



## CHAPTER II LITERATURE REVIEWS

### 2.1 Property of Mercury

Elemental mercury ( $\text{Hg}^0$ ), although it is a metal, is unique in that it is a liquid at normal temperatures. This property, plus its high specific gravity and electrical conductivity, has brought about its widespread use in industry and various types of laboratory equipment and instruments (Jones 1971, USEPA 1997, cited in Ebadian *et al.*, 1999). These applications include mercury-arc lamps, neon and fluorescent lamps, mercury boilers, electrodes in electrolysis, arc rectifiers, batteries, switches, thermometers, barometers, manometers, hydrometers, pyrometers, and related equipment. In addition to elemental mercury, other forms of mercury that have been widely used and found in the natural environment are inorganic mercury (II) compounds, such as mercury (II) hydroxide ( $\text{Hg}(\text{OH})_2$ ), mercury(II) sulfide ( $\text{HgS}$ ), and mercury(II) chloride ( $\text{HgCl}_2$ ); and organomercury forms, which include methylmercury species, such as monomethylmercury ( $\text{CH}_3\text{Hg}_x$ , where  $X =$  inorganic counter ions, such as  $\text{Cl}^-$  and  $\text{OH}^-$ ) and dimethylmercury ( $(\text{CH}_3)_2\text{Hg}$ ) (Henke *et al.*, 1993., USEPA 1997, cited in Ebadian *et al.*, 1999). Different mercury forms may exist at a contaminated site, and these compounds may also be transformed from one species to another under certain environmental conditions.

Decontamination for different mercury forms may require different techniques. Therefore, a thorough understanding of the physical, chemical, hydrological, mineralogical, and biological processes that affect the transport and fate of mercury in the environment is a primary and key step for successful decontamination and remediation efforts. This understanding will provide the basis for the selection and/or development of effective and economical decontamination and remediation techniques (Stepan *et al.*, 1993, cited in Ebadian *et al.*, 1999). Some basic physical, chemical, and biological properties are summarized here. More details can be found in the

literature (e.g., Henke *et al.*, 1993, USEPA 1997, cited in Ebadian *et al.*, 1999).

### 2.1.1 Properties of Elemental Mercury

Table 2-1 lists the most important physical and chemical properties for elemental mercury. The physical properties of a substance refer to those characteristics that are determined without altering its chemical composition, such as odor, color, density, melting point, and boiling point (Henke *et al.*, 1993, cited in Ebadian *et al.*, 1999). The elemental mercury metal is a heavy, silvery-white liquid at typical ambient temperatures and atmospheric pressures. The vapor pressure of mercury metal is strongly dependent on temperature, and it vaporizes readily under ambient conditions. The melting point of mercury is  $-38.87\text{ }^{\circ}\text{C}$  ( $-37.97\text{ }^{\circ}\text{F}$ ), and it has a boiling point of  $357\text{ }^{\circ}\text{C}$  ( $675\text{ }^{\circ}\text{F}$ ).

Elemental mercury is also extremely dense, being 13.5 times more dense than liquid water under ambient conditions. This high density, as well as the low saturation vapor pressure and high surface tension, control the immediate behavior of released elemental mercury on a land surface (Turner 1992, Henke *et al.*, 1993, cited in Ebadian *et al.*, 1999). Most of the mercury encountered in the atmosphere is elemental mercury vapor. The chemical properties refer to the characteristics of a substance that are intimately involved in chemical reactions with other substances. One of the most important chemical properties of different forms of mercury is the valance state (Henke *et al.*, 1993, cited in Ebadian *et al.*, 1999). Mercury can exist in three oxidation states:  $\text{Hg}^0$  (metallic),  $\text{Hg}_2^{2+}$  (mercurous), and  $\text{Hg}^{2+}$  (mercuric). The properties and behavior of mercury depend on the oxidation state. The valance states of mercury have important implications in human health and safety, in understanding mercury transport and fate, and in developing effective remediation technologies. Most of the mercury in water, soil, sediments, or biota (i.e., all environmental media, except the atmosphere) is in the form of inorganic mercury salts and organic forms of mercury. Solubility

data on elemental mercury and mercury compounds, especially in water, are important in understanding mercury transport and fate. Compared to some mercury compounds, elemental mercury tends to be relatively insoluble in water (see also next section for mercury compounds). Redox potential is another key parameter in governing the biogeochemical cycling of mercury (USEPA 1997, cited in Ebadian *et al.*, 1999).

**Table 2-1** Important Properties of Elemental Mercury (Henke *et al.*, 1993, Skoog *et al.*, 1998, cited in Ebadian *et al.*, 1999)

