CHAPTER II
BACKGROUND AND LITERATURE REVIEW

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

Elemental mercury and mercury compounds occur naturally in geologic hydrocarbon. At the ambient condition the elemental mercury is a liquid, high density, low saturation vapor pressure and high surface tension. The common physical properties of mercury are shown in Table 2.1

Normally, mercury that occurs in nature is in the zero (element), +1 (mercurus) or +2 (mercuric) valence state. Mercury occurs most prevalently in the element form, common mercuric compound include mercuric oxide, mercuric chloride, mercuric sulfide and mercuric hydroxide, organic mercury form also exist and consist of two main groups : R-Hg-X and R-Hg-R compounds, where R = organic species, of which methyl (-CH$_3$) is prominent, and X = inorganic anions, such as chloride, nitrate or hydroxide. The R-Hg-X group include monomethylmercury compound and the most prominent of R-Hg-R compounds is dimethylmercury.

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

Atomic number	80
Atomic weight	200.59 atomic mass units
Boiling point	357 °C (675 °F)
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 (68 °F)
Melting point	-38.87 °C (-37.97 °F)
Saturation vapor pressure	0.16 N/m^3 (pascal) at 20 °C (68 °F)
Surface tension (in air)	436 dyne/cm at 20 °C (68 °F)
Vaporization rate (still air)	0.007 mg/cm^2.hr for 10.5 cm^2(20 °C)

Mercury is difficult to oxidize in the natural environment and spilled mercury (in soil for instance) retains the elemental form indefinitely absent moisture and bacteria until evaporation. Mercury can be oxidized by the stronger oxidants including halogens, hydrogen peroxide, nitric acid and concentrated sulfuric acid.

The elemental mercury is highly adsorptive and adsorbs on metallic surfaces and on solid materials (sand) suspended in liquid. Under ambient conditions, silver, gold, copper, zinc and aluminum readily form amalgams with elemental mercury. The solubility of these metals in elemental mercury is relatively low. The solubility of zinc in mercury is approximately 2g Zn/100g Hg, while the solubility of gold in mercury is only 0.13g Au /100g Hg, and for silver, copper and aluminum have even lower solubility than gold. The affinity of mercury for gold is important in analysis and is applied as gold collector to trap vapor phase mercury.

2.2 Mercury in Petroleum (Wilhelm *et al.*, 2000)

The understanding of the chemistry of geologic mercury has evolved due to technical advances that allow differentiation of the various chemical forms of mercury in hydrocarbon matrices. Newly developed techniques can measure the concentration of mercury and mercury compounds in some hydrocarbon matrices to better than 0.1ppb.

Crude oil and gas condensate can contain several chemical forms of mercury, which differ in their chemical and physical properties. The various form of mercury can be classified as the following.

(1) Dissolved elemental mercury (Hg^0) – Elemental mercury is soluble in crude oil and hydrocarbon liquid in atomic form to a few ppm. Elemental mercury is adsorptive and adsorbs on metallic components (pipe and vessel) , suspended wax, sand and other suspended solid material in liquids. The measured concentration of dissolved element mercury typically decrease 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 (R-Hg-R and R-Hg-X, where R = alkyl and X = Cl⁻ or other inorganic anion) – Dissolved organic mercury compounds are highly soluble in crude oil and gas condensate. Organic compounds are similar to elemental mercury in adsorptive tendencies but differ in their boiling points solubility and thus they partition to distillation fraction in a different fashion from Hg^0.This category includes dialkylmercury (i.e., dimethylmercury, diethylmercury) and monomethylmercury halides (or other inorganic ion).

(3) Inorganic (ionic) mercury salts (Hg^{2+} X or $Hg^{2+}X_2$, where X is an inorganic ion) – Mercury salts (mostly halides) are soluble in oil and gas. Condensate but preferentially partition to the water phases in primary separators. 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 adsorbed to suspended particuls.

(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 many be present as suspended solid particals of vary small partical size.

(6) Suspended adsorbed mercury – This category included elemental and organic mercury that is not dissolved but rather adsorbed on inert particals 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.

The various chemical forms of mercury exhibit significantly different chemical and physical behavior. Each chemical form requires analytical methodology that is specific to its particular characteristics. Analytical procedures are formulated to take advantage of the differences in species adsorptive character, solubility and volatility. Boiling point of organic compounds (see table 2.2) assist prediction of the distribution of compounds in distillations of crude oil. The solubility of some mercury compounds in hexane are shown in Table 2.3 and are useful to predict the distribution of compound in phase separation (Wilhelm, 2000).

