

CHAPTER II

LITERATURE SURVEY

2.1 Background

2.1.1 Occurrence of Mercury

Mercury is present in the earth's crust at an average concentration of 0.08 mg/kg and it enters into the atmosphere through both natural and anthropogenic sources. The natural sources are volcanic activity, erosion of terrain, dissolution of mercury minerals in oceans, lakes and rivers and a variety of other venues that are not related to human activities. While most of the mercury in the atmosphere exists as vapor, it can exist in various forms in the earth's crust. This is because mercury goes through a cycle of physical and chemical transformation between atmosphere, land and water. The total amount of mercury in the world as a whole is constant while the amount in the biosphere is not. The amount of mercury released into the biosphere has increased markedly over time, especially from human activities since the beginning of the Industrial Age. The vast majority of mercury that enters the global mercury cycle from human activities comes from the combustion of fuels and the disposal of contaminated waste into air and water from petrochemical and refining industries, as, mercury is usually present in crude oil and natural gas in a concentration between 0.01 ppb to 10 ppm wt depending on geologic location (Wilhelm, 2001).

Typical crude oils may contain about 0.5 to 10 ppb of mercury. Higher levels of mercury are often found in hydrocarbon condensates from natural gas production. Concentrations between 50 and 300 ppb are present in the condensate from some fields.

2.1.2 Existing Forms of Mercury

Mercury is usually present in nature in the zero (elemental), +1 (mercurous) or +2 (mercuric) valence states. Mercurous compounds usually involve Hg-Hg bonds and are generally unstable and rare in nature. Mercury can be found in elemental, inorganic or in organic form. The more volatile Hg^0 is usually partitioned

to the lighter gas fraction while RHgR is the dominant species in liquid fractions. Therefore, if organic mercury is present in the reservoir, it would be found mostly in condensate, less so in gas, in those situations where hydrocarbon liquids separate due to natural cooling. On the other hand, ionic forms of mercury have been seen in all of the fractions but mostly in separated water (Edmonds *et al.*, 1996).

The solubility of Hg⁰ in produced hydrocarbons depends strongly on temperature, and hence, when saturated liquids are cooled, Hg⁰ can precipitate in equipment. Mercury is most stable in its reduced state and is difficult to oxidize in the natural environment. Mercury can, however be oxidized by strong oxidants including halogens, hydrogen-peroxide, nitric acid and concentrated sulfuric acid (Wilhelm, 2001).

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 ⁻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 ₂ O) | 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 |

The distribution of mercury in crude petroleum and condensates is well known, whereas the forms of mercury compounds present are uncertain. Evidence is growing that crude oil and gas condensate can contain several chemical forms of mercury, which differ in their chemical and physical properties, such as (Wilhelm and bloom, 2000):

1. Dissolved elemental mercury (Hg^0) – 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 $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$, etc. and $\text{X} = \text{Cl}$ 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 distillate fractions in a different fashion from Hg^0 .
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 Effects of Mercury

The adverse effects of mercury on processing systems include equipment degradation, toxic waste generation, increased risk to health and safety of workers and poisoning of catalysts such as palladium, alumina and similar catalysts which are often used in reforming and the hydrogenation process or the like. It is known if mercury is present in the hydrocarbon compound as an incidental impurity, the catalyst is poisoned such that modification may not fully take place (Kawazoc, *et al.*, 1991). In addition to the contribution to atmospheric pollution, the following problems are encountered while processing mercury:

1. Mercury deposits in cryogenic equipment sometimes cause cracking of welded aluminum heat exchangers. Numerous cases of cold box failure are recorded in older gas processing plants and steam cracking ethylene plants; however, the introduction of cold box designs that resist mercury have served to reduce the incidence of failure.
2. Mercury in gas plant products affects downstream processes. Gas plant products used for chemical manufacture, especially olefins, ethylene, aromatics and MTBE, are at risk in processing mercury in feeds due to the cited equipment problems and 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 sorbents 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.

Despite having so many adverse effects, little information is available in literature. This limited knowledge on mercury in condensate arises because:

1. The amount and type of organomercury compounds is not easy to determine. This is because the behavior of these compounds is not completely known and also the nature of these compounds is completely different in gas condensate as compared to gas mixtures.
2. The amount present is very low, and at such a low level, sophisticated techniques for analysis are required.

2.1.4 Condensates

Processed condensate is the C_5^+ fraction that can originate at several locations in a gas processing scheme. A generic unprocessed condensate is the hydrocarbon liquid that separates in the primary separator, either at the wellhead or at the gas plant. At this step the major quantity of the mercury content in the natural gas separates and accumulates in the obtained natural gas condensate. The typical steps in processing the liquid fraction of the wellstream do not reduce the amount of mercury in the liquid fraction leaving the separator. Thus a liquid fraction leaving the separator usually having a mercury content of about 220 $\mu\text{g}/\text{kg}$ (ppb) will yield a stabilized condensate containing about 220 ppb mercury (Audeh, 1990).

Gas and liquid processing can cause the transformation of one chemical form of mercury to another. For example, the mixing of gas and/or condensate from sour and sweet wells allows the reaction of elemental mercury with sulfur or ionic mercury with H_2S to form particulate HgS that can settle out in tanks and deposit in equipment.

Naphtha differs from gas condensates as it originates from the primary distillation of oil in the range of 37°C to 180°C, but the distribution of hydrocarbon compounds in both condensates and naphtha are similar, mostly in the range C₅ to C₁₀, and in condensate occurs in the wide range of 10 to 3000 ppb (Sarriazin *et al.*, 1993).