Physical Properties	
Atomic number	80
Atomic radius	1.5 Å
Atomic volume	14.81 cm <sup>3</sup> /g-atom
Atomic weight	200.59
Boiling point/rise in pressure	0.0746 °C/torr
Conductivity (heat)	0.022 cal/sec/cm <sup>3</sup> .°C
Contact angle	132 degrees
Density	13.546 g/cm <sup>3</sup> at 20 °C (0.489 lb/in <sup>3</sup> at 68 °F)
Diffusivity (in air)	0.112 cm <sup>2</sup> /sec
Electron configuration	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>
Heat capacity	0.0332 cal/g at 20 °C (0.060 Btu/lb at 68 °F)
Henry' s law constant	0.0114 atm m <sup>3</sup> /mol
Interfacial tension (Hg/H <sub>2</sub> O)	375 dyn/cm at 20 °C (68 °F)
Ionization potential (first)	10.4375 ev
Ionization potential (second)	18.751 ev
Isotope abundance	196(0.15), 198(9.97), 199(16.87), 200 (23.1), 201(13.18), 202(29.86), 204(6.87)
Melting point	-38.87 °C (-37.97 °F)
Odor	None
Reflectivity	71.2% at 5500 Å light
Resistivity (heat)	95.8 × 10 <sup>-6</sup> ohm/cm at 20 °C (68 °F)
Saturation vapor pressure	0.16 N/m <sup>2</sup> (pascal) at 20 °C (68 °F)
Specific gravity	13.546 at 20 °C (68 °F)
Surface tension (in air)	436 dym/cm at 20 °C (68 °F)

**Table 2-1 (Cont.)**

<b>Physical Properties</b>	
Vaporization rate (still air)	0.007 mg/cm <sup>2</sup> .hr.for 10.5 cm <sup>2</sup> droplet at 20 °C (68 °F)
Viscosity	1.554 cp at 20°C (68 °F)
<b>Chemical Properties</b>	
E° for Hg <sup>2+</sup> + 2e <sup>-</sup> = Hg (l)	0.854 V
E° for Hg <sub>2</sub> <sup>2+</sup> + 2e <sup>-</sup> = 2Hg (l)	0.788 V
E° for 2Hg <sup>2+</sup> + 2e <sup>-</sup> = 2Hg <sub>2</sub> <sup>2+</sup>	0.920 V
Electronegativity	1.92 (Pauling scale)
Solubility	In water: 60 – 80 µg/L at 20°C (68 °F)
	In benzene: 2000 µg/L at 20°C (68 °F)
	In dioxane: 7000 µg/L at 20°C (68 °F)
	In nitric acid: " soluble "
Valance state	0

### 2.1.2 Properties of Some Mercury Compounds

Tables 2-2 and 2-3 summarize some fundamental properties of selected inorganic mercury and organomercury compounds, respectively. Solubility information for some important mercury (organic and inorganic) compounds is listed in Table 2-4. Although water solubility values are available for elemental mercury and many inorganic mercury compounds, there is little quantitative information on the solubility of organomercury compounds in water (Henke *et al.*, 1993, cited in Ebadian *et al.*, 1999). However, some qualitative information is available from literature (Environment Canada, 1984, Henke *et al.*, 1993, cited in Ebadian *et al.*, 1999). Monomethylmercury compounds with highly electronegative inorganic anions, such as fluoride, nitrate, sulfate, or phosphate, tend to be more soluble in water and alcohol and less soluble in nonpolar solvent (for example, benzene), while the opposite is generally true for monomethylmercury compounds that contain hydroxide and less electronegative anions.

Solubility is also an essential parameter involved in the formation of amalgams between elemental mercury and various metals. Henke *et al.* (1993, cited in Ebadian *et al.*, 1999) summarized this information in their report to the U.S. Department of Energy. At ambient conditions, silver, gold, copper, zinc, and aluminum readily form amalgams in the presence of liquid or gaseous elemental mercury (Andren and Nriagu 1979, cited in Ebadian *et al.*, 1999). However, except for zinc, the solubility of these metals in elemental mercury is actually relatively low. Specifically, the solubility of zinc in mercury is 2.15 g/100g of mercury, while gold solubility in mercury is only 0.13 g/100g of mercury. Silver, copper, and aluminum have even lower solubilities than gold. Nevertheless, the solubility is sufficient so that only small amounts of liquid or gaseous elemental mercury can cause aluminum, certain steel and copper alloy pipes and valves to become corroded or embrittled. Galvanized metal, which contains zinc, is even more susceptible to corrosion from elemental mercury. In natural environments, the transport and fate of elemental mercury could also be affected by amalgamation with naturally occurring metallic minerals or metallic equipment that is at or near a mercury spill site (Henke *et al.*, 1993, cited in Ebadian *et al.*, 1999).

**Table 2-2** Properties of selected Inorganic Mercury Compounds (Lide 1997 and Henke *et al.*, 1993, cited in Ebadian *et al.*, 1999)

Compounds	Mol. W	Boiling point (°C)	Density at about 25°C (77 °F),g/cm <sup>3</sup>	Melting point(°C)
HgCl <sub>2</sub>	271.50	304	5.6	276
Hg(NO <sub>3</sub> ) <sub>2</sub>	324.60		4.3	79
HgO	216.59		11.1	Decomposes at 500 °C (932 °F)
HgS (Black)	232.66		7.70	Sublimes at 583.5°C (1082 °F)
HgS (red)	232.66		8.17	Transfer to black HgS at 386 °C

**Table 2-3** Properties of Selected Organomercury Compounds

	<i>Mol. W</i>	<i>Boiling point</i> (°C)	<i>Density at about 25°C</i> (77 °F),g/cm <sup>3</sup>	<i>Melting point(°C)</i>
CH <sub>3</sub> HgCl	251.09	Volat. At 100	4.063	170
(CH <sub>3</sub> ) <sub>2</sub> Hg	230.66	96	3.069	
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Hg	258.71	159	Liq. 2.444	