Table 2.2 Boiling point of volatile mercury compounds (Wilhelm, 2000)

Hg compound	Boiling point(C)
Hg^0	357
$(CH_3)_2Hg$	96
$(C_2H_5)_2Hg$	170
$(C_3H_7)_2Hg$	190
$(C_4H_9)_2Hg$	206

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

Species	Solubility (ppb)	Temperature (°C)
Hg^0	1,200	27.5
$HgCl_2$	11,500	27.5
CH_3HgCl	>1,000,000	20
$(CH_3)_2Hg$	∞	

Only limited data are available that allow examination of the distribution of concentrations of mercury compounds in hydrocarbon liquid

The production and processing practices can change the amounts and distribution of mercury species in crude oil. A common example is the reaction of elemental and/or ionic mercury in oil with sulfur compounds. The mixing of oil from different production zones and reservoirs in surface equipment and in pipelines can allow reactions of dissolved mercury with sulfur compounds in mixed oils to form particulate HgS that can settle out in tanks and deposit in equipment.

Tao *et al.,* (1998) reported the mercury concentration in gas condensates, naphtha and crud oil, as shown in figure 2.1. The origin (process location) of samples analyzed by Tao was not disclosed. Tao's data indicate that ionic mercury was the dominate species in condensate examined. Hg^0 did not exceed 25 percent of the total in any of the condensate samples. The diethyl species was detected (>10%) in some condensates. The monoalkyl species was detected but at very low concentration. Hg^0 was not seen in naphtha as would be expected assuming a normal distillation profile. The more volatile Hg^0 would be expected to partition to the lighter gas fraction. R-Hg-R appeared to be the dominate species in one naphtha sample. Ionic forms of mercury were seen in all of the samples.
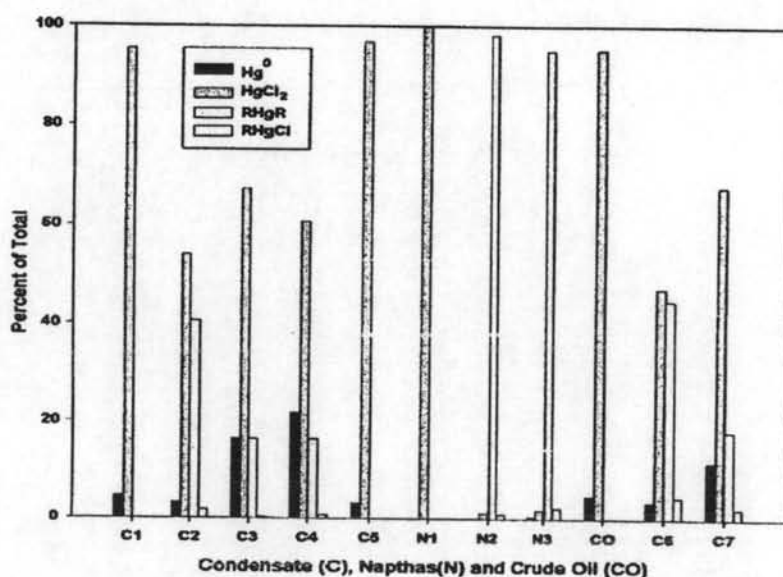

Figure 2.1 Distributions of Mercury Compounds in Liquids (Tao *et al.,* 1998)

Some comments have been found in the literature regarding the partition and nature of mercury and organomercury compounds in fluids. It is generally agreed that mercury in natural gas is almost all in element form, but in condensate and petroleum liquids mercury compounds are significant and may be the predominant form of mercury (Sarrazin *et al.*, 1993).

However, most literature on total mercury concentrations in condensate, naphtha and cruds oil do not fully disclose sampling procedures or analytical processing steps (filtration, centrifugation, exposure to air). For this reason, some data are questionable in some ways, e.g. total mercury concentrations reported could include a concentration from suspended form, or the distribution of compounds could reflect species conversion, for example, in the Aerobic processing the sample is suspended to promote oxidation of Hg^0 to ionic forms and thus to alter the distribution of species.

