

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

Mercury presented in gas condensate both organic and inorganic forms can give rise to both toxicological and equipment corrosion problems to industrial plant, particularly petrochemical plants. The inorganic form can be further divided into elemental mercury and mercuric salts. Organic mercury can be found in long and short alkyl and aryl compounds. With a small trace of mercury in mainstream it can be financially damage especially when unscheduled shut down are forced (Shafawi *et al.*, 2000). The nature of mercury compounds in condensate is not well known. Generally, this limited knowledge on mercury in condensate arises because:

1. The amount of mercury and the types of mercury species present are not easily determined. This is due to the nature of samples. Natural gas condensates are very volatile complex mixtures. In addition, the mercury species are volatile and can be transformed into different forms of mercury, caused by changes in their environment such as temperature, pressure, including the presence of active particles or impurities.

2. The techniques use for the determination of mercury content in different process streams are not standardized, validated or well documented.

3. Among laboratory technicians, some may not be aware of the advanced technical details required in determination, while others may not confide their skill.

4. With the mercury species content being unique to each type of condensate and at such low levels, sophisticated technique for an analysis is required.

However, Wilhelm and Bloom (2000) reported that the concentration of mercury in crude oil and natural gas is highly dependent on geologic location and varied between approximately 0.01 ppb and 10 ppm (wt.).

2.1 Properties of Mercury and Mercury Compounds (Wilhelm, 2001)

The common physical properties of element mercury (Hg^0) are listed in Table 2.1. Mercury occurs in nature in the zero (elemental), +1 (mercury[I] or mercurous), or the +2 (mercury[II] or mercuric) valence states. The mercurous compounds usually involve Hg-Hg bonds and are generally unstable and rare in nature. Widely, mercury occurs most in the elemental form or in the inorganic mercuric form such as mercuric oxide, mercuric chloride, mercuric sulfide and mercuric hydroxide.

Table 2.1 Physical properties of elemental mercury (Wilhelm, 2001)

Atomic number	80
Atomic weight	200.59 atomic mass units
Boiling point	367°C
Boiling point/rise in pressure	0.0746°C/torr
Density	13.546 g/cm ³ at 20°C
Diffusivity (in air)	0.112 cm ² /sec
Heat capacity	0.0332 cal/g at 20°C
Henry's law constant	0.0114 atm m ² /mol
Interfacial tension (Hg/H ₂ O)	375 dyne/cm at 20°C
Melting point	-38.87°C
Saturation vapor pressure	0.16 N/m ³ at 20°C
Surface tension (in air)	436 dyne/cm at 20°C
Vaporization rate (still air)	0.007 mg/cm ² hr for 10.5 cm ² droplet at 20°C

Organic mercury mainly consists of two types: R-Hg-X compounds and R-Hg-R compounds where X is inorganic anions, such as chloride, nitrate or hydroxide, and R is organic species, of which methyl (-CH₃) is prominent. The most common dialkyl mercury compound is dimethylmercury. Mercury in

nature is quite difficult to oxidize in the present environment. However, it can be oxidized by the presence of stronger oxidants such as hydrogen peroxide, nitric acid and concentrated sulfuric acid.

2.2 Mercury in Hydrocarbons

There is almost no information on typical amounts of organic mercury, said organomercury, compounds in gases and condensates. Mercury analysis techniques used for gas and condensates samples usually determine either total mercury, or elemental mercury, dimethyl and diethyl mercury only. At present organomercury compounds are not generally explicitly detected. Some comments have been found in literature regarding the proportion and nature of mercury and organomercury compounds in fluids. It is generally agreed that mercury in natural gas is almost all in elemental form, but in condensates and petroleum liquids organomercury compounds are significant and may be the predominant form of mercury (Edmonds *et al.*, 1996). Crude oil and gas condensate can contain several chemical forms of mercury, which differ in their chemical and physical properties.

