



## Mercury - LNG's problem

*Under some conditions mercury can be a major source for concern in LNG processing*

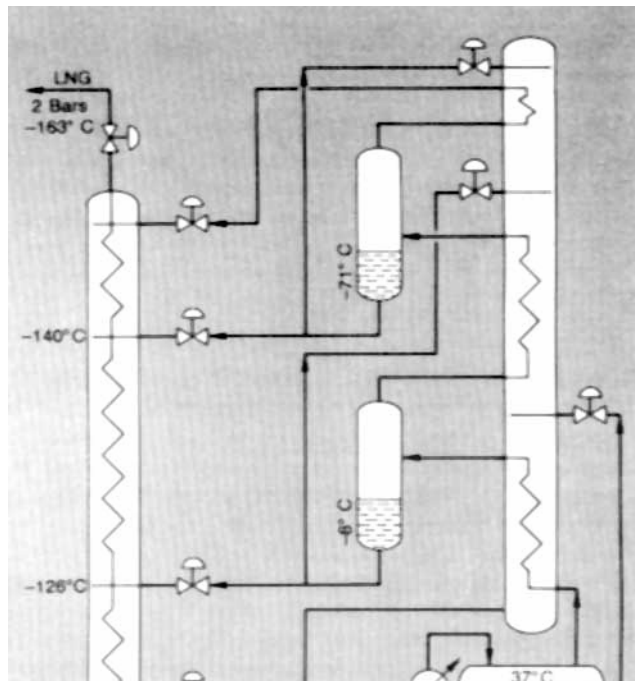
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Mercury induced corrosion in LNG plants using mixed refrigerant (Fig.1) can be severe on the cycle gas side of exchangers, primarily during warmup periods. The problem can be avoided by removing mercury from the feed and cycle gas liquid. Also, operating conditions during de-riming can be set to avoid or minimize the time during which corrosion can take place.

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 de-carbonation units, hold promise for mercury removal and merit further investigation.

### Problem Occurrence

Trace quantities of metallic substances are known to exist in natural gases including arsenic, selenium, mercury and uranium, but the significance was not recognized. Mercury was known to be in the Groningen gas (1969 or before) where severe corrosion was encountered on the gates and stems of wellhead valves, but carbon dioxide was considered to be the corroding substance. Although literature records the amount of mercury in the gas reduced in the transmission lines, this reduction was attributed to a mechanism based on the presence of hydrogen sulfide in the gas and iron oxide from the pipe.



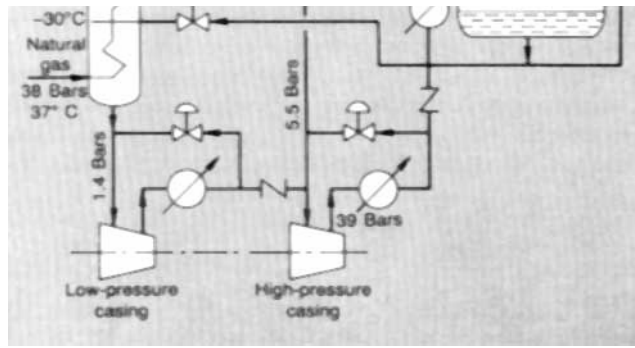


Fig. 1- A typical mixed refrigerant LNG plant.

More recently, failures occurred at the LNG plant at Skikda, Algeria, from tube corrosion in the spiral wound exchangers. Corroded tubes contained white deposits: aluminum oxide, aluminum hydroxide and aluminum carbonates, with traces of elemental mercury. It was generally assumed that the mercury might have been accidentally introduced. Later, traces of mercury, up to 12 micrograms per cubic meter, were found in the gas feed which led to considerable research and discussion on mercury removal methods, but no installation to remove the mercury.

## MERCURY CORROSION

Amalgamation (forming of an alloy) of mercury with almost all metals is exceedingly well-known. Mercury has been used to recover gold and silver since ancient times by amalgamation with the native noble metal, and recovery of the noble metal by distillation and recovery of the mercury.