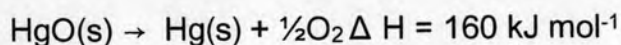
**Table 2-4** Solubility Information for Selected Mercury Compounds at about 20 °C (68 °F) (Modified from Henke *et al.*, 1993, cited in Ebadian *et al.*, 1999)

Compound	Solvent	Solubility	Reference
Hg <sup>0</sup>	Water	60 - 80 µg/L	Eichholz <i>et al.</i> , 1988
HgF <sub>2</sub>	Water	Hydrolyzes	Cotton <i>et al.</i> , 1999
HgCl <sub>2</sub>	Water	70,000,000 µg/L	Magos 1975
Hg <sub>2</sub> Cl <sub>2</sub>	Water	2,000 µg/L	Magos 1975
HgBr <sub>2</sub>	Water	6,205,000 µg/L	Cotton <i>et al.</i> , 1999
HgI <sub>2</sub>	Water	58,060 µg/L	Cotton <i>et al.</i> , 1999
HgO	Water	53,000 µg/L	Kaiser and Tolg 1980
Hg <sub>2</sub> O	Water	" very low"	Kaiser and Tolg 1980
HgS	Water	~ 10 µg/L	Lide 1990

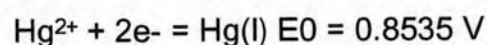
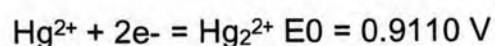
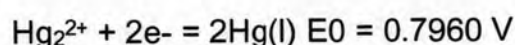
## 2.2 Some Important Reactions of Mercury

### 2.2.1 Reactions Involving Inorganic Mercury

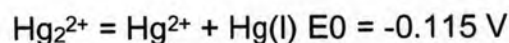
Mercury is obtained from its principal ore, cinnabar (HgS), by roasting to form HgO and then decomposing this at ca. 500 °C (Cotton *et al.*, 1999, cited in Ebadian *et al.*, 1999).



Univalent Mercury (Mercurous,  $\text{Hg}_2^{2+}$ ): As mentioned above, the  $\text{Hg}_2^{2+}$  ion is a very important species of mercury. In aquatic solution the  $\text{Hg}_2^{2+}$  ion is readily obtained by reduction of the  $\text{Hg}^{2+}$  ion. The transfer between different mercury species is often controlled by the potentials of a number of reduction/oxidation reactions. The following are some of the half reactions related to aqueous mercurous ion,  $\text{Hg}_2^{2+}$  (Cotton *et al.*, 1999, cited in Ebadian *et al.*, 1999):



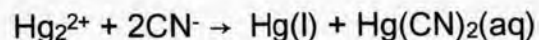
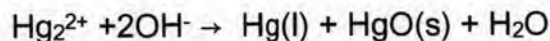
From these, the potential of the following rapid, reversible reaction is then calculated:



From this, the following equilibrium constant is obtained:

$$K = [\text{Hg}^{2+}]/[\text{Hg}_2^{2+}] = 1.14 \times 10^{-2}$$

It follows, then, that when a solution containing  $\text{Hg}^{2+}$  is treated with an equimolar or greater quantity of elemental mercury, a solution of  $\text{Hg}_2^{2+}$  is formed. This conclusion is obtained based on an assumption that only uncomplexed aqua ions are involved. In real aquatic environments, however, many anions exist. These anions tend to complex more strongly with  $\text{Hg}^{2+}$  than with  $\text{Hg}_2^{2+}$ , the marginal stability of the latter against disproportionation is easily altered and thus there are relatively few stable  $\text{Hg}_2^{2+}$  compounds (Cotton *et al.*, 1999, cited in Ebadian *et al.*, 1999). All anions or ligands such as  $\text{NH}_3$ , amines,  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ ,  $\text{S}^{2-}$ , and  $\text{acac}^-$  that complex or precipitate  $\text{Hg}^{2+}$  promote the disproportionation of  $\text{Hg}_2^{2+}$ .

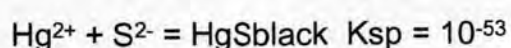


The rate-determining step in these disproportionations has been shown to be the cleavage of the Hg - Hg bond.

The four halides,  $\text{Hg}_2\text{X}_2$ , all occur, the chloride, bromide, and iodide all being insoluble in water.  $\text{Hg}_2\text{F}_2$  is rapidly hydrolyzed to HF, Hg(l), and HgO.  $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  are very soluble in water to give stable solutions from which the insoluble halides can easily be precipitated. Other compounds that contain weakly coordinating anions, e.g., sulfate, chlorate, bromate, iodate, and acetate, also occur. In general, oxygen-donor ligands such as oxalate, succinate,  $\text{P}_2\text{O}_7^{4-}$ , and  $\text{P}_3\text{O}_{10}^{5-}$ , which do not form strong complexes with  $\text{Hg}^{2+}$ , give stable complexes, such as  $[[\text{Hg}_2(\text{P}_2\text{O}_7^{4-})_2]^{6-}$ , with mercurous ion (Cotton *et al.*, 1999, cited in Ebadian *et al.*, 1999).