At ambient temperature, elemental mercury is soluble in crude oil and liquid hydrocarbons to a few (1-3) ppm, which is several times greater than its 0.05 ppm solubility in water (Wilhelm, 1999). Elemental mercury is adsorptive and adsorbs on suspended wax, sand and other solid materials suspended in liquids. It also reacts with iron oxide on pipe and equipment walls. The solubility of Hg^0 in produced hydrocarbons depends strongly on temperature. Therefore, when condensate is cooled in the process, Hg^0 can precipitate in equipment.

Organic mercury compounds are highly soluble in crude oil and gas condensate. Dialkylmercury compounds partition to hydrocarbon liquids in separation and to distillation fractions according to their boiling points shown in Table 2.2. However, the amount of dialkylmercury compounds presented in produced hydrocarbon is a matter of some debate. Monomethylmercury halides partition preferentially to water in primary separations. The existence

of organic mercury compounds is inferred when analysis for total mercury in a liquid matrix does not match mass balance with operationally speciated forms.

Table 2.2 Boiling points of volatile mercury compounds (Wilhelm and Bloom, 2000)

Hg compound	Boiling point (°C)
Hg ⁰	367
(CH ₃) ₂ Hg	96
(C ₂ H ₅) ₂ Hg	170
(C ₃ H ₇) ₂ Hg	190
(C ₄ H ₉) ₂ Hg	206

Inorganic mercury salts (Hg⁺²X or Hg⁺²X₂), mostly mercuric halides (HgCl₂), are about 10 times more soluble than Hg⁰ in oil and gas condensate, as shown in Table 2.3, but preferentially partition to the water phase of hydrocarbon/water separations. Mercuric halides also may be physically suspended in oil or may be attached (adsorbed) to suspended particles.

Table 2.3 Solubility of some mercury compounds in hexane (Wilhelm and Bloom, 2000)

Species	Solubility (ppb)	Temperature (°C)
Hg ⁰	1,200	27.5
HgCl ₂	11,500	27.5
CH ₃ HgCl	> 1,000,000	20.0
(CH ₃) ₂ Hg	∞	

Mercury (sulfur) complexes (HgK where K is an organic sulfide, thiol, thiophene or mercaptan) are presumed to exist in some crude oils and condensates. The existence of such compounds in produced hydrocarbons is uncertain at present. Specific complexes of mercury have not been identified

with certainty but their existence is inferred in some chromatographic and operational speciation experiments.

Generally, unprocessed hydrocarbon liquids contain suspended mercury compounds. The most common example is mercuric sulfide (HgS), which is insoluble in water and oil. Particle sizes are typically small. Elemental mercury can also be suspended in liquids that become saturated due to cooling such as in cryogenic liquid separations. Also including are mercury compounds that are not dissolved but rather adsorbed on inert particles such as formation fines.

Mercury removal systems (adsorbents) for hydrocarbon liquids are designed to react with elemental mercury and some mercury compounds. Removal systems are mostly ineffective in sorbing suspended mercury. This means that if suspended mercury is present in a liquid feed, it must be filtered to remove suspended solids. Similarly, some mercury removal systems are chemically specific to one form of mercury, usually elemental form. If the feed contains substantial amount of another mercury species such as dialkyl or complexed mercury, then the removal system may not achieve the design criteria for removal efficiency. Distinguishing the various mercury species by chemical analysis is a rigorous and difficult to work out. Just a few commercial laboratories can accomplish with verifiable accuracy.

2.3 Effects of Mercury on Processing

Wilhelm (1999) has previously summarized that mercury has several detrimental impacts on gas processing operations.

1. It deposits in cryogenic equipment, sometimes causing cracking of welded aluminum heat exchangers.

2. Mercury that distributes in gas plant products — organic mercury partitions to liquid fractions and elemental mercury equilibrates to both liquid and gas — reduces the quality and affects downstream processes. Gas plant products used for chemical manufacture, especially olefins, ethylene,

aromatics and MTBE, are at risk to mercury in process feeds due to the cited equipment problems and due to catalyst poisoning.

3. Mercury contaminates treatment processes such as molecular sieve and glycol dehydration units, and amine acid gas removal systems. Contaminated treatment liquids and spent mol-sieve adsorbents are difficult to dispose of and to regenerate.

