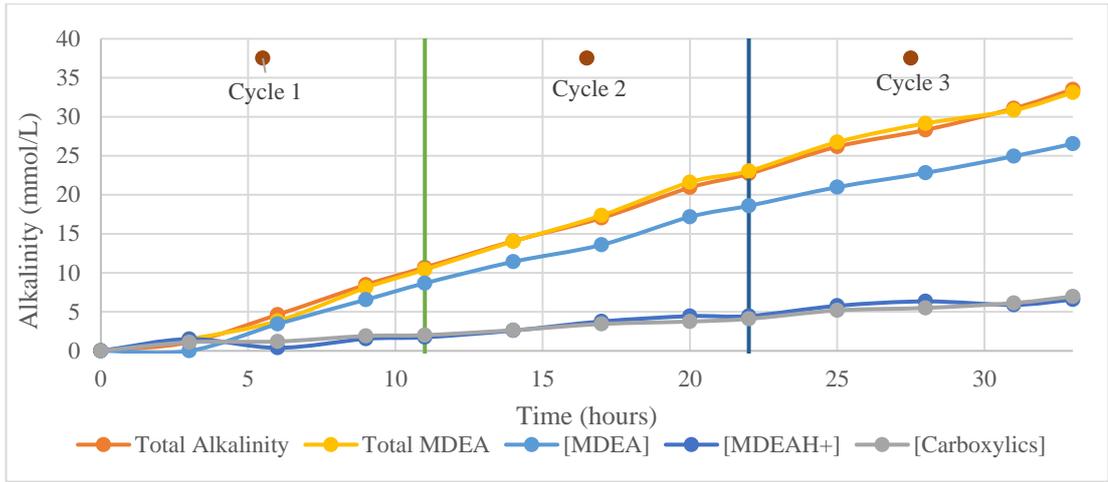


Figure 8-14 - Lean glycol alkalinity (RGT pH 7, MDEA)

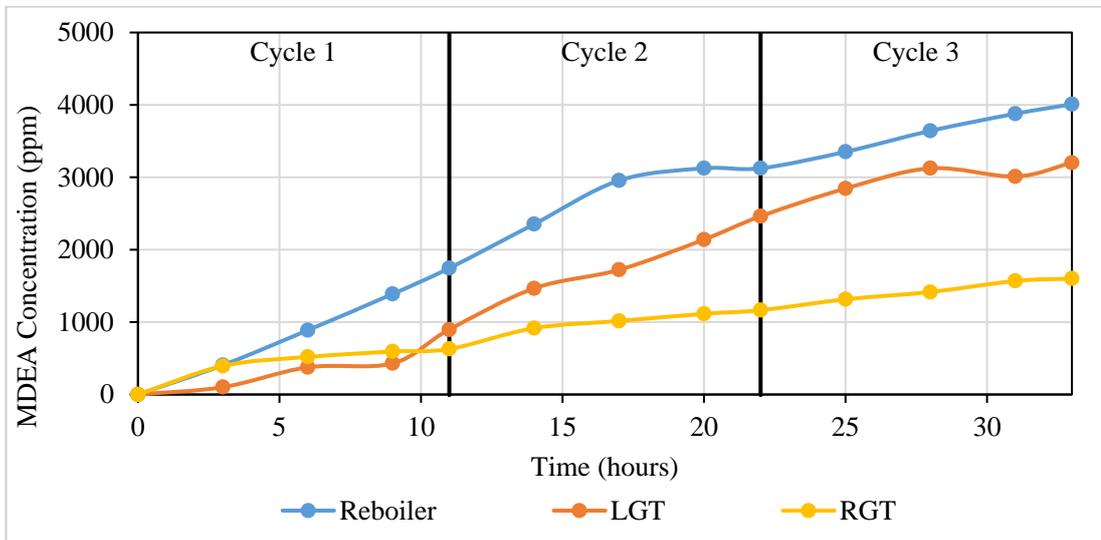
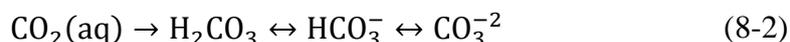


Figure 8-15 – Accumulation of MDEA

8.4.6 Comparison of KOH Usage between Operational Methodologies

Due to the higher RGT pH requirement of Experiment 2 (RGT pH 10.8) a greater dosage rate of KOH into the RGT system is expected and is illustrated in [Figure 8-16](#), and [Table 8-5](#), summarising the total KOH usage during the four tests. As a result of the stabilisation of system pH that occurred during Experiment 1, the KOH dosage rate into the RGT quickly stabilised reaching a constant rate. However, the KOH dosage rate required in Experiment 2 did not stabilise, instead gradually increased as time progressed. The increasing KOH dosage requirement occurred due to the increasing bicarbonate alkalinity within the system due to the high lean glycol pH. As the pH of the lean glycol rose, conversion of CO₂ to bicarbonate ([equation 8-2](#)) occurred within

the feed blender and its subsequent removal of CO₂ within the degasser was prevented. As such, as the bicarbonate containing rich MEG from the degasser entered into the RGT system, additional KOH was dosed to convert bicarbonate to carbonate. The rate of CO₂ conversion and hence KOH dosage rate should be expected to further increase during additional regeneration cycles due to continued increase of pH within the LGT.



