

# Regeneration and Reclamation of Mono-Ethylene Glycol (MEG) Used as a Hydrate Inhibitor: A Review

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**Abstract:** The use of Mono-Ethylene Glycol (MEG) as a hydrate inhibitor in wet gas pipelines is increasingly becoming widespread, especially in deep-water long-tie back pipelines where the use of low dosage hydrate inhibitor (LDHI) is not practical. MEG is a commonly used thermodynamic hydrate inhibitor (THI), and it prevents hydrate formation by lowering hydrate formation temperature. One significant advantage of MEG over other THIs is that MEG can be regenerated and reused, which minimises the cost of chemicals as large volumes of THIs are usually required. Over the years, significant research advances have been made in MEG recovery and the MEG Recovery Unit (MRU) design. This paper presents a comprehensive review of the evolution of MEG regeneration systems over the years and introduces recent developments, particularly on energy conservation. The entire MEG recycle and regeneration process is reviewed as well as the various sections and their functions. The different MRU configuration are discussed and factors that affect the performance of the MRU as well as Corrosion and corrosion mitigation in the MRU. This review shows that there are a number of new improvements in the MRU application that are yet to be fully explored as well as some technical challenges that are yet to be fully understood.

**Keywords:** Mono-Ethylene Glycol, MEG Regeneration Unit, Hydrate Inhibitor

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## 1. Introduction

Hydrate formation and its prevention remains a technical challenge for flow assurance in wet gas pipelines. Gas hydrates are crystalline solids formed from water and hydrocarbon gases molecules at low temperatures and elevated pressures. Gas hydrates formation starts with a nucleation step where microcrystalline hydrate particles form. They subsequently agglomerate and grow into large structures that may eventually obstruct the flow inside the pipeline. Hence, hydrate prevention and its management is one of the major focuses for flow assurance [1].

A combination of four essential parameters – water, gas, temperature and pressure – must be present within the hydrate stability region, as defined by the hydrate equilibrium curve, for hydrate formation to be initiated [2]. A typical pressure-temperature diagram showing the hydrate stability region and equilibrium curve is shown in Figure 1.

Consequently, eliminating one of the four hydrate formation requisites can prevent hydrate formation. However, as the composition of gas produced from the gas wells and the reservoir pressure cannot be controlled, the hydrate onset temperature is the only parameter that can be controlled with the least effect on the production. Operating at temperatures and pressure outside the hydrate stability region can delay the onset of hydrate formation. Still, the ability to operate outside the hydrate stability temperatures and pressured is vastly limited, especially in deep-water, long-distance tie-backs, of which there have been many developments in recent times. The use of thermodynamic hydrate inhibitors (THI) to reduce the hydrate stability region and increasing the window for operation outside the hydrate region is a common approach for hydrate prevention.

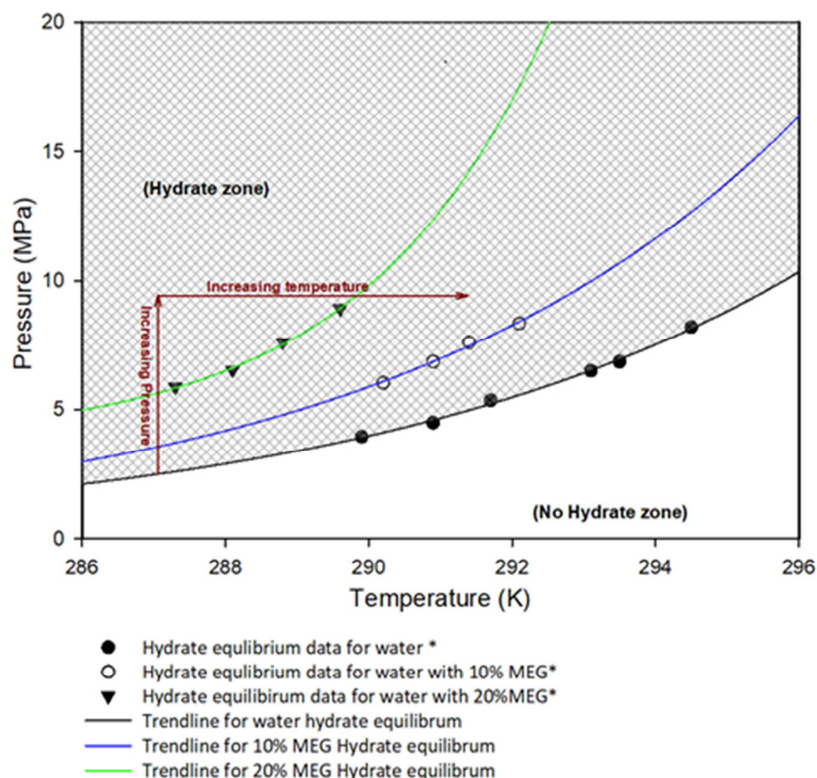


Figure 1. Typical Hydrate equilibrium plot \* Data from [3] and trendlines were determined by polynomial regression fitting.

Additionally, the kinetics of hydrate formation – how fast the hydrates grow and increase in size – can be controlled. There have been positive advances in the application of low dose hydrate inhibitors (LDHI) in the form of kinetic hydrate inhibitors (KHI) and anti-agglomerates (AA) for hydrate management and prevention. KHIs typically have a lactam or caprolactam functional group and they act by suppressing the nucleation and accumulation of gas hydrates [4]. As the name implies, LDHIs are applied in lower dose rates, i.e., between 0.25 to 5 vol. % of the produced water, compared to THIs that are applied in much larger volumes (up to 90 vol%) [5].

While LDHIs have proven effective in hydrate prevention, they are not robust for use across all field applications. The mechanism of hydrate inhibition typically limits the application of AAs to a water cut less than 50 to 75% as they require the presence of a hydrocarbon phase to remain effective [5]. In addition, the efficiency of KHIs appeared to be influenced by the operating pressure. Lederhos et al. (1996) investigated the efficiency of poly(N-vinylcaprolactam) (PVCAP), N-vinylpyrrolidone/N-vinylcaprolactam/N,N-dimethylaminoethyl-methacrylate (VC-713), and N-vinylpyrrolidone-co-N-vinylcaprolactam (VP/VC) at controlling hydrate formation and reported a fivefold increase in hydrate inhibition efficiency when pressure increased from about 6Mpa to 10Mpa while induction times remained unaffected [6]. This study also reported that a reduction in temperature by 8°C, from 285.6 K to 277 K, rendered some inhibitors inactive and that KHIs were more effective at low dose rates and in water with high salt content, such as with seawater and with formation water

breakthrough. Nonetheless, water with high salt content is not favourable in oil and gas production as it increases the corrosivity and complications of fluids separation, resulting in more significant financial implications. On the contrary, Brustad et al. reported that KHIs demonstrated high performance at high pressures [7], highlighting the controversies that still exist in the field of KHI application. Further research effort is needed in this field. AA application also requires further study as they have not been proven to be effective at high pressures [8]. Furthermore, with increasingly strict regulations on global environmental protection, the use of KHI and LDHI are not favoured due to their low biodegradability [9]. Therefore, increasing research focus is now being placed on developing novel “green” LDHIs and KHIs [9, 10].