Mercury amalgams are used in industrial processes, such as the manufacture of caustic soda or caustic potash with the mercury cell and sodium amalgam decomposer.<sup>2</sup>

Failure of metals, notably 70-30 cartridges brass, by exposure to metallic mercury is also well-known, in the re-use of brass firearms cartridge cases. Previously fired cases exposed to a primer containing fulminate of mercury exhibit de-zincification of the brass by corrosion. The metallic mercury can be readily seen on such a brass failure by light etching with a weak acid, and the de-zincification is evident by the characteristic red color of copper crystals.

Another example of mercury corrosion occurred during a private industrial research project to reproduce the published results of research on the solubility of elemental sulfur in sour natural gases.<sup>3</sup> During this research, 316 L stainless steel was severely corroded when subjected to temperatures of 65 to 121°C, pressures of 207 to 276 bars absolute, and an atmosphere of CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S. Reaction of the mercury with the hydrogen sulfide occurred to some extent (even at atmospheric pressure in glass vessels), provided water was present. Corrosion of the stainless steel was also expected but did not occur unless both mercury and liquid water were present. No elemental sulfur was formed under these conditions.

The records lead to the following conclusions:

- The mechanism postulated for the reduction of mercury in the pipe line is incorrect, as will be shown later by thermodynamic data, since elemental sulfur was not formed in the sour gas research.
- Mercury is regenerated in elemental form following corrosion, as shown by the example of mercury attack on 70-3- cartridge brass.
- It is probable that liquid water must be present for such corrosion or attack to occur.
- A key element in corrosion is the tube material, since aluminum is corroded and copper is not.

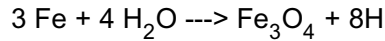
It also follows that the mechanism of all corrosion caused by the presence of metallic mercury takes place in the following sequence:

- Elemental mercury amalgamates with the surface layer of the metal being corroded.

- o The minute amount of the base metal alloyed with the elemental mercury is exposed intimately in an un-passivated state to the action of the corroding medium or, to state it alternatively, a short-circuited corrosion cell is formed between the mercury and the base metal with liquid water as an electrolyte.
- o If only pure water is present and inert gases, the base metal in the amalgam is corroded gradually by reaction with water:



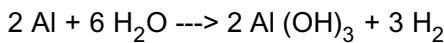
This mechanism can and does occur in boilers by the reaction:



If an acid anhydride, such as  $\text{CO}_2$  or  $\text{H}_2\text{S}$  is present, the corrosion product is the metal carbonate or sulfide.

**Thermodynamic examination** of some systems of un-passivated (no oxide film present) metals and liquid water show the effect that this reaction mechanism has on the metals most used in a cryogenic plant.

**ALUMINUM.** The reaction to the hydroxide takes the form:



The thermodynamics of the reaction are:

$$\begin{aligned} & \dots\dots\dots \text{Al}^{\circ} + 3 \text{H}_2\text{O}^{\circ} \rightarrow \text{Al}(\text{OH})_3 + 3 \text{H}_2 \\ \sim \text{H}^{\circ} \text{ (Kcal/mol, 18 }^{\circ}\text{C)} & \dots\dots\dots 0^{\circ} - 68.37^{\circ} \dots\dots\dots -304.9^{\circ} \dots\dots\dots 0 \\ \sim \text{G}^{\circ} \text{ (Kcal/mol, 25 }^{\circ}\text{C)} & \dots\dots\dots 0^{\circ} - 56.69^{\circ} \dots\dots\dots -272.9^{\circ} \dots\dots\dots 0 \\ \sim \text{H}^{\circ} \text{ (net)} & = (2) (-304.9) - (6) (-68.37)^{\circ} =^{\circ} -199.58 \\ \sim \text{G}^{\circ} \text{ (net)} & = (2) (-272.9) - (6) (-56.69)^{\circ} =^{\circ} -205.66 \end{aligned}$$

Since net enthalpy and net free energy changes are both highly negative, the reactions will strongly liberate heat and go to completion at essentially room temperature. The reason aluminum is not normally attacked by water is its tightly adhering oxide film, which is not present when aluminum is amalgamated with mercury in an anaerobic atmosphere.