**Divalent Mercury:** An important process by which mercury concentration in solution could increase is through the dissolution of mercury minerals. The most common mercury minerals are cinnabar (red HgS) and metacinnabar (black HgS). Cinnabar is most commonly found as an ore mineral, whereas metacinnabar is often found in anoxic, Hg-contaminated sediments (Barnett *et al.*, 1997, Ravichandran 1999, cited in Ebadian *et al.*, 1999).

The addition of  $\text{H}_2\text{S}$  or alkali metal sulfides to aqueous  $\text{Hg}^{2+}$  precipitates the highly insoluble, black mercuric sulfide, HgS.



This black solid when heated or treated in other ways is changed into a red form that is identical to the mineral cinnabar (Cotton *et al.*, 1999, cited in



Ebadian *et al.*, 1999). In this red form, HgS has a distorted NaCl structure in which the  $(\text{Hg-S})_{\infty}$  chain can be recognized. Red cinnabar on irradiation in aqueous KI is converted to black cinnabar, which has the ZnS structure and also occurs in nature.

The addition of  $\text{OH}^-$  to aqueous  $\text{Hg}^{2+}$  precipitates HgO as a yellow solid of fine particles. When prepared in other ways, e.g., by gentle thermolysis of  $\text{Hg}_2(\text{NO}_3)_2$  or  $\text{Hg}(\text{NO}_3)_2$ , or by direct combination of Hg and  $\text{O}_2$ , it is red.

All four halides,  $\text{HgX}_2$ , are known. Mercury (II) fluoride has the fluorite structure and is not volatile. It is decomposed by water as might be expected since HgO and HF are both weakly dissociated. No fluoro complex is known (Cotton *et al.*, 1999, cited in Ebadian *et al.*, 1999). The other three halides can all be vaporized as  $\text{XHgX}$  molecules, and such molecules can also occur in solution.

Salts of oxo anions, such as the nitrate, perchlorate, and sulfate, are appreciably dissociated in aqueous solution, but because of the weakness of mercuric oxide as a base, the solutions must be acidified to be stable (Cotton *et al.*, 1999, cited in Ebadian *et al.*, 1999). An aqua ion,  $[\text{Hg}(\text{H}_2\text{O})_6]^{2+}$ , apparently exists, but this readily hydrolyzes to  $\text{Hg}(\text{OH})^+(\text{aq})$  and then to  $\text{Hg}(\text{OH})_2(\text{aq})$  in which there is a linear  $\text{HO} - \text{Hg} - \text{OH}$  unit. The dissolved nitrate is mainly present as  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{Hg}(\text{NO}_3)^+$  and  $\text{Hg}^{2+}$ , but in the presence of excess  $\text{NO}_3^-$ , the complexes  $\text{Hg}(\text{NO}_3)_3^-$  and  $\text{Hg}(\text{NO}_3)_4^{2-}$  are formed.

**Mercury (II) Complexes:** Mercury is a distinctly soft cation, showing a strong preference for Cl, Br, I, P, S, Se, and certain N-type ligands. It displays coordination numbers of 2 through 6, with a preference for the lower ones. Its marked preference for linear 2-coordination, is a distinctive feature (Cotton *et al.*, 1999, cited in Ebadian *et al.*, 1999). Several important mercury (II) complexes are shown below.

Halogen and pseudohalogen complexes are an important category. In aqueous solution, mercury forms complexes  $\text{HgX}_n^{-(n-2)}$  for  $n = 1-4$ . At  $10^{-1}$  M  $\text{Cl}^-$ , for example, approximately equal amounts of  $\text{HgCl}_2$ ,  $\text{HgCl}_3^-$ , and  $\text{HgCl}_4^{2-}$  are present, but at 1 M  $\text{Cl}^-$  essentially only  $\text{HgCl}_4^{2-}$  is present.

Mercury (II) has a great affinity for ligands with sulfur and the other chalcogenides as the ligating atom and forms more complexes with such ligands than with any other types (Cotton *et al.*, 1999, cited in Ebadian *et al.*, 1999). Indeed, the name mercaptan for thiols arose from their affinity for mercury. In biological systems Hg (II) invariably binds to cysteine thiolate groups.

In aquatic environments, hydroxide, chloride, and sulfide are considered to control the speciation of mercury (Schuster 1991, Ravichandran 1999, cited in Ebadian *et al.*, 1999). At circum-neutral pH conditions, hydroxidemercury species ( $\text{Hg}(\text{OH})_2$ ,  $\text{HgOH}^+$ ) are expected to be predominant in freshwater (Hudson *et al.*, 1994, Stumm and Morgan 1995, cited in Ebadian *et al.*, 1999). Chloride-mercury complexes are expected to be important at low pH and/or high chloride concentrations found in real aquatic environment, such as marine and estuarine. For example, Leermakers *et al.* (1995, cited in Ebadian *et al.*, 1999) estimated that more than 90% of mercury would be found as  $\text{HgCl}_2$  at salinity greater than 25%. In anoxic aquatic environments containing dissolved sulfide ( $\text{HS}^-$ ), mercury is expected to combine with sulfide to form mercuric sulfide species such as  $\text{HgS}_{\text{solid}}$  and  $\text{Hg}(\text{SH})_2(\text{aq})$  (Dyrssen and Wedborg 1991 Hudson *et al.*, 1994; Ravichandran 1999, cited in Ebadian *et al.*, 1999).

