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Application of Mercury Removal Technology in the Gas Project

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Abstract: *Mercury can be observed in many of the world's natural gas fields. Natural gas process facilities with brazed aluminum heat exchangers, including LNG facilities and nitrogen rejection units, are particularly susceptible to corrosive attack by mercury. There is an increased awareness on the part of gas processors to better protect their assets and address environmental concerns by removing mercury at the most appropriate location from their facilities. There are many mercury removal technologies for natural gas, oil and produced water process facilities. Metal sulfide adsorbents and activated carbons are popular technique to remove mercury from natural gas and oil. However, there are some difficulties in mercury removal from oil. The reservoir properties data of the gas wells showed that the well fluids contain a maximum of 70 µg/Sm^3 of mercury. The presence of mercury in the produced water , hydrocarbon liquids and export gas in the gas project were discussed. Technical and economical comparison were conducted between the all available technology methods for the removal of mercury from gaseous hydrocarbon, such as impregnated activated carbon, sulphided Zn/Cu oxide and mixed metal sulphides. It's recommended the use the sulphur impregnated metallic oxide technology for mercury removal in the gas stream and also concluded that the mercury removal unit should be located immediately after the inlet separator, upstream of CO_2 removal, to avoid venting of mercury vapours from the CO_2 vent and glycol still column overhead and to limit possible contamination of pipework especially the drain and vent lines. There is no apparent advantage to locating the mercury removal unit downstream of gas dehydration*

Keyword: *Mercury, CAPEX, OPEX, Alumina, Activated Carbon, Metal Oxide*.

1. Introduction

Mercury occurs naturally in soil and rock and is also released into the environment by volcanic eruptions. Mercury metal is a silver-gray liquid. Because of its unique properties as a liquid metal, metallic mercury is especially challenging to control[1,2]. When exposed to the air or if spilled, mercury metal vaporizes into the air where it can be breathed into the lungs[3]. Mercury and most of its compounds are extremely toxic. It can be inhaled and absorbed through the skin and mucous membranes. The most toxic forms of mercury are its organic compounds which can cause both chronic and acute poisoning. The warmer the temperature, the more quickly the mercury gets into the air. A temperature increases from 64.4 F to 78.8 F doubles mercury's vapor pressure[4-6].

It is also released from human activities such as mining and coal combustion. For the past 150 years, increased human industrial activity has also generated significant environmental releases of mercury. A recognized toxin, exposure to mercury can result in adverse human health effects ranging from acute to chronic. Mercury has a range of forms with varying levels of toxicity[7-9].

Natural gas wells and oil wells may contain a small amount of mercury. The origin of mercury in the oil and natural gas is atmospheric mercury deposition or enhanced mercury concentrations resulting from interaction of hydrocarbon fluids with mercury rich sediment, such as coal and carbonaceous shale. Almost all hydrocarbons contain mercury. In the case of natural gas and natural gas liquids it is likely to be present as elemental mercury. In the case of crude oil, it may also be present as organo-metallic and ionic mercury[10-12].

Mercury can cause amalgam corrosion of aluminum heat exchangers in liquefied natural gas (LNG) plants, mercury in condensate and crude oil can cause catalyst poisoning in oil refineries and petrochemical plants. It is highly required to remove mercury from natural gas and oil in oil & gas process facilities for environmental issues , occupational health and safety in the oil and natural gas facilities[13-15]

Mercury should be measured select the best technical and economical method for mercury removal from the natural gas & oil process facilities[16]. Removing mercury from the oil & natural gas process facilities is essential to meet the required export gas and oil specification, protecting the gas & oil process facilities and for environmental compliance, mercury levels must be known based on the samples taken from the oil & natural gas reservoir[17]. To design a mercury removal unit, accurate mercury measurement is critical to properly size the system and to avoid having a system that is overly large and uneconomical or too small to satisfy the required outlet mercury specifications[18,19]. For the existing natural gas & oil process facilities, mercury levels must be monitored for changing inlet levels that might exceed the designed capabilities of the mercury removal unit[20].

Delphine et al., studied the optimization of fixed bed design for natural gas mercury removal by sulfur doped into porous activated carbon, they found that the obtained Hg^0 adsorption capacity using sulfur doped porous activated carbon was obviously higher than that of raw activated carbon and after optimizing all conditions[21].

Tao et al., studied gas-phase elemental mercury removal by nano-ceramic material, they found that different Hg^0 concentration, adsorption temperature, gas flow rate and different gas components have significant effects on the mercury removal performance of nano-ceramic, and the adsorption removal rate of nano-ceramic can be 75.58% under the optimal experimental conditions[22].