Copper needs heat input, for the reaction to be sustained and will not proceed to completion.

$$\begin{aligned} & \dots\dots\dots \text{Cu}^{\circ} + 2 \text{H}_2\text{O} \rightarrow \text{Cu}(\text{OH})_2 + \text{H}_2 \\ \sim \text{H}^{\circ} \text{ (Kcal/mol)} & \dots\dots\dots 0^{\circ} - 68.37^{\circ} \dots\dots\dots -106.8^{\circ} \dots\dots\dots 0 \\ \sim \text{G}^{\circ} \text{ (Kcal/mol)} & \dots\dots\dots 0^{\circ} - 56.69^{\circ} \dots\dots\dots -85.5^{\circ} \dots\dots\dots 0 \\ \sim \text{H}^{\circ} \text{ (net)} & = -106.8 - (2) (-68.37)^{\circ} =^{\circ} + 29.94 \\ \sim \text{G}^{\circ} \text{ (net)} & = -85.5 - (2) (-56.69)^{\circ} =^{\circ} + 27.88 \end{aligned}$$

Therefore, copper would not be expected to be attacked by liquid water under any conditions, except at quite elevated temperatures, even in an amalgam, and such attack would require sustained heat input to continue. We would expect corrosion on copper in the presence of  $\text{CO}_2$ , but not in the absence of oxygen. Over a long period of time, copper will be weakened by alteration in the crystal structure caused by amalgamation.

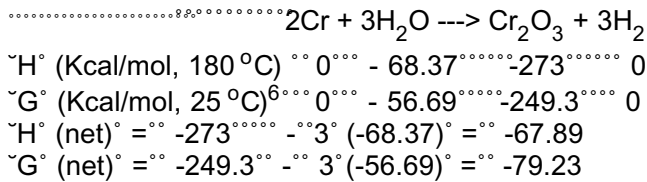
**Stainless Steel.** The corrosion resistance of stainless steel is dependent on a hard, tough, chromium oxide film that is self-repairing under oxidizing conditions. This oxide film is not self-repairing in reducing or neutral conditions. If the film is disturbed, corrosion will result. Here again, we can postulate metallic mercury forming an amalgam with the chromium, iron, or nickel; with subsequent corrosion by liquid water or an aqueous acidic phase.

The nickel reaction needs some heat to go forward and probably would not be corroded by this mechanism.



$$\begin{aligned} \Delta H^\circ (\text{Kcal/mol}) &= 0 - (-68.37) - (-58.4) = 9.97 \\ \Delta G^\circ (\text{Kcal/mol}) &= 0 - (-56.60) - (-53.03) = 3.68 \\ \Delta H^\circ (\text{net}) &= -58.4 - (-68.37) = +9.97 \\ \Delta G^\circ (\text{net}) &= -53.03 - (-56.69) = +3.68 \end{aligned}$$

On the other hand, the chromium reaction will proceed readily at room temperature if the chromium oxide film is broken.



Based on these examinations, the corrosion of the wellhead valves in the Groningen Field was due, in part, to the chromium-water reaction in the presence of mercury, but most probably was largely due to carbon dioxide, since the mercury concentration was so small and no mechanism existed for concentration.

The following generalizations can be made about corrosion induced through mercury amalgamation:

- Liquid water must be present.
- The metal involved must be above nickel in the electromotive series of metals for the reaction to proceed spontaneously at room temperature.

## 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 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, C<sub>1</sub> through C<sub>5</sub>.

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 dewpoint 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

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 microporous 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 dewpoint at the plant inlet. Zinc oxide is readily reduced for use at the site by a reducing gas generator using natural gas as fuel.