Thailand is currently producing natural gas and condensate from 1,225 wells. In May 2001, Thailand natural gas production averaged 1,950 million cubic feet per day while the accompanying condensate production averaged 55,830 barrels per day. Produced water is the highest volume waste source in the offshore oil and gas industries. For offshore platforms in the Gulf of Thailand, mercury has been found in natural gas, condensate, produced water and condensate sludge obtained from tank cleaning in the condensate floating storage unit. The range of mercury concentrations in the gas, condensate and produced water, which are produced in the Gulf of Thailand fields, is presented in Table 2.2. Some gas is flared off at the central process platforms, which would allow some mercury to enter the atmosphere.

Table 2.2 Mercury found by Unocal, Thailand (Chongprasith *et al.*, 2001)

| Source | Range of mercury |
|----------------|-------------------------|
| Natural gas | 10-25 µg/m ³ |
| Condensate | 500-800 µg/l |
| Produced water | 30-800 µg/l |

The distribution of mercury for an Asian condensate is shown in Figure 2.1. For this particulate condensate, the large majority of mercury is found in C3 and C4 fractions, (Didillion *et al.*, 2000).

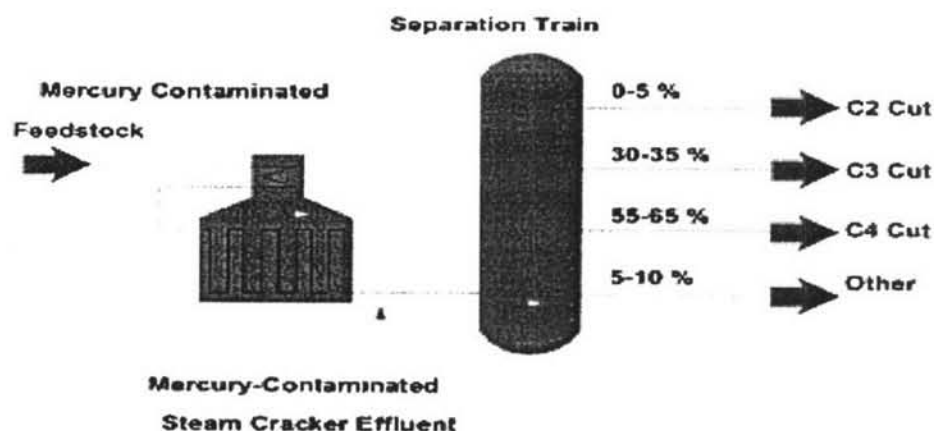


Figure 2.1 Mercury repartition in the steam cracker effluents (Didillon *et al.*).

2.1.5 Mercury Removal Systems

Mercury removal sorbent beds are used to scavenge mercury from gas and liquid hydrocarbon streams. The sorbents 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. Strictly speaking, sorbents are more correctly described as chemisorbents because they function by reacting mercury (or a mercury compound) to a chemical form (HgS, HgI₂ or amalgam) that is insoluble in the hydrocarbon liquid and is chemically inert to a process stream. Table 2.3 shows various mercury removal systems:

Table 2.3 Mercury removal systems for hydrocarbons (Wilhelm, 1999)

| Reactant | Substrate | Complex form | Application |
|------------------------------------|--|------------------|-------------------|
| Sulfur | Carbon, Al ₂ O ₃ | HgS | Gas |
| Metal sulphide | 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 |

There are several factors which have been considered while designing an efficient removal system, such as, various chemical forms of mercury that exhibit very different chemical and physical behaviors. For example, in a gas separation plant having both gas and liquid feeds, adding a gas phase mercury removal system does not eliminate mercury in liquid fraction. Apart from type of mercury species present in feed, there are several factors affect the reaction of mercury with the sorbent such as temperature, pressure, flow rate, hydrocarbon composition, water content, and minor contaminants like arsenic, sulfur, organic halides, etc.

The key rate-determining factors are adsorption and chemical reactivity of the reactive component. Adsorption depends upon the adsorbent. For example, alumina-based systems are less adsorptive. This means that they are somewhat less sensitive to hydrocarbon composition and are not as strongly affected by contaminants as carbon-based systems. Carbon-based systems are more strongly adsorptive and more sensitive to feed composition. On the other hand, capacity is affected by reactant loading on the substrate and available surface area. If a sorbent has a high loading of active reactant (MS, Ag, KI), it will hold more reacted mercury; but high loading can decrease the available surface area.

2.1.5.1 Mercury in Gas

Gas-phase treatment systems primarily consist of sulfur impregnated carbon, regenerative molecular sieve (Ag on zeolite) and metal sulfide on carbon or alumina. The most widely used system for the removal of mercury in a gas-treatment system is a sulfur-impregnated carbon sorbent in which elemental mercury (Hg°) physically adsorbs on carbon and then reacts to form nonvolatile mercuric sulfide:



The resulting mercuric sulfide is nonvolatile, insoluble and is retained on the bed. The reaction is rapid and high levels of mercury can be absorbed onto the bed. However, there are a number of drawbacks. There is no commercial use for the spent material. The only environmentally acceptable route of disposal is combustion

followed by condensation of the mercury evolved. Many operators have to rely on some form of landfill for disposal. Moreover, sulphur 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 downstream equipment. This is why, sulphur impregnated carbon bed has to be located downstream of the molecular sieve dryers. Also, the gas-phase reaction of C-S with organic mercury is slower (than for elemental); however, the percentage of organic mercury in gas is usually low.

Molecular sieve (mol-siv) sorbents that contain certain metals (silver) selectively capture mercury by an amalgamation process:



The advantage is that the system can be regenerative in that mercury is released as mercury vapor when heated in the regeneration cycle and can be recovered by condensation. Due to limited capacity these systems require a regeneration system that cycle frequently. And, also, the system cannot work in the presence of high H_2S .