Furthermore, it was observed that dosing of Baker Hughes OS directly increased the amount of KOH required to maintain the desired pH, whether 7 or 10.8 within the RGT. *Table 8-5* summarises the total amount of KOH required over five regeneration cycles compared to no oxygen scavenger corresponding experiments, and indicated that approximately 1.4-1.5 times the amount of KOH was required when OS was present.

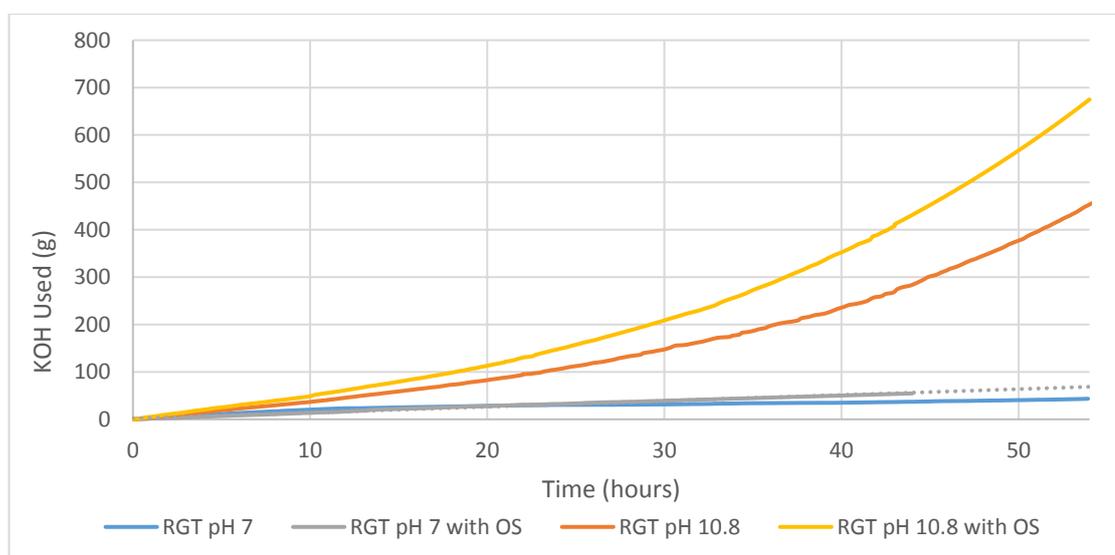


Figure 8-16 Comparison of KOH usage between operational methodologies

Table 8-5 Comparison of KOH usage at different operation conditions

RGT pH	7	7 (with OS)	10.8	10.8 (with OS)	7 (MDEA)
Total Days	5	4	5	5	3
Total KOH used (g)	43.4	54.62 (66.7)	470.4	674.9	106.6 (140)
Comparative KOH usage	1	1.53	10.84	15.55 (1.43*)	-

1. * Total KOH used after five days compared to RGT pH 10.8 with no oxygen scavenger present

8.5 Conclusions

Under the current lean glycol pH and alkalinity control methodology for field 3 using potassium hydroxide, both rich glycol target pHs (7 and 10.8) produced a final lean glycol product with pH in excess of the maximum pH specified in the current operating philosophy (pH11.2). The resulting lean glycol pH under both rich glycol operating conditions will pose a risk of subsea scaling if sudden formation water breakthrough occurs. The removal of excess carbon dioxide during the regeneration process in combination with the change in MEG concentration resulting in a concentration of the hydroxide present, ultimately causing a large increase in pH. If the use of KOH for pH and alkalinity control is to be performed, a rich glycol pH of 7 should be targeted to minimise the hydroxide and carbonate alkalinity produced in the lean glycol product to reduce the risk of scaling. Furthermore, the presence of OS within the regeneration system did not appear to have any significant impact in terms of pH or alkalinity accumulation.

Additionally, through the testing conducted the use of MDEA was found to be a strong alternative to KOH for rich glycol pH control. The use of MDEA to control the rich glycol pH produced a far more favourable final lean glycol pH and alkalinity compared to KOH and will ultimately reduce the risk of scaling if sudden formation water breakthrough occurs. Therefore, it is recommended that the use of MDEA for pH control at field 3 be further investigated as an alternative to KOH addition.

