

MERCURY MANAGEMENT SOLUTIONS FOR THE OIL AND GAS PROCESSING INDUSTRY

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ABSTRACT

Natural gas, being produced from gas fields around the globe, along with a large number of other harmful substances (CO₂, H₂S, RSH, COS, etc.), often contains mercury. Mercury's potentially harmful effect on humans and on the ecological system as a whole as well as the risk regarding mercury's corrosive effects to the very sophisticated and expensive process material, equipment and catalysts is making its removal an imperative.

Gas plants reduce mercury in natural gas with mercury removal units (MRUs). MRUs use fixed bed absorbers, often with sulfur-impregnated carbon or other chemisorbents as the active material.

Mercury removal by sulfur-impregnated activated carbon is the best commercial method for treating the main gas stream, provided the carbon is not blinded by adsorbed hydrocarbon. However, it is not suitable for treating liquids because of solution of the sulfur. Solid beds of iron sulfide, and sodium vanadate in the treating solution in the decarbonation units, hold promise for mercury removal and merit further investigation.

This paper will evaluate and compare the various mercury removal technologies namely Activated Charcoal-Sulfur System, Oxidizing Solutions, Acids, Metals, Metal Sulfides and other new methods.

Ultimately the objective is to produce a system that assures the safety of plant operation thus all have to be addressed when considering corrosion management.

KEY WORDS :mercury removal unit, corrosion, sulfur-impregnate, activated carbon, natural gas, new method

INTRODUCTION

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.

The concentration of mercury in natural gas varies widely from 450 to 5000 µg/Nm³ to less than 0.01µg/Nm³ in some parts of the US and Africa. Mercury has a high boiling point (356.7°C) but has a high vapour pressure at ambient temperature and is surprisingly mobile.

Although the levels of mercury recorded are low, the tonnages of liquid hydrocarbons handled are enormous so downstream processing equipment is exposed to a substantial amount of mercury. Thus a typical 10,000 tes/day LNG plant would use 600 mmscfd of natural gas and if this contained 100 µg/Nm³ mercury the plant would receive 582 kg mercury per year.

Even in small amounts, mercury and its compounds have an extremely harmful effect on human health.[1,2]

MERCURY CORROSION

Investigations determined that mercury corrosion caused the failure and that the mercury likely came from an accidental source, such as test instruments used in plant and field start-up.

most if not all of the mercury in natural gas is in the elemental form and that no natural gas processing plant problems are suspected to have been caused by organic or inorganic mercury compounds, and that elemental mercury is the probable cause of mercury corrosion problems. Even more, trace quantities of H₂S, very often present in the natural gas, are the

catalyst for the reaction of mercury with iron oxide from the pipe (vessel/reactor).

Although the concentration of mercury in a given natural gas may be considered extremely low, its effect is cumulative as it amalgamates. Elemental mercury forms an amalgam with the surface layer of the metal it contacts.

To date, the most serious problems reported by the industry owing to mercury corrosion have been the result of mercury forming an alloy with aluminum (amalgam), which is much weaker than the metal itself and is often referred to as an embrittlement. To initiate aluminum corrosion, the tightly adhering aluminum oxide layer on the surface of the aluminum must be removed. The mercury/aluminum amalgam process removes this oxide layer. Saunders et al observed that brazed aluminum plate-fin heat exchangers are the predominant choice for cryogenic service. Aluminum is used due to its brazeability, excellent mechanical properties at cold temperatures, and superior heat transfer characteristics... They further state that mercury can damage the aluminum used in these exchangers and must be completely removed to no detectable levels in upstream equipment.[2,4]

MERCURY-INDUCED CORROSION

Two major types of mercury corrosion can be observed. These are amalgam corrosion and liquid metal embrittlement (LME). Amalgam induced corrosion is shown by any metal capable of forming an amalgam with mercury. Most metals owe protection from corrosion to the presence of an oxide layer. If this protective layer is damaged in the presence of liquid mercury, the metal can show its full reactivity and attack by air or water is rapid.

LME involves the diffusion of mercury into the grain boundaries and results in cracks developing along the grain boundary. This type of attack does not involve air or water and once initiated progresses rapidly. This type of corrosion affects a broad range of materials (aluminium alloys, copper based alloys eg Monel 400 and some types of steel eg 316 L). Figure 1 is a photomicrograph showing mercury embrittlement on a failed heat exchanger

Corrosion is a particular concern for LNG plants and for this reason a mercury limit of $< 0.01 \mu\text{g}/\text{Nm}^3$ is set on the feed.[1]

LNG PLANT CORROSION

Mercury in an LNG plant containing trace amounts of mercury in the feed gas should concentrate in the heavier liquid phases, such as the de-carbonation treating solution or butanes plus (including liquids from the dehydrators).