The application of THIs is much more established as they have been proven effective in other environments, such as antifreeze used in the automotive industry. Research and field experience of THIs in other environment apply to oil and gas production. THIs are effective in most conditions but require a high inhibitor volume and higher handling cost. However, they remain the most viable option in most cases today.

Low molecular weight alcohols and glycols are effective THIs, with Tri-Ethylene Glycol (TEG) and Mono-Ethylene Glycol (MEG) being the most commonly used THIs. Although methanol presents a higher sub-cooling per unit volume used compared to TEG and MEG, but the choice of MEG as a THI in wet gas pipelines is largely favoured because MEG can be regenerated and reused over a number of cycles. THIs are generally used in large quantities, as

much as 20 vol% of combined pipeline liquid phase [11] (combined pipeline liquid phase here means the combination of MEG, water, and liquid hydrocarbon). Hence, the ability to be recycled and reused provides long term economic advantages, making MEG a highly favoured choice for THI.

THIs also provide other benefits, such as reducing the scale formation tendency and corrosivity of the aqueous phase. Fan et al. (2011) demonstrated that MEG and methanol decreased barite scale induction [12]. MEG at 10 wt.% increased the induction time for barite scale formation by 1.5 times compared to water. However, further increasing MEG concentration in the aqueous phase (MEG-water co-solvent) from 10 wt.% to 30 wt.% had little effect on induction time of barite nucleation. MEG also increases the induction time for the formation of the  $\text{CaCO}_3$  polymorphs [13]. Methanol at 10 wt.% was also effective in scale inhibition as it increased the scale induction time by 1.4 times compared to water. On the other hand, the efficiency of methanol was highly affected by its concentration in the aqueous phase (Methanol-water cosolvent). An Increase in methanol concentration from 10 wt.% to 30 wt.% resulted in a 35% increase in scale induction time. This study showed that both THIs demonstrated a positive effect on hydrate inhibition and scale inhibition.

While methanol was shown to inhibit hydrate formation more effectively than MEG, MEG offers another benefit, i.e., corrosion rate reduction. The corrosion inhibition property of MEG is considered a great benefit to flow assurance. The corrosion inhibition afforded by MEG is further discussed later in section 4.1.3.

## 2. MEG Recovery Unit (MRU) Operational Sections

The process of recycling MEG is commonly referred to as MEG recovery. Rich MEG returning from pipeline and process facilities enter the MRU with high water and salt content and is processed into lean MEG with lower water and, occasionally, salt content for re-injection into the pipeline near the wellhead. Rich MEG typically has 30-50% water content whereas lean MEG typical has less than 20% water content [15]. The entire MEG recovery process consists of three dominant sections. These are pre-treatment, dewatering and desalination. The dewatering process is commonly referred to as regeneration, while the desalination process is referred to as reclamation. These words may be used interchangeably in the rest of this paper.

### 2.1. Pre-treatment

The aqueous phase returning from the gas pipeline is a mixture of MEG, water, and other water-soluble components. This feeds into the MRU for the recovery of MEG. However, the critical function of the MRU is the separation of MEG from an aqueous phase of water and salts; hence, MRUs are generally not equipped to handle other water-soluble

contaminants from the pipeline and process that may partition into the aqueous phase. It is, thus, critical to minimise the quantity of contaminants entering the MRU. For this reason, the pre-treatment process upstream of the MEG regeneration and reclamation units is required.

The common contaminants found in oil and gas pipelines and process aqueous phase are entrained hydrocarbons, corrosion product scales, and residual pipeline chemical additives such as scale, dissolved ions from produced water and corrosion inhibitors. These contaminants can cause fouling and MRU process upsets and they are removed from the rich MEG stream as a first step in the MRU before the dewatering and desalination processes [14].

The pre-treatment in the MRU starts with the separation of entrained hydrocarbons from rich MEG, which is not typically fully separated in the gas process slug catcher. The presence of emulsion is common due to many reasons. Agitation from high production flow rate or pressure differentials within the flow line can stabilize emulsions of hydrocarbons and MEG. A second factor that facilitates the formation of hydrocarbon in MEG emulsion is the low operating temperature typical of gas pipelines, as reported in a MEG regeneration technical meeting (2009) [15]. Other contaminants like chemical treatment residuals (i.e., corrosion inhibitors), naturally occurring surfactants from the reservoir, and suspended particles also stabilize hydrocarbons in MEG emulsion [14].

The process upsets in the MRU as a result of emulsion is frequently reported [16-20]. If the emulsion phase is not fully separated, light hydrocarbons can flash off during the regeneration process, resulting in a decrease in the system operating temperature and contamination in the MRU water streams [21]. The heavy hydrocarbons, on the other hand, can accumulate in the MRU bottom MEG stream resulting in increased MEG viscosity and fouling in reboilers and heat exchangers [14]. The increase in MEG viscosity can also enhance loading on MEG recycle pump. The entrained hydrocarbons were reported to stabilise suspended particles in the MEG stream and make it difficult to settle out these particles [22]. Burping in MEG distillation column is also frequently associated with entrained hydrocarbon carryover in MEG [15]. Burping occurs when there is periodic build-up and collapse of a vapour blanket in the distillation column. when built-up, the vapour blanket causes localised increased pressure preventing further boiling until the blanket collapses; these cycle of increase and decrease in pressure results in severe flooding that increased the product loss in the distillate stream [23].

Methods to demulsify hydrocarbon in MEG emulsion and removal of entrained hydrocarbons in MEG are dependent on the type of emulsion formed. According to Latta 2018 [24], fractional interface coalescence efficiency ( $f_{ice}$ ) is used to determine methods and equipment for minimising hydrocarbon content effluent in the aqueous phase. A high  $f_{ice}$  means that the dispersed phase in the emulsion has a high propensity to coalesce and separate from the aqueous phase, and vice versa. Hydrocarbons with higher API gravity

generally have a higher  $f_{ice}$  and separation can be easily achieved by gravitational separation in a settling tank with minimal residence time. In a series of lab bottle tests, liquid iso-paraffin with API gravity of 53.2 completely separated from MEG-water mixture in under one minute after shearing was stopped [25]. For this type of light hydrocarbon, a settling tank with a skimming pump may be sufficient to remove entrained oil upstream of the MRU; especially when there is the facility to maintain or provide warm temperature as well as baffles/weirs to allow for separation of the hydrocarbon phase in the settling tank. A more difficult case of separation is experience with heavy oil with low API gravity [26], in this case the  $f_{ice}$  for the emulsion is low and complete separation requires the use of multiple size exclusion filters.

A second major pre-treatment step in the MRU is the removal of low solubility divalent ion salts from the rich MEG. Common divalent ion salts found in the MRU are carbonate scales of calcium and magnesium ions, which have very low solubility and readily precipitate at high temperatures. As such, there is tendency for carbonate scale precipitation in unfavourable high temperature regions like the reboiler and/or pumps. As MEG is heated, the dissolved  $CO_2$  is removed causing the pH to rise. A one unit increase in pH across the MEG reboiler inlet and outlet has been reported [27]. At these high temperatures and pH, the residual divalent cations can precipitate in the MRU as carbonate scales, which are hard to clean up and can cause fouling and gunking. For this reason, the precipitation of these divalent ion salts is usually controlled so they are easily removed from the system.

