Technologies for Mercury Management in Operations

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Abstract

Mono-ethylene glycol (MEG) is pumped from an LNG facility to the wellheads to prevent hydrates forming in the pipeline. The incoming fluids from the wells are received at the onshore inlet area and include; natural gas, condensates, and rich MEG. The rich MEG is separated and then treated to remove hydrocarbons, excess water, and suspended solids to obtain a lean MEG solution in a closed loop system. As is common throughout industry, mercury in its various forms is present in the incoming stream. Mercury is carried across to the rich MEG fluid streams and the regeneration system, building-up inside the system over time. The aim of this project is to identify technologies to remove mercury from rich MEG. The successful design of a mercury removal solution will minimise decontamination requirements and the duration of turnarounds. Furthermore, removing mercury to a level that is as low as reasonably practicable will reduce exposure risks to personnel undertaking any break in containment work. The project objectives were to investigate all technologies pertinent with removing mercury from rich MEG and to provide a recommendation for a technology which can be applied at an LNG facility.

1. Introduction

Elemental, inorganic, and organic mercury are all naturally forming compounds present throughout the world. In industry, mercury levels may vary from below 0.01 $\mu g/m^3$ to well above 1,000 $\mu g/m^3$ depending on the geographical region. Southeast Asia and Australia are all considered highly mercuriferous regions, where mercury concentrations in natural gas and condensates range between 200-300 $\mu g/m^3$ and 10-800 ppb respectively (Chalkidis et al., 2020).

Mercury in its various forms can cause multiple risks to LNG plants. If left unmitigated it risks poisoning catalysts, contaminating equipment, and increasing corrosion, particularly in aluminium cryogenic heat exchangers. Additionally, it can cause health and safety risks, equipment failure, and requires additional decontamination. As a result of this, mercury management solutions have been implemented in onshore facilities around the world.

Traditional mercury management strategies have revolved around its removal from natural gas, water, and liquid hydrocarbon streams. These technologies have since become mature, however there are still opportunities to improve mercury removal from rich or lean MEG. Due to MEG's recent use at LNG facilities, this project deals with further means to optimise mercury management strategies. Specifically, it investigates technologies to remove various forms of mercury from rich MEG entering the MEG regeneration train.

1.1 Onshore Inlet Area

As shown in Figure 1, mercury enters the onshore facility via slugcatchers used to separate gases and liquids. The liquids are subsequently sent to a feed separator to remove condensates, resulting in a rich MEG stream (shown in red). This stream has a composition of 40-50% MEG where the remainder is predominantly water.