9 Conclusions and recommendations

9.1 Conclusions

In This Chapter, the various studies from the previous technical chapters are summarised to give the overall conclusions for this thesis.

9.1.1 Design, operation and control of MEG plant

- At this stage of research, the MEG bench scale pilot plant was successfully designed, constructed, and operated to serve the actual field conditions.
- It was designed to simulate different scenarios that could possibly occur during the operation of certain gas wells back to the onshore production facility, such as clean up to host study, switchover between different corrosion management strategies, oxygen scavenger evaluation, pH- Alkalinity control
- It was proposed to use realistic simulated production fluids, such as condensate mixtures and simulated formation water/brines.

9.1.2 Mono-ethylene Glycol bench scale clean up study, operating results using field data

In this chapter, the MEG bench top regeneration and reclamation system was used to simulate the start-up conditions of both field 1 and field 2. The actual composition for these two fields were used as well as same drilling mud and demulsifier. The results showed;

- The presence of drilling mud facilitates and increases the emulsion formation tendency in both fields.
- Without the demulsifier addition, the majority of the drilling mud partitions via emulsion formation into the MEG phase and is carried over into the MEG pre-treatment vessel (MPV).
- Adding the demulsifier results in the accumulation of the drilling mud at the MEG/condensate interface inside the three-phase separator (TPS) and the resulting drilling mud carryover into the MPV is significantly reduced.
- Most of the drilling mud carried over into the MPV is not discharged with the rich MEG leaving the vessel and it accumulates within the vessel at the condensate/rich MEG interface for both scenarios.

- Calcium ions were removed in the MPV only after raising the alkalinity with 1 mole/L NaOH solution to adjust the pH above 8.

9.1.3 Study the Performance of Pre-Treatment System in MEG Pilot Plant during Switch over Corrosion Management Strategies (pH Stabilisation to Film Forming Corrosion inhibitor)

- A pH above 8 is required in the MED pre-treatment vessel (MPV) to precipitate calcium ions for field 1.
- For field 2 field, similar pH is required in the MPV to remove divalent ions.
- Addition alkalinity to the MPV resulted an elevated pH in the feed to the reboiler via the rich glycol tank (RGT) and the pH value is further increased in the reboiler after boiling off the carbon dioxide, resulting in a produced lean glycol with a pH above 10 for both field 1 and field 2
- The MDEA downstream the facility was not removed due to the high pH in the reclaimer and it was estimated that about 30 inventory turnovers are required to reduce the MDEA concentration to below 10mM.
- Some scale formation was observed inside the tubing for field 1 conditions. Scale formation was also noticed in the reboiler and on the reboiler heating coil when applying field 2 field conditions.

9.1.4 The performance of Pre-treatment System during switchover experiment (from FFCI to pH and follow up vice versa using a modified HCl dosing point)

- The experimental work undertaken in the MEG benchtop facility has demonstrated the switchover from FFCI to MDEA is feasible with the current operating procedure.
- The dosage rates for sodium hydroxide changed rapidly once MDEA is dosed to the system and returns to the MEG regeneration and reclamation facility. Therefore, extra care is needed for controlling the alkalinity in the MPV.
- The switchover strategy using the modified HCl dosing points was found to be working much faster and more efficient if an additional HCl dosing point is installed in the feed to the reboiler and if the feed is adjusted to pH 6.

- For field 2, it would take about 30 inventory turnovers to remove the MDEA concentration to levels <10 mM. However, with the additional dosing point, the same could be expected in about 10 inventory turnovers.

9.1.5 pH and Alkalinity Control of Lean MEG for Field 3

- The resulting lean glycol pH under both rich glycol operating conditions will pose the risk of subsea scaling if sudden formation water break through occurs.
- Rich glycol pH of 7 should be targeted to minimise the hydroxide and carbonate alkalinity produced in the lean glycol product to reduce the risk of scaling.
- The presence of OS within the regeneration system did not appear to have any significant impact in terms of pH or alkalinity accumulation.
- Through the testing conducted the use of MDEA, it was found to be a strong alternative to KOH for rich glycol pH control as the use of MDEA to control the rich glycol pH produced a far more favourable final lean glycol pH and alkalinity compared to KOH and will ultimately reduce the risk of scaling if sudden formation water breakthrough occurs.

9.2 Recommendations

The following recommendation for future work could be investigated on the MEG pilot plant:

- 1- More experiment work could be done on the MPV section using different operating conditions and parameters such as temperature, pressure and pH.
- 2- Different circulation rates could be used on the MPV circulation heater.
- 3- Different alkalinity controllers could be used on the plant to control the precipitation of divalent salts in the MPV.

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