

CHAPTER I
INTRODUCTION



Corrosion Problems of Equipments For Gas Production

Since natural gas was discovered in the gulf of Thailand and started producing in 1981, the economic status of the country has been progressively better. This is due to having natural gas used as source of energy in various factories and as essential feedstock for petrochemical industry. These imply that natural gas has been enormously useful. However, the natural gas taken up from its reservoir for use can also damage the related field industries enormously as well. That is due to corrosion caused by trace quantity of mercury contained in natural gas, which it will be described below.

UNOCAL THAILAND has been producing natural gas since 1981 and selling it to the Petroleum Authority of Thailand (PTT) at the entrance of the gas pipeline on the UNOCAL platforms in the gulf of Thailand. Being produced with the gas is natural gas condensate which is separated out at the platforms and loaded into a floating 400,000 barrel condensate barge that acts as a storage facility. It is well-known that the condensate can be used as excellently feedstock for ethylene plants or the other petrochemical units. The condensate is then either sold to PTT or exported directly by UNOCAL THAILAND. The production rates as of early 1990 were 550 MMSCFD of natural gas and 20,000 barrels per day (bpd) of condensate.

As of 1984, elemental mercury was found in the natural gas and some was actually recovered in form of liquid mercury on the platforms. The remaining mercury was carried over into the gas being flown through the 425-mile long pipeline to PTT's gas separation plant in Mab Ta Put and some was carried over to the liquid condensate in the condensate barge.

In the condensate barge, it is believed that there is some of mercury reaction occurred between the liquid and the surface of condensate barge and mercury is deposited in an unknown chemical form onto the walls of the condensate barge. As the walls of condensate barge are regularly cleaned by seraping off rust and other deposits, a fair amount of hydrocarbon sludge is obtained. This sludge cannot be dumped as it contains some 0.15 to 1.0 weight percent of mercury which is considered high. It is not only damage the walls of the condensate barge, but it is well known that some mass-ppm of mercury or less contained in the condensate resulted in corrosion of equipments in many processing plants concerned with use of the condensate, especially, corrosion of aluminium alloy material in cryogenic servics. In addition to corrosion of equipments in many plants, it is also found that the mercury in the condensate resulted in poisoning of noble metal catalysts in some processes[1,2].

In the case of mercury mixed in the natural gas, it causes the same results to equipments in the processes as the condensate does. Before natural gas enters production processes of any gas separation units, including that in Mab Ta Put, it must have been passed through the mercury removal unit, which most, if not all, of the mercury was caught here. It may have the least amount of mercury leaked from this unit and gone low but its effect can be cumulative

at any points on metal surface as it can amalgamate[3] It can then damage various equipments. This is the main cause of equipment failure, especially, failure of the aluminium heat exchanger, which the gas separation units of PTT at Map Ta put itself had been already encountered this problems until it must be shut down for a period of 4-5 months. It makes the country lost income obtained by this for several hundred millions baht.

Organic mercury compounds are typical mercury derivative that are commonly formed with elemental mercury in natural gas[4]. Most of organomercury compounds are liquids which are remarkably volatile[5,6]. No mercury removal units can catch them. To catch them, it is essential to decompose and convert them to the form of elemental mercury either by thermal or catalyst together with thermal[7]. Organomercury which has already passed through mercury removal units contacts with various equipments for a long time to the present time it is still lack of investigations of organomercury effect on metal corrosion. There are results caused by elemental mercury only. The behavior of organomercury compounds on metal corrosion has been payed attention to by this research. Dimethylmercury, which is among those compounds is selected to be represent to study their corrosive behavior because it is commercially available in high purity.

Mercury Corrosion and Literature Review

1. Mercury Corrosion in Natural Gas

Any processes associated directly between metal-mercury are very rare because mercury is a corrosive substance and dangerous to mankind.

Although there is a few examples of that, such as, thermoumeter and fluorescent lamp, both of them are the mercury-glass system on which corrosion problem is not existed. Thus if it is desired to continue inquiries about metal corrosion with mercurial substance, it is difficult to avoid mentioning about natural-gas produsing in which the metal-mercury corrosion process is hidden.