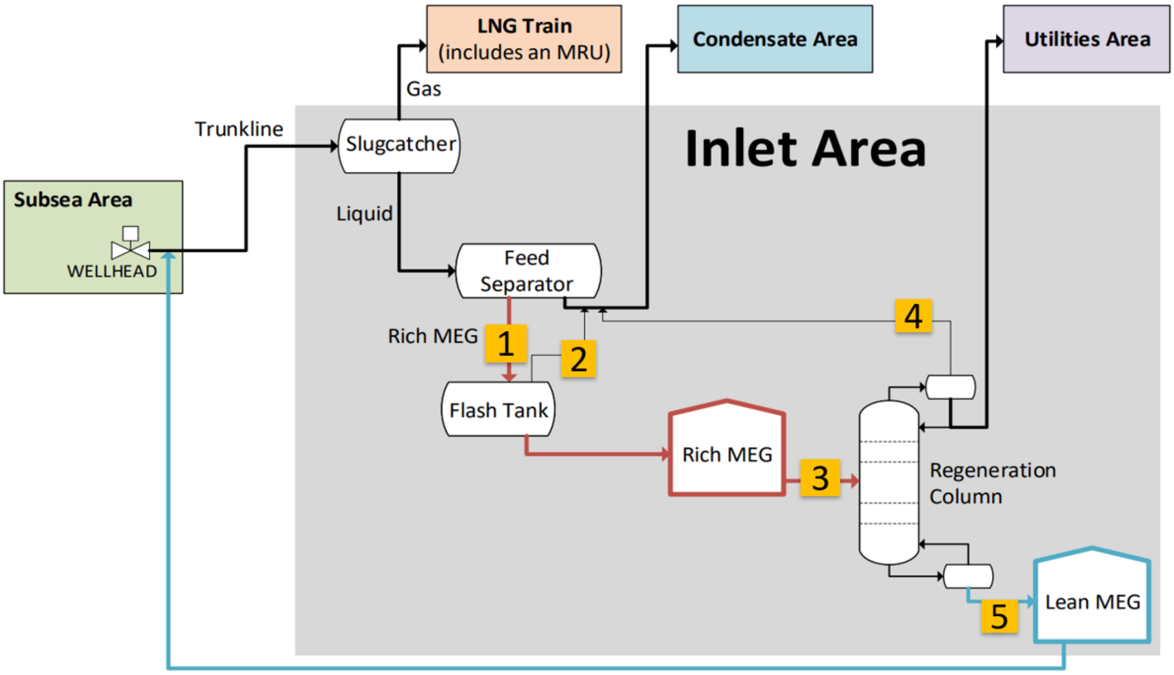

Figure 1 Process flow diagram of the onshore LNG facility's inlet area.

Stream Number	Approximate Mercury Fraction
1	100%
2	50%
3	50%
4	45%
5	5%

Table 1 Estimated mercury fraction by weight for the streams shown in Figure 1. The fraction is as a percentage of the total mercury entering the MEG regeneration system.

Approximately 50% of the mercury entering the flash tank in stream 1 is lost through the overheads as elemental mercury is driven into the vapour phase. These vapours are recompressed and routed back to the gas processing trains where mercury is removed using a traditional mercury removal unit. The remaining mercury is sent to a rich MEG tank and subsequently to the MEG regeneration column to obtain a lean MEG solution (approximately 70-80% MEG). During this process, around 45% of the original inlet mercury exits the column via the overheads. Finally, lean MEG containing approximately 5% of the incoming mercury is pumped to the offshore wells for hydrate inhibition in a closed circuit.

Although elemental mercury levels remaining in the lean MEG stream are negligible, mercury sulfide (particulate mercury) remains to accumulate over time. Some of these particulates are removed by the various centrifuges, filters, and storage tanks in the inlet area. However, there is the potential for particulate mercury levels to accumulate over time.

The presence of mercury only poses a risk to unprotected personnel once a break in containment is performed. This break in containment generally occurs during turnaround periods where vessels are decontaminated, cleaned, and subsequently inspected. The presence of mercury increases decontamination requirements, resulting in additional time and work to ensure any equipment is inherently safe prior to vessel entry.

1.2 Project Objectives

The project objectives are:

- Investigate all current mercury management technologies for use with rich MEG. This will take the form of a literature review.
- Implement a decision method to evaluate technologies and provide a recommendation.
- High level, early phase design engineering of the recommended technology for use at an LNG facility.
- Develop engineering documentation (datasheets, process flow diagrams) for the integration of the recommended mercury management technology.
- Provide a way forward, outlining the next steps required for implementation.

These deliverables will better inform mercury management technologies that can be implemented at an LNG facility. This project will also assist in optimizing future plant turnarounds through; reducing decontamination requirements, lowering turnaround durations, and minimising financial costs associated with deferred production.

2. Process

This project has two key phases; the research and the high level design phase. The research phase revolves around investigating all potential technologies that can be used or applied to remove mercury from glycols. Following a "funnel approach", numerous technologies featuring various literary sources were investigated and subsequently evaluated. Once assessed, technologies were continually eliminated throughout the project phase to obtain a few high potential solutions. These remaining technologies were thoroughly investigated as part of the literature review, enabling the recommendation of a technology.

The second phase of the project focuses on the high level engineering design of the recommended technology. This includes producing process flow diagrams and heat & material balances for the implementation of the technology at an LNG facility. Additional units and equipment were also sized to produce datasheets of key equipment.

3. Literature Review

Following the outlined "funnel approach", each proposed technology was evaluated using the following selection criteria; CAPEX, OPEX, health & safety, effectiveness, technical maturity, disposal volume, and operability. The remaining technologies were subsequently separated in three categories; particle separation, liquid-liquid contact, and solid-liquid contact.