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 as it is bonded with the support and it is less sensitive to water, so it can be applied for both dry and wet gases. MS systems, therefore are more suited to moist, heavy feeds in which some hydrocarbon condensation is possible. In an alumina (Al_2O_3) supported system, mercury directly reacts with the MS:



It is believed when the adsorbent comprising the substrate having the sulfur element for removing mercury, the reason why the removal efficiency improves, as compared to the adsorbent having no sulfur element introduced, resides in the fact that sulfur in the adsorbent acts as a donor. It is also believed that, particularly when

active carbon is used as the substrate the adsorption reaction by the active carbon occurs and therefore the removal efficiency is enhanced (US Patent No. 4,839,029).

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

2.1.5.2 Mercury in Liquid Hydrocarbons

Mercury-removal processes for liquids consist of iodide impregnated carbon, a mol-siv amalgam system and a two-step process consisting of a hydrogenation conversion catalyst followed by MS reaction with elemental mercury.

Sulphur-impregnated materials are not suitable for the removal of mercury from liquid hydrocarbons. This is due to the solubility of elemental sulphur and this is particularly serious if aromatic species are present. Table 2.4 shows the equilibrium level of sulphur obtained with three liquid hydrocarbons (Openshaw and Woodward, 2001).

Table 2.4 Solubility of Sulphur in Liquid Hydrocarbons at 25°C (Openshaw and Woodward, 2001)

| Hydrocarbon Solubility | ppm |
|------------------------|------|
| Pentane | 300 |
| Heptane | 500 |
| Toluene | 2500 |

Metal sulfide systems, which are successful for mercury removal from gas fraction, cannot 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. 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) impregnated alumina (Al₂O₃).



The main advantage of MS systems are that they are relatively insensitive to sulfur in feed, water and aromatics, and they have a high capacity. Also, after breakthrough the spent material can be regenerated through metal smelters. This is made possible by the use a combination of metals and an inorganic support that is compatible with smelting processes (Abbott and Openshaw, 2000). The major drawback of this system is that the hydrogenation step requires hydrogen and elevated temperature.

The carbon/iodide system consists of potassium iodide impregnated carbon with a large pore diameter.



The 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 iodide-impregnated carbons are sensitive to liquid phase water and process locations where water condensation may occur must be avoided.

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 that dialkylmercury compounds do not amalgamate rapidly; hence the mol-sieve amalgamation sorbents may not have high efficiencies if organic forms of mercury are present in significant concentrations.

Metal oxide systems for liquid fractions are similar to the metal oxide systems for gas and consist of metal oxides that are "activated" by reaction with H_2S . They function in generally the same manner as MS systems. Metal oxide systems are less affected by contaminants (sulfur compounds; aromatic, olefinic and heavy hydrocarbons) than carbon-based sorbents.

2.1.5.3 Mercury in Water

Water discharges from refineries and petrochemical plants have been identified as sources of aquatic mercury contamination. Under anaerobic conditions, inorganic mercury present in water can be transformed by microorganisms into organic mercury compounds and be taken up by aquatic organisms, making them unacceptable for human consumption.

The primary separation of water in gas or oil production separates the majority of ionic species into the water phase. In petroleum production operations, produced water may contain >100 ppb concentrations of total dissolved mercury mostly in ionic or suspended forms, while a lesser amount of Hg^0 (<50 ppb) can be found because of the low solubility of Hg^0 in water.

A common method for the removal of mercury from aqueous process effluents is chemical precipitation by oxidation and sulfide addition. The sulfide reacts with the ionic forms of mercury to form the insoluble HgS that is separated by coagulation and filtration. Specially formulated activated carbons are used to adsorb (chemisorb) elemental, ionic and complex mercury from water streams that do not contain significant amounts of hydrocarbons. Activated carbons are specific and selective for mercury, but typically do not have high capacity and are used mostly for waste streams that are relatively low in mercury content. Waste water streams can also be treated with thiol resins that can achieve very low mercury concentrations in the resin bed effluent and are used in situations where regulatory requirements are stringent.

Table 2.5 Mercury removal systems for water (Wilhelm, 1999)

| Method | Waste stream | Lower limit of treatment capability $\mu\text{g/L}$ |
|-----------------------|----------------------|---|
| Sulfide precipitation | HgS sludge | 10–20 |
| Other precipitant | Sludge, Hg complex | 1–10 |
| Ion exchange | Resin, Hg solution | 1–5 |
| Iron cementation | Hg metal, iron oxide | 0.5–5 |
| Activated carbon | Carbon + Hg complex | 0.25 |
| Thiol resins | Resin + Hg complex | <0.1 |

2.2 Literature Review and Developments

Various mercury removal processes have been developed and applied during the last few decades. However, improvements in existing processes and new developments are always under progress depending upon the present scenario, requirements and problems encountered (technical and economical).

As stated earlier, the presence of mercury and its compounds in crude oil or in raw condensates can cause environmental pollution, equipment corrosion and reduction of the catalyst lifetime. So, the reduction of such contaminants is of prime concern today. The maximum acceptable concentration of mercury in water is 0.001 mg/l as water can be contaminated by mercury through several industrial activities such as effluents from char-alkali industries, pulp and paper industry, mining, gold and other ore recovery processes and irrigation pesticides, etc. There are several techniques available for mercury removal from water, which includes iron coagulation, alum coagulation and lime softening which are quite effective in removing inorganic mercury from water. The ion exchange method is capable of removing about 98% and reverse osmosis can remove 80% of organic and inorganic mercury from water. However, the behavior of mercury and its compound is very different in more complex mixtures of petroleum fractions, such as light naphtha and gas condensates, and is not yet completely understood. The inorganic form of mercury, usually present in water, can be easily removed but mercury is mostly

present in metallic or in organo-metallic form in petroleum fractions which is difficult to remove due to its different solubility and small amounts.