The main objective of this paper is to discuss the presence of the mercury in the gas project based on reservoir properties data of the gas wells and the best available technology which should be used to eliminate mercury from the export gas. Technical and economical comparison were made between the all available technology for the removal of mercury from gaseous hydrocarbon, such as impregnated activated carbon, sulphided Zn/Cu oxide and mixed metal sulphides

2. Process Facilities Description

Figure 1 displays the schematic diagram for the gas and condensate process facilities in the natural gas project. The natural gas project in the North Africa will consists of eight gas wells, Manifold and gas & condensate process facilities. The natural gas coming from various gas wells will be separated into condensate and export gas. The natural gas processing in the gas project will involve inlet separator for liquid & gas separation, mercury removal unit, CO_2 removal unit by using Amine unit, dehydration by trie ethylene glycol unit for water vapor removal and a hydrocarbon dew-pointing unit to meet the export gas specifications.

The condensate separated from the gas in the inlet facilities is stabilized to meet the RVP specification for export condensate. The gas will be exported via export gas main pipeline. The condensate will be exported via export pipeline to the oil terminal.

The analysis of the samples which were taken from the natural gas wells showed that the natural gas from wells contains mercury, the concentration of mercury was 70 ng/Sm^3. No Sulphur, no wax and no paraffin. Also, the H_2S content of the wells is zero.

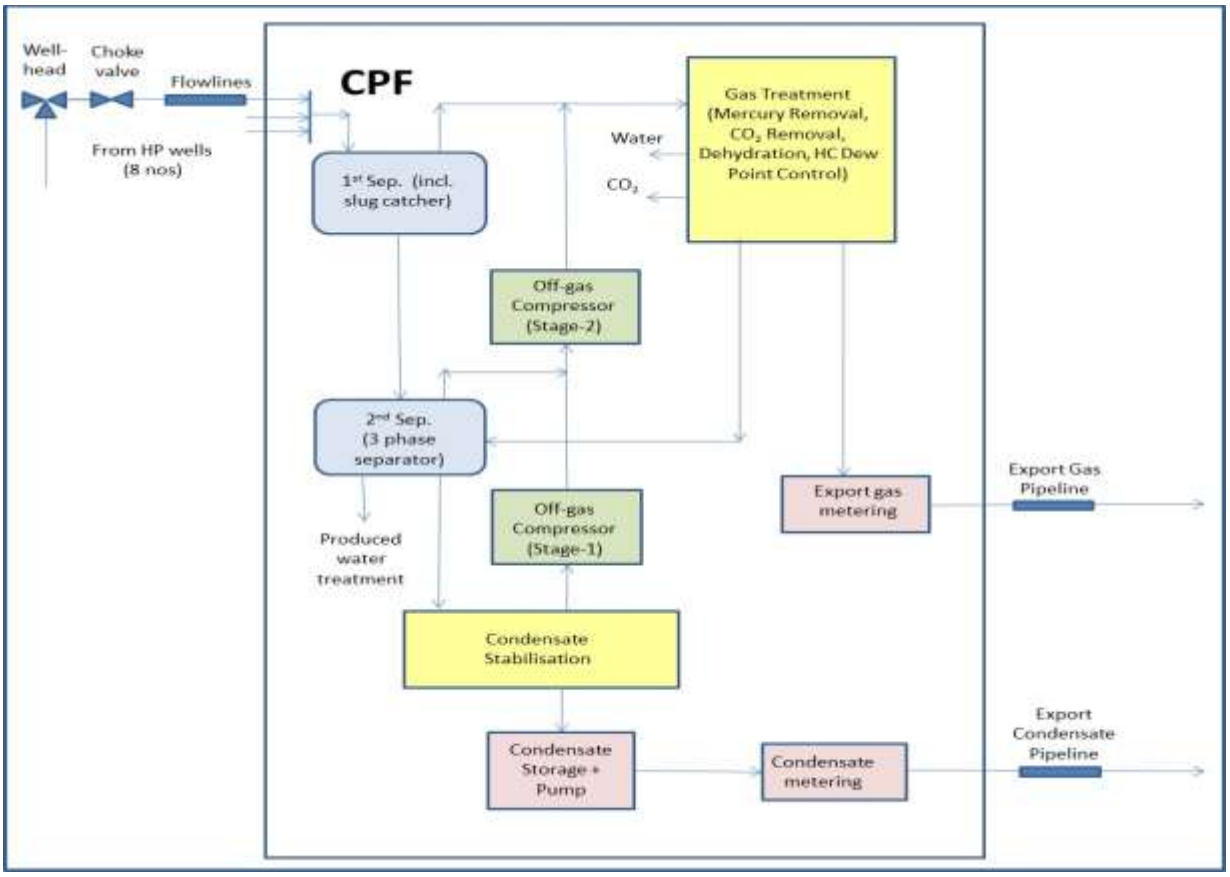

Figure 1: Schematic of the CPF Process Units

3. Gas Project Design Capacities

The natural gas project in North Africa will be designed to handle maximum 2.7 MSCMD export gas and maximum 0,000 STB/day export condensate. Table 1 shows the design flowrates for the for the export gas , export condensate and water of the natural gas project.