3.1 Particle Separation

An established method for removing heavy metals, including mercury, from oily waters and glycols in the oil and gas industry is through precipitation (Gallup, 2014). This is implemented through addition of a precipitant and a flocculant (or coagulant) to form mercury-containing compounds. The particle separation process can then be performed by physical separation through filtration, settling in tanks, or using centrifuges (Jensen, 2012). Whilst centrifuge separation is based on the density difference between precipitated mercury and rich MEG, filtration and settling is dependent on the size of the precipitated mercury particles.

Making use of a centrifuge bank upstream of the MEG regeneration column and adding a flocculant and precipitant solution was found to be a highly prospective solution. However, it is limited by the relatively large disposal volume from the creation of a mercury-laden process sludge (Ebadian, 2001). Other compounds in the rich MEG would be removed with mercury, resulting in large disposal volumes.

By increasing the addition rates of the precipitant and flocculant solutions, mercury can be removed through settling in the rich MEG tank. Based on the size of the precipitated mercury particles and the degree of mixing between rich MEG and the added streams, this solution takes advantage of the existing sump pump in the rich MEG tank.

3.2 Liquid-Liquid Contact

A potential method for removing mercury from rich MEG is through the addition of a solvent solution. Based on the mercury solubility difference between a solvent and rich MEG, liquid-liquid contact can be achieved using two packed bed columns and a solvent in a closed loop system. The first column would be a cross-stream liquid-liquid extraction column, used to maximise the contact area between liquid solutions and migrate mercury to the solvent. The second column will feature a packed bed using sulphide pellets to adsorb mercury from the solvent, enabling the solvent to be regenerated in a closed loop system.

The extent of mercury removal using this solution is based on the solvent used. It must be immiscible with rich MEG, have a high mercury solubility, and have the ability to be efficiently regenerated whilst minimising entrainment or plug formations. Long-chained alcohols were found to be most suitable, specifically n-octanol (Gallup et al., 2017).

3.3 Solid-Liquid Contact

Solid-liquid contact technologies can remove mercury through the formation of amalgams, or through adsorption in a packed bed. Unique to elemental mercury, amalgamation is a process where certain metals form a semisolid alloy with mercury. For this technology to be successful the added metal must be added in sufficient amounts and with sufficient agitation to amalgamate mercury, converting it to an easily processed form. This was primarily investigated through the addition of a metal powder (nickel, zinc, and tin) using in-line mixers to remove mercury through settling the amalgams in the rich MEG tank.

Based on the historical use of glycols for dehydration and mercury removal from natural gas prior to liquefaction, packed beds can be used to regenerate a glycol solvent (Wang & Economides, 2009). This process resulted in the formation of a rich glycol stream, having a similar composition to that of rich MEG. The packed bed column would feature non-regenerable metal sulphide adsorbent pellets to form mercury sulphide on the pellets' surface.

4. Results and Discussion

Evaluating the technologies with respect to the outlined decision criteria resulted in two technologies being recommended for application; particle separation through settling and a packed bed solution (solid-liquid). Whilst these differ in their implementation method, they both have the advantage of having a relatively high technical maturity. Essential to the project, both of these technologies have a low impact on operators, ensuring a minimal additional workload. Upon review of the literature, it was decided to progress both technologies into the next phase of design work.

The packed bed column was designed to maximise the lifetime of the non-regenerable adsorbent packings whilst satisfying the design constraints. These include current pressure limitations (not installing additional pumping), ensuring sufficient liquid velocities, and high residence times. To maximise the contact area between the oncoming rich MEG and the absorbent pellets whilst reducing the risk of plugs forming, spherical pellets were selected over other packing types containing higher specific surface areas.

Variable	Value	Variable	Value
Column Height	28.3 m	Total Pressure Drop	775 kPa
Column Diameter	3.75 m	Residence Time	3.6 hrs
Volume	243 m^3	Column Capacity	2.1 yrs
Number of Stages	9	% MEG Treated	40 wt%
Packing Type	Copper Sulphide	Packing Size	1.59 mm

Table 2 Packed bed column design summary.