2.3 Fate of Mercury in Refinery and Gas Processing (Edmonds *et al.*, 1996 and Bloom, 2000)

It is necessary to understand how mercury partitions in separations, distillations and catalytic processes so as to be able to predict the amounts of mercury in emissions or effluents as a function of the known amount in feeds. Optimally one would have this type of information for each of the various mercury species presenting in hydrocarbon feeds to the processing. Very little data are presently available for providing evidence of the fate of mercury in refining and gas processing. Most of the reported information concerning mercury in processes is anecdotal and consists of observation of mercury deposition in equipment and detection of mercury in waste streams.

Vapor pressure and solubility for elemental mercury are seasonably well known or easily estimated. The solubility of dialkylmercury compounds in hydrocarbons is assumed to be infinite over the range of temperature encountered in most petrochemical processes. Partitioning of mercury species between liquid and gas phase can be estimated using chemical approximation principles and some limited empirical data.

In low temperature processes, chemical reaction to transform one mercury species to other typically do not occur so a species mass balance is assumed. Oxidation of Hg^0 to ionic compounds and/or HgS likely occurs in some high temperature refinery processes, thus making predictive calculation more difficult. Distillations and separations produce major redistribution of mercury compounds in refinery as does blending crude feeds having differing amounts of reactive sulfur compounds.

Desalting is a process by which oil is washed with water to remove soluble salts and is applied upstream of the atmospheric distillation. The partition of mercury in desalting is similar to that which occurs in primary phase separations. The greater amount of water and the longer residence times of crude oil in the desalter make it more efficient to remove suspended mercury and those ionic species that have affinity for water. As a result, the mercury in crude oil after desalting should be depleted.

It is easier to predict the fate of mercury in gas processing because the process is simpler and less transformation of species initially present. In treatment for contaminants, the element in gas will dissolve in the liquid glycol dehydrators and increase concentration until equilibrium is reached. Some portion of elemental mercury in a glycol dehydrator is removed in the cycle. If the concentration of mercury in gas is sufficiently high, elemental mercury can condense in the glycol reboiler vapor condenser. In amine systems, it is postulated that mercury may react with the H_2S scavenged by the amine and thus be removed from the process as HgS in the amine filters. In the separation process, if the concentration of elemental mercury is sufficiently high in the gas, the opportunity for condensation (precipitation) of elemental mercury can occur in cryogenic process (Wilhelm, 2001).

2.3 Impact of Mercury on Petroleum Processing Systems

Mercury is universally detrimental to petroleum and petrochemical processing. In chemical manufacturing and refining, mercury poisons catalysts and contaminates waste water, thus impacting regulatory compliance. In gas processing, mercury damages equipment and fouls cryogenic heat exchangers.

Wilhelm *et al.*, (2000) has summarized several detrimental impacts on gas operations.

(1) The mercury deposits in cryogenic equipment cause cracking of welded aluminum heat exchangers.

(2) The mercury in gas plant products affects downstream processes. Gas plant products used for chemical manufacturer, especially olefins, ethylene, aromatics and MTBE are as risk to mercury in process feeds due to the cited equipment problems and catalyst poisoning.

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

(4) Mercury sorbent materials used for gas or liquid treatment, when spent, constitute a regenerated 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 level of mercury must be treated by removing mercury prior to discharge thus adding significant costs plant.

In order to eliminate the impact of mercury in the processing, the best way is to limit the amount of mercury entering to the system by limiting the amount of high mercury condensates being processed. Thus, the preferred location to install the mercury removal unit is a place before hydrocarbon streams entering the plant.

2.5 Conventional Mercury Removal Systems (Wilhelm *et al.*, 2000)

Several commercial removal processes are available for removing mercury and mercury compounds from hydrocarbons (see Table 2.5). Some are targeted at the gas phase treatment and some at liquid phase treatment.

Table 2.4 Mercury Removal Systems for Hydrocarbons (Wilhelm *et al.*, 2000)

| Reactant	Substrate	Complex Form	Application
Sulfur	Carbon	HgS	Gas
Metal Sulfide	Al_2O_3; Carbon	HgS	Gas, Condensate
Iodide	Carbon	HgI_2	Condensate
Hydrogen, Metal Sulfide	Al_2O_3	HgS	Condensate
Ag Zeolite	Ag/Hg	amalgam	Gas, Condensate
Metal Oxide	Sulfided metal oxide	HgS	Gas, Condensate

Mercury has low vapor pressure and low solubility. Therefore, any mercury removal process must be effective at very low concentrations. Adsorption is such a process. Unimpregnated activated carbon is a fair adsorbent for mercury. But its capacity is significantly increased by impregnation with a material that chemically reacts with, and holds, the mercury. The choice of impregnant is dictated by the process conditions and the composition of the fluid. Sizing of adsorption equipment is determined by the flow rate of the fluid stream and the desired operational life of the adsorbent.