However, the presence of mercury is of little consequence in the de-carbonation unit, unless it



Figure 1
Liquid metal embrittlement failure on brazed aluminum heat exchanger

builds to an equilibrium level and re-enters the gas stream. Most likely the damaging mercury concentration will occur in the cycle gas stream where losses are made up from plant products, C1 through C5.

Since mercury-induced corrosion occurs only in the presence of liquid water, the temperature at which the corrosion occurs must be between approximately 0 C and the highest temperatures at which a water dew point can occur. There is only one condition of operation in which this temperature can occur: when the plant is allowed to warm above 0 C, either for deriming, or through shut-down for any other reason. Therefore, warming cryogenic exchangers should be prevented whenever possible. Also, there is more risk of failure from mercury-induced corrosion on the cycle gas side of the exchangers, and more risk in general with a mixed refrigerant plant than with

a cascade cycle (since a cascade system uses no refrigerant heavier than propane).

REMOVAL METHODS

Separation processes represents a practical and cost effective approach for eliminating pollution substances from petroleum and chemical processing applications. Mercury is very often removed as an

impurity and environment pollutant from process fluid gas streams by adsorption on a fixed activated carbon bed. The adsorbent is primarily designed to extract elemental mercury, i.e. mercury in its vapor state.

Physical forces of adsorption are not always sufficient for total adsorption of a particular component, e.g. mercury. In this case, the large inner surface may serve as a carrier of the active component and/or chemical compound, i.e. to take over and distribute an optimum quantity of impregnating agent. The impregnation process increases the activated carbon capacity significantly, in order to produce a special type of sulfur impregnated activated carbon with a great adsorption capacity for mercury vapors. The mercury removal process is based on principle of adsorption and of chemical reaction (chemisorption) of mercury present in natural gas using impregnated elemental sulphur in a micro-porous adsorbent.

This reaction results in a stable and insoluble compound, the mercury sulfide.

Several factors are influencing efficiency of mercury removal from natural gas: composition of gas as well as concentration of mercury vapor, presence of higher hydrocarbons, water and other impurities, temperature, pressure, gas flow rate, activated carbon characteristics, contact time, etc. It is extremely hard to design the breakthrough curve, or to accurately predict the effective capacity and expected bed life. To solve all problems a multidiscipline approach to a mercury removal problem is necessary.[2,5]

Characteristics required of any mercury removal system should include:

- A very active mercury removal agent; preferably one that bonds to the mercury, so it cannot be released again to the treated stream.
- A removal agent that will remain active; with a high resistance to blinding by components in the stream being treated.
- A removal agent that will not harm natural gas or downstream components.

Desirable characteristics should include:

- A system that provides ready separation of the mercury from liquid hydrocarbons (propanes, butanes and pentanes plus) for use with the cycle gas stream or makeup.

- A removal agent that is inexpensive, readily available, or easily regenerated.

A removal agent that will hold mercury in a solid form or in a liquid form from which it can be precipitated readily for filtration and disposal.

ACTIVATED CHARCOAL-SULFUR SYSTEM

is a proven commercial process. Sulfur, the active ingredient, securely fixes mercury as sulfide in the micro porous structure of the activated carbon. If the charcoal is not blinded by heavy hydrocarbon, it is definitely the preferred system and there is no reason that it could not be used on liquids, except that the treated liquids would dissolve sufficient sulfur to eventually exhaust the capacity. Also, the treated liquids would be corrosive to copper alloys which could cause corrosion of the brazed exchangers.

Thus, sulfur impregnated activated charcoal is the best system for the main gas stream, provided its effectiveness is proven when saturated with pentanes plus; but is unsuitable for cycle gas liquids or cycle gas make-up liquids.

OXIDIZING SOLUTIONS

Strongly oxidizing solutions, such as potassium permanganate, will oxidize elemental mercury, but might have side-effects if carried over to downstream equipment.

ACIDS

Strong acids might absorb mercury, but principally through oxidizing actions, since mercury is below hydrogen in the electromotive series of the metals. The downstream results and corrosion effects could be serious.

METALS

A commercial system that readily comes to mind is a reduced zinc oxide bed used for synthesis gas purification. The problem here is that while the mercury would be trapped by the zinc, a zinc corrosion would start by the same water mechanism if liquid water were present. Subsequently, this would collapse the absorption bed and zinc oxide dust would be carried downstream. This may not be a problem, since the gas should be above the water dew point at the plant inlet. Zinc oxide is readily reduced for use at the site by a reducing gas generator using natural gas as fuel.

Other than reduced zinc oxide, the other metals above hydrogen in the electromotive series have tough oxide films not easily reduced or are unsuitable from the standpoint of reactivity or ease of amalgamation.