Seiersten and Kundu 2018 published an extensive review on the scale management in MEG systems [28]. In brief, rich MEG is slightly heated to about 50-60°C and dosed with a hydroxide or carbonate alkali to increase its pH to facilitate the precipitation of divalent ions such as calcium, magnesium, iron, and strontium [28]. The precipitates are given time to settle in the settling tank and suspended particles are removed alongside any other particles in the final step, i.e., filtration.

However, most but not all MRUs have this pre-treatment step. If the MRU has other means of handling salt precipitates prior to the dewatering stage, this pre-treatment step may not be required. With other MRU design configurations that do not have a salt handling capability upstream of dewatering in a distillation column, this pre-treatment step is crucial to minimize scaling in the reboiler and associated pumps. Nonetheless, the use of scale inhibitor is recommended for all MRU reboilers [28, 29].

Filtration is the final pre-treatment step to remove any oil wetted fine solid particles that may be suspended in the rich MEG upstream of the MRU, following the alkali treatment of rich MEG to precipitate the divalent ion salts. These particles also include corrosion products accumulated from the pipelines as reported by Soames et al (2019). These particles demonstrate strong tendency to remain afloat when they are oil wetted [22]. Filtration ensures that all these

very fine particles do not enter the MRU, where they can cause fouling [26].

## 2.2. MEG Dewatering

A critical function of the MRU is to reduce water content from its feed rich MEG stream to produce a lean MEG stream with much less water content. The rich MEG stream typically holds 40-50 wt.% water while the lean MEG stream typically holds less than 20% water [30]. The dewatering of rich MEG to lean MEG is thus a vital step in the MEG regeneration process. Due to the difference in boiling points of MEG and water (100°C @1 atm for water and 197°C @ 1 atm for MEG), the dewatering step is achieved by reflux distillation in an atmospheric distillation unit. A typical MRU distillation column operating temperature is about 120°C. Considering that there is a relatively low vapour load during dewatering, the packed distillation column is the most commonly used as it can maintain a low pressure drop and achieve high efficiency of separation with the expected vapour load [31]. Important factors to consider during MEG dewatering are the windows for operating temperature, pressure and MEG salt loading. The window for operating temperature must be balanced to achieve required separation efficiency with consideration for MEG degradation onset temperature and process energy consumption [32]. MEG losses as a result of thermal oxidative degradation can impact operating cost for regular MEG top-up [32] and cause process upsets due to the reduction in pH as organic acids are degradation products of MEG [27].

The energy requirement for dewatering MEG using the conventional distillation method is significant and can account for up to 60% of the energy consumption of the entire MRU. Reducing energy consumption while achieving efficient dewatering remains a challenge. Pries et al. (2020) compared the Destubcal technology, a falling film distillation method, with conventional distillation [33]. The technology allows uniform temperature distribution along the distillation column, hence more effective energy usage. According to Pries et al. (2020) the Destubcal technology consumed 46.3% less energy than the convention distillation column to concentrate 66 wt.% (rich) MEG to 88.61 wt.% (lean) MEG. Destubcal technology reported by Pries et al. (2020) is a series of distillation tests performed with a single tube falling film distillation column assisted by a thermosyphon system operating at atmospheric pressure [33]. this technology is yet to be deployed commercially and the effects of salt loading and possible fouling of tube walls were not evaluated in this study.

Recent research developments have also investigated the membrane distillation method as another low energy alternative for dewatering MEG [34]. Membrane distillation is a combination of thermal distillation and membrane technology in which volatile vapour is transferred from a hot aqueous distillation bottom through a microporous hydrophilic membrane because of the partial pressure difference created due to the temperature difference on both sides of the membrane [35]. In 1999, Rincon et al. confirmed

the feasibility of the membrane distillation for water-MEG separation from used coolant liquid [36]. Later in 2005, Mohammadi T. and Akbarabadi M. used vacuum membrane distillation to reconcentrate MEG from used coolant solution using a flat-sheet polypropylene membrane [37]. Vacuum is applied to create the required vapour pressure difference across the membrane to drive a flux during distillation. With this process, Mohammadi T. and Akbarabadi M. distilled water (with less than 1 wt.% MEG) from 60 wt.% MEG solution at 60°C. The vacuum membrane distillation technology demonstrated promising results in recovering used coolant liquid but much research is still required to apply this technology in the THI application where a high salt loading is expected.

In 2019, Ajdar et al. explored the use of air gap membrane distillation to dewater MEG. In this technique, a stagnant air gap between the membrane and a condensation surface inside the distillation unit generates the flux required to drive the separation [34]. One major advantage of the air gap membrane distillation over other types of membrane distillation is that there is no contact of the permeate (i.e., top distillate) with the membrane, thus resulting in a relatively higher flux, less fouling tendency, and less heat loss [38]. The permeate is the vapour that passes through the membrane and is recovered as a top distillate and the permeate flux is the quantity of the permeate produced per unit time and unit membrane area [39]. Ajdar et al. used a polysulfone hollow fibre membrane surface coated with polydimethylsiloxane to improve hydrophobicity and was able to achieve a 26 kg/(m<sup>2</sup>h) permeate flux rate. Energy consumption figures were not published for this membrane distillation technology as it is yet to be scaled up for commercial application.

### 2.3. MEG Desalination

After the pre-treatment and dewatering steps, the lean MEG stream generally has low water contents (<20 wt.% on a salt free basis) and low divalent salts. However, in some cases where the pre-treatment step is absent before the dewatering step, divalent salts concentration can still be considerable. Prior to reinjecting the lean MEG into the pipelines, these salts need to be removed to below acceptable limits. The final process of the MRU is the desalination.

The desalination of MEG in the MRU is the removal of salts from MEG, commonly achieved by the difference in volatilities of the salts and MEG. The desalination process is classified into monovalent and divalent cation salts removal. The principles of divalent salts removal have already been discussed in the pre-treatment section. When the concentrations of divalent ions are low and do not reach the saturation points of carbonate scales, the scaling tendency is low. In this case, divalent ion salts can be removed together with the monovalent ion salts in the desalination step. Otherwise, the removal of the divalent ions is usually accomplished as part of the MRU pre-treatment section, where the mono-valent ion removal is usually stand-alone in the desalination unit.

Monovalent ion salts (most commonly sodium and potassium chlorides) are usually very soluble with less tendency to cause fouling in the system. However, regardless of solubility, they need to be removed from the MEG stream to avoid build-up.

The conventional desalination process involves the recovery of a solvent by boiling. The boiling point of pure MEG at one atmosphere is 197°C. However, MEG thermal oxidative degradation reportedly occurs at 162°C [40]. Therefore, heating MEG to its boiling point of 197°C is not a viable option as this can lead to MEG losses due to degradation and adverse effects from the degradation products, which are volatile fatty acids. Additionally, raising MEG temperature to 197°C requires large energy demand and thus operational cost. Hence, vacuum evaporation is employed to evaporate MEG at a relatively lower temperature (e.g. < 150°C) to minimise the aforementioned downsides.