Though a variety of metallic compounds has been known to be in light and heavy cuts from the distillation of crude (nickel, vanadium, arsenic, mercury) or in condensates from natural gas (mercury, arsenic) but mercury and arsenic need special facilities. This is because thermal or catalytic cracking of the hydrocarbon cuts, such as steam cracking for conversion into lighter hydrocarbon cuts, allows the elimination of certain metals (like nickel, vanadium etc). On the other hand, metals (like mercury, arsenic) are likely to form volatile compounds and tend to distribute in different fractions depending upon boiling point. Also, behavior of mercury compounds in liquid condensate is different from a gaseous mixture, as mercury tends to form organo-metallic compounds with hydrocarbon chains containing two, or more than two, carbon atoms (US Patent No. 4,911,825).

Techniques for removing mercury present in trace amounts in hydrocarbons have been described in numerous reports. In one method, mercury in waste water is removed with the aid of a chelating agent, sulfur, activated carbon, an ion-exchange resin, etc. In another method, mercury in waste gases, such as combustion gases and air, are removed using a molecular sieve, lead sulfide, an alkaline reducing agent, a chelator supporting activated carbon or an aqueous solution of permanganate. These methods of mercury removal are mostly intended for use in environmental pollution control (Torihata *et al.*, 1990).

As for natural gas, the following two methods have been proposed:

1. Cooling-condensation method, and
2. Adsorption (absorption) method.

The former method is employed in natural gas liquefaction plants. However, the method is not applicable for removal of mercury from liquid hydrocarbons such as natural gas liquid, because the method includes a cooling step by adiabatic expansion which is employable for gaseous material only.

The latter method uses various adsorbents; for example, an alumina or a zeolite impregnated with silver, an activated charcoal or a molecular sieve impregnated with potassium iodide or sulfur or the like. There are, however, problems with them in that some of them are expensive or some of them are low in

adsorption capacity, inherently or as the result of the reduction of the mercury adsorbing capacity due to the co-adsorption of hydrocarbons (Furuta *et al.*, 1990)

Also, to attain lower concentration levels requires the use of relatively large adsorption beds and relatively low mercury loading. If non-regenerable, the capital and adsorbent costs are uneconomical, and if regenerable, the regeneration media requirements are not only large, but also result in a large mercury-laden bed effluent, which must itself be disposed of in an environmentally safe manner. Furthermore, the high volume of regeneration gas required to be first heated and then cooled to recover the mercury can result in oversized regeneration equipment which increases the capital and utility costs of the process installation (Markovs, 1989).

In addition, the various liquid removal systems have both advantages and disadvantages, depending on feed composition and stream location. 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 complex mercury, then the removal system may not achieve the design criteria for removal efficiency. Also, 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 filter treated to remove suspended solids if the system is to function effectively. Moreover, removal system chemistry is sensitive to minor feed contaminants. So the search for a mercury removal process is still needed.

So far, extensive research has been undertaken in order to find ways to remove mercury from both gaseous and liquid hydrocarbons streams. In general, there are two types of mercury removal technologies, namely mercury trapping, and mercury displacement. Both involve contacting the gas/liquid stream with a mercury removal unit, containing a sulfur-based bed or equivalent adsorbent. The former method consists of trapping the element until the bed becomes spent, and must be replaced. The latter involves trapping the mercury and regenerating the unit in a cyclic process. Universal Oil Products (UOP) (mercury displacement) with Hg-SIV, and Institut Français du Pétrole (IFP) (mercury trapping) with their CMG273, are the two big competitors for mercury removal technology based on the new technology. They both claim excellent trapping efficiency for their marketed products.

In U.S. Patent 4,874,525 (Markovs *et al.*, 1989) disclosed the UOP HgSIV process for effective mercury removal using adsorption molecular sieve. 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 (metal) and selectively capture mercury by an amalgamation process on the outside surface of the molecular sieve pellet or bead due to 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 in the particle. zeolites having the faujasite, i.e. zeolite X and zeolite Y, are found to be superior sorbents and are particularly preferred. Now this mercury amalgam can be recovered as mercury vapors by heating in regeneration cycle, thus producing a mercury-free dry process fluid. So, adding a layer of the HgSIV adsorbents to an existing dryer can remove both water and mercury without requiring a larger dryer. A regeneration cycle limits the capacity of the system:



Later, IFP raised a major problem associated with mercury removal, which is the diverse Hg species present in raw condensate, or in crude oil, and then suggested a two step process permitting the elimination of both As and Hg impurities with very high efficiencies, as appearing in U.S. Patent 4,911,825 (Roussel *et al.*, 1990). According to the process in a first step, 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-aluminas, silica, zeolites, clays, activated carbon and alumina cements.

The first step requires passing the contaminant-containing feed over a fixed bed reactor loaded with a hydrogenolysis catalyst where both catalytic hydro-

genolysis reaction and As captation occur in a presence of hydrogen required to hydrogenolyse the organomercury compounds based on the following reaction:



The arsenic free-feed is subsequently cooled and fed to the second stage in the presence of a trapping material. The second step involves the simple chemical bonding of metallic Hg to selective trapping masses:



The process described above can be used for feedstocks 10^{-3} to 1 milligram of Hg per kilogram of charge and possibly from 10^{-2} to 10 milligrams of arsenic per kilogram of charge.