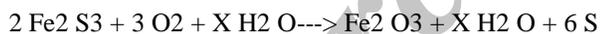
Of the metals below hydrogen, gold or silver are certainly suitable but would be prohibitively expensive, even on an inert substrate. Finely divided copper should be an excellent absorber, provided its surface is bright and clean. Its capacity is limited.[2]

METAL SULFIDES

The metallic sulfides hold particular attention as potential mercury removal agents because:

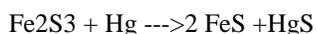
- A crystalline structure precludes deactivation by absorption of liquids.
- They are readily available.
- The available sulfur content varies fore reaction.

Iron sulfide is particularly attractive, since it has been identified in at least nine crystalline forms, which vary from 3.37 to 53.4 weight percent sulfur. The existence of iron sulfides of even higher sulfur content has been inferred by work on corrosion products. A common commercial process involving iron sulfide, the so-called "dry-box" method of removing hydrogen sulfide from gas, operates on two basic reactions:



This illustrates that upon oxidation, Fe_2S_3 liberates 3 atoms of sulfur per molecule.

If iron sulfide is considered as a source of sulfur to react with mercury, a reaction could be:



$$\text{H (net)} = 2(-23.1) + (-10.7) + 7.7 = -49.2$$

$$\text{F (net)} = 2(-22.9) + (-6.8) + 32.7 = -19.9$$

The free energy change of this reaction is negative and the reaction would, therefore, proceed at room temperature. A potential problem would be dusting from reaction, but with the amount of mercury involved; and with the amine unit and gas filters downstream, this would hardly be a problem.

Iron sulfide would have particular merit for mercury removal from a side-stream of mixed refrigerant liquid from the first cycle gas separator. In this manner, mercury could be removed from the cycle gas stream, without the risk of sulfur dissolving in the cycle gas.

The reaction would probably require the injection of minute amounts of water as a catalyst, but this could readily be removed with a cartridge-type liquid dehydrator.

All existing and future LNG units have an excellent liquid-gas contact system in the decarbonation system. Logically, a chemical might be added to the de-carbonation to remove mercury, without disturbing the de-carbonation system or any other plant unit.

OTHER METHODS

For example, a trace amount of hydrogen sulfide might be injected into the gas stream with subsequent removal of the H_2S by the de-carbonation unit:



While this reaction does proceed, the idea is not desirable of:

- Possible objections to the introduction of H_2S to the gas stream.
- Difficulty in obtaining H_2S .

Or consider additional oxidizing compounds. Potassium permanganate, mentioned earlier, is unsuitable since it oxidizes amine in the treating solution. A further examination of the periodic table shows that chromium and vanadium are next below manganese in their combination with oxygen and, thus, in the oxidizing power of their oxides.

Sodium vanadate is strongly recommended by Dow Chemical Co. as a corrosion inhibitor for aqueous monoethanol amine solutions, particularly for CO_2 removal system. Although enough thermodynamic data has not been developed to prove that this system will oxidize metallic mercury, there is a strong possibility that it will. This system merits further investigation if it will oxidize mercury because:

- It could be used in existing units.

- It would have a beneficial effect on existing systems due to corrosion inhibition. [2,3]]

POSSIBLE LOCATIONS OF MRU

There are three possible locations for the MRU. These are shown in Figure 2 and are after the molecular sieve driers (C), before the molecular sieve driers (B) and before the acid gas removal (A). Undoubtedly the easiest duty is after the molecular sieve driers as the gas is cleanest and the rate lowest. However, there are concerns about this location. Mercury will have contaminated all of the upstream plant equipment and mercury will be released to the atmosphere. Plant measurements have found up to 30,000 ng/m³ in the acid gas removal stripper gas. In the case of molecular sieves, mercury is released throughout the regeneration cycle with peaks of up to 60,000 ng/m³. Acid gas removal stripper gas is likely to be vented locally. Molecular sieve regeneration gas will enter the fuel gas system but the water removed together with entrained mercury will go to drain. Flash gas and stripper gas from MEG and TEG dryers is likely to be vented locally.