4. Mercury sorbent materials used for gas or liquid treatment, when spent, constitute a generated hazardous waste that plant operators must store or process for disposal.

5. Mercury deposition in equipment poses a health and safety risk for workers involved in maintenance or inspection activities.

6. Sludge containing mercury from water treatment systems, separators, desalters, and heat exchangers represents a toxic waste stream that is difficult to store or process for disposal.

7. Waste water streams that contain high levels of mercury must be treated to remove mercury prior to discharge thus adding significant costs to plant operational expense.

2.4 Mercury Removal Systems

Mercury removal adsorbent beds are used to scavenge mercury from gases or liquid hydrocarbon streams. The adsorbents are a granular or palletized material consisting of a substrate support (zeolite, activated carbon, metal oxide or alumina) and a reactive component (Ag, KI, CuS, metal sulfide, etc.) that is bonded to the support. Mercury removal systems for hydrocarbons have been summarized in Table 2.4 (Wilhelm, 1999).

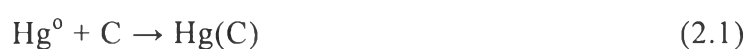
Adsorbents function by reacting mercury or a mercury compound to a chemical form (HgS , HgI_2 or amalgam) that is insoluble in hydrocarbon liquid and chemically inert to the components of process stream. Several commercial processes are available for removing mercury and mercury compounds from hydrocarbons. Some commercial mercury removal systems are targeted at gas phase treatment and some are targeted at liquids. In gas phase treatment (Table

2.4), the systems primarily consist of sulfur-impregnated carbon, metal sulfide on carbon or alumina, and regenerative molecular sieve (Ag on zeolite).

Table 2.4 Mercury removal systems for hydrocarbons (Wilhelm, 1999)

Reactant	Substrate	Complexed form	Application
Sulfur	Carbon, Al ₂ O ₃	HgS	Gas
Metal sulfide	Carbon, Al ₂ O ₃	HgS	Gas, Liquid
Iodide	Carbon	HgI ₂	Dry liquid
Pd+ H ₂ ; metal sulfide	Al ₂ O ₃	HgS	Liquid
Ag	Zeolite	Ag/Hg amalgam	Gas, light liquid
Redox/ion exchange	Resin	Hg ²⁺	Gas
Metal oxide/sulfide	Oxide	HgS	Gas, liquid

In a gas-treatment system that uses a sulfur-impregnated carbon adsorbent, elemental mercury physically adsorbs on carbon and then reacts to form non-volatile mercury sulfide (Wilhelm, 1999):



The reaction between Hg⁰ and sulfur is a redox reaction in which mercury is oxidized and sulfur is reduced. The resulting mercuric sulfide is nonvolatile, insoluble and is retained on the bed.

Metal sulfide (MS, where M = Cu, Mo, Co and others) systems for gas have the advantages that the MS is not soluble in liquid hydrocarbon and it is less sensitive to water. Therefore, metal sulfide systems are more suited to moist, heavy hydrocarbon feeds in which some hydrocarbon condensation is possible. In a MS mercury removal system for gas with an alumina (Al₂O₃) substrate, mercury directly reacts with the metal sulfide. Adsorption on the support is less kinetically favoured than for carbon and is not strictly required for the reaction to occur:



Molecular sieve adsorbents that contain certain metals (silver) selectively capture mercury by an amalgamation process. The system is regenerative in that mercury is released as mercury vapor when heated in the regeneration cycle.



Because of limited capacity, these systems require a regeneration system that cycles frequently and a mercury removal system for the regeneration gas.

Metal oxide removal systems for gas are oxides that are partially converted to sulfides by activation with organic sulfides or H_2S . The resulting adsorbent has adsorptive characteristics of the oxides and reactive characteristics of a metal sulfide. Metal oxide systems have the advantage that they are not harmed by sour gas.

