CHAPTER II
LITERATURE REVIEW

2.1 Background

2.1.1 Occurrence of Mercury

Mercury metal is widely distributed in nature, usually in quite low concentrations. The terrestrial abundance is on the order of 50 parts per billion (ppb), except in mercuriferous belts and anthropogenically contaminated areas. In soils, the average mercury content is about 100 ppb, ranging from 30 to 500 ppb. In rocks, mercury content ranges from 10 to 20,000 ppb. Surface waters, except where special geological conditions prevail or where anthropogenic sources occur, generally contain less than 0.1 ppb total mercury. The average mercury content of sea waters has been found to range from 0.1 to 1.2 ppb (Iverson *et al.*, 1978). The most important mineral of mercury is cinnabar (HgS), found in rocks near recent volcanic activity or hot spring areas and in mineral veins or fractures as impregnations. In addition to cinnabar, corderoite ($Hg_3S_2Cl_2$), livingstonite ($HgSb_4S_8$), montroydite (HgO), terlinguaite (Hg_2OCl), calomel (HgCl) and metacinnabar, a black form of cinnabar, are commonly found in mercury deposits (Cammarota, 1975). The numerous other mercury minerals are rare and not commercially significant.

In petroleum such as natural gas, condensate and crude oil, mercury is found in wide range. The presence and variety of mercury species are highly dependent on the source and type of petroleum. The concentration of mercury in crude oil and natural gas varies between approximately 0.01 ppb and 10 ppm (wt) (Wilhelm, 2001). In natural gas, concentrations of mercury are typically reported as μg per "normal" cubic meter, where normal (N) indicates standard temperature and pressure. Concentrations of mercury in natural gas vary from 0 to > 300 $\mu g/Nm^3$ with some of the highest concentrations occurring in the Indonesian Arun and Dutch Groningen fields (see Table 2.1). Concentrations of mercury vary from 10 to 3,000 ppb (Sarrazin *et al.*, 1993) and 0.5 to 10 ppb (Yan, 1996) in natural gas condensate and crude oil, respectively.

Table 2.1 Published concentrations for various natural gases and oils

Field	Location	Hydrocarbon	Hg Concentration	Reference
Groningen	Netherlands	Gas	0.001-180 μg/Nm^3	Bingham, 1990
Unknown	Netherlands	Gas	0-300 μg/Nm^3	Gijselman, 1991
Arun	Sumatra	Gas	180-300 μg/Nm^3	Muchlis, 1981; Situmorang and Muchlis, 1986
Unknown	Middle East	Gas	<50 μg/Nm^3	Hennico *et al.*, 1991
Unknown	South Africa	Gas	100 μg/Nm^3	Hennico *et al.*, 1991
Unknown	Far East	Gas	50-300 μg/Nm^3	Hennico *et al.*, 1991
Cymric	San JoaquinVly, CA	Oil	1.9 - 21 ppm	Bailey *et al.*, 1961

2.1.2 Forms of Mercury

Mercury can occur in three chemical forms: elemental, inorganic and organic. The chemical forms that have been considered important for mercury in environmental samples are listed in Table 2.2.

1. **Elemental mercury** refers to the metallic element (Hg°), also known as quicksilver or metallic mercury. In this form, mercury can exist as a shiny silver liquid or a colourless, odourless gas vapor at room temperature, and it is insoluble in water.
2. **Inorganic mercury** (Hg^{1+} and Hg^{2+}) refers to mercury in combination with other element such as sulphur, chlorine, and oxygen.
3. **Organic mercury** refers to mercury compounds that include carbon, such as methylmercury (CH_3Hg^+). Each of these forms exhibits unique chemical and biological characteristics and has a different degree of toxicity.

Table 2.2 Major mercury species in environmental samples (Morita *et al.*, 1998)

Elemental mercury		Hg°
Inorganic mercury species	Mercuric ion	Hg^{2+}
	Mercurous ion	Hg^{+}
	Mercury sulfide	HgS
Organic mercury species	Methylmercury	CH_3Hg^{+}
	Ethylmercury	$C_2H_5Hg^{+}$
	Phenylmercury	$C_6H_5Hg^{+}$
	Dimethylmercury	$(CH_3)_2Hg$

Mercury exists almost exclusively as elemental mercury in natural gas. In contrast, condensate and crude oil contain mercury in a variety of forms, including elemental, ionic and organometallic. Table 2.3 shows various chemical forms of mercury in naturally occurring hydrocarbons (Wilhelm, 2001).

Table 2.3 Approximate natural abundance of mercury compounds in hydrocarbons

Compound	Coal	Natural Gas	Gas Condensate	Crude Oil
Hg°	T	D	D	D
$(CH_3)_2Hg$	?	T	T, (S?)	T, (S?)
$HgCl_2$	S?	N	S	S
HgS	D	N	Suspended	Suspended
HgO	T?	N	N	N
CH_3HgCl	?	N	T?	T?

Abundance: D (dominant) – greater than 50% of total
S (some) – 10 – 50%
T (trace) – less than 1%
N (none) – rarely detected
? – data not conclusive

As mentioned above, the forms of mercury compounds present are uncertain in crude oil and condensates. They can exist in several chemical forms following the

difference in their chemical and physical properties such as (Wilhelm and Bloom, 2000):

1. Dissolved elemental mercury (Hg°) – Elemental mercury is soluble in crude oil and hydrocarbon liquids in atomic form to a few ppm. Elemental mercury adsorbs on metallic components (pipes and vessels), suspended wax, sand and other suspended solid materials in liquids. The measured concentration of dissolved elemental mercury typically decreases with distance from the wellhead due to adsorption, reaction with iron, conversion to other forms and loss of the suspended fraction.

2. Dissolved organic mercury (RHgR and RHgX, where R = CH_3, C_2H_5, etc. and X = Cl or other inorganic anion) – Dissolved organic mercury compounds are highly soluble in crude oil and gas condensate. Organic mercury compounds are similar to elemental mercury in adsorptive tendencies but differ in their boiling points and solubility and thus they partition to distillation fractions in a different fashion from Hg°.