The mercury removal sorbent beds consist of granular or palletized sorbent material that consists of a substrate support (zeolite, activated carbon,

metal oxide or alumina) and reactive component (Ag, KI, CuS, metal sulfide, etc.) that is bounded to the support. The proprietary nature of commercial sorbents derives from the chemistry of the reactive component, the adsorptive nature of support and the method by which the reactive component is attached to the support. Sorbent function by reacting mercury or mercury compound to a chemical form (HgS, HgI_2 or amalgam) that is insoluble in hydrocarbon liquid and chemically inert to the component of process stream.

The substrates (supports) are designed to selectively adsorb mercury compounds but do not react with them directly; the reactant compound is designed for this task. Most support materials are porous with the pore size carefully controlled to selectively adsorb mercury and avoid adsorption of high molecular weight hydrocarbons. For efficient mercury removal bed function, the adsorptive capacity of the support is equal in importance to the reactive nature of the mercury-scavenging compound.

In a gas treatment system that utilizes sulfur-impregnated activated carbon (AC), mercury (Hg^0) physically adsorbs and then reacts to form non-volatile mercuric sulfide (see equation 2.1). The reaction between Hg^0 and sulfur is a redox reaction in which mercury is oxidized and sulfur is reduced. Because the percentage of amount of mercury in gas is usually very low, the efficiency to react with organic mercury is less critical. Sulfur is soluble in liquid hydrocarbon and is removed by contact with liquid hydrocarbon rendering it ineffective. Sulfur/carbon sorbents are relatively less effective to treat heavy gas where some liquid condensation is possible (Nishino *et al.* 1995, Matviya *et al.* 1987).

$$Hg^0 + S(AC) \longrightarrow HgS + AC \qquad (2.1)$$
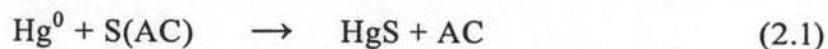
Metal sulfide (MS) systems for gas have the advantage that the metal sulfide is not soluble in liquid hydrocarbon and has less sensitivity to water. The MS systems are therefore more suited to moist feeds or those in which hydrocarbon carry over or condensation may occur. In a metal sulfide

mercury removal system for gas having an alumina (Al_2O_3) support, mercury reacts with the metal sulfide directly, adsorption on the alumina substrate is less kinetically favored than for carbon and is not required for the reaction to occur (Sugier *et al*. 1978;Barthel *et al*. 1993).

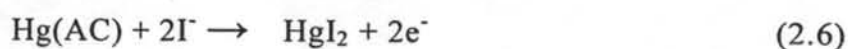$$Hg^0 + SM \quad \longrightarrow \quad HgS + M^0 \qquad (2.2)$$
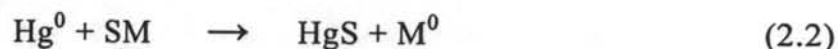
Mol-siv (molecular sieve) sorbents that contain metals (silver) selectively capture mercury by an amalgamation process. Mol-sieve treaters serve a dual role to dehydrate and to remove mercury. The mercury is released as mercury vapor upon heating in the regeneration cycle. The regeneration gas in these systems is treated with a conventional mercury removal bed to prevent sales gas contamination or a mercury condensation system is employed in the regeneration cycle (Markovs, 1988).

$$Hg^0 + Ag^0 \qquad \longrightarrow \quad HgAg \qquad (2.3)$$

$$HgAg + heating \quad \longrightarrow \quad Hg^0 + Ag^0 \qquad (2.4)$$
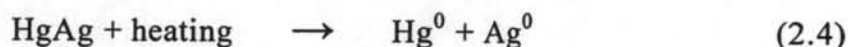
Liquid removal processes consist of iodide impregnated carbon, metal sulfide on carbon and alumina, silver (on zeolite), mol-sieve and two step process consisting of a hydrogenation catalyst followed by metal sulfide capitation.
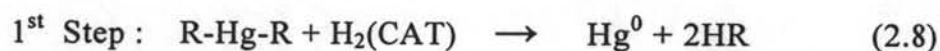
The carbon/iodide system consists of iodide-impregnated carbon having a large pore diameter. In the iodide system, mercury must oxidize to react with iodide. In theory the oxidation step is assisted by carbon, which provides catalytic assistance to the oxidation step. The carbon/iodide adsorbent will scavenge elemental and organic mercury.