Mercury occurs naturally in trace quantities in air and natural gas, but it is difficult to generalize mercury concentrations in air which is typically in a range of 1 ng/m^3 to 10 ug/m^3 ($1 \text{ ppm by volume} = 10,000 \text{ ug/m}^3$). Some author[8] have reported that natural gas typically contains mercury concentrations between 1 and 200 ug/m^3 , but concentrations are probably best evaluated on a producing-formation basis. Osborne reported that there was organomercury formed and mixed with elemental mercury in natural gas[5]. Therefore, if any account on mercury in natural gas is mentioned, it should be meant the account resulted from all forms of the mercury

The implication of the effects of mercury in natural gas was not reported until 1973, when a catastrophic failure of aluminium heat exchangers occurred at the Skikda liquefied natural gas plant in Algeria[9]. Investgations determined that mercury corrosion caused the failure and that the mercury seemed to come from an accidental source, such as test instruments used in plant and field start up.

After the Skikda failure, a study of Groningen field in Holland revealed similar corrosion in the gas-gathering system. CO_2 was thought to be

the cause[10], but later investigations[11] pinpointed mercury, with concentrations ranging from 0.001 to as high as 180 ug/m³.

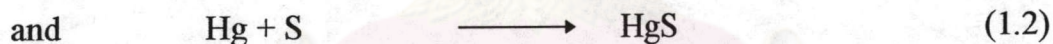
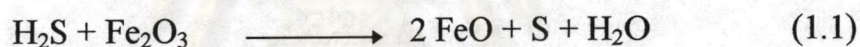
Phannenstiel et al.[11] state that most if not all of the mercury in natural gas was in the elemental form and that no natural gas processing plant problems were suspected to have been caused by organic or inorganic mercury compound. These statements would imply that elemental mercury was the probable cause of mercury problems. Although the concentration of mercury in a given natural gas may be extremely low, Audeh[12] observed that its effect was cumulative as it amalgamates.

Amalgamation is the formation of an alloy. Up to date the most serious problems reported by the industry owing to mercury corrosion have been the result of mercury forming an alloy with aluminium. Copper has also been presented some problems[13]. Saunders et al.[14] observed that brazed aluminium plat-fin heat exchangers were the predominant choice for cryogenic service. Aluminium was used for making that equipment due to its brazability, excellent mechanical properties at cold temperatures, and superior heat transfer characteristics. They further stated that mercury could damage aluminium used in these exchangers and must be completely removed to nondetectable levels in up stream equipments. Unfortunately, complete removal is not economical. But fortunately, the design of systems capable of minimizing operating problems associated with mercury in natural gas is currently being emphasized.

1.1 Operating Implication of Mercury in Natural Gas

The problems associated with mercury can begin at each producing well. Both the high investment required and the remote nature of wellsites prohibit mercury removal at these location. Thus, mercury is introduced into the wellbore and gathering systems simply by gas production

As mercury enters gathering-system pipeline, the mercury content of the natural gas is reduced because of chemisorption onto steel pipe walls. Leeper[10] suggested the following reactions as the driving force behind this reduction



Trace quantities of H_2S are the catalyst for the reaction of mercury with iron oxide from the pipe. The mercurous sulfide precipitates and is adsorbed onto the pipe wall. Grotewold et al.[13] reported that for one 68-mile pipeline, mercury content decreased from about 50 to 20 $\mu\text{g}/\text{m}^3$. This reduction was influenced by pipe-wall roughness and adhesive forces. Similar reduction were also experienced on pipe and vessel walls in facilities and plants

Other factors influence mercury distribution in following streams. Mercury condenses into the liquid phased of hydrocabons and gas-treating chemicals because of its greater solubility with higher-molecular-weight streams. Most facilities and processing plants that handle natural gas have

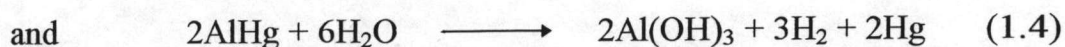
some form of separation, sweetening, and/or dehydration equipment. The amount of mercury reduction resulting from contact with higher-molecular-weight solutions is difficult to define owing to the wide range of hydrocarbon saturations and treating conditions. Grotewold et al. reported that some 50% to 60% of the inlet mercury accumulated at the bottom of the glycol absorber and that 15% to 20% was separated in scrubbers. This left 20% to 35% of the mercury entering the plant or facility to carry over into down-stream processing equipment and /or transportation pipelines.