3. Inorganic (ionic) mercury salts ($Hg^{2+}X$ or $Hg^{2+}X_2$, X being an inorganic ion) – Mercury salts (mostly halides) are soluble in oil and gas condensate but preferentially partition to the water phase in primary separations. Mercuric chlorides have a reasonably high solubility in organic liquids (about 10 times more than elemental mercury). Ionic salts also may be physically suspended in oil or may be attached (adsorbed) to suspended particles.

4. Complex mercury (HgK or HgK_2) – Mercury can exist in hydrocarbons as a complex, where K is a ligand such as an organic acid, porphyrin or thiol. The existence of such compounds in produced hydrocarbons is a matter of speculation at present depending in large part on the particular chemistry of the hydrocarbon fluid.

5. Suspended mercury compounds – The most common examples are mercuric sulfide (HgS) and selenide (HgSe), which are insoluble in water and oil but may be present as suspended solid particles of very small particle size.

6. Suspended adsorbed mercury – This category includes elemental and organic mercury that is not dissolved but rather adsorbed on inert particles such as sand or wax. Suspended mercury and suspended mercury compounds can be

separated from liquid feeds to the plant by physical separation techniques such as filtration or centrifugation.

2.1.3 Physical and Chemical Properties

The common physical properties of elemental mercury are listed in Table 2.4. Elemental mercury is a liquid at ambient conditions. Its melting point is -38.87 °C and it has a boiling point of 356.9 °C. Elemental mercury is quite dense (13.5 times more than liquid water under ambient conditions). The high density, the low saturation vapor pressure and high surface tension control the behavior of elemental mercury in solid, liquid and gaseous matrices.

Table 2.4 Physical properties of elemental mercury (Wilhelm, 2001)

Atomic distance[a]	0.30 nm
Atomic number	80
Atomic weight	200.59 atomic mass units
Boiling point[a]	356.9 °C
Boiling point/rise in pressure	0.0746 °C·torr^{-1}
Density	13.546 g·cm^{-3} at 20 °C
Diffusivity (in air)	0.112 cm^2·sec^{-1}
Heat capacity	0.0332 cal·g^{-1} at 20 °C
Henry's law constant	0.0114 atm m^2·mol^{-1}
Interfacial tension (Hg/H_2O)	375 dyne·cm^{-1} 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^{-1} at 20 °C
Vaporization rate (in air)	0.007 mg·cm^{-2}·hr^{-1} for 10.5 cm^2 droplet at 20 °C

[a] Ref. Gordon *et al.*, 1957

Mercury is capable of existing in three oxidation states: 0, +1 and +2. In the atmospheric environment, mercury exists predominantly in the elemental form (oxidation state 0) and in the +2 oxidation state, with the +1 oxidation state being very rare, if it exists at all. The chemical and physical properties of mercury and its

compounds dominate their behavior in the atmosphere and their significance as environmental contaminants. Selected physical and chemical properties of some environmentally relevant mercury species are summarized in Table 2.5. Inspection of Table 2.5 reveals the extremely wide range of physicochemical properties (ranging many orders of magnitude in the case of vapor pressure, water solubility and Henry's law coefficients) which characterizes elemental mercury and its environmentally significant inorganic and organic compounds.

Table 2.5 Physical and chemical properties of mercury and some of its compounds (Schroeder *et al.*, 1991)

Property	Hg°	$HgCl_2$	HgO	HgS	CH_3HgCl	$(CH_3)_2Hg$
Melting point (^{0}C)	-39	277	decomp. @ + 500 ^{0}C	584 (sublim.)	167 (sublim.)	-
Boiling point (^{0}C)	357 @ 1 atm	303 @ 1 atm	-	-	- @ 1 atm	96
Vapor pressure (Pa)	0.18 @ 20 ^{0}C	8.99×10^{-3} @ 20 ^{0}C	9.20×10^{-12} @ 25 ^{0}C	n.d.	1.76 @ 25 ^{0}C	8.30×10^{3} @ 25 ^{0}C
Water solubility (g/L)	49.4×10^{-6} @ 20 ^{0}C	66 @ 20 ^{0}C	5.3×10^{-2} @ 25 ^{0}C	$\sim 2 \times 10^{-24}$ @ 25 ^{0}C	~ 5-6 @ 25 ^{0}C	2.95 @ 24 ^{0}C
Henry's law coefficient [Pa m^3 mol^{-1}]	729 @ 20 ^{0}C 0.32[a] @ 25 ^{0}C 0.18[a] @ 5 ^{0}C	3.69×10^{-5} @ 20 ^{0}C	3.76×10^{-11} @ 25 ^{0}C	n.d.	1.6×10^{-5} @ 15 ^{0}C and pH = 5.2	646 @ 25 ^{0}C 0.31[a] @ 25 ^{0}C 0.15[a] @ 0 ^{0}C
Octanol-water partition coefficient	4.2[a]	0.5[a]	-	n.d.	2.5[a]	180[a]

[a] Dimensionless units

2.1.4 Mercury Distribution

Pressure and temperature changes during processing have an effect on the distribution of mercury compounds. In low temperature processes, transformations of one mercury species to another typically do not occur. However, thermal transformation of Hg° to ionic compounds or HgS likely occurs in some high

temperature refinery processes. Thus, determination of the mercury distribution is more difficult.

The distribution of total mercury in crude oil to primary distillation products is shown in Figure 2.1 and generally trends toward lower concentration in the higher temperature fractions. The distribution of mercury for a Southeast Asian condensate is shown in Figure 2.2. For this particular condensate, the large majority of mercury is found in the naphtha and kerosene fractions.