$$Hg^0 + AC \quad \longrightarrow \quad Hg(AC) \qquad (2.5)$$

$$Hg(AC) + 2I^- \longrightarrow \quad HgI_2 + 2e^- \qquad (2.6)$$

$$R\text{-Hg-R} + 2I^- \longrightarrow \quad HgI_2 + 2R^- \tag{2.7}$$

The metal sulfide and mol-sieve mercury removal system for condensate are conceptually equivalent to those employed for gas. Metal sulfides on alumina do not react efficiently with liquid phase organomercury. The main advantage of metal sulfide system is that they are relatively insensitive to sulfur, water and aromatics, and they have high capacity. The large capacity translates into smaller bed size and longer bed life (Mcnamara, 1994).

Organic mercury (dialkylmercury) is more prevalent in hydrocarbon liquids. The ability of sorbents to react with the organic variety is less certain. One system addresses this situation by using a two-step process in which the first step is hydrogenolysis of the dialkylmercury using the catalyst and hydrogen. The dialkylmercury is converted to elemental mercury that is scavenged in the second step using a metal sulfide sorbent (Roussell et al., 1990).

$$1^{st} \text{ Step}: \quad R\text{-Hg-R} + H_2(CAT) \quad \longrightarrow \quad Hg^0 + 2HR \tag{2.8}$$

$$2^{nd} \text{ Step}: \quad Hg^0 + SM \quad \longrightarrow \quad HgS + M^0 \tag{2.9}$$

This process has the advantage of insensitivity to moisture and high molecular weight compounds—it will withstand plant inlet conditions in some case. The major disadvantage is that in the 1st step (hydrogenation step) requires hydrogen and high temperature.

2.6 Zeolite (Govind et al., 2002)

Zeolite molecular sieves are crystalline, highly porous materials, which belong to the class of aluminosilicates. These crystals are characterised by a three-dimensional pore system, with pores of precisely defined diameter. The corresponding crystallographic structure is formed by tetrahedras of (AlO_4) and

(SiO₄) and giving rise to three-dimensional networks of channels and cages as shows in Figure 2.2.
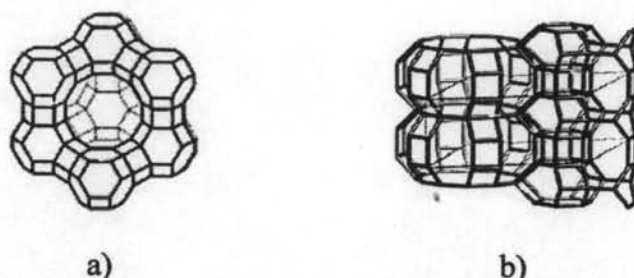

a)   b)

Figure 2.2 The structure type of zeolite, a) Cage-structure (Zeolite Y), b) Channal-structure (Zeolite L).

Due to the presence of alumina, zeolites exhibit a negatively charged framework, which is counter-balanced by positive cations resulting in a strong electrostatic field on the internal surface. These cations can be exchanged to fine-tune the pore size or the adsorption characteristics.

The up-take of water or other species in zeolites is called adsorption and functions on the basis of physisorption. The main driving force for adsorption is the highly polar surface within the pores. This unique characteristic distinguishes zeolites from other commercially available adsorbents, enabling an extremely high adsorption capacity for water and other polar components even at very low concentrations.

Siriwat T., (2003) has been studies the affinity in adsorption of DPM on cage-structure of zeolite, 3A, 4A, 5A, X and Y. In this research work, the channel structure zeolite was selected to study the capable in DPM adsorption. The zeolite Omega, L and Beta were chosen based on their Si/Al ratio and surface area that comparable to zeolite X and Y. The information of zeolite Omega, L and Beta are shown as following.

1) Zeolite Omega (Keffer *et al.*, 1996) -- has one-dimensional 12-ring channels. However, the channels of Omega are more circular in cross-section with a nominal diameter of 7.4 Å. The accessible volume is a tube

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centered in the pore with varying diameter, it is widest to either side of the 12-ring and narrowest at the 12-ring.
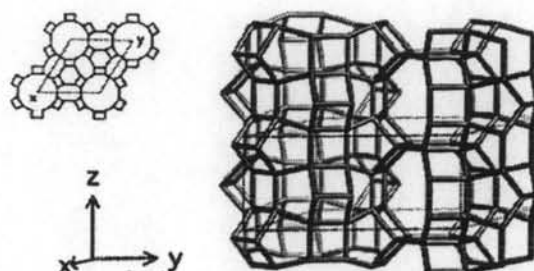

Figure 2.3 The channel structure of Zeolite Omega viewed to [001].