1.2 Corrosion Mechanism of Mercury and Aluminium

Elemental mercury forms an amalgam with the surface layer of the metal contacted. With aluminium, the amalgam is much weaker than the metal itself and is often referred to as an embrittlement. To initiate aluminium corrosion, the tightly adhering aluminium oxide layer on the surface of the aluminium must be removed. The mercury/aluminium amalgam process removes this oxide layer. The layer can be removed chemically or mechanically and is catalyzed by the presence of an aqueous electrolyte. Phannenstiel et al. reported their study that mercury/aluminium amalgamation generally does not occur as a direct chemical reaction because the base-metal aluminium is usually protected by the oxide film.

The aqueous corrosion cell forms aluminium hydroxide and gaseous hydrogen through the following reactions :





These reactions leave the previously amalgamated mercury free to form the additional amalgam with the base metal in a continuous corrosion processes.

Observations of the physical nature of the corrosion indicate that the amalgamation/corrosion is preceded by small half-moon intrusion that forms a continuous network as edges of the intrusions joined together. The formation of aluminium hydroxide can be identified by a grayish-white “whisker” appearance. Rapid pining is common because mercury tends to effect in localized area

Operating conditions conducive to corrosion in plant containing aluminium heat exchangers include deriming and shutdown. Deriming is heating cycle on the exchangers that removes “frost” (frozen water, hydrates, and CO₂ frost) buildup from exchanger internals. To melt the frost, the exchanger typically is taken out of service and hot, dry gas is passed through it. The hot gas melts the frost and is intended to vaporize and purge out moisture and other impurities. Thaw gas is continuously passed through the exchanger until the effluent dewpoint is significantly reduced or until design limits on exchanger core temperature or heat exposure time are reached. Shutdown occurs when gas is not passed through the system, heat exchange no longer occurs, and the exchangers are allowed to warm to ambient conditions. Deriming is necessary periodically to improve exchanger efficiencics lost to frost buildup on exchanger core surfaces; however, deriming and shutdown frequency should be as low as possible to minimize the potential for a corrosive

environment. Liquid water is present during both deriming and shutdown. When thaw gas is passed through the exchanger or when operation are resumed, gas containing trace concentrations of mercury is allowed to contact the aluminium in an aqueous environment.

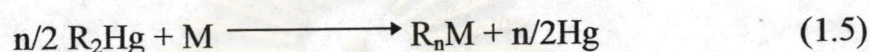
Deriming operations stopped before completion can also lead to the formation of mercury corrosion cells. Any liquids left in the cryogenic aluminium equipment will be lying in low spots along with any condensed mercury. Care should be exercised during the mechanical design stage to eliminate low spots and pockets, and low-point drains should be installed where possible. These drains can be opened during operations to sweep liquid out of the system with hot thaw gas.

2. Decomposition and Reaction of Dimethylmercury[15,16]

The metal-carbon bond in organomercury compounds is rather unreactive in comparison with that in organic compound of other group II metals. Thus organomercurials are a poor source of nucleophilic carbon and usually do not react with compounds such as alcohols, aldehydes, ketones or alkyl halides. Nevertheless, many of the principal reactions that they can undergo involve electrophilic substitution at carbon, the best-characterised example being reactions with metal salts, acid, and halogens. In these substitutions the fully organic mercurials (R_2Hg) are generally more reactive than the corresponding organomercury compound salt ($RHgX$) since the presence of the x group attenuates the nucleophilicity of R. The Hg-C bond in aryl derivatives is more readily cleaved than its counterpart in aliphatic systems.