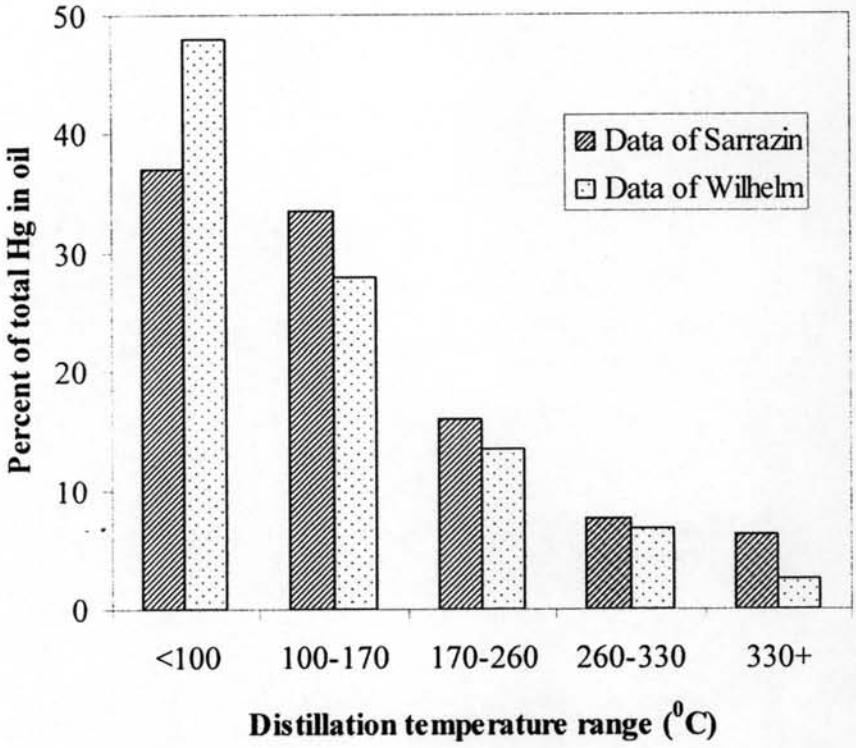

Figure 2.1 Distribution of mercury compounds in distillation cuts (Wilhelm and Bloom, 2000).

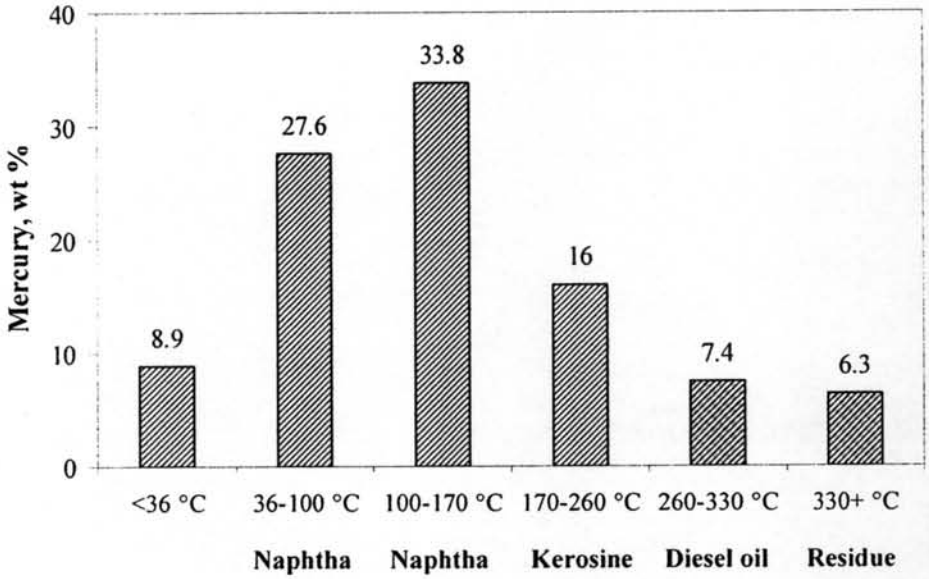

Figure 2.2 Distribution of mercury in condensate (Sarrazin *et al.*, 1993).

2.1.5 Problems Caused by Mercury

Mercury in natural gas, condensate and crude oil can adversely affect hydrocarbon production and processing in a variety of ways. Specifically:

A) Hg forms amalgams with a variety of metals, including aluminum, copper, brass, zinc, chromium, iron, and nickel. When these amalgams form with metal components of processing equipment, corrosion of the equipment results, because either the amalgams are weaker than the mercury-free metal (Leeper, 1980; Bingham, 1990), or, as is the case with the aluminum amalgam, the amalgam reacts with moisture to form a metal oxide plus free mercury, which then can continue the corrosion process (Crippen and Chao, 1997). Specific examples include corrosion of aluminum in cryogenic heat exchangers, gates and stems of wellhead valves. Such mercury-induced corrosion of aluminum heat exchangers resulted in catastrophic failure of exchangers at the Skikda LNG plant in Algeria (Kinney, 1975).

B) Hg poisoning of catalysts reduces the catalyst life (e.g., Hennico *et al.*, 1991).

C) Hg amalgam formation on steel pipe walls can result in classification of production and processing equipment as hazardous waste.

2.1.6 Mercury Removal Processes

Table 2.6 shows the various methods for removing mercury from hydrocarbons.

Table 2.6 Mercury removal systems for hydrocarbons (Wilhelm, 2001)

Reactant	Substrate	Complex Form	Application
Sulfur	Carbon	HgS	Gas
Metal Sulfide	Al_2O_3, Carbon	HgS	Gas, Condensate
Iodide	Carbon	HgI_2	Condensate
Pd + H_2; Metal Sufide	Al_2O_3	HgS	Condensate
Ag	Zeolite	Ag/Hg amalgam	Gas, Condensate
Metal Oxide	Sulfide metal oxide	HgS	Gas, Condensate

Some of the most commonly used methods are discussed below (Coleman *et al.*, 2005):

2.1.6.1 Reaction of Mercury with Sulfur

Process involves passing the feedstock over a bed of adsorbent material, consisting of an inert support on which a reactive compound has been bonded. The reactive species chemically reacts with the mercury to form a stable compound which is retained on the bed. Reactive compounds include sulfur or metal sulfides, which react with mercury to form mercuric sulfide. Supports include activated carbon and aluminum oxide.