Several other technologies with potential to reduce energy demand have been investigated. Among them, ion exchange for MEG desalination has gained research attention as a possible means of lower energy desalination. One of the earliest publications on ion exchange for MEG MRU desalination is the patent developed by Phelps D. W. and Fernandez L. in 2012. This patent presented a system to remove divalent cations from rich MEG using a cation exchange resin that adsorbs the divalent cations in the rich MEG prior to its entry into a flash separator [41, 42]. In 2020, He S. et al., published their work on an electrically regenerated mixed bed ion exchange resin for MEG desalination [43]. Ion exchange for MEG desalination is claimed to be less energy intensive compared to the volatility-based desalination by heating under vacuum. Further, electrically regenerated resin consumes less chemical for resin regeneration compared to conventional chemically regenerated ion exchange resins. More so, He S. et al. proposed the use of much less voltage for ion backward migration, which eliminated the need for ultra-pure water. In their work, 70wt% MEG with 47.1mmol/L NaCl rich MEG composition was used; After regeneration of the resin bed for 1 hour at a voltage lower than 73 V, 33.83% of NaCl in 5.16 bed volume (BV) simulated rich MEG liquid was removed. After 15 cycles of repeated operation, the performance of the resins remained stable. The result indicated that the electrically regenerated mixed-bed ion exchange could be a promising prospect for MEG desalination in deep-water gas field operations. In recent times, research has shown a successful application of an ion exchange technology for MEG desalination [43]. The technical challenge as of today is the development of efficient regeneration of the ion exchange resin used for the MEG desalination.

## 3. MEG Recovery Unit (MRU) – System Operation and Design

There are various MRU units around the world with

different design configurations. This section discusses key MRU designs.

MRU design configurations can be largely classified into three major categories.

- Traditional MRU designs with dewatering in a distillation column and no desalination capability (Figure 2);
- Integrated MRU designs with a flash drum for desalination prior to dewatering in a distillation column (Figures 3 and Figure 4);
- Reclamation and regeneration MRU design with a desalination unit downstream of the distillation column (Figure 5).

### 3.1. Traditional MRU Design

The traditional MRU design closely resembles system previously used for Tri-Ethylene Glycol (TEG) regeneration in TEG dewatering applications. Some of these early MRUs were actually retrofitted versions of the TEG regeneration unit [7]. This MRU design is essentially a distillation column that separates water from MEG and has no desalination capabilities, as described schematically in Figure 2. The rich

MEG skimmer in this diagram is not unique to this design configuration and is meant for the removal of carryover hydrocarbon in MEG as a pre-treatment.

The main challenge with the direct transfer of technology from TEG regeneration to MEG regeneration is that TEG was mainly used in gas dehydration units with little dissolved condensed water and salt contents. On the contrary, MEG is used in gas fields where formation water or seawater breakthrough is possible. Formation water is water associated with the oilfield reservoir formation and can hold total dissolved solids generally more than  $10^5$  mg/L [44], with a high concentration of divalent ions (primarily calcium and magnesium salts). While this traditional MRU design is simple, compact, and easy to deploy, it is not suitable to handle the high salt content in rich MEG, as it has led to multiple reports of scaling and reboiler fouling [7]. A salt slurry may be occasionally removed by de-bottoming the settling tank in Figure 2. However, it is worth mentioning that there are plenty of examples of MRU which do not handle formation water in which case, MEG had been recovered and recycled for nearly 30 years with minor top-up [45].

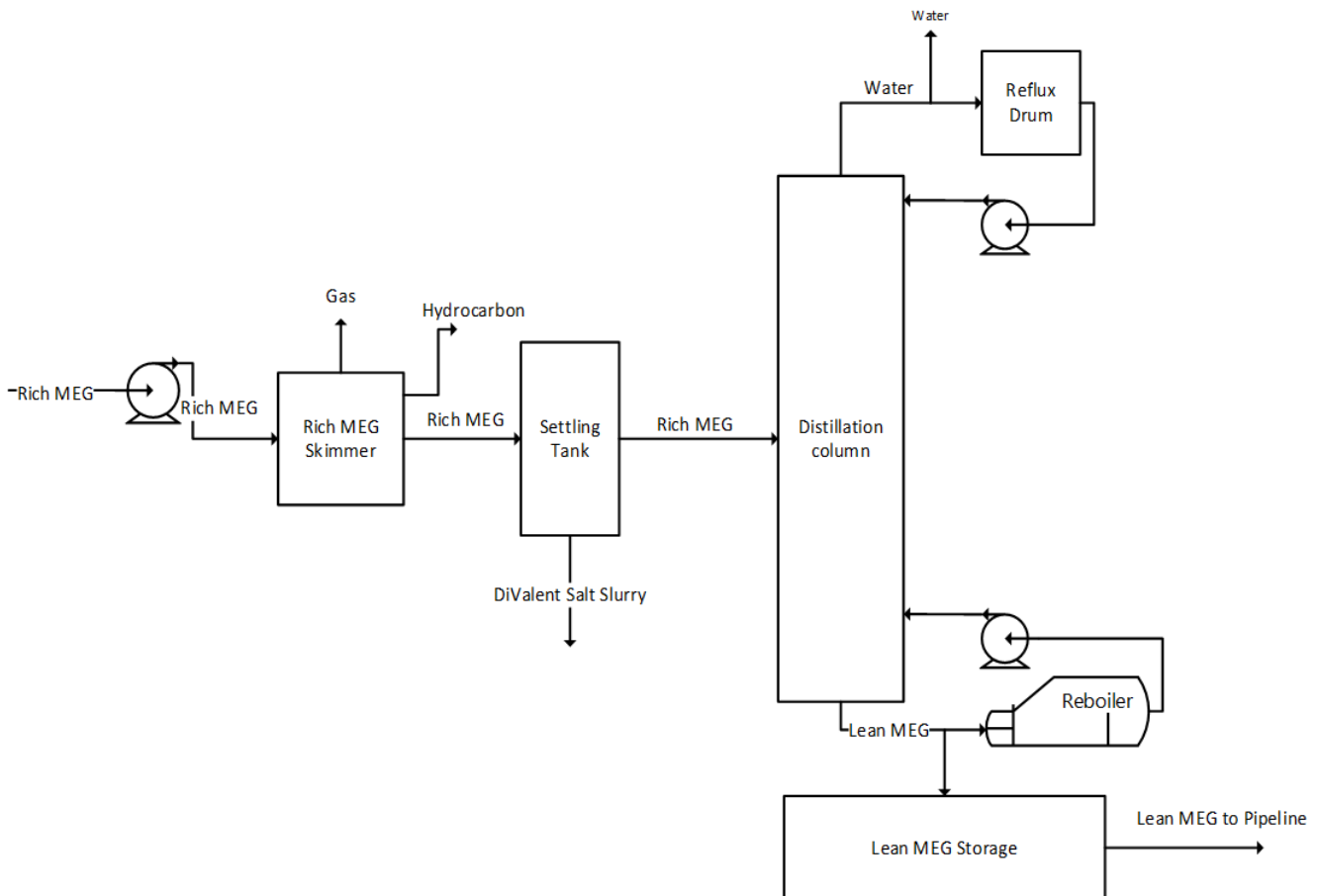


Figure 2. Traditional MRU design.