2) Zeolite-L (Keffer *et al.*, 1996) -- Like Omega, zeolite-L has one-dimensional 12-ring channels with an only slightly smaller nominal diameter of 7.1 ´ . However, L has only one 12-ring per unit cell length of channel. The diameter of the accessible volume tube varies more widely than in zeolite-Omega.
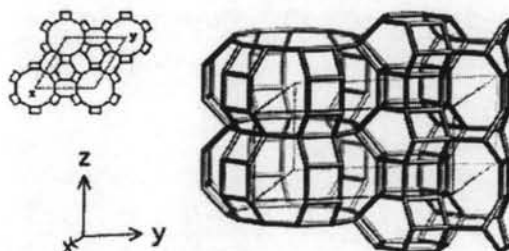

Figure 2.4 The channel structure of L viewed to [001].

3) Zeolite Beta (Keffer *et al.*, 1996) -- has a there-dimensional network of 12-ring straight channels with nominal principal axes of 7.6 and 6.4 ´ along [010] and [100]. The accessible volumes are intersecting cylinders running in two directions, reflecting the pore structure.
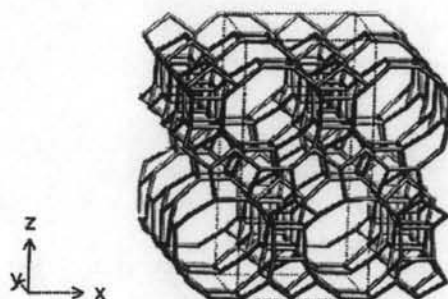
Figure 2.4 The channel structure of Zeolite Beta viewed to [001].

2.6 Kinetic Models

Numerous publications in literature on adsorption kinetics (Shie, *et al.*, 2005) are available. The typical kinetics model normally considers both external and internal mass transfer resistances. A general model involves complicated mathematical computation to obtain the related diffusion coefficients of the model.

Therefore, for the simplicity and practical use of engineering applications, the global kinetic expressions such as Lagergren Pseudo 1st order and 2nd order, and Elovich rate equations, were tested to describe the adsorption kinetics (Chang, *et al.*, 2004).

a) For pseudo 1st order of the Lagergren equation, the kinetic rate can be expressed,

$$\frac{dq_t}{dt} = k_{e1}(q_e - q_t). \qquad (2.10)$$

Integrating Eq. (2.10) with the conditions ($q_t = 0$ at $t = 0$; $q_t = q_t$ at $t = t$),

$$\ln(q_e - q_t) = \ln(q_e) - k_{e1}t, \qquad (2.11)$$

where q_t and q_e is the adsorption capacity at time t and at equilibrium, and k_{e1} is the equilibrium rate constant of the pseudo 1st order sorption.

b) For the pseudo 2nd order, the kinetic rate can be written,

$$\frac{dq_t}{dt} = k_{e2}(q_e - q_t)^2.$$ (2.12)

Integrating Eq. (2.12) with the conditions (q_t = 0 at t = 0; q_t = q_t at t = t) yields

$$\frac{t}{q_t} = \frac{1}{k_{e2}q_e^2} + \frac{t}{q_e},$$ (2.13)

where k_{e2} is the equilibrium rate constant of the Pseudo-second-order sorption.

c) The rate expression of Elovich equation can be expressed,

$$\frac{dq_t}{dt} = a\, e^{(-bq_t)}.$$ (2.14)

Integrating Eq. (2.14) with the conditions (q_t = 0 at t = 0; q_t = q_t at t = t) and subsequent linearization results,

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t + t_0),$$ (2.15)

where a and b are the parameters of the Elovich rate equation; t_0 is equal to $1/(ab)$. If $abt \gg 1$, Eq. (4.6) can further be simplified as:

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t).$$ (2.16)

Azizian *et al.* (2004) reported theoretical analysis for the Pseudo 1st and 2nd order model. The analysis shows, the adsorption of lower solute

concentrations obeys Pseudo 2nd order rate kinetics. While, Pseudo 1st order rate kinetics can be applied to higher initial concentrations of solute.