1. Sulfur-Impregnated Activated Carbon (Nishino *et al.*, 1985)

Gas phase treatment

The most widely used system for the removal of mercury in a gas-treatment system is sulfur-impregnated carbon sorbent in which elemental mercury (Hg°) physically adsorbs on carbon and then reacts to form nonvolatile mercuric sulfide:

$$Hg^{\circ} + C \rightarrow Hg(C) \tag{2.1}$$

$$Hg(C) + S \rightarrow HgS \tag{2.2}$$

The reaction between Hg° 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. However, sulfur can be lost by sublimation and by dissolution in hydrocarbon liquids. This not only reduces the capacity for mercury but also leads to fouling of down stream equipment. This is why sulfur impregnated carbon bed has to be located downstream of the molecular sieve dryers. Because the percentage amount of organic mercury in gas is usually very low, the efficiency to react with organic mercury is less critical.

Liquid phase treatment

Sulfur impregnated materials are not suitable for the removal of mercury from liquid hydrocarbons. This is due to the solubility of elemental sulfur and this is particularly serious if aromatic species are present. Table 2.7 shows the equilibrium level of sulfur obtained with three liquid hydrocarbons.

Table 2.7 Solubility of sulfur in liquid hydrocarbons at 25°C (Abbott *et al.*, 2001)

Hydrocarbon Solubility	ppm
Pentane	300
Heptane	500
Toluene	2500

2. Metal Sulfide on Activated Carbon

Gas phase treatment

Metal sulfide (MS, where M = Cu, Mo, Co and others) systems for gas have the advantages that the metal sulfide is not soluble and has less sensitive to water but their inherent reactivity to mercury may be somewhat less than some other systems, thus requiring longer bed residence time. The metal sulfide systems are therefore more suited to moist feeds or those in which hydrocarbon carry over or condensation may occur.

$$Hg^{\circ} + CuS \rightarrow HgS + Cu^{\circ} \tag{2.3}$$

Liquid phase treatment

MS systems can be used for liquid removal by an initial hydrogenation step in which organic mercury is converted (reduced) to elemental mercury on a catalyst. Elemental mercury is then captured by a metal-sulfide (CuS or other metal sulfide).

$$XHgX + H_2(Pd) \rightarrow Hg^{\circ} + 2HX \tag{2.4}$$

$$Hg^{\circ} + CuS \rightarrow Cu^{\circ} + HgS \tag{2.5}$$

Main advantages of metal sulfide systems are that they are relatively insensitive to sulfur, water and aromatics or high molecular weight compounds, and they have a high capacity. The large capacity translates into smaller bed size and longer bed life. But the major drawback is that the hydrogenation step requires hydrogen and high temperature.

3. Metal Sulfide on Alumina (Sugier *et al.*, 1978)

Gas phase treatment

In a metal sulfide mercury removal system for gas with an alumina (Al_2O_3) substrate, mercury reacts with the metal sulfide directly. Adsorption on the substrate is less kinetically favoured than for carbon and is not strictly required for the reaction to occur:

$$Hg^{\circ} + CuS \rightarrow HgS + Cu^{\circ} \quad (2.3)$$

Liquid phase treatment

Metal sulfide systems can not be applied directly for liquid fraction as it contains organic mercury. The metal sulfide systems are chemically specific to the elemental form and do not react with covalently bound mercury compounds.

2.1.6.2 Hydrogenolysis of Organometallic Mercury followed by Adsorption (Roussell *et al.*, 1990)

Process involves first passing liquid hydrocarbon feedstock over a nickel on alumina bed along with hydrogen. Organometallic Hg is converted into metallic mercury. The effluent then passes over a bed of adsorbent material consisting of metallic sulfide bonded to an inert support. The resultant mercuric sulfide is retained on the second bed.

2.1.6.3 Reaction of Mercury via Amalgamation with Metal on a Molecular Sieve Support (Markovs, 1989)

Process involves the reaction of mercury with another metal, such as silver, bonded to a support, such as a molecular sieve. The mercury is released into the regeneration gas when the molecular sieve bed is regenerated. This technology has been widely used in natural gas processing, but has been installed in at least 15 ethylene plant dryers worldwide.

Gas phase treatment

Mol-siv sorbents that contain certain metals (silver) selectively capture mercury by an amalgamation process. Mol-sieve treaters serve a dual role to dehydrate and to remove mercury. Because of limited capacity, these systems require a regeneration system that cycle frequently and a mercury removal system for the regeneration gas. The mercury is released as mercury vapor upon heating in the regeneration cycle. The regenerated gas in these systems must be treated with a

conventional mercury removal bed to prevent sales gas contamination or a mercury condensation system must be employed in the regeneration cycle.

$$Hg^{\circ} + Ag^{\circ} \rightarrow HgAg \tag{2.6}$$

$$HgAg \rightarrow Hg^{\circ} + Ag^{\circ} \tag{2.7}$$

Liquid phase treatment

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 regenerated gas. The advantage is that sorbent can be regenerated. The disadvantage is dialkylmercury compounds do not amalgamate rapidly hence the mol-sieve amalgamation sorbents may not high efficiencies if organic forms of mercury are present in significant concentrations.

2.1.6.4 Reaction of Mercury with Iodide-Impregnated Activated Carbon (McNamara, 1994)

Process involves passing mercury-containing hydrocarbon liquid over a carbon bed impregnated with iodide. The mercury must be oxidized to react with the iodide.

Liquid phase treatment

The carbon/iodide system consists of potassium iodide impregnated carbon with a large pore diameter and it will scavenge elemental and organic mercury. Nevertheless, this system is sensitive to liquid phase water and process locations where water condensation can occur must be avoided.

$$Hg^{\circ} + C \rightarrow Hg(C) \tag{2.8}$$

$$Hg(C) + 2I^{-} \rightarrow HgI_2 + 2e^{-} \tag{2.9}$$

$$XHgX + 2I^{-} \rightarrow HgI_2 + 2X^{-} \tag{2.10}$$

In the iodide system, mercury must oxidize to react with iodide. In theory the oxidation step is assisted by carbon which provides catalytic assistance to the oxidation step.