Table 1: Flowrates Design Production

Design Capacity of the Natural Gas Project	Unit	Value
Natural Gas Wells Flowrate	MSCMD	2.9 (lean gas) 3.3 (rich gas)
Maximum Export Gas	MSCMD	2.7
maximum Export Condensate	STB/d	10,000
Water-cut	% Vol.	10

3.1 Product Specifications

The required export gas specifications from the natural gas project are as follow:-

- Water dew point in the export gas: -12°C.
- Hydrocarbon dew point at 35 barg in the export gas: +10°C.
- CO_2 content in the export gas: < 2.0 mole %.

Some margins should be assumed for each parameter during the design phase of the natural gas project i.e., water dew point should be -15°C, Hydrocarbon dew point should be 6.5°C and CO_2 content should be 1.8% vol. These design margins will allow gas export to continue in the event of off-specification gas production. The online gas chromatograph will be used to for export gas analyses.

The condensate stabilization unit is designed to achieve a true vapor pressure (TVP) < 0.8 bara at 60°C, which gives the Reid vapor pressure (RVP) < 0.4 bara.

4. Results & Discussions

The reservoir properties data of the gas wells showed that the well fluids contain a maximum of 70 µg/Sm^3 of mercury. In calculating the maximum possible concentration of mercury in various areas of the CPF, the maximum standard gas flow in the inlet stream to the CPF has been taken (3.3 MSCMD in rich winter which would equate to a total mass flow of mercury of 9.38 mg/h). This total mass flow has been considered in each of the sections in the CPF due to lack of information regarding the nature of mercury expected.

Environmental standards recommend that the emission of heavy metals into the atmosphere (at standardized conditions of temperature (273 K) and pressure (101.3 kPa)) should be limited to <0.05 mg/Sm^3 for each metal but < 0.1 mg/Sm^3 in total[23]. Alkyl mercury compounds are more toxic than mercury vapor and divalent mercury compounds.

4.1. Mercury Migration

Elemental mercury will tend to migrate with propane/butane components. Thus, a majority of the elemental mercury will follow the liquid hydrocarbon steam but part of it will also follow the gas stream. It is also expected to get recycled to the gas stream along with the vapors from condensate stabilization column.

Inorganic mercury tends to follow the heaviest liquid or aqueous stream. organic mercury follows liquid hydrocarbon products. A typical distribution of mercury around a gas processing facility is shown in figure 2.