Dissolved organic matter (DOM), which is ubiquitous in aquatic environments, is known to bind trace metals strongly, affecting their speciation, solubility, mobility, and toxicity (Buffle 1988, Ravichandran 1999, cited in Ebadian *et al.*, 1999). Many metals in natural waters have solubilities much higher than expected from calculations based on complexation with

inorganic ligands. The enhanced solubility is predominantly due to the complexation of these metals with DOM. There is increasing evidence that DOM plays an important role in the speciation of mercury in aquatic environments. This evidence is largely based on positive correlation observed between mercury and dissolved organic carbon (DOC) concentration in natural waters (Andren and Harriss 1975, Lindberg and Harriss 1975, Mierle and Ingram 1991, Driscoll *et al.*, 1995 Watras *et al.*, 1995, Varshal *et al.* 1996 Cai *et al.*, 1999, Ravichandran 1999, cited in Ebadian *et al.*, 1999).

Knowledge of the complexes formed between mercury and different ligands (inorganic and organic) is very important in understanding mercury transport and fate and in developing effective remediation technologies. Some important stability constants of complexes between mercury and various inorganic and organic ligands and between mercury and DOC are summarized in Tables 2-5 and 2-6, respectively.

**Table 2-5** Stability Constants of Complexes between Mercury and various Inorganic and Organic Ligands (From Martell *et al.*, 1998, Ravichandran 1999, cited in Ebadian *et al.*, 1999)

Ligand <sup>a</sup>	Formula	HgL		HgL <sub>2</sub>	
		Log K	T (°C) I (M)	Log K	T (°C) I (M)
Chloride	Cl <sup>-</sup>	7.3	25, 0	14	25, 0
Carbonate	CO <sub>3</sub> <sup>2-</sup>	11.0	25, 0.5	--	--
Hydroxide	OH <sup>-</sup>	10.6	25, 0	21.8	25, 0
Sulfate	SO <sub>4</sub> <sup>2-</sup>	1.3	25, 0.5	--	--
Bromide	Br <sup>-</sup>	9.1	25, 0.5	17.3	25, 0.5
Fluoride	F <sup>-</sup>	1.0	25, 0.5	--	--
Ammonia	NH <sub>3</sub>	8.8	25, 2.0	17.4	22, 2.0
Sulfide	HS <sup>-</sup>	--	--	37.7	20, 1.0
Phosphate	PO <sub>4</sub> <sup>3-</sup>	9.5	25, 3.0	--	--
Acetic acid	CH <sub>3</sub> (COOH)	3.7	24, 0.1	8.4	25, 3.0
Citric acid <sup>3-</sup>	HOC(CH <sub>2</sub> ) <sub>2</sub> (COOH) <sub>3</sub>	10.9	25, 0.1	--	--

**Table 2-5 (Cont.)**

Ligand <sup>a</sup>	Formula	HgL		HgL <sub>2</sub>	
		Log K	T (°C) I (M)	Log K	T (°C) I (M)
Nitrilotriacetic acid <sup>3-</sup>	N(CH <sub>2</sub> COOH) <sub>3</sub>	14.3	25,0.1	--	--
Ethylenedinitrilo-tetraacetic acid <sup>4-</sup>	(HOOCCH <sub>2</sub> ) <sub>4</sub> (NCH <sub>2</sub> ) <sub>2</sub>	21.5	25,0.1	--	--
Cysteine <sup>2-</sup>	HSCH <sub>2</sub> CH(NH <sub>2</sub> )COOH	14.4	25,0.1	--	--
Glycine <sup>-</sup>	NH <sub>2</sub> CH <sub>2</sub> COOH	10.3	25,0.5	19.2	20,0.5
Thiourea <sup>-</sup>	H <sub>2</sub> NCSNH <sub>2</sub>	11.4	25,0.5	22.1	25,0.5
Thioglycolic acid <sup>2-</sup>	HSCH <sub>2</sub> COOH	--	--	43.8	25,1.0

<sup>a</sup> The superscripts in organic ligands are the charge on the ligand when they are fully ionized, for which the binding constants are given.

**Table 2-6 Stability Constants of Mercury-DOC Complexes Reported in Literature (Modified from Ravichandran 1999, cited in Ebadian *et al.*, 1999)**

Method	Type of organic matter	pH	Log K	Reference
Ion-exchange	Marine sedimentary humic acid, commercial humic acid	5.0	5.2	Strohal and Huljev (1971)
Iodide selective electrode	Soil fulvic acid	3.0 4.0	4.9 5.1	Chem and Gamble (1974)
Iodide selective electrode	Soil humic substances	4.5	4.69	Yin <i>et al.</i> (1997)
Titration	Bog water-concentrated organic matter	4.0	10.4	Lovgren and Sjoberg (1989)
Gel Filtration Chromatography	Lake and river humic substances	8.0	18.4 - 21.1	Mantoura and Riley (1975) and Mantoura <i>et al.</i> (1978)
Ultrafiltration	Surface water organic matter	7.0 - 7.6	4.85 - 6.66	Cai <i>et al.</i> (1999)