Mercury removal processes for liquid hydrocarbons consist of iodide-impregnated carbon, metal sulfide on carbon or alumina, a mol-sieve amalgam system and a two-step process consisting of a hydrogenation conversion catalyst followed by MS reaction with elemental mercury. The various liquid removal systems have both advantages and disadvantages that depend on feed composition and stream location (Wilhelm and Bloom, 2000). Their function reacts primarily with elemental mercury and with some mercury compounds to form insoluble chemical form. Removal systems are ineffective in reacting with suspended mercury such as HgS . If HgS is present in a liquid feed, the feed liquid must be filtered (or otherwise treated) to remove suspended solids in order to that the system is to function effectively. Most mercury removal systems for liquids are chemically specific to one form of mercury, usually elemental. If the feed contains substantial amounts of ionic, dialkyl or

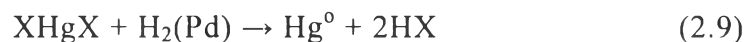
complexed mercury, then the removal system may not achieve designed criteria for removal efficiency.

The carbon/iodide system consists of potassium iodide impregnated carbon with a large pore diameter. The carbon/iodide adsorbent will scavenge elemental and organic mercury.



The mercury must be oxidized to react with iodide. In theory, the oxidation step is assisted by carbon, which provides catalytic assistance to the oxidation step. Main advantages of MS systems are that they are relatively insensitive to sulfur, water and aromatics, and they have a high capacity. The large capacity translates into smaller bed size and longer bed life.

Reportedly, metal sulfides on alumina do not react efficiently with liquid-phase organic mercury. For feeds that contain a significant amount of organic mercury, one system uses an initial hydrogenation step in which organic mercury is converted to elemental mercury on a catalyst. Elemental mercury is then captured by a metal-sulfide (CuS or other metal sulfides) impregnated alumina (Al_2O_3).



However, this process has the advantage that it is relatively insensitive to moisture and high molecular weight compounds—it will withstand plant inlet conditions in some cases. But the major drawback is that the hydrogenation step requires hydrogen and high temperature.

The liquid-phase regenerable molecular sieve (zeolite) system is analogous to the gas-phase system using silver to amalgamate with mercury. Amalgamative systems require regeneration and a separate mercury-treatment

system for the regeneration of gas. But water condensed from these systems also will contain mercury.

Metal oxide mercury removal systems for liquid-phase treatment are similar to the metal oxide systems for gas and consist of metal oxides that are activated by reaction with H₂S. They function in generally same manner as metal sulfide systems. Metal oxide systems are less affected by contaminants (sulfur compounds, aromatic, olefinic and heavy hydrocarbons) than carbon-based adsorbents.

2.5 Background of the Invention

According to Sugier and La Villa (1978), metals such as gold, silver and copper formed amalgams with mercury are used to extract or trap mercury from the main streams, but these metals have not been used industrially on a large scale because the volume of feed per volume of adsorbent and per hour is very small. Also, the use of activated carbon support impregnated with a silver salt reported is ineffective to remove mercury in hydrocarbon. They have proposed the use of copper sulfide and a support selected from the group formed by silica, alumina, silica-alumina, silicates, aluminates, and aluminosilicates where a specific surface area of the adsorbents between 20 and 250 m²g⁻¹ were used to remove mercury from gas or liquid hydrocarbons. The results show that these adsorbents are effective in removing mercury, which the efficiency level is defined by:

$$\frac{\text{Hg content on entry} - \text{Hg content on outlet}}{\text{Hg content on entry}} \times 100 \quad (2.11)$$

They also claimed that an average pore diameter at least equal to 100 Å has an increased stability in the presence of feed containing condensable hydrocarbon (C₄ or above C₄). In reference to what they have been said, the temperature range where the adsorbents are effective is generally between -50°C and +200°C. If the operating temperature is more than that, it may lead

to melting of the copper and a decrease in activity. These adsorbents can be carried out at atmospheric pressure or under a higher or lower pressure, whereby the total pressure can reach, for example, 200 bars. Finally, they claimed that the volume of feed per volume of adsorbent and per hour in the case of hydrocarbon liquids is preferably between 0.1 and 50. The mercury removal device that they use in their experiment comprises three reactors in series. However, the device can comprise a single reactor or at least two reactors in parallel, but at least two reactors in series are preferred.