2.2 Literature Review and Developments

Mercury vapor contained in natural gas corrodes heat exchanger made of aluminum and other types of equipment in the process of gas liquefaction is responsible for serious disasters. Also, mercury vapor contained in incinerator waste gases and waste gases from factories handling mercury is regarded as controversial from the standpoints of air pollution control and working environmental preservation.

Therefore, it becomes necessary to remove mercury vapor in these gases by means of some appropriate treatment. The method for removing mercury vapor in gas conventionally known is washing with chemical solutions and dry adsorption with the use of adsorbents such as activated carbon and ion exchange resins. Nevertheless, the process of washing with chemical solution suffers from the fact that removal efficiency of mercury vapor is poor and that waste solutions are produced, while the dry adsorption method, with its small capacity to adsorb mercury vapor, is far from satisfactory.

A process for the removal of mercury vapor from a gas, which comprises contacting the gas with an adsorbent comprising activated carbon as the support with one or more components included in one of the three groups shown in Table 2.8 and one or more components included in the remaining two groups shown in Table 2.8, efficiently adsorb mercury vapor in gas and also exhibit an outstandingly increased adsorption capacity.

Table 2.8 Group of components supported on activated carbon (Nishino *et al.*, 1985)

Group	Component
I	sulfur
II	sulfate and nitrate of Al, V, Fe, Co, Ni, Cu, Zn or NH_4
III	oxide of iodine, oxyacid corresponding to the oxide of iodine, salt of said oxyacid, and bromide and iodine of K, Na or NH_4

The activated carbon that is used in this case may be any type, so long as it is manufactured by known process from wood charcoal, coal, coconut shells, resins,

etc. employed as raw materials and exhibits a specific surface area of 200 to 2000 m^2/g.

However, these adsorbents are only effective when relatively large concentrations of mercury are present and, each adsorbent has a lower limit, below which, mercury vapor either inefficiently adsorbed or not adsorbed at all.

It has been discovered that carbon molecular sieves impregnated with a mercury reactive material are effective adsorbents especially of very low concentrations of mercury vapor. It was also found that carbon molecular sieves impregnated with sulfur are less adversely affected by water and temperature. Examples of the mercury reactive materials which may be used include oxidizing agents and amalgamating metals. Examples of oxidizing agents include: S, $FeCl_3$, sulfide (such as CuS, AgS), KI_3, KIO_3, NaOCl, MnO_2 and $PbCl_2$. Examples of metals include: gold, silver, tin and copper (Matviya *et al.*, 1987).

For liquid condensate which is by-products of gas production (natural gas, associated gas) and crude penetration, they can contain numerous metallic compounds in trace amounts, generally present in the form of organometallic compound in which the metal forms bonds with one or more carbon atoms of the organometallic radical. These metallic compounds are poisonous to catalysts used in petroleum transformation process. In particular, they poison hydrotreating and hydrogenation catalysts by being progressively deposited on the active surface. Metallic compounds are particularly found in heavy cuts from the distillation of tanker crude (nickel, vanadium, arsenic, mercury) or in condensates of natural gas (mercury, arsenic).

Institut Français du Pétrole (IFP) has been a pioneer in the invention of such technologies, appropriate for the processing of liquid hydrocarbon feedstocks boiling in the naphtha range and heavier, as appeared in U.S. Patent 4,911,825 (Roussel *et al.*, 1990). According to the process, a mixture of feed and hydrogen was contacted on a catalyst containing at least one metal from a group consisting of iron, cobalt, nickel and palladium (nickel or a combination of nickel with palladium are preferably used) followed by a trapping material, including sulfur or a metal sulfide deposited on a support chosen from the group consisting of alumina, silica-alumina, silica, zeolites, clays, activated carbon and alumina cements.

The RAM II process (removal of arsenic and mercury) developed by the IFP, shown in Figure 2.3, is ideally suited for simultaneous removal of arsenic, mercury and lead if present, from contaminated feedstocks upstream of aromatic complexes or steam-cracking units. Typical results are excellent, less than 3 ppb of each contaminant in the process effluent as threshold limit for analysis, 1 ppb of each as expectation. Mercury removal from a hydrocarbon cut is not as simple as the same operation from a gas or LPG feed. The very nature of the mercury compounds, to be found in such a cut, requires a two-step process in which the organomercuric species are decomposed into hydrocarbons and metallic mercury in a first step, the latter being subsequently absorbed on a trapping mass in a second step (Didillon *et al.*, 2000).

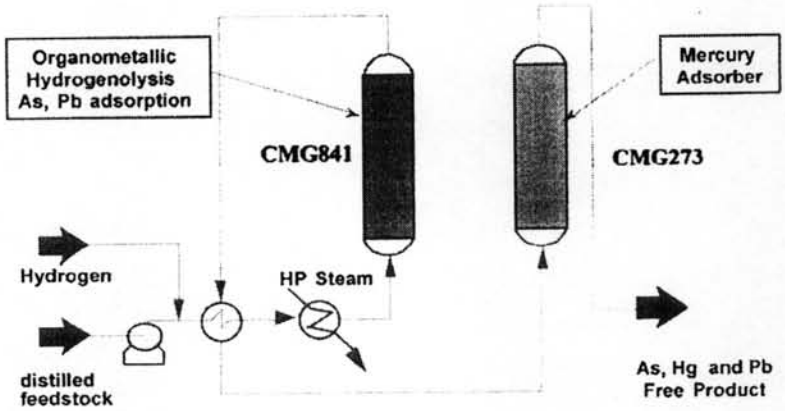

Figure 2.3 The IFP RAM II process.