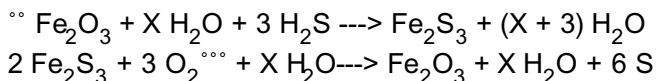
Other than reduced zinc oxide, the other metals above hydrogen in the electromotive series have tough oxide films not easily reduced or are unsuitable from the standpoint of reactivity or ease of amalgamation.

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.

**Metal Sulfides.** The metallic sulfides hold particular attention as potential mercury removal agents because:

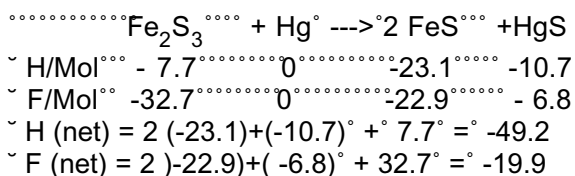
- A crystalline structure precludes deactivation by absorption of liquids.
- They are readily available.
- The available sulfur content varies fore reaction.

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.<sup>7</sup> 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<sup>7</sup>, operates on two basic reactions:



This illustrates that upon oxidation, Fe<sub>2</sub>S<sub>3</sub> 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:



The free energy change of this reaction is negative and the reaction would, therefore, proceed at room temperature.

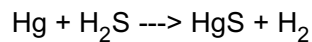
A potential problem would be dusting from reaction, but with the amount of mercury involved; and with the amine unit and gas filters downstream, this would hardly be a problem.

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.

**Other Methods.** All existing and future LNG units have an excellent liquid-gas contact system in the de-carbonation 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.

For example, a trace amount of hydrogen sulfide might be injected into the gas stream with subsequent removal of the H<sub>2</sub>S by the de-carbonation unit:



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

- Possible objections to the introduction of H<sub>2</sub>S to the gas stream.
- Difficulty in obtaining H<sub>2</sub>S.

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 mono-ethanolamine solutions, particularly for CO<sub>2</sub> removal system.<sup>9</sup> 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.

## LOCATION OF REMOVAL FACILITIES

Mercury removal facilities on the main gas stream should be located between the inlet knockout vessels and the de-carbonation unit.

Since mercury will be concentrated in the cycle gas system and in the butane and heavier, it is desirable to remove mercury from the butane make-up to the cycle gas system, or alternatively from the cycle gas liquid from the final cycle gas separator. The latter is preferable, even if only a small side-stream is treated, since in this fashion the mercury level in the cycle gas stream can be prevented from rising due to concentration.

### Literature Cited:

<sup>1</sup> Activated Carbon Handbook

<sup>2</sup> Shreve, R. Norris, Chemical Process Industries, 3rd Edition, McGraw-Hill, 1967, pp.237-239.

<sup>3</sup> Wieland, Denton R., Solubility of Elemental Sulphur in Methane, Carbon Dioxide and Hydrogen Sulfide Gas, Doctoral Dissertation, Texas A & M, January, 1958.

<sup>4</sup> Lange, N.A., *Handbook of Chemistry*, Handbook Publishers, Inc., Sandusky, Ohio, 1946, pp. 1532-1561.

<sup>5</sup> Hougen, O.A. and Watson, K.M., *Chemical Process Principles*, John Wiley & Sons, New York, 1947 - Volumes 1 and 2.

<sup>6</sup> Chilton, C.H., *Chemical Engineer's Handbook*, 5th Edition, McGraw-Hill, 1973

<sup>7</sup> Meyer, F.E., et al, "Corrosion Products of Mild Steel in Hydrogen Sulfide Environments", Corrosion, National Association of Corrosion Engineers, Vol. 24, February, 1958, pp. 69-75.

<sup>8</sup> *ibid*, Chemical Process Industries, p. 86

<sup>9</sup> "Sodium Vanadate as a Corrosion Inhibitor in Aqueous Mono-ethanolamine Solutions," Customer Service Report, Dow Chemical Company, Midland, Michigan, April 1959.

#### **Acknowledgement**

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#### **About the author**



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