Later, U.S. Patent 5,384,040 (Mank et al., 1995) described a process for eliminating mercury from a liquid hydrocarbon feed, comprising two steps, a step for transforming compounds containing mercury into elemental mercury and a step for fractionating the effluent from the first step. The metallic mercury from the first step is distributed in at least two cuts: one light fraction that is enriched in mercury and has a boiling point of less than 180°C , which is treated using a metallic mercury adsorption mass, and at least one heavy fraction with a boiling point of more than 180°C , with a reduced mercury content.

In a latest invention, U.S. Patent 6,878,265 (Didillon *et al.*, 2005) disclosed a method in which feed was first distilled instead of directly treated as described in above methods. Distillation in the range 20°C to 600°C allows the mercury distribution in a variety of cut(s). Lighter cuts would likely contain metallic mercury while the organometallic compounds would be concentrated in the heavier cut(s). The sludge would essentially go in the heaviest cut. Thermal decomposition of organometallic mercury compounds and sludges increases the amount of mercury in lightest fraction thus reduces the mercury concentration in the heaviest cuts. This

change in mercury distribution is completely unexpected since the boiling point of mercury metal is 356°C and the mercury should be concentrated in the heavy fraction. However, distillation cannot decompose all of the species of mercury to metallic mercury, and thus the non-metallic mercury species remain in concentrated form in the intermediate cuts.

Demercuration of the lightest cut thus requires installing a simple metallic mercury adsorber while the heavier cuts (>100°C) containing organometallic mercury compounds can now be decontaminated by installing a two-step process. Further, the heaviest cut, sludge (>170°C), containing mercury can also be completely demercurised. An overall demercuration efficiency of more than 99% can be achieved by installing a simple mercury adsorber in each of these produced cuts. The disadvantage of this approach is that it does not provide protection for upstream heat exchangers and does not eliminate the complications of toxic sludge accumulation in upstream separators or effluent water contamination by mercury.

In lab experiments, Shafawi *et al.* (2000) tested three commercially available mercury removal systems. Both real and substitute condensate samples i.e. hexane containing dimethylmercury (DMM), diethylmercury (DEM) and dibutylmercury (DBM) species, were used in the test. The systems were designated AA (using a hydrogenolysis catalyst to convert organic and inorganic mercury to elemental mercury and then using a sulfide-containing alumina for the removal of elemental mercury), BB (a carbon-based adsorbent which contained sulfur as the active material) and CC (a molecular sieve-based adsorbent with undisclosed active material). The tested results show that all three pilot plants can reduce the mercury content of the final product. For the adsorbent system AA, elemental mercury measured in the liquid product from first reactor was only about 30% of the total mercury content. Incomplete conversion of the organomercury species to mercury metal by this reactor may be due to competition between the organomercury species and the unsaturated compounds in the matrix during the hydrogenolysis reaction. The second reactor, for mercury trapping, was able to efficiently adsorb elemental mercury present in the liquid stream (the product from the first reactor) but was unable to remove the organomercury content from the condensate stream. However, the main types of mercury present in the condensate which are organometallic

(>80%) was discussed in this context. For system BB, the results showed no peaks of three organomercury species in the product samples after the reactor. Therefore, the efficiency in removing spiked DMM, DEM and DBM from the n-hexane hydrocarbon sample was close to 100%. Finally for the CC system, efficiency of removal for different mercury species spiked into the n-hexane was variable. The overall performance of the adsorbent in removing DMM, DEM and DBM species was 55, 80 and 22%, respectively.

In a previous work, 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 affects the adsorption capacity and the 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 the bulky size of the diphenylmercury molecule. A bi-Langmuir model was fitted well with the experimental data. The adsorption of the diphenylmercury 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.

2.3 Zeolites

Zeolites are getting much interest nowadays because of its well-defined molecular structure. zeolites are crystalline aluminosilicates, connected with 4 tetrahedral framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration. There are large numbers of natural zeolites (chabazite, mordenite, faujasite, etc.) and more than 150 have been synthesized (Ruthven, 1984). In this context attention is paid only on zeolites X, Y, L, Omega and Beta which are used in separations. All these zeolites have large pore openings.

2.3.1 Zeolites X and Y

The synthetic zeolites X and Y and the natural zeolite faujasite all have the same framework structure, which is shown in Figure 2.2. The

crystallographic unit cell consists of an array of eight cages containing a total of 192 AlO_2 and SiO_2 tetrahedral units. The framework may be thought of as a tetrahedral lattice of sodalite units connected through six-membered oxygen bridges, or equivalently as a tetrahedral arrangement of double six-ring units. The resulting channel structure is very open with each cage connected to four other cages through twelve-membered oxygen rings of free diameter $\sim 7.4 \text{ \AA}$. The difference between the X and Y sieves lies in the Si /Al ratio which is within the range of 1-1.5 for X and 1.5-3.0 for Y. There is a corresponding difference in the number of exchangeable univalent cations, which varies from about 10-12 per cage for X to as low as 6 for high silica Y (Ruthven, 1984).

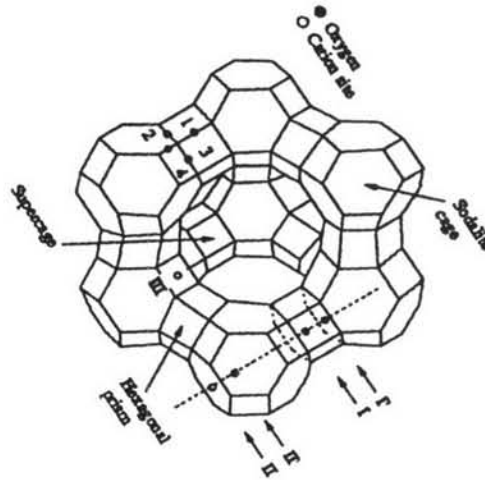


Figure 2.2 Framework of X and Y type zeolites

2.3.2 Zeolite L, Omega and Beta

Zeolite Omega (Figure 2.3) has a pore size about 7.5 \AA with a Si/Al ratio varies in the range of 3-10. The framework is built of gmelinite cages superimposed to form parallel columns. Adjacent columns are cross-linked to form two different types of channels; the large channels are composed of 12-member rings surrounded by 6 cages while smaller channels are formed by distorted 8-member rings between adjacent pairs of cages (Keffer *et al.*, 1996).