When salts are present, the traditional MRU system needs to be regularly replenished with fresh MEG to maintain salt content within a threshold. The replenishment process

minimises the accumulation of salt content after MEG has been circulated for a period of time. However, the salt content still reportedly accumulates beyond its solubility



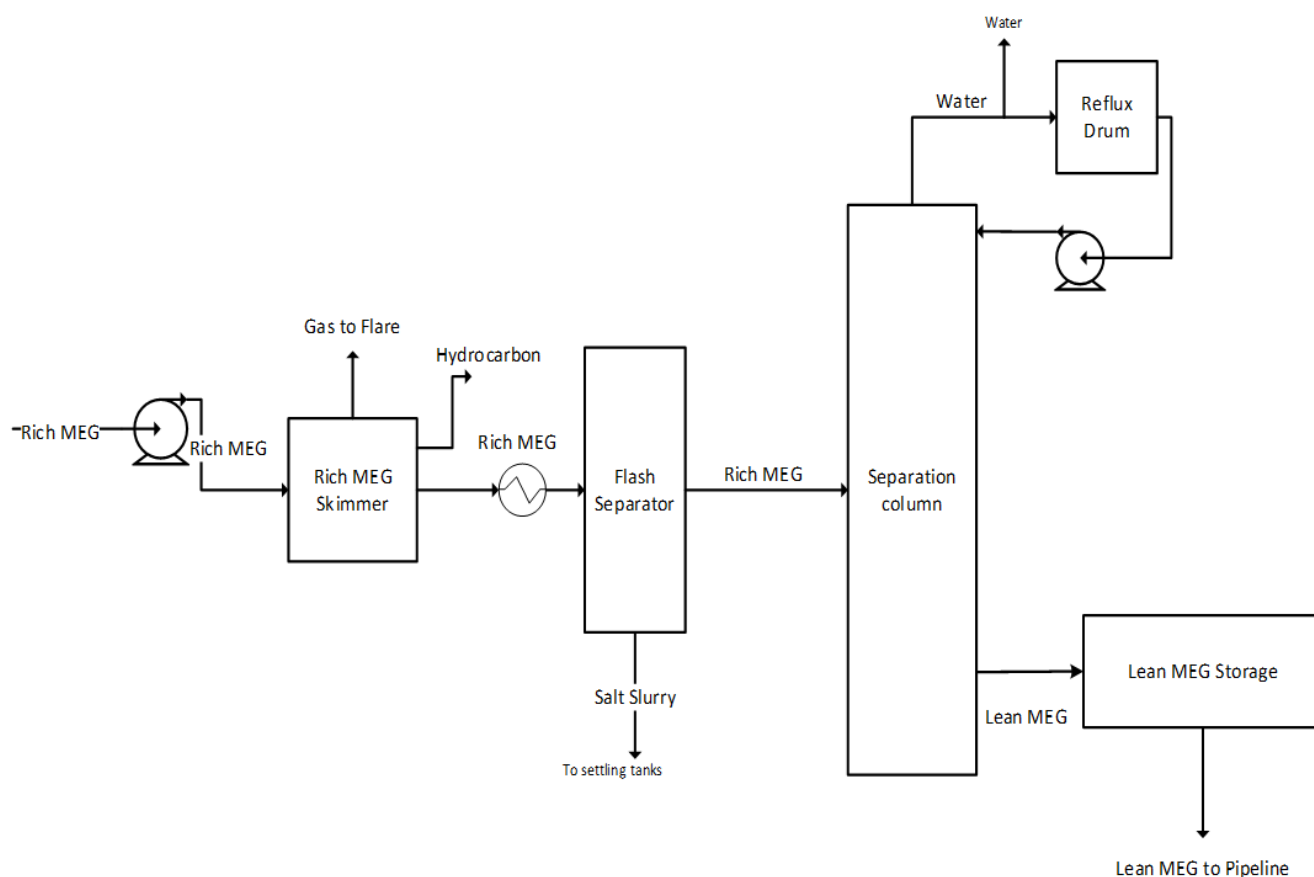
limits in the MEG stream, especially in facilities that have formation water breakthrough. Consequently, salts precipitate at undesirable points either in the production pipeline, topsides or even in the MEG cycle, causing blockage and process upsets. Brustad et al. reported the case of scaling in the MRU inlet heater, column and reboiler with this traditional MRU configuration and formation water in the Statoil operated Troll (Kollsnes) gas plant [45, 46]. The scaling problem encountered with the traditional MRU design prompted a modification to improve the effectiveness of the MEG recovery process. High MEG waste and losses are also drawbacks of this MRU system, frequent replacement and top-up are required with salt accumulation and salt slurry removal within the system [45, 46].

### 3.2. Integrated MRU Design

The integrated MRU design was introduced to reduce scaling problem in the MEG regeneration distillation column by desalinating rich MEG upstream of the distillation column. Nazzer and Keogh (2007) describes this design configuration as used in New Zealand's Maui gas plant in the early 90s and the schematic of this design is

shown in Figure 3 [47].

In this design configuration, rich MEG is desalinated in a flash separator operating under vacuum and about 100°C temperature [48]. Hayhoe (1993) did not specify vacuum pressure for operation, but Boschee (2012) reported operating the flash separator between 3 to 4 psia and about 135°C at the Independence Hub FPSO in the Gulf of Mexico [26]. As MEG with its high salt content enters the flash separator, salt free rich MEG flashes off overhead the separator leaving the salt slurry at the bottom of the separator. The salt slurry is then syphoned to a settling tank to allow salts to crystallize. Recovered MEG from the settling tank is recirculated back into the flash separator by mixing with the rich MEG post the skimmer tank. The overhead salt-free rich MEG vapour is then further concentrated in a vacuum distillation column downstream of the flash separator. The benefits of this design configuration are two-fold. It reduces the salt loading in the MEG distillation column and design eliminates the need for a reboiler in the distillation column as the rich MEG enters the column as vapour. Hence, it is easily fractionated into distilled water and lean MEG at the overhead and bottom of the column, respectively.



**Figure 3.** Integrated MRU Design: extracted from Schlumberger PureMEG unit - Cameron, a Schlumberger company proprietary design [15, 51].

Nonetheless, Nazzer and Keogh et al. reported that the flash separator bottom recycle stream encountered a very high salt content resulting in scaling inside the recycle pump [47]. Boschee 2012, also reported that high divalent salt content, especially calcium ions, increased the viscosity of

the flash separator recycles MEG stream putting more strain on the recycle pump. As a result, the viscous MEG stream had to be periodically replenished. The replenishment increases operating cost as well as significant environmental cost to dispose used MEG [26].

A variation of the integrated MRU design was developed to minimise scaling at the recycle pump [49, 15]. In this variation, a downcomer extension is connected to the bottom part of the flash separator as shown in Figure 4; the recycle pump is positioned higher than the flash separator downcomer. Due to differences in density and gravity of MEG with varying salt content, the high salts concentration MEG pools to the bottom of the downcomer [49]. Therefore, the recycle pump which is positioned above the downcomer receives MEG in low salt content. This design may also include an integrated slip stream divalent ion removal system in which divalent ions can be precipitated by pH adjustment with chemical treatment.