The first step requires passing the contaminant containing feed over a fixed bed reactor operated under mild conditions loaded with a hydrogenolysis catalyst (CMG 841, nickel-on-alumina), where both catalytic hydrogenolysis reaction and As removal occur in the presence of hydrogen required to hydrogenolyse the organomercury compounds. Hydrogenolysis is the cleavage of a bond in an inorganic compound with simultaneous addition of a hydrogen atom to each fragment. The catalyst causes the Hg-C and As-C bonds to rupture, generating As adsorption and metallic Hg formation. Both ionic and organomercury species are converted to metallic mercury, base on the following reactions, this first stage adsorbs also arsenic and lead impurities present in the feed.

$$AsR_3 + M\text{-}H \rightarrow M\text{-}AsR_2 + RH \quad (2.11)$$

$$R\text{-}Hg\text{-}R + 2M\text{-}H \rightarrow Hg^{\circ} + 2RH \quad (2.12)$$

The As-free feed is subsequently cooled down and fed to the second stage which operates at low temperature in the presence of a trapping material (CMG273, a metal sulfide supported on alumina) where mercury is captured. The second step involves the simple chemical bonding of metallic Hg to selective trapping masses:

$$Hg^{\circ} + MS \rightarrow HgS + M^{\circ} \quad (2.13)$$

Mercury present in used catalyst is a stable sulfide compound, cinnabar (HgS), which is the most common form of mercury mineral in mercury ores and so can be classed as a secondary raw material for the production of mercury. Disposal of non-regenerable used catalysts is organized according to local regulations.

In U.S. Patent 5,336,835 (McNamara, 1994), enhanced mercury removal capability from liquid hydrocarbon is achieved by the impregnation of activated carbon with at least one metal halide consisting of the halides of I, Br and Cl. The metal I, Br and Cl halides facilitate the mercury conversion and removal process. The use of one or more of these impregnants on activated carbon efficiently converts organomercury and weakly adsorbable compounds to the desired inorganic mercury halides and/or reduces non-elemental mercury compounds to elemental mercury. Once converted to a more adsorbable form, after which adsorption of that mercury can efficiently occur. The advantages of this process over other ways of removing mercury include that the activated carbon may selectively adsorb efficient levels of mercury that would otherwise escape less effective mercury removal systems. As a result of the reactant-impregnated carbon's ability to convert mercury to more readily adsorbable forms, these carbons perform their mercury removal function in a manner not previously contemplated, and in a manner that significantly increases the capacity of filters using these carbons in removing trace levels of mercury that is not possible through the use of other activated carbons.

New developments have been undertaken in order to find ways to remove mercury from both gaseous and liquid hydrocarbons streams. In U.S. Patent 4,094,777 (Sugier *et al.*, 1978), the invention relates to a process for eliminating

mercury present in a gas or liquid, and substantially comprises bringing the gas or liquid into contact with an adsorption mass containing copper in the sulphurized state and a support selected from among silica, alumina, silica-alumina, silicates, aluminates and silico-aluminates. These adsorption masses are both very active, particularly copper sulfide, and relatively inexpensive. Their activity is much greater than those containing metallic copper and can be obtained more easily than the latter.

Universal Oil Products (UOP) has developed the UOP HgSIV process for effective mercury removal using adsorption molecular sieve, as presenting in U.S. Patent 4,874,525 (Markovs *et al.*, 1989). Since cryogenic plants need to have dry inlet streams, molecular sieve dryers already exist in most plants with natural gas liquid recovery. HgSIV adsorbents are molecular sieve products that contain silver on the outside surface of the molecular sieve pellet or bead. Mercury from the process fluid (either gas or liquid) amalgamates with silver, and a mercury free dry process fluid is obtained.

$$Hg^{\circ} + Ag^{\circ} \rightarrow HgAg \tag{2.6}$$

$$HgAg \rightarrow Hg^{\circ} + Ag^{\circ} \tag{2.7}$$

The advantage of this process include that the costs of using silver exchanged zeolites for the selective removal of mercury can be greatly reduced without a corresponding reduction in the effectiveness of the process. This cost reduction is based on the discovery that the effectiveness of the silver constituent of the zeolite on the outer portion of the adsorbent particle is many times greater than silver values located more deeply into the particle. zeolites having the faujasite, i.e. zeolite X and zeolite Y, are found to be superior adsorbents and are particularly preferred.

NUCON International, Inc. (NUCON) has developed the MERSORB® family of adsorbents (based on sulfur and/or metal sulfide on activated carbon) for almost every type of mercury removal application. For processing natural gas, hydrocarbon liquids and small air streams, fixed beds of pelleted MERSORB® adsorbents are used. Even though the adsorbents are optimized for maximum mass transfer rates, the relatively slow reaction rate of the mercury vapor with impregnant

requires a relatively long residence time. The amount of adsorbent required to achieve high removal efficiency will generally give a very long service life.

When mercury is present at very low concentrations in relatively large gas streams (such as effluent gases from coal fired power plants or waste incinerators), powdered adsorbents can be used. The powdered adsorbents can be injected into the gas stream and, after an appropriate residence time, filtered out in a dust collector. Tests have shown various degrees of effectiveness.

In a previous work, Taechawattanapanich (2004) studied the removal of diphenylmercury (DPM) from simulated condensate by using the molecular sieve, i.e. 3A, 4A, 5A, NaX and NaY zeolites. The results showed that the pore size of those zeolites affects the adsorption capacity and the adsorption isotherm revealed that DPM molecules can penetrate into the supercage of NaX and NaY zeolites, but only partially of the 5A zeolite due to the bulky size of the DPM molecule. A bi-Langmuir model was fitted well with the experimental data. The adsorption of the DPM occurs only on the external surface of 3A and 4A zeolites. In the kinetic study of the adsorption at 25 °C, very low diffusivity constants indicate limitation of DPM molecule adsorption.

Namprai (2005) studied the removal of diphenylmercury (DPM) from South East Asian condensate by using NaX, NaY zeolites and the commercial CMG273 (CuS supported on alumina). The results indicated that the presence of water content in zeolite in the range of 0-7 wt% affected the adsorption capacity of NaX zeolite while the adsorption capacity of NaY zeolite was significantly decreased by increasing the water content. This is due to the Lewis acid sites that prefer to adsorb DPM molecule was decreased. Moreover, influenced of alicyclic and aromatic hydrocarbons were studied. The result indicated that the adsorption capacity decreased when increasing aromatic hydrocarbon content due to the competitive adsorption of aromatic molecule which is able to adsorb chemically on adsorption site and physically on the window linked together with the supercage of NaX and NaY zeolites. The characteristic of physical adsorption was observed in NaX and NaY zeolites, i.e., the higher the temperature, the lower the adsorption isotherm.