The Elovich rate equation is commonly used to describe those kind of sorption in which the rate slows down after a very rapid initial sorption (for eg removal of DPM on Zeolites Omega and Beta in this study). The constants a and b, in the Elovich rate equations represent the rate of sorption and surface coverage, respectively. Although the values of R^2 for the Elovich rate equation are good enough still less than Pseudo 2nd order kinetic rate model. This is why Pseudo 2nd order kinetic rate model is selected to study adsorption kinetics of DPM removal from n-heptane on Zeolites Omega, Beta, L and CMG273.

In recent years, Pseudo 2nd order rate expression has been widely applied to the adsorption of pollutants from aqueous solutions onto adsorbents (Ho, *et al.*, 2005). Chang, *et al.* (2004) studied and applied the Pseudo 2nd order rate model for the kinetics of adsorption of naphthalene on zeolite DAY.

2.6 Background of Invention (Shafawi, 2000)

The removal systems for mercury are ill suited to treating unconditioned hydrocarbons due to the fact that raw produced hydrocarbons contain numerous contaminants that interfere with the operation of mercury removal systems (Wilhelm, 1999).

However the natural gas (gas phase) that contains mostly elemental mercury is easier to treat. The success of the absorbent that is used to remove elemental mercury has been achieved. The two largest competitors of commercial mercury removal technology are UOP^{TM}HgSIV^{TM} (silver-impregnated zeolite) from Universal Oil Products (UOP), USA and CMG$^{®}$273^{TM} (copper sulfide supported alumina-silica) from Institut Français du Pétrole (IFP), France. Both claim that their technologies have excellent trapping efficiency for marked products.

The removal of mercury in the liquid hydrocarbon is different from natural gas due to the mercury species (>80% of organomercury (Shafawi,

2000)) and the lack of knowledge of the distribution of mercury species that highly depends on geological. The removal process used in the gas phase can not be applied. The mercury removal process for the liquid hydrocarbon are under development, some improvement is made by two step processing, first by converting organomercury into elemental mercury form followed by trapping by adsorbent on the second step. However this process still has problem of incomplete conversion of organomercury in the first step. The other application that has high potential in order to remove organomercury is adsorption by molecular sieve.

Wilhelm *et al.* (1999) stated that the several mercury removal systems for liquids are commercially available but performance is sometimes difficult to predict because very few commercial applications have been documented.

In 2000 the IFP de-mercurisation and de-arsenification process (IFP RAM II) was successfully applied catalyzed to the purification of a natural feedstock. A kinetic model is developed to describe the involved chemical reactions and is used now as a predictive model for industrial units. This technology is based on a two-step procedure operating under liquid phase. The first step is a fixed bed reactor operate under mind conditions loaded with a hydrogenolysis catalyst, CMG®841™, both ionic and organomercury species are converted to metallic mercury. The feed is subsequently cooled down and fed to the second stage which operats at low temperature in the presence of a trapping material, CMG®273™, where the mercury is captured. The second step involves the sample chemical bonding of metallic mercury to selective trapping masses.

Shafawi *et al.* (2000) studied three commercially available mercury removal processes designated AA (using hydrogenolysis catalyst to convert inorganic and organomercury to elemental mercury and then using a sulfide containing alumina for removal of elemental mercury), BB (a carbon based adsorbent which contained sulfur as the active material and CC (molecular sieve-based adsorbent with un disclosed active material). All three pilot plants used both real and substitute condensate i.e. hexane that containing dimethylmercury (DMM), diethylmercury (DEM) and dibuthylmercury (DBM)

species as feedstock. The result showed that all three pilot plant-tested mercury-removal systems AA, BB and CC showed a reduction in the mercury content of the final products. For the adsorbent system AA, the hydrogenolysis reator was able to convert some of the organomercury present in the gas condensate feed to metallic mercury. However the amount of elemental mercury measured was only about 30% of the total mercury content. Incomplete conversion of organomercury species to mercury metal may be due to competition between the organomercury species and the unsaturated compounds in the matrix during the hydrogenolysis reaction. The result from the first reactor (hydrogenolysis) also showed a higher total mercury content compared with the feed condensate. The second reactor (mercury trapping) was able to adsorb elemental mercury present in the stream (the product from the first reactor) but was unable to remove the organomercury content from the condensate stream. For the single-stage adsorbent systems BB, the efficiency in removing spikes of DMM, DEM and DBM from the n-hexane hydrocarbon sample was very high. Removal efficiency of the species was 100% with no indication of mercury present in the product. For adsorbent systems CC, efficiency of removal for the different mercury species spiked into the n-hexane was variable. Over 50% of DMM was removed using the adsorbent, while the DEM showed a range of 60-80% removal. For the DBM the initial adsorbed efficiency was less than 80% at 2 h but was rapidly released back into the product stream after 4 h.