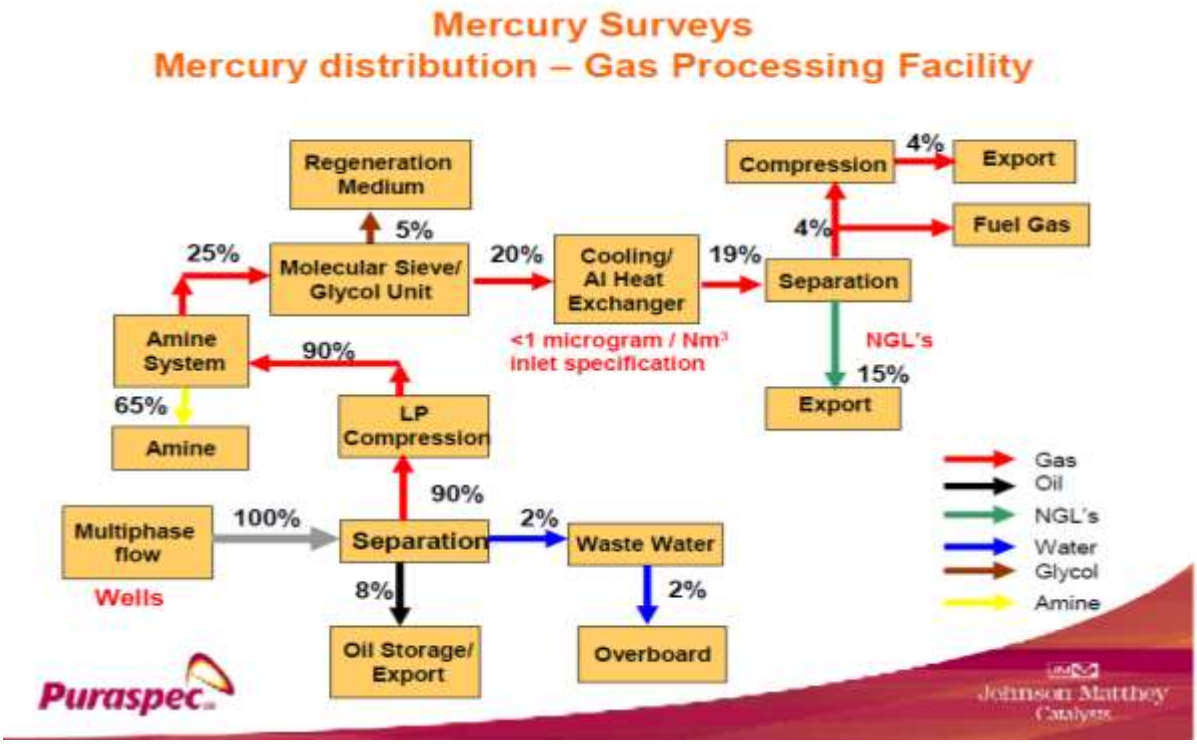

Figure 2 :Typical Distribution of Mercury in a CPF [Ref. 27]

4.2.Typical Mercury Removal Systems

Inorganic mercury will follow the produced water stream; whereas organic mercury will distribute almost exclusively to the hydrocarbons, a majority of which will follow the condensate stream and the balance will remain in the gas stream.

Mercury removal requirement is normally specified to be a level of <0.01 µg/Nm^3. In essence systems are designed for 100 % removal.

The mercury removal chemicals generally used are impregnated activated carbon, sulphided Zn/Cu oxide, mixed metal sulphides or molecular sieve. For example, the Puraspec range of absorbents are mixed metal sulphides available from Johnson Matthey. Used absorbents are typically returned to the supplier for reprocessing.

The mercury removal bed can be installed at the well head provided the flowing temperature is below 95°C and free liquid is removed upstream (water and hydrocarbon condensate). It acts as a guard bed for downstream equipment and requires little or no maintenance between scheduled replacements of the absorbent. Because mercury builds up in the pipeline over a period of time and its subsequent release can be unpredictable, the guiding principle is to remove mercury as far upstream as possible.

It can be also be installed at the inlet facilities in the CPF. As shown in figure 3, this unit can be located downstream of the amine absorber suction drum as well.

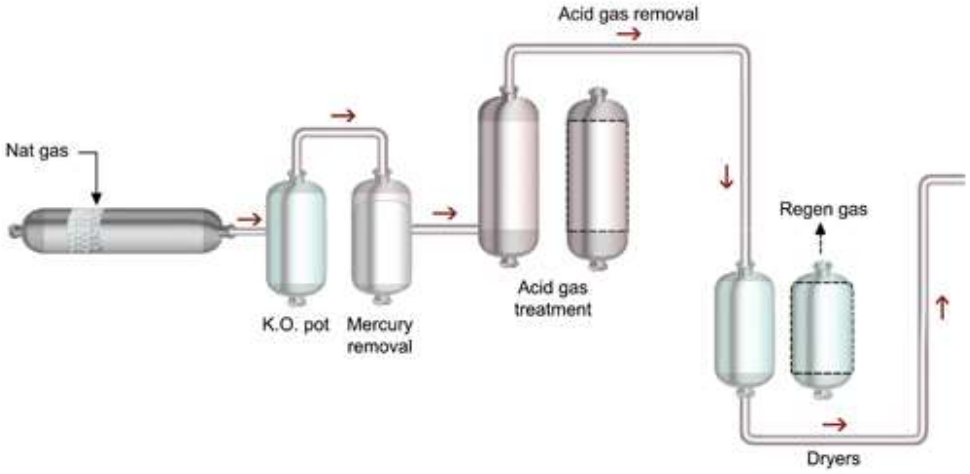

Figure 3: Typical Location of Mercury Removal Bed in CPF [Ref. 28]

Similarly, these mercury removal beds can also be installed in liquid hydrocarbon streams. It is recommended that a filter is installed upstream of the mercury removal bed to avoid the fixed-bed acting like a filter and getting fouled.