### 2.2.2 Organomercury Compounds

The vast majority of organomercury compounds are of the  $\text{RHgX}$  or  $\text{R}_2\text{Hg}$  types, in which the  $\text{C} - \text{Hg} - \text{X}$  or  $\text{C} - \text{Hg} - \text{C}$  units are linear (Cotton *et al.* 1999, cited in Ebadian *et al.*, 1999). Among a number of organomercury compounds that have been synthesized over the years, the case of  $\text{R} = \text{CH}_3$  is of special interest because of its presence in environmental and biological samples and its toxicity to animals and human beings. The  $\text{CH}_3\text{Hg}^+$  ion exists in aqueous solution in one or more of the following forms, depending on pH:  $\text{CH}_3\text{Hg}(\text{H}_2\text{O})^+$ ,  $\text{CH}_3\text{HgOH}$ ,  $(\text{CH}_3\text{Hg})_2\text{O}$ ,  $(\text{CH}_3\text{Hg})_3\text{O}^+$ . The  $\text{CH}_3\text{Hg}^+$  is very persistent and can form a great variety of  $\text{CH}_3\text{HgX}$  compounds (Geiser and Gross 1989, cited in Ebadian *et al.*, 1999), where  $\text{X}$  may be a unidentate group or a polydentate one such as a tripod ligand, whereby a tetrahedral complex is formed (Ghilardi *et al.*, 1992, Midollini *et al.*, 1994, cited in Ebadian *et al.*, 1999). Formation constants for 18 methylmercuric complexes ( $\text{CH}_3\text{HgX}$ ) in water are summarized in Table 2-7 (Baugman *et al.*, 1973, cited in Ebadian *et al.*, 1999), and degrees of dissociation of 10 organomercury compounds in aqueous solution at 25 °C are listed in Table 2-8. Reactions of  $\text{CH}_3\text{Hg}^+$  with proteins, peptides, nucleotides, and other biological molecules are presumably the reason for its toxicity. The interactions between methylmercury and DOC in aquatic environments have been investigated recently (Hintelmann *et al.*, 1997, Cai *et al.*, 1999, cited in Ebadian *et al.*, 1999). Strong complexation between methylmercury and small molecular weight DOC fractions has been observed with distribution coefficients ( $\log K$ ) ranging from 3.85 to 5.28 (Cai *et al.*, 1999, cited in Ebadian *et al.*, 1999).

**Table 2-7** Logarithms of Formation Constants for 18 Methylmercuric Complexes ( $\text{CH}_3\text{HgX}$ ) in water (from Baugman *et al.*, 1973)

Ligand X <sup>a</sup>	Log[ $\text{CH}_3\text{HgX}$ ]/[ $\text{CH}_3\text{Hg}^+$ ][X] <sup>a</sup>	
F <sup>-</sup>	9.37	(9.5)
Cl <sup>-</sup>	5.25	(5.45)
Br <sup>-</sup>	6.62	(6.7)
I <sup>-</sup>	8.60	(8.7)
OH <sup>-</sup>	9.37	(9.5)
OC <sub>6</sub> H <sub>5</sub> <sup>-</sup>		(~6.5)
OCOCH <sub>3</sub> <sup>-</sup>		(~3.6)
HPO <sub>4</sub> <sup>2-</sup>	5.03	
HPO <sub>3</sub> <sup>2-</sup>	4.67	
S <sup>2-</sup>	21.2	
SCH <sub>2</sub> CH <sub>2</sub> OH <sup>-</sup>	16.12	
SR <sup>-</sup> (cysteine)		(15.7)
SO <sub>3</sub> <sup>2-</sup>	8.11	
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	10.90	
SCN <sup>-</sup>		(6.1)
NH <sub>3</sub>	7.60	(8.4)
NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	8.25	
CN <sup>-</sup>	14.2	

<sup>a</sup> Values in parentheses taken from Simpson (1961) (ionic strength = 0.5, temperature 25 °C; other values from Schwarzenbach and Schellenberg (1965) (ionic strength = 0.1, temperature 20 °C).

### 2.3 Mercury in Environment

Both anthropogenic and natural processes emit mercury (USEPA 1997, cited in Ebadian *et al.*, 1999). Due to its chemical properties, environmental mercury is thought to move through various environmental matrices, possibly changing form and species during this process. Measured data and modeling results indicate that the amount of mercury mobilized and released into the biosphere has increased since the beginning of the industrial age. Several types of emission sources contribute to the total atmospheric

loading of mercury. Once in the air, mercury can be widely dispersed and transported thousands of miles from likely emission sources. The distance of this transport and eventual deposition depends on the chemical and physical form of the mercury emitted. Studies indicate that the residence time of elemental mercury in the atmosphere may be on the order of a year, allowing its distribution over long distances, both regionally and globally, before being deposited to the earth. The residence time of oxidized mercury compounds in the atmosphere is uncertain but is generally believed to be on the order of a few days or less. Even after it deposits, mercury commonly is emitted back to the atmosphere either as a gas or in association with particulates to be re-deposited elsewhere. Mercury undergoes a series of complex chemical and physical transformations as it cycles among the atmosphere, land, and water. Elemental mercury may also oxidize in soils, sediment, water, or air. Once the elemental mercury has oxidized to mercury (II) ions forms, the ions may sorb onto organic matter and minerals; chemically precipitate as mercury (II) form, such as mercury sulfide (HgS); migrate to some extent in the subsurface; methylate; and be reduced back to the elemental form (Schuster 1991, Rogers 1992, Henke *et al.*, 1993, cited in Ebadian *et al.*, 1999).