In 2001, Spiric, reported that several factors are influencing efficiency of mercury removal from natural gas; composition of gas as well as concentration of mercury vapor, presence of higher hydrocarbons, water and other impurities, temperature, pressure, gas flow rate, activated carbon characteristics, contact time, etc. Upon investigating the mercury removal technology available, Croatian scientists concluded that according to the best world experience, sulfur impregnated activated carbon was the best suited for achieving the mercury removal objective at Molve, Croatia natural gas processing plant. The results of the innovative approach in the process control for more than seven years of practical field experience obtained by research of

mercury removal unit efficiency during production and enhancement of natural gas at Molve, Croatia. it was found that mercury removal efficiency is strongly related to the mercury removal unit inlet stream temperature. This finding provides some fundamental data for research into sulfur impregnated activated carbon mercury removal inefficiency caused by the loss of active species. Considering that elevated temperatures promote the chemical reaction with sulfur, forming mercury sulfide and the possibility that mercury occurs in its vapor state increases, it is desirable to obtain the mercury removal at the highest possible temperature. Moreover, natural gas is saturated with steam, and condensation of water within carbon pores should be prevented. This problem can also be solved by application of the corresponding temperature regime. When the problems with condensation in the activated carbon bed, as well as reduction of sulfur content in activated carbon become evident, a process improvement was introduced, related to change of flow direction.

In 2002, UOP has made recent advances in low level mercury analysis, which aid in the detection of mercury in the hydrocarbon streams. The benefit to the gas processor is that each sample can now be gathered and analyzed within hours, not days or even longer as with an off-site facility. Before the analytical team departs, the level of mercury in a treated or untreated stream has been quantified. This information can determine whether streams need to be treated for mercury or to confirm that an existing mercury removal system is functioning as designed. They also claimed that the UOP™ HgSIV™ regenerative mercury removal adsorbents not only dry these streams but also remove mercury to less than 0.01 ppb. The HgSIV™ adsorbents are their 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 the silver, and a mercury-free dry process fluid is obtained. These HgSIV adsorbents are loaded into an adsorption vessel in the same way as are conventional molecular sieves. The disposal requirements are also the same as for conventional molecular sieves. Currently, UOP has installed HgSIV adsorbents in over 25 gas dryers and 7 liquid dryers. These

units are located in the Far East, Middle East, Africa, South America and the United States.

Recently, Lee *et al.* (2003) studied the gas-phase mercury removal by carbon-base sorbents. The mercury adsorption performances of virgin activated carbon (AC) and sulfur impregnate AC were compared. The research result showed that virgin AC with large oxygen functional groups was superior in mercury adsorption performance. In particular, when sulfur is impregnated, it is essential to select an AC with a large pore diameter. If the pore characteristics of AC are different, the AC capacities also differ even if sulfur is impregnated. There are two types of sulfur impregnated into AC, one of this desorbs at 250 °C and the other evaporates at 400 °C. If amount of sulfur that is strongly bonded to the carbon was large, the AC has better mercury adsorption performance. The developed sulfur-impregnated AC manufacturing process may be more economical than the existing sulfur impregnation method, and the result might be applied to the AC injectors or power plants.

Most recently, Mr. Siriwat Taechawattanapanich (2004) studied the removal of diphenylmercury from simulated condensate by using the molecular sieve i.e. 3A, 4A, 5A, NaX and NaY Zeolite. He found that the pore size of those zeolites effect the adsorption capacity and adsorption isotherm revealed that the diphenylmercury molecules can penetrate into the supercage of the NaX and NaY zeolites but only partially of the 5A zeolite due to bulky size of the diphenylmercury molecule, and bi-Langmuir model can fit well with the experimental data. The adsorption of the dipenylmercury occurs only on the external surface of the 3A, 4A zeolites. In the kinetic study of the adsorption at 25 °C, very low diffusivity constants indicate the limitation of diphenylmercury molecule adsorption.