Markovs (1993) from UOP describes the use of a large non-regenerated adsorption bed in combination with regenerated secondary adsorption bed to reduce sequestered mercury that reintroduce into the environment by means of the spent gas used to periodically regenerate the fixed beds. Using the combination bed is from the fact that if mercury is removed from the process streams by use of non-regenerable adsorbents, very large adsorption beds are required because sufficient adsorbent must be present not only for the long term equilibrium capacity, but also enough adsorbent to contain the mass transfer (reaction) zone. Contrastingly, if the case where mercury is removed by regenerative means, less adsorbent is required since only the adsorbent for containing the mass transfer zone is required. If regenerable, the regeneration media requirements are not only large but result in a large mercury-loaded bed effluent which must itself be disposed of in an environmentally safe manner. Such a combination allows for (a) attaining the lowest possible mercury levels in the process streams, (b) making full utilization of the non-regenerative mercury removal adsorbent, and (c) disposing of the mercury in an environmentally safe manner. His invention involves the removal of mercury from either in the hydrocarbon liquid phase or the gas phase, which the potential component is elemental mercury, by using the copper sulfide loaded on alumina in the non-regenerable adsorption bed operated at mild condition while the adsorbent particles in the regenerable adsorption bed comprise crystallites of aluminosilicate zeolite such as zeolite X and zeolite Y containing at least one metal selected from the group consisting of silver, gold, platinum and palladium.

McNamara (1994) claimed the use of activated carbon containing metal halides for removal of mercury from liquid hydrocarbons, particularly even trace levels of mercury, where the metal is selected from the group consisting of K, Ca, Fe and Zn and halide is selected from the group consisting of Br, Cl, and I. With the experimental condition, ambient temperature and pressure, it was found that the adsorbent was quite effective to remove even the trace amount of mercury presented.

Yan (1996) presented the suitable adsorbents for use in removing mercury from oil. He intended not only to develop the process that can be an add-on to an existing system, but also to improve the life cycle of the adsorbents to minimize the operating cost and to reduce the spent adsorbent disposal cost. He reported that the useful adsorbents used for removing mercury from gases and liquids, which have been proposed previously, are copper sulfide on alumina or silica alumina, silver, silver/gold, nickel or copper on support and sulfur on zeolites. Even though these adsorbents are generally quite effective in removing mercury from condensate, their cycle life for mercury adsorption is only about 1-3 months depending on the mercury concentration of the condensate, which is too short to be commercially useful. In his study, four types of adsorbents were experimented; (1) copper oxide on alumina ($\text{CuO}/\text{Al}_2\text{O}_3$), (2) copper sulfide on alumina ($\text{CuS}/\text{Al}_2\text{O}_3$), (3) silver on alumina ($\text{Ag}/\text{Al}_2\text{O}_3$), and (4) copper sulfide on activated carbon (CuS/C). In his work, the mercury removal from the condensate increases with temperature, indicating that it is a reactive adsorption involving chemical reaction and not a simple physisorption. He also found that the organic mercury can be removed effectively by using activated carbon as the support of the CuS adsorbent, but it is ineffective in the case of Al_2O_3 when dimethylmercury was compared. Thus, the process is based on high temperature chemisorptions for selective adsorption of mercury and uses a special CuS/C adsorbent which is effective for removal of most types of mercury compounds. However, he claimed that the spent CuS/C is not easily regenerated. Little mercury was stripped off using hot N_2 gas at 340°C . Substantial decomposition of HgS only takes place at temperature above

500°C, but heat treating at such a high temperature, the activity of CuS/C was greatly reduced. Nevertheless, he claimed that the CuS/C adsorbent has a long life of more than 1 year. Regeneration of the adsorbent using an elaborating operation is not economically justified, and it should be disposed of.