4.3. Mercury Removal Systems for the Gas Project

4.3.1. Mercury in Produced Water:

Since inorganic mercury will follow the produced water stream, the mercury level in the produced water stream is expected to be in the range of 1 ppb-wt. to 16 ppb-wt. The lower level is estimated based on the maximum produced water flowrate of 240 m^3/day and the higher level is based on the condensed water from the production gas and no formation water. These are not significantly high values; typical mercury limits for effluents from petroleum refining facilities is 0.02 mg/l i.e., approximately 20 ppb-wt. The disposal of evaporation pond residue will utilize contractors well versed in handling noxious liquids and capable of following adequate HSSE principles.

4.3.2. Mercury in Export Gas:

Based on the available data, it is assumed that the maximum mercury content in the produced gases could be 70 ng/Sm^3. This is a likely scenario in the lean gas composition case, when negligible hydrocarbon liquids are expected and all the mercury in the well fluids will follow the gas route. If mercury is not removed upstream, then it is expected that a significant proportion will be vented to atmosphere through the CO_2 vent from the amine regeneration and also through the vent from the glycol regeneration column .

Based on the maximum mercury content of 70 ng/Sm^3, the total inlet mass flow rate of mercury into the amine absorber is 9.38 mg/hr. If this was all to exit in the vent from the amine regeneration package, this would be at a concentration between 0.0039 and 0.0051 mg/Sm^3 for lean winter and rich summer respectively; which is below current environmental emission (< 0.05 mg/Sm^3) and exposure limitations (long-term exposure limit of 0.025 mg/m^3 . Table 2 illustrate the calculation for mercury content in the export gas

Table 2: Calculation for Mercury Content in Export Gas

Maximum total mercury mass flow	9.38	mg/hr.
Vent flow rate (rich summer – lean winter)	1845 – 2413	Sm^3/hr.
Mercury concentration at outlet (lean winter - rich summer)	0.0039 – 0.0051	mg/Sm^3

Mercury may accumulate in cold dead legs, e.g., instrument impulse lines and drains, and represents a hazard to maintenance personnel. Since mercury has been detected in a number of wells, it is recommended that it be removed upstream of the gas processing train. It would be advantageous if future wells are also tested for mercury as the mercury content in these wells could differ. The corrosion problems in the downstream gas processing train, the risk of accumulation in the condensate train or the release of vapor

phase mercury from an evaporation pond would be minimized. This would also avoid exposure of workers to mercury during maintenance operations.

It is recommended to consider a fixed bed mercury removal bed, designed to reduce the mercury levels in the gas from 70 ng/Sm^3 to 10 ng/Sm^3. A mercury removal bed also allows aluminum based heat exchangers to be used downstream. This means that brazed aluminum plate fin heat exchangers may be considered for the gas / gas heat exchanger duties if found to be competitive in terms of CAPEX.

4.3.3. Mercury in Hydrocarbon Liquids:

Even if it is assumed that the entire organic mercury content in the well fluids is passed into the hydrocarbon liquid phase, the maximum mercury expected in the condensate stream downstream of the water/condensate separator is approximately 0.69 mg/Sm^3, i.e., 1 ppb-wt. Such a level of mercury is considered low and a neutron activation analysis would be required to detect mercury in such levels in liquid hydrocarbons .Table 3 reveals the calculation for mercury content in hydrocarbon liquids of the gas project.

Table 3: Calculation for Mercury Content in Hydrocarbon Liquids

Maximum total mercury mass flow	9.38	mg/hr.
Mass flow to condensate stabilisation (lean summer – rich winter)	9801 - 43428	kg/h
Volumetric flow to condensate stabilisation (lean summer – rich summer)	13.5 – 77.0	Sm^3/hr.
concentration of mercury (rich winter – lean summer)	0.22 - 0.96	ppb-wt.
concentration of mercury (rich summer – lean summer)	0.12 – 0.69	mg/Sm^3

Mercury removal technology is available for hydrocarbon liquid streams, such as using a Sulphur impregnated carbon bed. However, there is no mercury limit specified for the export condensate, but typically condensate quality requires mercury content below 30 ppb-wt. If all the mercury ends up in the condensate, then mercury concentration remains well below this level and removal need not be considered. If mercury content was to increase during future plant life, the use of a mercury removal unit for the hydrocarbon liquids should be reviewed.