Zeolite-L (Figure 2.3) also has one-dimensional 12-ring channels with the framework formed by hexagonal lattice connected through double six-ring

units. Zeolite L has pores of about 7.1 Å with Si/Al ratio typically 3.0. (Keffer *et al.*, 1996).

Zeolite Beta (Figure 2.3) is a tetragonal crystal structure with straight 12-membered ring channels (7.6 x 6.4 Å) with crossed 10-membered ring channels (5.5 x 6.5 Å). It is a three dimensional network (Keffer *et al.*, 1996).

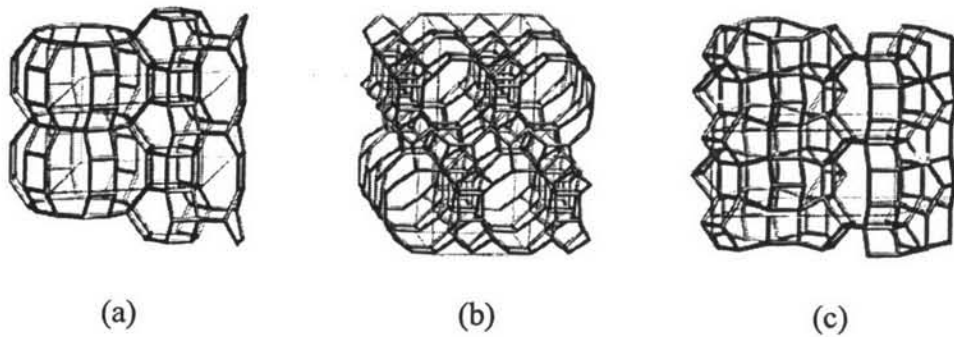


Figure 2.3 Framework of zeolites: a) L, b) Beta and c) Omega

2.4 Mathematical Model

The mathematical model of the isothermal, dynamic adsorption breakthrough process in a fixed bed is based on transient material balance, gas or liquid phase, intrapellet mass transfer and adsorption equilibrium relationship. The kinetic aspects are also taken into account along with adsorption equilibrium which can be described by Langmuir equation. The mass transfer rate is represented by Linear Driving Force (LDF) model which is a lumped-parameter model for particle adsorption. The estimation of intrapellet mass-transfer coefficient, k , is an important step in the resolution of the simulation problem.

2.4.1 Modeling Approach

The phenomenon of adsorption is an attraction of adsorbate molecules to an adsorbent surface. The phenomenon arises due to the different concentration of adsorbate in the bulk phase and in the adsorbent or solid phase. During an adsorption process, overall mass transfer adsorbate specie is depend on various kind of mass transfer resistances and the determination of these resistances is the major step in

order to understand slowest mechanism. However, in many cases (Ghorai, *et al.*, 2005; Brosillon, *et al.*, 2001; Singh *et al.*, 2004), overall rate of mass transfer may depend on more than one mass transfer resistance. So, it is important to understand the effects of various mass transfer resistances on overall process, in order to solve a predictive model.

Figure 2.4 (a cross section of column) shows a general adsorption process, indicates various mass transfer resistances namely;

1. External film resistance (due to the interaction of solid and liquid)
2. Internal (macro and micro) resistance (due to the geometry of adsorbent)
3. Rate of adsorption (due to active sites on surface of adsorbent)