A number of reviews on the transport and fate of mercury in the environment can be found in the literature (e.g., Henke *et al.*, 1993, USEPA 1993, cited in Ebadian *et al.*, 1999). Some of the transport and fate mechanisms have been widely studied and are partially understood (Henke *et al.*, 1993, USEPA 1997, cited in Ebadian *et al.*, 1999). For example, inorganic, organic, and elemental mercury forms are known to have strong tendencies to adsorb onto materials that are common in many soils and sediments, including natural organic matter, clays, and mineral oxides (Fang 1978 and 1981, Adriano 1986, Bodek *et al.*, 1988, Andersson *et al.*, 1990, Schuster 1991, cited in Ebadian *et al.*, 1999). These strong sorption tendencies may suggest that inorganic mercury would not be very mobile in subsurface soils and sediments. However, this suggestion is still uncertain, since local

conditions, such as the presence of significant methylating agents, colloid materials, chloride-rich groundwater, may hinder mercury sorption or favor the desorption and mobilization of mercury in the surface.

Bacterial and abiotic chemical processes can methylate mercury (II) ions in both waters and geological materials (Stepan *et al.*, 1995, cited in Ebadian *et al.*, 1999). Many animals and certain plants, such as algae, can readily uptake methylmercury. Compared to elemental mercury, methylmercury is more easily absorbed by fish and other aquatic fauna, either directly through the gills or by ingestion of contaminated aquatic plants and animals. Human exposure may result via three dominant pathways: inhalation, ingestion, and dermal absorption. The most widespread mercury-related health problem among humans involves the consumption of water fauna, such as fish, that have been contaminated with methylmercury (Stepan *et al.*, 1995 USEPA 1997, cited in Ebadian *et al.*, 1999).

## **2.4 Mercury in Thailand' s Context**

### **2.4.1 Distribution of mercury in the environment**

Recently, Sirirattanachai (2001) found that total mercury concentrations in precipitation of some areas in Bangkok and Chonburi were in the range of 0.001 to 0.019  $\mu\text{g/l}$ . Total mercury concentrations of surface water in the coastal areas and the Gulf of Thailand during 1999 - 2001 were in the range of 0.001 - 0.022  $\mu\text{g/l}$ . The annual loading of mercury to the Gulf of Thailand would be about 5.4 metric tons per year (Tetrattech, 1997, cited in PCD. 2001). As mercury is of concern, mercury concentrations in waters, sediments, and marine organisms have been monitored.



#### 2.4.1.1 Mercury levels in waters

1) Rivers; Mercury is one of the parameters set out for the Thailand Surface Water Quality Standard. Inland Water Quality Sub-Division of Pollution Control Department (PCD) under Ministry of Science, Technology and Environment (MOSTE) has been monitoring mercury concentrations two to four times a year depending on annual financial status allocated by the Thai Government. Water quality in 16 rivers (Bang Pa Kong, Chao Phra Ya, Tha Chin, Mae Klong, Rayong, Phang Rat, Trad, Phetchaburi, Pranburi, Lang Suan, Tapee, Pak Phanang, Tepa, Trang, Pattani, Sai Buri) is measured and determined whether mercury level is higher than the Thailand Surface Water Quality Standard level, 2 of  $\mu\text{g/l}$ . Total mercury concentrations measured during 1996 to 2000 in rivers ranged from less than 0.05 to 1.5  $\mu\text{g/l}$ . In addition, Siriratanachai (2001, cited in PCD. 2001) applied ultra clean technique as well as atomic fluorescence to determine mercury concentrations and reported that total mercury concentrations in the Chao Phraya river ranged from 0.024 to 0.133  $\mu\text{g/l}$ .

2) Coastal water; The PCD has annually conducted a monitoring of coastal water quality along the whole coastline in the Gulf of Thailand and Andaman Sea. In some years, the monitoring program had been assigned to the consulting companies to conduct the study. Total mercury is one of the parameters that have been monitored. The samplings were carried out at 100, 500 and 2,500 meters offshore with 218 stations in wet and dry season. The results during 1998-1999 showed that the concentrations of total mercury ranged from less than 0.01 to 0.54  $\mu\text{g/l}$  with the average of less than 0.1  $\mu\text{g/l}$  (PCD, 1997, cited in PCD. 2001). Generally, samples taken in wet season had higher concentrations of mercury than those in dry season. The method used to determine mercury in 1998 was EPA 1631, cold vapor/ atomic fluorescence, and in 1999, atomic absorption spectrophotometer (cold vapor technique) was applied.

3) Industrial estates; Water quality in some coastal areas, where the major industrial estates are located, is also monitored. During January 1995 - December 1999, coastal water from 161 stations around Map Ta Phut Industrial Estate (Rayong Province) was sampled. Concentrations of total mercury ranged from 0.002 to 0.48  $\mu\text{g/l}$  with the average of  $0.052 \pm 0.037 \mu\text{g/l}$ . Laem Chabang Industrial Estate, located in Chonburi Province, is also one of the major industrial estates in the eastern coast of Thailand. It was found that total mercury concentrations of samples taken in 1998 ranged from 0.01-0.02  $\mu\text{g/l}$  (PCD, 1999).