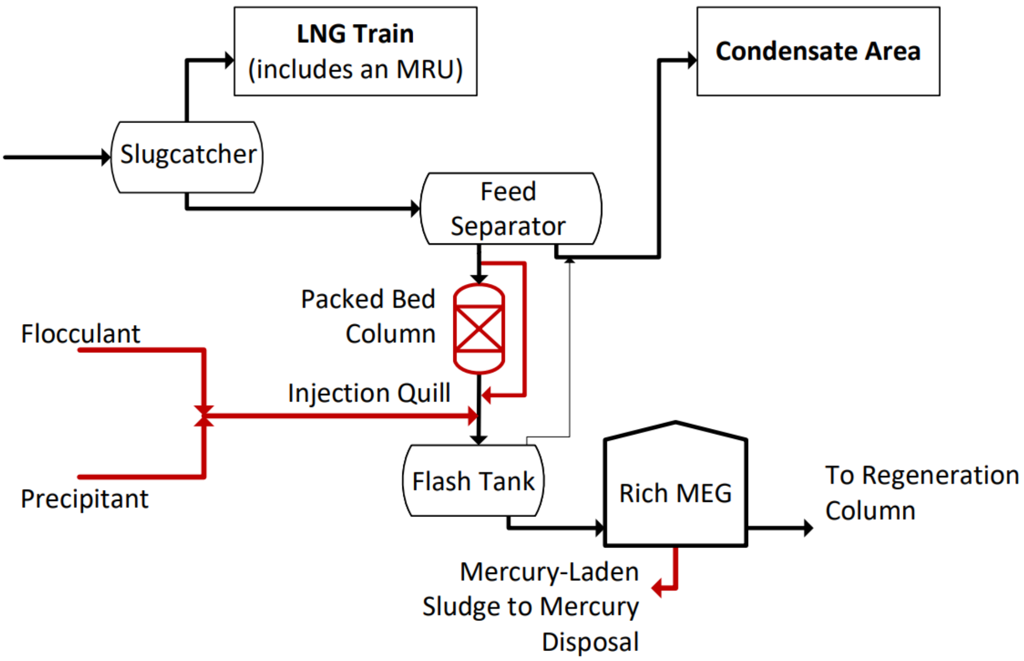

Figure 2 Inlet area with added mercury management units shown in red.

As shown in Figure 2, to maximise the column's lifetime a bypass stream around the column is suggested. This will theoretically enable 40% of the total incoming rich MEG to be treated by the column, with the remainder to be treated by sodium hydrosulfide (precipitant) and ammonium sulphate (flocculant).

Located upstream of the flash tank, the existing injection quill is used for chemical addition. At this point, highly turbulent incoming rich MEG flow increases the mixing potential of the added solutions. To ensure settling occurs inside the rich MEG tank, a total dosing rate of 1.9 m^3/h is required to obtain the minimum mercury sulfide particle size of 4 μm.

5. Conclusions and Future Work

This project was successfully able to identify and evaluate various technologies to remove mercury from rich MEG. Due to the relatively high technical maturity, low health & safety risk, and low additional workloads (or disruptions) to operations, both a packed bed column and particle separation via settling were suggested technologies that could potentially be progressed for further assessment.

The packed bed column was optimised to meet constraints, treating 40% of the rich MEG and achieving a bed lifetime of 2.1 years. To align with LNG facility turnarounds every four years, it is recommended to install two columns, swapping from one to the other once the first bed is consumed. The remaining mercury will be precipitated using NaHS to form mercury sulfide particles that are large enough to settle in the rich MEG tank.

Due to MEG's increasing use at LNG facilities around the world, this project provides a basis from which operators are able to further optimise their mercury management operations. Prior to implementation, future laboratory trials should be performed to determine the reaction kinetics inside the column and that of the precipitant. Additionally, the impact other compounds present in rich MEG have on the adsorbent bed and on the total disposal volume inside the rich MEG tank should be determined to further optimise this design.

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7. References

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