Rakrood (2006) studied the removal of diphenylmercury (DPM) from liquid hydrocarbon by using Beta, Omega, L zeolites and CMG273. In batch system, the

adsorption of DPM on Beta, Omega and L zeolites was mainly physisorption. The DPM molecule prefers to adsorb on zeolite that has high Si/Al ratio. Moreover, the adsorption of DPM in heavy naphtha was studied. The result showed that the adsorption capacity was reduced due to the complexity of hydrocarbons in heavy naphtha (also the same result as Namprai, 2005). For the continuous system, alumina had less DPM adsorption efficiency than CMG273 (CuS support on alumina). Therefore, copper sulfide can increase the adsorption capacity of DPM on alumina support.

The removal of metallic mercury from simulated gas condensate was studied by using NaX, NaY, Beta, Omega, L zeolites and CMG273 (Ullah, 2006). The results from previous work indicated that the moisture content affected the adsorption capacity, therefore adsorbents must be preheated before use. Thermogravimetric analysis (TGA) showed that the appropriate temperature to preheat adsorbents is around 350°C. From kinetic studies, Beta, Omega and L zeolites have no affinity towards metallic mercury (only 15% removal was achieved for Omega and Beta zeolites and only 10% for L zeolite) while NaX and NaY zeolites have some affinity towards metallic mercury (30% removal was achieved). For CMG273, it effectively adsorbed metallic mercury (over 95% was achieved). The mathematical model comprising the steps of: 1) external mass transfer, 2) internal mass transfer (micropore and macropore resistance) and 3) surface adsorption/reaction was studied. The result indicated that the external mass transfer has little effect on overall mass transfer. In addition, pore diffusion and surface adsorption may be the limiting step for CMG273 and NaX, NaY zeolites, respectively.

2.3 Adsorbents

2.3.1 Alumina

Alumina is a porous high-area form of aluminium oxide, prepared either directly from bauxite ($Al_2O_3 \cdot 3H_2O$) or from the monohydrate by dehydration and recrystallization at elevated temperature. The surface is more strongly polar than that of silica gel and has both acidic and basic character, reflecting the amphoteric nature of the metal.

Annual world production of alumina is approximately 65 million tonnes, over 90% of which is used in the manufacture of aluminium metal. Major uses for aluminium hydroxide include the manufacture of water treatment chemicals such as aluminium sulphate, poly aluminium chloride and sodium aluminate. Large tonnnages are also used in the manufacture of zeolites, coating titania pigments and as a fire retardant/smoke suppressant. The major uses of speciality aluminium oxides are in refractories, ceramics, polishing and abrasive applications. Minor uses include use in toothpaste formulations, and as a medium for chromatography. In this latter application alumina is available in the so-called Brockmann types neutral, basic (pH 9.5) and acidic (pH 4.5 when in water). Aluminium oxide also used in preparation of coating suspensions in compact fluorescent light lamps.

2.3.2 Activated Carbon

Activated carbon is normally made by thermal decomposition of carbonaceous material followed by activation with steam or carbon dioxide at elevated temperature (700-1100°C). The activation process involves essentially the removal of tarry carbonization products formed during the pyrolysis, thereby opening the pores.

The structure of activated carbon consists of elementary microcrystallites of graphite, but these microcrystallites are stacked together in random orientation and it is the spaces between the crystals which form the micropores. The pore size distribution is typically trimodal. The actual distribution and the total pore volume associated with each pore size range are however sensitive to the conditions of the initial pyrolysis and activation procedures. Typical ranges are given in Table 2.9, but by special procedures it is possible to prepare activated carbons with even higher porosity, surface area and adsorptive capacity.

Table 2.9 Pore sizes in typical activated carbons (Ruthven, 1984)

	Micropores	Mesopores or Transitional pores	Macropores
Diameter (Å)	<20	20-500	>500
Pore volume (cm^3/g)	0.15-0.5	0.02-0.1	0.2-0.5
Surface area (m^2/g)	100-1000	10-100	0.5-2
(Particle density 0.6-0.9 g/cm^3; porosity 0.4-0.6)			

The surface of carbon is essentially nonpolar although a slight polarity may arise from surface oxidation. As a result, carbon adsorbents tend to be hydrophobic and organophilic. They are therefore widely used for the adsorption of organics in decolorizing sugar, water purification and solvent recovery systems as well as for the adsorption of gasoline vapors in automobiles and as a general purpose adsorbent in range hoods and other air purification systems. In order to decrease the mass transfer resistance, the activated carbons used for adsorption from the liquid phase generally have somewhat larger pore diameters than those used for adsorption from the gas phase.

2.3.3 Zeolites

Zeolites are porous crystalline aluminosilicates. The zeolite framework consists of an assemblage of SiO_4 and AlO_4 tetrahedral, joined together in various regular arrangements through shared oxygen atoms. Each aluminum atom introduces one negative charge on the framework which must be balanced by an exchangeable cation. The exchangeable cations are located at preferred sites within the framework and play a very important role in determining the adsorptive properties.

The Si/Al ratio in a zeolite is never less than 1.0 but there is no upper limit. The adsorptive properties show a systematic transition from the aluminum-rich sieves, which have very high affinities for water and other polar molecules, to the microporous silicas such as silicalite which are essentially hydrophobic. The transition from hydrophilic to hydrophobic normally occurs at a Si/Al ratio of between 8 and 10. By appropriate choice of framework structure, Si/Al ratio and

cationic form, adsorbents with widely different adsorptive properties may be prepared.

The pores can be classified as cages and channels. High aluminium content zeolite tends to be a cage structure framework while high silica content zeolite tends to be a channel structure framework. The window is a pore aperture of the framework structure. Classification of zeolites based on size of windows is shown in Table 2.10. In zeolites such as a sodalite the channels are constricted by six-membered oxygen rings with free diameter of about 2.8 Å. These pores are so small that only small polar molecules such as H_2O and NH_3 can penetrate. In the small-pore zeolites such as type A, chabazite and erionite, the limiting constrictions are eight-membered oxygen rings with free diameter of 4.2 Å while in the large-pore zeolites , X and Y and mordenite access is through twelve-membered oxygen rings which have free diameters of 7-7.4 Å.