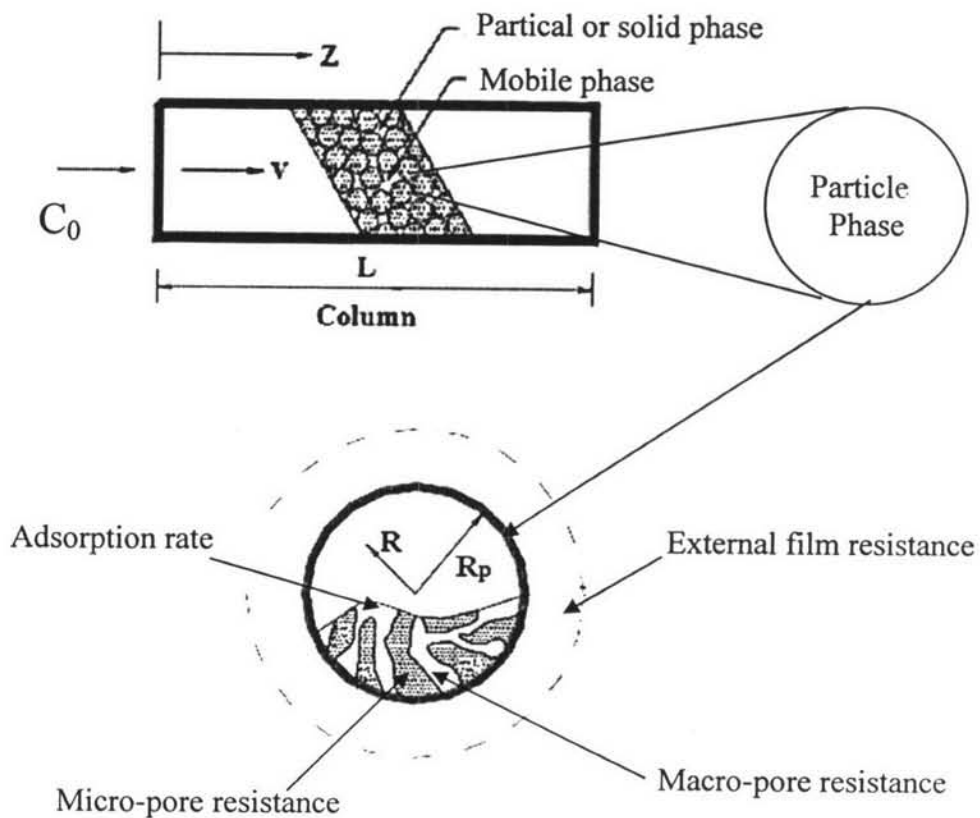


Figure 2.4 Various resistances during adsorption phenomena (Ruthven, 1984).

2.4.2 Model Formulation

In an adsorption column, the differential mass balance for an element in bulk fluid phase and in solid phase provides the starting point for developing a mathematical model in order to describe the dynamic behavior of the system. Figure 2.5 shows a cross section of column, and mass balance for a specie 'i' can be given as:

$$\left[\begin{array}{l} \text{Rate of increase} \\ \text{in moles of } i \\ \text{per unit volume} \end{array} \right] = \left[\begin{array}{l} \text{Net rate of addition} \\ \text{in moles of } i \text{ per unit} \\ \text{volume by convection} \end{array} \right] + \left[\begin{array}{l} \text{Rate of addition of} \\ \text{moles of } i \text{ per unit} \\ \text{volume by diffusion} \end{array} \right] - \left[\begin{array}{l} \text{Rate of loss of moles} \\ \text{of } i \text{ per volume by} \\ \text{physical adsorption} \end{array} \right] \\ - \left[\begin{array}{l} \text{Rate of loss of moles} \\ \text{of } i \text{ per volume by} \\ \text{physical adsorption} \end{array} \right] - \left[\begin{array}{l} \text{Rate of loss of } i \text{ per volume} \\ \text{due to deactivation by aging} \\ \text{poisoning, cocking} \end{array} \right]$$

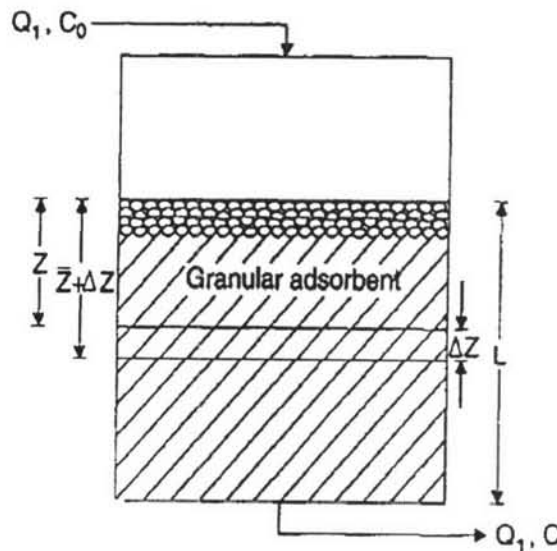


Figure 2.5 Differential mass balance over the packed bed

where C_0 , C are the inlet and outlet fluid phase concentrations to adsorber, Q_1 is the volumetric flow rate of fluid, z the distance measured from column inlet, ϵ the porosity of adsorption bed Under the isothermal conditions and the only concentration gradient in the radial direction, above expression can be written as:

$$\frac{\partial c}{\partial t} = \left\{ -\frac{\partial(vc)}{\partial z} \right\} + \left\{ D_L \frac{\partial^2 c}{\partial z^2} \right\} - \left\{ \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial \bar{q}}{\partial t} \right\} - (-r_i) - A \quad (2.16)$$

$$-D_L \frac{\partial^2 c}{\partial z^2} + v \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \left(\frac{1-\varepsilon}{\varepsilon} \right) \frac{\partial \bar{q}}{\partial t} + (-r_i) + A = 0 \quad (2.17)$$

where D_L is the axial dispersion coefficient and, v the interstitial velocity of fluid, \bar{q} the adsorbate concentration averaged over crystal and pellet, A is representative term for deactivation and $(-r_i)$ is rate of chemical adsorption and for a first order reaction can be given as:

$$(-r_i) = K \cdot c \quad (2.18)$$

where K is rate constant for chemical reaction.

The rate of adsorption can be described by linear driving force (LDF) equation as indicated below:

$$\frac{\partial \bar{q}}{\partial t} = k(q^* - \bar{q}) \quad (2.19)$$

where k is the LDF mass transfer coefficient (Appendix D) in the unit of s^{-1} and q^* represents the equilibrium adsorbed phase concentration which can be determined from the concentration in the mobile phase using the Langmuir equation as indicated below:

$$q^* = \frac{q_{max} b \cdot c}{1 + b \cdot c} \quad (2.20)$$

where q_{max} and b are Langmuir isotherm parameters. The term $\partial \bar{q} / \partial t$ represents the overall rate of mass transfer for adsorbed component average over a particle.

Substituting equation (2.18) and equation (2.19) into equation (2.17),

$$- D_1 \frac{\partial^2 c}{\partial z^2} + v \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + k \left(\frac{1 - \varepsilon}{\varepsilon} \right) (q^* - \bar{q}) + K.C + A = 0 \quad (2.21)$$

The dynamic response of the column which is concentration profiles in the mobile (c) and adsorbed phase (\bar{q}) along the packed bed adsorber can be determined by solving equation (2.21) subject to the following initial and boundary conditions:

$$\begin{aligned} \text{Initial conditions: } & t = 0, z > 0, & c = c(0,z) \text{ and } q = q(0,z) \\ \text{Boundary conditions: } & z = 0, t > 0, & c = c_{inlet} \\ & z = L, t > 0, & \frac{\partial c}{\partial z} = 0 \end{aligned}$$

where c_{inlet} represents the initial feed concentration or concentration of bulk fluid.