It is possible to use small mercury removal units to treat some of the emissions. Location upstream of the driers will reduce some of the mercury emissions and avoids any delays to start up. However, this location will carry the risk of fouling by carryover. Treatment of the raw gas is undoubtedly the preferred location. This avoids emissions of mercury to the atmosphere and contamination of plant equipment. This will ensure any NGLs produced are free from mercury. However, this location is more of a challenge for the mercury removal absorbent. [1]

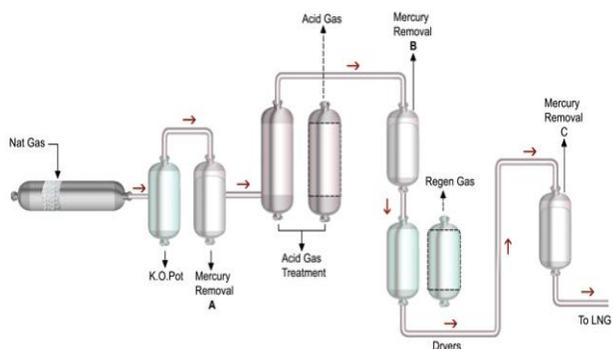


Figure 2
Possible locations for MRU

CHOICE OF ABSORBANT

Traditionally mercury has been removed using sulphur impregnated carbon. Typically this will contain 10 to 15% w/w sulphur and mercury is removed by reaction to form HgS. The reactivity with mercury depends on the allotrope of sulphur present on the carbon. This can vary from S₈ down to S₂ with the lower allotropes having higher activity but these are the harder to form as they require higher impregnation temperatures [10].

There are other problems inherent with this type of absorbent.

- Sulphur Loss – sulphur is lost in service by sublimation and leaching by liquid hydrocarbons. LNG operators have found sulphur at the top of the bed of a discharged reactor to be as low as 3.7 to 4.2%. Whilst this is still enough to trap mercury there must be a concern as to where the sulphur has gone. Table 3 shows the solubility of sulphur in liquid hydrocarbons.
- Capillary condensation – the nature of the material and the method of manufacture give a high surface area support (typically 1000 m²/g with average pore size <20Å). This type of material is vulnerable to capillary condensation by C₅+ hydrocarbons with aromatic compounds a particular concern .
- Start up delays – carbon based absorbents need to equilibrate with the process gas and can release sulphur during commissioning. This can delay introduction of feed gas to the cryogenic plant for up to three days. On a 10,000 tpd plant this is worth \$5.6 M in lost production.
- Disposal of spent absorbent – the material cannot be sent for landfill in most locations. It is difficult to free the spent absorbent from hydrocarbons and mercury can only be removed by a thermal process.
- Handling – the material is likely to contain dust and carries the risk of self heating.

Recognition of these problems has led to the development of inorganic based absorbents. These rely on the high reactivity of mercury with the metal

sulphides of certain variable valency metal sulphides.



The reactive metal is incorporated in an inorganic support and the absorbent is supplied with reactive sulphide resin or this is formed in situ by reaction with H₂S in the hydrocarbon to be treated. The “inorganic” approach has a number of advantages over the “sulphur impregnated carbon” approach:

- The spent mercury absorbent can be recycled through metal smelters. This is made possible by the use of a combination of metals with an inorganic support that is compatible with smelting processes.
- The materials can be used on wet and dry gases.
- The reactive species and the support have meso-porous structures with little affinity for hydrocarbons. There is little risk of capillary condensation even when used with gases at very high pressures (120+ bar)
- There is no risk of sulphur migration by sublimation or dissolution.
- The absorbents can be used to process liquid hydrocarbons.

[1,6]

Table 1
Solubility of sulphur in liquid hydrocarbons

Hydrocarbon	Solubility (ppm)
Pentane	300
Heptane	500
Toluene	2500

CONCLUSIONS

Development of new high activity mercury removal absorbents allows greater flexibility in the design of LNG plants. It is now possible to locate the MRU upstream of the main gas processing plant and

thus avoid mercury emissions and contamination of any co-produced NGLs. The high activity allows for smaller beds, which coupled with ew reactor designs, allows for savings in compression costs. The new absorbents can be recycled through metal smelters to give an auditable and environmentally acceptable route for disposal.

ACKNOWLEDGMENTS

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REFERENCES

1. Peter J H Carnell and Vince A Row & Rachel McKenna, “A re-think of the mercury removal problem for LNG plants”.
2. Zdravko Spiric, “INNOVATIVE APPROACH TO THE MERCURY CONTROL DURING NATURAL GAS PROCESSING”, INA-Naftaplin, Subiceva 29, 10000 Zagreb, Croatia
3. J. E. Leeper, “Mercury - LNG's problem”, Partec Lavalin Inc., Calgary, Alta., Canada(15)
4. Saunders J.B., Pahade R.F. and Delnicki W.V. Cryogenic Nitrogen rejection, Proc. ASME Annual Energy- Sources Technology Conf. Hydrocarbon Process Symposium, Dallas, pp. 43-49, Feb.15-18,1987.
5. Carnell, P., J., H. and Foster, A. “Control of Mercury Emissions from Gas Processing Plant Dryers” Mercury 2006 Conference on Mercury as a global pollutant, Madison, USA, August 6–11, 2006.
6. J. H., Openshaw, P. J. ”Mercury Distribution on Gas Processing Plants” 83rd Annual GPA convention March 14-17,2004, San Antonio, TX, USA