Table 2.10 Classification of zeolites based on size of windows

	Pore size (Å)		Examples
Small	4-5	8-T ring	Zeolit A, Chabazite, ZK-5, Rho and Erionite
Medium	5-6	10-T ring	ZSM-5, Theta-1, Ferrierite and ZSM-48
Large	7-8	12-T ring	Faujasite, Mordenite, Offretite, Zeolite Beta and L
Extra large	12	18-T ring	VPI-5
	13	20-T ring	Cloverite
Mesoporous	16-100	variable	MCM-41 and MCM-48

In this context attention is paid only on Beta zeolite which is used in this study.

Beta zeolite (Figure 2.4) is a tetragonal crystal structure with straight 12-membered ring channels (7.6 x 6.4 A) with crossed 10-membered ring channels (5.5 x 6.5 A). It is a three dimensional network (Keffer *et al.*, 1996).

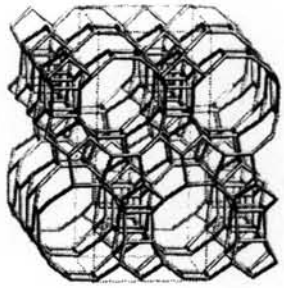

Figure 2.4 Framework of Beta zeolite.

2.4 Kinetic Models

2.4.1 The Pseudo First Order Equation

The pseudo first order equation is given as (Mall *et al.*, 2006):

$$\frac{dq_t}{dt} = k_{p1}(q_e - q_t) \tag{2.14}$$

where q_t is the amount of adsorbate adsorbed at time t (mg/g), k_{p1} is the rate constant of pseudo first order kinetics (min^{-1}) and t is the time (min). The integration of Eq. (2.14) with the initial condition, qt = 0 at t = 0 leads to the pseudo first rate equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_{p1}}{2.303}t \tag{2.15}$$

The rate constants, k_{p1}, and correlation coefficients, R^2, are determined from the plot of $\log(q_e\text{-}q_t)$ against t.

2.4.2 The Pseudo Second Order Equation

The pseudo second order model can be represented in following form (Ho and McKay, 1999):

$$\frac{dq_t}{dt} = k_{p2}(q_e - q_t)^2 \tag{2.16}$$

where k_{p2} is the pseudo second order rate constant (g/mg min). Integrating Eq. (2.16) and noting that q_t= 0 at t = 0, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{k_{p2}q_e^{\ 2}} + \frac{1}{q_e}t \tag{2.17}$$

The initial adsorption rate, h (mg/g min), as $t \rightarrow 0$ can be defined as

$$h = k_{p2} q_e^{\ 2} \tag{2.18}$$

The value of q_e is obtained from the slope while k_{p2} and h are obtained from the intercept of the plot between t/q_t and t.

2.4.3 The Intraparticle Diffusion Equation

The intraparticle diffusion is explored by using the intraparticle diffusion model (Mall *et al.*, 2006):

$$q_t = k_{id} t^{1/2} \tag{2.19}$$

where k_{id} is the intraparticle diffusion rate constant. According to Eq. (2.19), a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{id} when adsorption mechanism follows the intraparticle diffusion process.

2.5 Adsorption Isotherm Models

2.5.1 The Brunauer-Emmett-Teller (BET) Model

The Brunauer-Emmett-Teller (BET) model extends the Langmuir model, which is a monolayer adsorption, to include multilayer adsorption phenomena. The BET isotherm model is:

$$q_e = \frac{K_B C_e q_{\max}}{(C_s - C_e)[1 + (K_B - 1)(C_e / C_s)]} \tag{2.20}$$

The BET equation can be linearized as

$$\frac{C_e}{(C_s - C_e) q_e} = \frac{1}{K_B q_{\max}} + \left(\frac{K_B - 1}{K_B q_{\max}}\right)\left(\frac{C_e}{C_s}\right) \tag{2.21}$$

where q_e is the amount adsorbed per unit weight of adsorbent (μmol/g), C_e is the concentration of solute remaining in solution at equilibrium (μmol/L), C_s is the saturation concentration of the solute (μmol/L), q_{max} is the amount of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface (μmol/g), and K_B is the constant expressive of the energy of the interaction with the surface. A plot of C_e/C_s versus $C_e/[(C_s-C_e)q_e]$ results in a straight line with a slope of $[(K_B -1)/ K_B q_{max}]$ and intercept of $1/ K_B q_{max}$.

2.5.2 The Freundlich Model

The Freundlich expression is an empirical model using for nonideal adsorption that involves adsorption on a heterogeneous surface. The Freundlich model is commonly presented as

$$q_e = K_F C_e^{1/n} \tag{2.22}$$

and the equation can be linearized by taking logarithms

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{2.23}$$

The constants K_F (μmol/g) and $1/n$ which related to the adsorption capacity and adsorption intensity of the adsorbent can then be evaluated from the intercept and slope of $\ln q_e$ against $\ln C_e$ plot.

2.5.3 The Langmuir Model

According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, once an adsorbate occupied a site, no further adsorption can take place at this site. The Langmuir model is expressed as

$$q_e = \left(\frac{bC_e}{1 + bC_e} \right) q_{\max} \tag{2.24}$$

where $q_{\max}$ is the maximum amount of metallic mercury adsorbed (μmol/g), b is the adsorption equilibrium constant (L/μmol), q_e is the amount of metallic mercury adsorbed at equilibrium (μmol/g), and C_e is the equilibrium concentration (μmol/L). The constants $q_{\max}$ and b can be evaluated from the linear form represented by the equation

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{bq_{\max}} \right) \frac{1}{C_e} \tag{2.25}$$

A plot of $1/q_e$ versus $1/C_e$ results in a straight line with a slope of $1/bq_{\max}$ and an intercept of $1/q_{\max}$.