There are several types of the reactions of mercury-carbon bond as follows :

1. replacement of mercury by other metals (Organometallic synthesis) which can be written in general form of those as follow :



2. replacement of mercury by hydrogen, which it can be separated to be acidolysis, reduction implemented by other hydrogen donor and thermal decomposition

3. replacement of mercury by carbon substituents

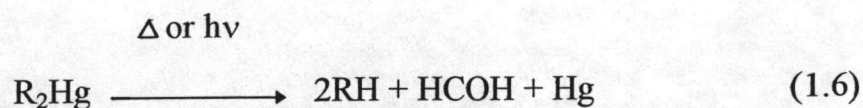
4. replacement of mercury by oxygen substituents

5. replacement of mercury by halogens

The most interested types of all which associated with this research is replacement of mercury by hydrogen, those are acidolysis and reduction.

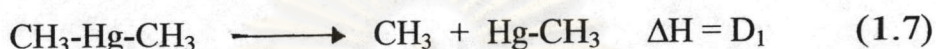
Reduction

Reductive demercuration of diorganomercurials can be accomplished by pyrolysing or photolysing in the presence of a hydrogen donor, such as methanol, which is according to general form of the following equation ;



or in the presence of other hydrocarbon solvents, such as benzene, etc.

DMM is one of alkyl diorganomercurials, which it is rather small molecule with low intermolecular force, but it is rather more stable than the other. Skinner[18] had organized its thermochemical data as follow ;



The energy required to initiate disruption is 51.5 ± 2 kcal/mole, and the energy required to complete the break-up of the molecule,

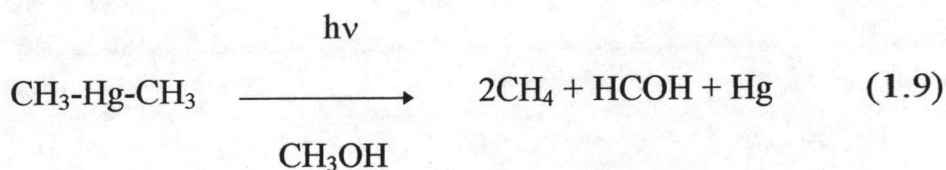


is 6.9 ± 3 kcal/mol, compared with those of HgCl_2 , which are

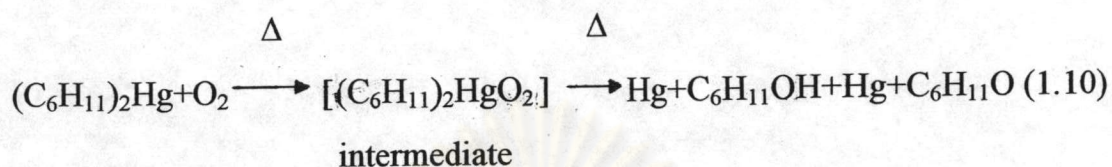
$$D_1 = 81 \pm 1 \text{ kcal/mol and}$$

$$D_2 = 24 \text{ kcal/mol}$$

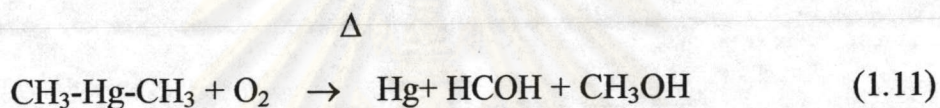
It is found that those of $\text{CH}_3\text{-Hg-CH}_3$ are much lower than that of HgCl_2 . It must not forget that HgCl_2 is the severe corrosive agent to metals in both organic and inorganic solvent, then it is believed that DMM can also do that. K.C. Bass[17] had organized the data of decompositions obtained by pyrolysing and photolysing of organomercurials in both alcohol and other hydrocarbon solvent. One instant of those data is photolysis of DMM in methanol as follow;