It is considered probable that mercury in the condensate stream will be vaporized in the stabilization column, and progress through the off-gas compression trains to the main process gas train. If it is assumed that the entire organic mercury content is passed into the off-gas compression unit, the maximum mercury expected in the gas stream is approximately 0.022 mg/Sm^3, i.e., 10 ppb-wt. Table 4 shows the calculation for mercury content in the off gas compression

Table 4: Calculation for Mercury Content in Off-Gas Compression

Maximum total mercury mass flow	9.38	mg/hr.
Mass gas flow through off-gas compression (lean summer – rich winter)	618 - 8394	kg/hr.
Volumetric gas flow through off-gas compression (lean summer – rich winter)	423 – 6476	Sm^3/hr.
concentration of mercury (rich winter – lean summer)	0.76 - 10.3	ppb-wt.
concentration of mercury (rich winter – lean summer)	0.0014 - 0.022	mg/Sm^3

If this was to be released to the atmosphere as relief gas directed to a non-burning flare, it would not exceed current environmental emission (<0.05 mg/Sm^3) and exposure limitations (15 minute exposure limit of 0.03 mg/m^3).

4.3.4. “Not Normally Manned” Operation

The process facilities of the gas project shall be designed such that it will be possible to support a “not normally manned” operation. Vendors (e.g., Axens, Calgon Carbon and Johnson Matthey) were contacted with regards to any detrimental effects on the mercury removal unit’s operation under such conditions and all confirmed that, as static items, the mercury removal bed should not be affected by such operation.

4.4. Mercury Removal Unit CAPEX & OPEX

There are many technologies available for the removal of mercury from gaseous hydrocarbon, such as impregnated activated carbon, sulphided Zn/Cu oxide and mixed metal sulphides. Depending on the technology used, the location of the mercury removal bed should vary to ensure minimal degradation to the mercury removal chemical and other process units. A comparison of the beds available, alongside quotes from typical vendors is provided below in table 5.

Table 5: Cost Comparison of Mercury Removal Technologies

Type	Alumina	Activated Carbon	Metal Oxide
Vendor Name	Axens	Calgon Carbon	Johnson Matthey
Cost of bed (US$ per m^3) [1]	13,790	5,621	21,310
Volume of bed required (m^3)	8.715 (including 2.1 m^3 of inerts)	10	5
Cost of bed (US$)	91,219	56,207	106,552
Additional Costs (US$)	7,669 (Inert Ceramic Balls)	N/A	N/A
Estimated Cost of Vessel (US$) [2]	298,699	298,699	194,315
Total Cost for Unit – CAPEX (US$)	397,588	354,906	300,867
Total Installed Cost (US$) [6]	1,351,798	1,206,681	1,022,948
Cost for servicing of bed (US$) [3]	50,105	80,295	48,177
OPEX (US$) [4]	141,324	136,502	154,729
Bed life expectancy (years)	>5	>10	>10
Overall cost for 25 years (US$) [5]	1,403,281	1,146,141	996,820

Notes:

1. Vessel for alumina and activated carbon assumed to be 2.1 m ID x 3.3 m T/T. Vessel for metal oxide assumed to be 1.8 m ID x 2.6 m T/T. Carbon steel clad vessel cost assumed $8900/te
2. Cost of servicing includes removal of depleted bed and the replacement with a new bed, but excludes the cost of the new bed.
3. OPEX is based on the cost of a new bed and the cost for servicing of the bed, provided by the vendor.
4. Values based on assumption of 3% inflation and 10% discount per annum, using the cost of servicing and replacement of a new bed as the OPEX
5. Lang factor of 3.4:1 is used to calculate the total installed costs based on cost estimate
6. Contacted vendors have suggested that the best achievable outlet concentration is comparable for all types of technologies on the market (< 10 ng/Sm^3).

All vendors contacted offer a service for the removal and disposal of spent beds. These services allow the bed to be collected and regenerated by the vendor, whilst a fresh bed is delivered and installed as replacement (activated carbon bed cannot be regenerated and would be sent to hazardous disposal or incinerated). The cost for this servicing has been included, in addition to the cost of a fresh bed, as the OPEX cost.

Loading and unloading procedures vary for different bed types, with differing requirements for inserting of the removal bed during loading and unloading procedures. Some vendors require high purity nitrogen (99.9%) for loading and discharge of the bed, which would be supplied in bottles/tanks as the nitrogen generation unit is insufficient to provide this purity of nitrogen.

The mercury contaminated beds are hazardous. Mercury will react with the Sulphur in the beds to create a sulphide. When exposed to air, the sulphide will preferentially remove oxygen from the air, creating a sulphate product. This is an exothermic reaction, so will generate some heat, but will also create a harmful environment for personnel. The reaction, however, is slow and by using suitable precautions, such as using nitrogen blanketing, the risk to personnel is minimized. Transportation of mercury is internationally monitored in accordance with the Basel convention.

Vendors recommend that a filter coalescer should be located upstream of mercury removal unit to reduce liquid content to <0.1 ppmv. Liquids can potentially damage the bed if allowed to get enter the vessel. Some vendors also recommend the use of a 5°C superheater upstream of the mercury removal bed, again to reduce the liquid content in the inlet stream.