### 3.3. Regeneration and Reclamation MRU Design

A schematic of a third MRU configuration is shown in Figure 5. For this MRU design configuration, divalent salts are first removed in the settling tank (pre-treatment). Subsequently, MEG is dewatered in a distillation column. Lean MEG then is desalinated under a vacuum-operated flash separation downstream of the distillation unit. MEG is evaporated in the desalination unit, thereby reducing the salt content in reclaimed MEG. Original MEG reclamation units

are based on vacuum evaporation and crystallization where MEG is heated, under vacuum, to temperatures below 150°C. MEG is flashed off, leaving salts and non-volatiles in the flash drum.

The major advantage of this configuration is that it can interchange between a full stream or slipstream reclamation. The full stream is when the entire MEG stream passes through the desalination unit, while the slipstream reclamation accommodates only a fraction of the MEG stream. A slipstream reclamation operation is suitable when salt contents are low, i.e. an early well life. As the formation water starts to break through, the salt content rises, and the operation can be switched to the full stream reclamation. Other benefits of this design include the independence between each process. The desalination unit, whether full or slipstream, does not impact the operation of the distillation [51]. This is because the removal of water in the distillation column amounts to less volume of lean MEG requiring desalination compared to the volume of rich MEG being desalinated in design configurations 1 and 2. The small desalination unit is beneficial as it requires lower capital costs and less space requirement [51].

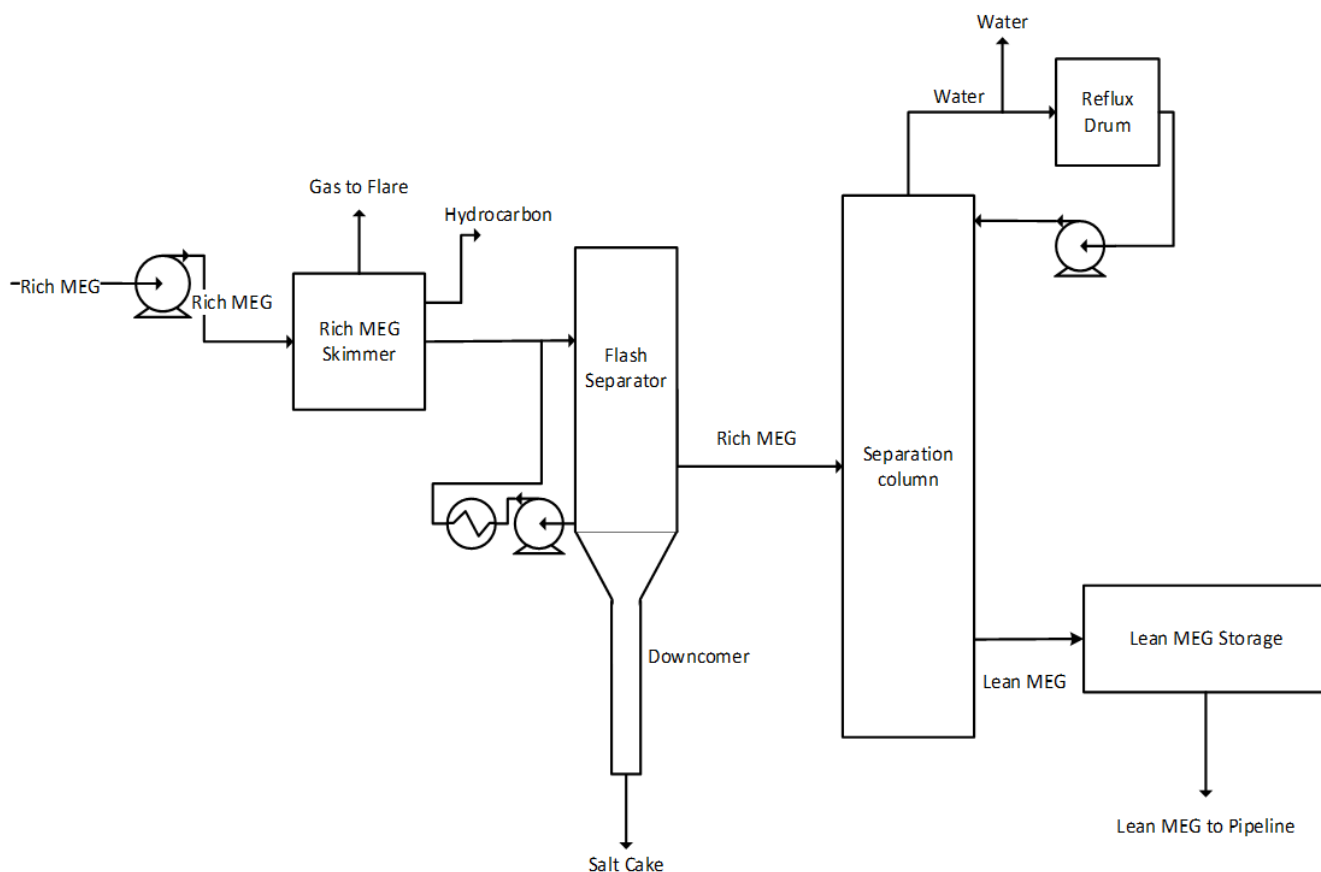


Figure 4. Integrated MRU design with downcomer extension to the flash separator.

MEG reclamation is an energy intense system. It was calculated that energy efficiency in an MRU drops about 1% when a slip stream reclamation unit is added to a regeneration only MRU and about 5% when a full stream

reclamation is employed [52]. As a result, a slip stream reclamation system is commonly employed to minimise energy consumption and optimise overall efficiency.



## 4. MRU Factors and Efficiency

Simply put, the efficiency of a system is a measure of the system's ability to convert its inputs into the desired output. For an MRU, the desired output is the lean MEG meeting certain pre-defined specifications, whereas the input is rich MEG returning from the pipeline. Factors and efficiency discussed in this section address general operational issues that may not have been mentioned earlier in this paper but impact the efficiency and the feasibility of the entire MRU process. Key factors affecting the efficiency of the MRU are the quality of rich MEG and the specification for lean MEG. There is limited control over the quality of rich MEG returning from the gas pipeline. However, understanding the impact of pipeline flow assurance events on the quality of rich MEG and consequent effects on the MRU is crucial. The specification for lean MEG output from the MRU, on the other hand, can be defined to achieve thermodynamic hydrate inhibition, preventing scaling, corrosion and fouling inside the pipeline, and minimising cost implications for operating the MRU. Some of the essential lean MEG specifications that need to be defined are minimum MEG content, salt content, organic acid content, dissolved oxygen content, recyclable

chemical additives, such as pH stabilizers, corrosion inhibitor and scale inhibitor residuals, etc. [53].