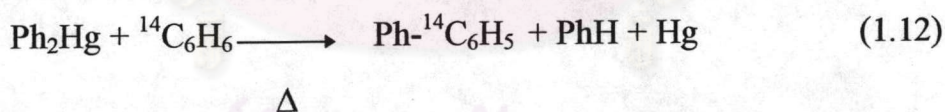
He had shown the decomposition instant of dicyclohexylmercury in the presence of oxygen according to the following reaction ;



then the corresponding reaction of DMM with the above should be



In the case of thermal decomposition of organomercurials in other hydrocarbon solvents, that of dirphenylmercury in ^{14}C -labelled benzene in the presence and absence of oxygen was shown for example as follow ;



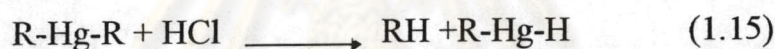
It is believed that DMM accomplish the corresponding reaction with the above by supporting of the similar condition and enviroment.

Acidolysis

Both alkyl groups can be removed from diorganomercurial by mineral acid as in general form of the following reactions ;



but more vigorous conditions are required for the second stage. Organic acids, which they are weak acid, such as acetic acid, can react with fully organic mercurials but not normally with organomercury salts. Dessy and Kim[19] had studied mechanism and rate of the reactions between various dialkyl mercurials and hydrogmn chloride in various solvent systems according to the general form of the equations



They reported that reaction rate of cleavage of C-Hg bond in DMM was slower than the others and that the following solution systems, such as 91% methanol-9% water, 67% dioxane-33% water, and DMSO:Dioxane at 10:1, can be used as solvents. Formation of symmetrical diorganomercurials can be obtained the reaction of two unsymmetrical diorganomercurials according to the following general form[15]



The reaction is reversible and in fact the position of equilibrium is normally well to the left. The forward reaction, known as "symmetrisation", is affected through the agency of an anionic or neutral ligand (L) when the inorganic product is the complex $\text{HgX}_2 \cdot \text{L}_2$, or with a reducing agent when mercury is

formed. It is found by equations (1.15) and (1.16) that HgCl_2 can be obtained by adding HCl , as shown in equation (1.16)

3. Dimethylmercury Corrosion on Metal

It is recognized that Hg and HgCl_2 are corrosive agents well, thus if any metal is immersed in the DMM solution either with heat or with acid, then it should be corroded by either the elemental Hg or HgCl_2 resulted by one process as mentioned.

Scope of Investigation

Nowadays natural gas production in the gulf of Thailand has been encountering the problem of mercury cumulative on various equipments, both in storage units and production units, which it is difficult to solve. Although the elemental mercury had been already eliminated at the mercury removal unit, those equipments have been still damaged as mentioned. Therefore, the main research project associated with mercury substance in natural gas has been aimed to find out how to remove mercury from natural gas and to prevent corrosion to various equipments. This research is only one part of the project and really is the subset of that. It is mainly aimed to study and collect the data of various metal corrosions caused by dimethylmercury. That is due to DMM as one of organomercury mixed in natural gas. Although quantity of organomercury compounds is too low-in ppb, but DMM seems to be predominant rather than the others. Metal selected to study the corrosion rates are, for example, carbon steel and aluminium, because both of them are the main metal used to make the equipments for producing and have ever been

corroded by mercury substance as previously mentioned. In addition to collect the corrosion rates of the metal obtained by DMM, the effects of various factors on the corrosion rates are also studied, such as concentration of corrosive media, the exposure temperature and velocity of corrosive solutions. Another important study included in this research is investigation of the corrosion appearances on specimen surface after exposure in corrosive solutions in order to identify forms of corrosion which it is private manner of one pair of metal-corrosive media, for example, uniform corrosion, pitting, intergranular corrosion and etc. The forms of corrosion appeared on specimen surface can be used as data for evaluating methods of corrosion prevention resulted from mercurial substance later. This research will not be aimed at mechanisms of corrosion reactions occurred because it is not the main interested issue and is time constraint

Objectives

This research is aimed to study the following main issues;

- 1 To study corrosion of carbon steel and aluminium metal by dimethylmercury including their corrosion rates
- 2 To study the effects of various factors, such as concentration of corrosive media, the exposure temperature and velocity of corrosive solution, on the corrosion rates
- 3 To investigate the corrosion appearance on specimen surfaces obtained by exposure in corrosive solutions.