It is recommended that an after-filter should be incorporated downstream of the mercury removal unit to trap any particles which might escape the bed. This would also be necessary to prevent any possible foaming in the amine absorber or the TEG contactor, as well as reduce the risk of erosion to piping, instrumentation and equipment.

4.5 Mercury Removal Possible Locations in the Gas Project

In general, there are two possible locations for the mercury removal unit as represented in figure 4. First location is upstream of CO_2 removal unit and the second location is downstream of hydrocarbon dewpointing

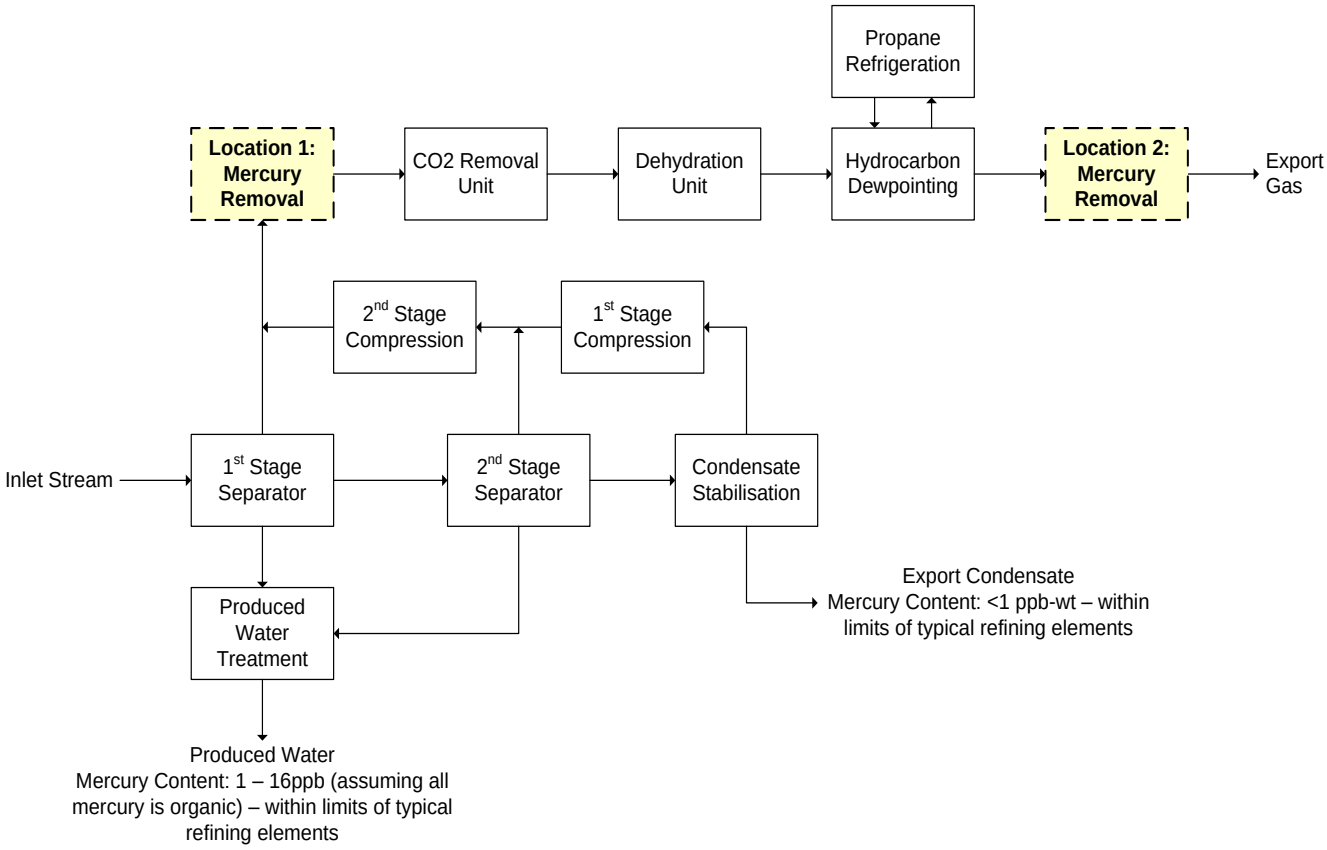

Figure 4: Possible Locations for Mercury Removal Unit

4.5.1.Upstream of CO_2 Removal Unit:

Sulphided Zn/Cu oxide, alumina and mixed metal sulphide technologies are not degraded due to water content in the gas, therefore can be located upstream of the CO_2 removal unit, when the gas is partially saturated, without adverse effects.