### 4.1. MEG Quality

The MEG system is a closed-loop process. Consequently, the quality of MEG in the MRU and that of MEG in the pipeline are interrelated. The performance of the MRU determines the quality of its lean MEG output while the rich MEG returning from the pipeline feeds the MRU and, in turn, influences the efficiency of the MRU to produce the required quality lean MEG for re-injection into the pipeline. The suppression of the hydrate onset temperature and delay in hydrate formation time by MEG depends on produced gas composition, MEG concentrations, and quality [54-57]. Thus, the percentage of MEG in lean MEG output from the MRU should be high enough to suppress the hydrate onset temperature. As a general rule of thumb, the industry application of lean MEG is somewhere between 80-95wt% MEG content. A more accurate determination of the MEG-hydrocarbon vapour phase equilibria can be predicted by thermodynamic modelling [56] or simpler empirical correlations [54, 58].

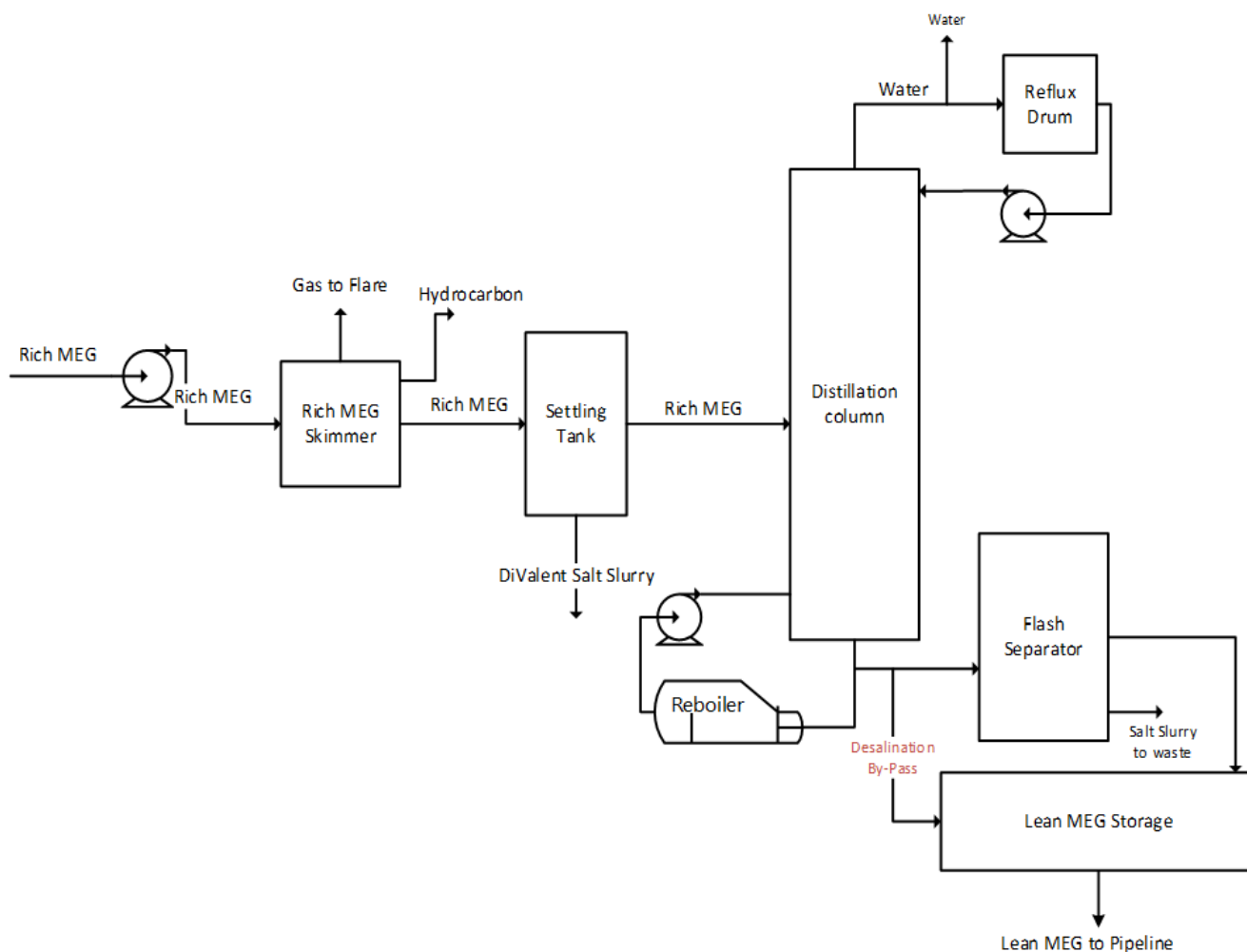


Figure 5. Regeneration and Reclamation MRU design.

The salt content in the lean MEG may contribute to its hydrate inhibition effect. Lee and Kang (2011) reported that the addition of 3.5 wt.% NaCl in MEG reduced the hydrate formation temperature by 2.8-3.2 K. Masoudi et al. (2005) also showed that the presence of hydrated chloride salts in MEG increases hydrate inhibition efficiency [59]. Even though high concentrations of salts have not been experimentally tested for this synergistic effect, salts are not expected to contribute to hydrate formation in the pipeline. However, salts above their saturation point in lean MEG will deposit inside the pipeline causing a build-up of scale and fouling, which can be difficult and costly to clean up. The primary culprits contributing to scaling are carbonates of low solubility divalent ions; these salts will cause scaling and fouling in the MRU as discussed under MRU pre-treatment and scale-up inside the pipeline. Studies have shown specific divalent ions are more insoluble in the presence of MEG [53] [60]. As it is a close loop system, the divalent ions can accumulate and over-time exceed their saturation points, causing scaling of the pipelines and MRU.

Organic acids are inherently present in some hydrocarbon fields and also are a by-product of the thermal oxidative degradation of MEG, which is accelerated at high temperature conditions such as in dewatering and desalination processes within the MRU [61, 62]. As mentioned, the thermal degradation of MEG starts at 167°C. Moreover, salt and long-term exposure are shown to reduce the degradation onset temperature and also increase the rate of thermal degradation. Monteiro et al. (2019) used an experimental simulation of an MRU flash separator to show that MEG degrading at temperatures below 140°C and the percentage of MEG degraded after 56 hours of long-term exposure sharply increased to 21.1% when the salt content increased to 5.52 wt.% [63].

Aside from thermal oxidative degradation of MEG, organic acids may also enter the MRU from the pipeline condensed water phase or formation water [30]. The presence of organic acid in lean MEG poses several operational issues, including bottom-of-line and top-of-line corrosion of carbon steel pipelines and process equipment [64, 65]. The organic acid content in MEG also reduces hydrate inhibition efficiency of MEG. AlHarooni et al. (2017) reported that organic acid content in MEG as a result of thermal degradation even in neat MEG increases the hydrate onset temperature by up to 2.6°C at 50 bar [66]. The removal of excess organic acid can be achieved during desalination and dewatering if the pH within the system is adequately controlled [26, 67].