The response to a perturbation in the feed composition involves a mass transfer zone or concentration front which propagates through the column with a characteristic velocity determined by the equilibrium isotherm. The location of the front at any time may be found simply from an overall mass balance, but in order to determine the form of the concentration front Eqs. (2.18) and (2.20) must be solved simultaneously (Ruthven, 1984).

2.4.3 Numerical Algorithm

The method of lines (MOLs) can be applied to discretize partial differential equations presented in Eq. (2.21) into a set of ordinary differential equations (ODEs) by using the central finite difference method. Then, the 4th order Runge-Kutta method available in the MATLAB[®] programming language can be applied to solve ODE in order to predict the mercury concentration in the fluid phase leaving the adsorber with time.

2.4.3.1 The method of lines (MOLs)

This explicit method will convert PDE into a set of first-order ODE's with initial value problem. For 1st order derivative, $\partial c / \partial z$ in terms of central finite differences with error of order h^2 can be expressed in terms of their respective definitions:

$$\frac{dc_i}{dz} = \frac{1}{2\Delta z}(c_i - c_{i-1}) + O(\Delta z^2) \quad (2.22)$$

For 2nd order derivative term, $\frac{\partial^2 c}{\partial z^2}$ in terms of central finite differences with the error of order h^2 can be expressed in terms of their respective definitions:

$$\frac{d^2 c_{i,j}}{dz^2} = \frac{1}{\Delta z^2}(c_{i+1,j} - 2c_{i,j} + c_{i-1,j}) + O(\Delta z^2) \quad (2.23)$$

where i is the step size number of axial direction and j the step size number of time. Finally, MATLAB language is programmed to solve the set of ODEs.

As a summary, a general solution procedure for solving mathematical model is shown in Figure 2.6.

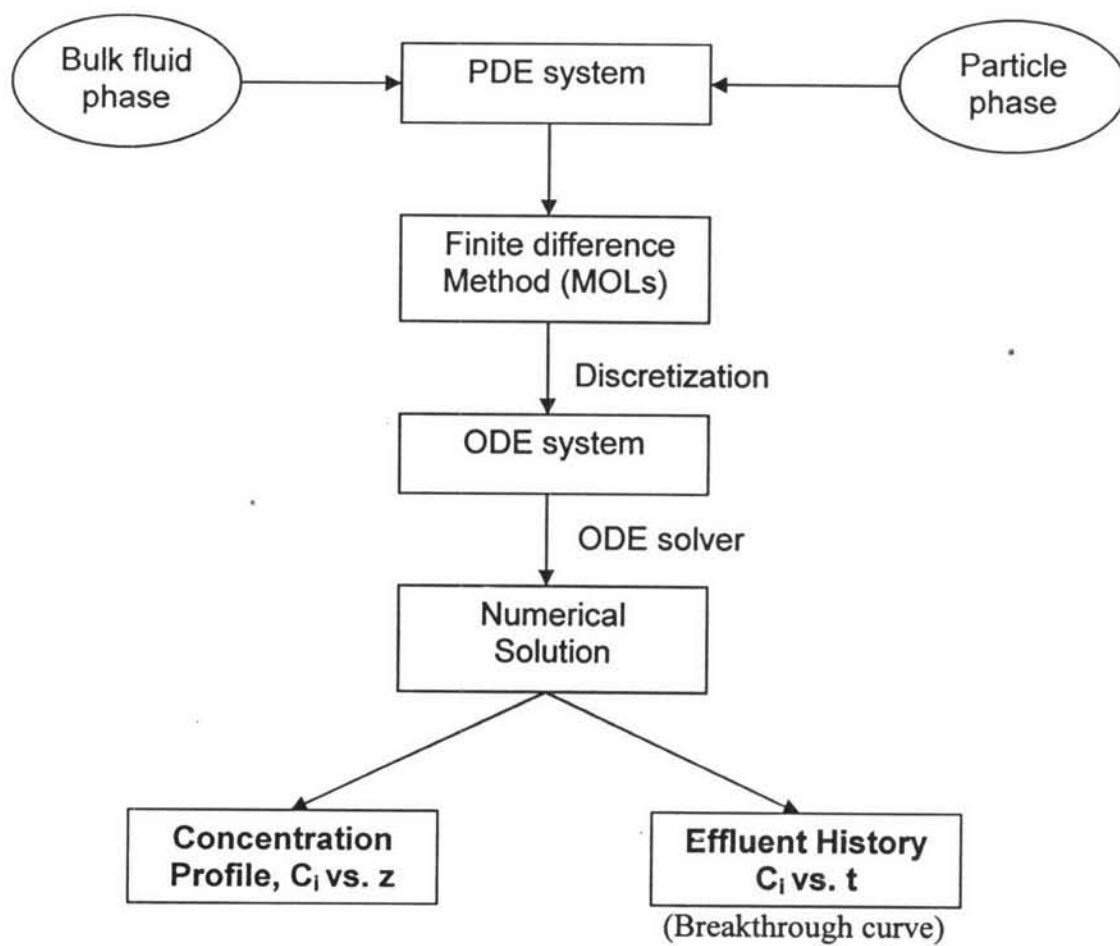


Figure 2.6 General solution strategy for solving a mathematical model