The primary advantage of this location is to reduce the mercury contamination in the amine (used for CO_2 removal) and TEG (used for dehydration), and it will allow aluminum-based heat exchangers to be used downstream of the bed, as stated above.

The main disadvantage is that impregnated activated carbon beds cannot be located here, as the saturated water in the gas will be favourably adsorbed onto the bed, which will reduce the quantity of clean bed for adsorbing mercury, thus shortening the lifespan of the bed. Therefore, this limits which technology can be practically used for mercury removal.

4.5.2.Downstream of Hydrocarbon Dewpointing:

Though all mercury removal technologies investigated are capable of functioning downstream of hydrocarbon dewpointing, the main benefit of this would be for the impregnated activated carbon beds. Water, as well as other heavy hydrocarbons such as ketones and BTEX, adsorb onto the carbon bed better than mercury, therefore their presence will greatly reduce the lifespan of the bed. The dehydration unit and hydrocarbon dewpointing will remove the majority of the water and heavy hydrocarbons, thus allowing carbon-based mercury removal technologies to be used. Other mercury removal technologies, such as alumina and metal oxides, will also work well in this location.

The primary advantage is that the mercury removal technology is not limited, and it will still allow aluminum-based heat exchangers to be used downstream of the bed.

The main disadvantage will be the potential for contamination of amine and TEG, which will create a maintenance hazard, and the potential release of mercury to atmosphere through the CO_2 and dehydration vents. Though these are within current exposure and environmental limits, avoiding all emissions of mercury is inherently safer – assuming the containment of the mercury contaminated bed is adequate. In addition, the amount of mercury may increase in the future for drilled wells and the content could differ for new wells to be drilled.

5. Conclusions

It will only be necessary to use mercury removal units on the gas stream in the CPF as mercury concentrations in the water, condensate and off-gas streams are low. The design of the mercury removal unit is not expected to change if the CPF is to be designed for “not normally manned” operation, because the bed is considered a static item with minimal operational requirements.

It’s recommended to install the mercury removal unit immediately in the gas project either after the inlet separator or having the unit after the gas dehydration. The advantage of removing mercury upstream of CO_2 removal is to avoid venting of mercury vapors from the CO_2 vent and glycol still column overhead, and to limit possible contamination of pipework especially drain and vent lines. There is no apparent advantage to locating the mercury removal unit downstream of the gas dehydration. The proposed location is considered ideal and have no problem with the gas being water saturated at temperatures less than 95°C. A KO drum or filter separator upstream of the mercury removal bed is recommended to remove liquid hydrocarbon droplets from the feed. If water/condensate ingress (vapors, drop-outs or carryover) in the mercury removal bed, then the lifetime of the removal bed may significantly decrease

The life span of the mercury removal bed is a function of pretreatment of the feed gas rather than its location in the gas train. Installing the bed downstream of the CO_2 removal unit does not protect against hydrocarbon liquid drop out in the mercury removal bed. Filtration of the gas is required irrespective of its location in the gas train.

CAPEX: Based on the information available, it is apparent that the design based on metal oxide catalyst is the cheapest, primarily due to a smaller vessel size requirement. There is no CAPEX advantage in using activated carbon beds.

OPEX and overall cost: Based on current values, the cost of a single activated carbon bed is cheapest, and as the life expectancy is similar to that of metal oxide beds, it provides the cheapest OPEX of all technologies. Based on the overall cost over a 25 year lifespan, the metal oxide technology is the lowest cost option.

6. Recommendations

It is recommended that metal oxide technology is used in the mercury removal unit, as this can be located upstream of the CO_2 removal unit, is comparable or better than all other technologies on overall cost and offers the lowest CAPEX and acceptable OPEX.

Abbreviation	Description
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
CAPEX	Capital Expenditure
CGR	Condensate to Gas Ratio
CPF	Central Processing Facilities

HC	Hydrocarbon
HSSE	Health, Safety, Security and Environment
ID	Internal Diamter
KO	Knock Out
LPG	Liquefied Petroleum Gas
L	Lean
MSCMD	Millions of Standard Cubic Meter per Day
ng	Nano gram
OPEX	Operating Expenditure
ppm	Part per million
ppb	Parts per billion
RVP	Reid Vapor Pressure
R	Rich
SBPD	Standard Barrels Per Day
SCF	Standard cubic feet
STb	Standard tank barrel
TCF	Trillion cubic feet
TEG	Tri Ethylene glycol
TVP	True Vapor Pressure

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