In principle, closed-loop MRUs operate under oxygen-free conditions. However, oxygen contamination is not uncommon. The presence of oxygen in aqueous phase can accelerate thermal degradation of MEG and cause corrosion of both carbon steel and corrosion resistant alloys (CRAs). Dissolved oxygen concentration as low as 52 ppb initiated corrosion at stainless steel weldments due to the strong oxidizing effect of oxygen [68]. Ferrite dissolution and

crevice corrosion were reported for duplex stainless steel with 620 ppb oxygen in salt-saturated MEG at 108°C [69]; highlighting the detrimental impact of dissolved oxygen in MEG on pipelines and process equipment. The dissolved oxygen in MEG is thus a major cause for concern in MEG regeneration and injection into the pipelines.

#### 4.2. MEG Loss in the MRU

The primary culprit for MEG losses in the MRU is the loss during hydrocarbon condensate skimming due to emulsification of MEG and condensate [70]. MEG loss also occurs during the dewatering step in the distillation column. The sudden changes in the column reflux level and accumulation of the water condensate increase boil-off liquid from the reboiler [21, 70]. Consequently, more MEG in the reboiler is vaporised and lost to the reflux drum. However, Son et al. showed that the desalination step (salt removal by centrifuge) in the MRU system with design configuration 2 led to more MEG losses than the dewatering step [32]. From desktop modelling, the desalination step accounts for up to 221 \$(/kg/h) of MEG feed, whereas the dewatering step accounts for up to 25\$(/kg/h), without factoring in MEG loss during dewatering due to fluctuations in the distillation column reflux rate [32]. At the cost of 1250 \$ per tonne of MEG in Son et al.'s work, these losses amount to 176.8 kg MEG/h during the desalination and 20 kg MEG/h during the dewatering step. These results showed that the desalination could cause significant MEG loss from removing the precipitated salt slurry. Conversely, Kim et al. (2019) reported operational losses of 1.8 m<sup>3</sup> MEG/month in the reboiler [70]; assuming uninterrupted operation of 24 h in a 30-day month, which amounts to 2.5 kg/h. Kim et al. (2019) reported that MEG loss in the operating facility was reduced by up to 75.2% when freshwater was introduced into the distillation column reflux system [70]. Another significant factor contributing to MEG loss in the MRU is accumulation of highly soluble salts in the reclaimers. Examples are salts of organic acids like sodium acetate, which can accumulate to 10 wt.% [15]. or more and thereby increase the boiling temperature and the viscosity of the liquid in the reclaimers to levels that are not manageable. The only solution today, seems to be bleeding of the reclaimers slurry. This bleeding amounts to significant loss of MEG. Another process that leads to MEG loss, albeit a small quantity, is the thermal degradation of MEG.

#### 4.3. Corrosion and Corrosion Mitigation in the MRU

Corrosion mitigation remains a technical challenge for maintaining the asset integrity of the MEG system. High process temperatures, high shear stress, produced or formation water, and acid gases can cause corrosion concerns with the MRU construction materials [71].

The material selection and metallurgy for use in the MRU generally takes into consideration operating conditions of the

MRU, e.g., operating temperatures, presence of acid gases in the system (if any), the salt loading and potential contaminations of the liquid phase at any point in the system, and the capital cost of the unit. Corrosion resistant alloys (CRA) are generally used in parts of the MRU where a high salt loading or low pH resulting from acid gases is expected [72]. While oil and gas pipeline metallurgy and material selection are widely published [53, 73], there are limited reports on the specific material used in MRUs. However, austenitic stainless steel (UNS S31600/03) and duplex stainless steel (UNS S32205) is relatively common, as well as Inconel® alloy 625 grade steel (UNS N06625) [72, 74-76].

For example, the overhead of the distillation unit is exposed to distilled water from the dewatering process and acid gas, especially CO<sub>2</sub>. As such, this area is prone to acid gas corrosion, and the use of CRAs would be appropriate [67]. Latta et al. 2016 mentioned an operational example of the use of carbon steel in an MRU dewatering overhead being “severely corroded”, albeit corrosion rate figures were not reported in their publication [14].

For carbon steel, such as in pipelines, corrosion mitigation uses either a film forming corrosion inhibitor (FFCI) or pH stabilization. FFCI is a surfactant that forms a thin inhibitor film on the metal surface and as a protective layer, suppressing corrosion of carbon steel. pH stabilization prevents corrosion in two ways; first, by neutralizing acidic components in the aqueous phase, eliminating the cathodic reaction and reducing the corrosion rate. Secondly, by stabilizing pH at about 8 – 9, the formation of FeCO<sub>3</sub> is facilitated. The adherent FeCO<sub>3</sub> then acts as a barrier to prevent corrosion [77]. The optimal operating pH range in MRU is where corrosion is suppressed, but the scale precipitation is not facilitated. The effects of temperature on corrosion of carbon steel components in the MRU can be complex. The consensus is that the corrosion rate of carbon steel can be effectively reduced in MEG at lower temperatures but not at elevated temperatures, such as in the reboiler condition.

Corrosion rates increase with increasing temperature when the protective corrosion product scale does not form. A 2.8 times rise in the corrosion rate of carbon steel in rich MEG solutions was reported when temperature was increased from 25°C to 60°C [78]. A similar trend was found when the temperature was raised from 80°C to 120°C in lean MEG solutions (80 wt.% MEG) saturated with CO<sub>2</sub> [79]. Even though the corrosion rates markedly reduced from 15.25 mm/y in MEG-free solutions to 3.18 mm/y (80 wt.% MEG) under the same condition, the resulting corrosion rate was still much greater than the accepted industry standard of 0.1 mm/y. Another study mimicked the reboiler condition with N<sub>2</sub> atmosphere [78]. In this case, the corrosion rate was much milder (0.43 mm/y) and was effectively mitigated with the pH stabilization method using mono-ethylamine.

However, most literature on corrosion in MEG solutions has focused on carbon steel and not on the corrosion of MEG on other construction metals, such as duplex stainless steel

and other corrosion resistant alloys (CRAs), especially for corrosion in the MEG regeneration context. Indeed, further research is needed to fill the current gaps.

## 5. Summary

As MEG is widely used as a hydrate inhibitor, its regeneration and reclamation processes become vital to the overall natural gas production and processing. A review of this process is presented in this paper, which covers the use of MEG as a hydrate inhibitor and the need for regeneration and reclamation, MRU processes and the common MRU design configuration. Important factors affecting the efficiency of the MRU system were also discussed. Despite considerable research on the design and operation of the MRU system, there seems to be significant gaps in some specific aspects of the MRU operation, as highlighted below.

Frequent fouling in the MRU remains a technical challenge with MRU operations; the cause of fouling and a credible prevention method is yet to be fully studied and understood. MRU treatment chemical additives has been suspected to contribute to fouling. However, the mechanism of this fouling is yet to be fully understood. There is also a significant knowledge gap in the mechanism of MEG degradation during MRU operation, with or without chemical additives. More work is required to explore the potential corrosive behaviour of thermally degraded MEG for MRU asset integrity.

Foaming and emulsion are also major challenges with MRU operations as it minimizes the efficiency of the MRU. The presence of foaming and stable emulsion formation in the MRU are frequently reported but no systematic study has been conducted to elucidate the causes of these incidents and prevention methods. Besides, the interaction of MEG with pipeline fluids causing foaming and stable emulsion could be further explored.

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