4) Offshore; Two hundred and ninety six water samples from 61 stations in the Gulf of Thailand were monitored in 1995, 1996, and 1998. The concentrations of total mercury ranged from less than 0.01 to 0.69  $\mu\text{g/l}$  on the average of 0.06  $\mu\text{g/l}$  (PCD, 2000).

#### 2.4.1.2 Mercury levels in sediment

##### 1) Coastal sediment

PCD also has monitored mercury in sediments along coastlines and river mouths. In 1998, total mercury concentrations were found in a range of 0.005 to 1.05  $\mu\text{g/g}$  (dry weight) with the average of 0.11  $\mu\text{g/g}$  (dry weight). The samples taken in 1998 were analyzed by BrCl cold oxidation and detected by atomic absorption spectrophotometer. In 1999, the range of total mercury concentrations was from 0.001 to 0.872  $\mu\text{g/g}$  (dry weight) with the average of 0.059  $\mu\text{g/g}$  (dry weight). The method used for mercury in 1999 was EPA 7471, cold vapor technique.

##### 2) Industrial estates

PCD has monitored total mercury concentrations in sediments around Map Ta Phut Industrial Estate area. Marine sediments were collected 5 times during 1995 – 1998. It was found that total mercury concentrations ranged from less than 0.005 to 0.134  $\mu\text{g/g}$  (dry weight). At Laem Chabang

Industrial Estate, organic mercury concentrations ranged from 0.006 - 0.032  $\mu\text{g/g}$  (dry weight), and inorganic mercury concentrations ranged from 0.005 - 0.01  $\mu\text{g/g}$  (dry weight) in 1998 (PCD, 1999).

### 3) Offshore

The measurement of heavy metals in sediment is an indicator to determine if there is any heavy metal contamination around such area. In 1996 and 1998 samples were taken from the Gulf of Thailand. The range of mercury concentrations in sediment was 0.01 to 0.12  $\mu\text{g/g}$  (dry weight) with the average of 0.02  $\mu\text{g/g}$  (dry weight) (PCD, 2000). There was a study by Unocal, Thailand on mercury concentrations in sediment that was carried out by Tetra Tech (1998, cited in PCD, 2001). It was reported that the samples collected at Erawan Platform contained average mercury concentration of 1404  $\mu\text{g/g}$  (dry weight) in 1997 and 863  $\mu\text{g/g}$  (dry weight) in 1998. Samples around surrounding stations were also taken with the concentrations ranging from 206 - 292  $\mu\text{g/g}$  (dry weight). However, the evidence derived from the three types of analyses (total mercury, particulate mercury, and the relative bioavailability of the mercury) indicates that mercury in the sediments surrounding the Platong and Erawan Platforms is present as metacinnabar (mercuric sulfide). It was also reported that less than 0.2 percent of the total mercury in the sediments could be considered bioavailable and that between 95 and 98 percent was present as either crystalline or strongly bound amorphous mercury.

#### 2.4.1.3 Mercury levels in aquatic tissues

##### 1) River mouths

To ensure that human health is protected, mercury levels in aquatic organisms are also measured in some particular areas and in the Gulf of Thailand. Various biological samples such as fish, shrimps, and shells were collected from 15 river mouths of Thailand in 1998 and 1999. The local

fishermen were asked to catch any organisms by their artisan gears. The results showed that total mercury concentrations of all biological samples were in the range of 0.041 - 0.64, and 0.01 - 0.6  $\mu\text{g/g}$  (dry weight) in 1998 and 1999, respectively, which were lower than the standard of Food Containing Contaminant (0.5  $\mu\text{g/g}$  (wet weight), or approximately 1.25  $\mu\text{g/g}$  (dry weight), Ministry of Public Health, Thailand, 1986, cited in PCD, 2001).

## 2) Coastal areas

Cheevaporn et al. (2000) stated that mercury levels of fish and other marine organisms (390 samples) collected from the East Coast of Thailand were within the safety limit (0.5  $\mu\text{g/g}$  (wet weight)). However, biological magnification of mercury residue in marine food chain was observed. Organisms of higher trophic levels have higher mercury residue than those in lower trophic levels.

## 3) Industrial estates

At Map Ta Phut Industrial Estate area, the monitoring was carried out in year 1996 to 1998. The results showed that the concentrations of total mercury in tissues varied between 0.03 and 1.04  $\mu\text{g/g}$  (dry weight), which were lower than the standard of Food Containing Contaminant. In 1998, samples were also taken at Laem Chabang Industrial Estate. The ranges of total mercury concentrations in mussels and crabs were 0.008 - 0.012  $\mu\text{g/g}$  (dry weight), and 0.027 - 0.028  $\mu\text{g/g}$  (wet weight) respectively. Organic mercury concentration in mussel was 0.005  $\mu\text{g/g}$  (wet weight) and organic mercury concentration in crab tissues was in the range of 0.02 - 0.025  $\mu\text{g/g}$  (wet weight) (PCD, 1999).

#### 4) Offshore

PCD collected 119 marine tissue samples by trawling from seven locations in the Gulf of Thailand in 1998. The results showed that the range of mercury concentrations varied from 0.02 to 1.57 g/g (dry weight) and mercury concentrations in two samples were higher than the standard of Food Containing Contaminant. DMR, Ministry of Industry, had assigned the Aquatic Resources Research Institute to measure mercury concentrations in fish tissues collected from the vicinity of the central production platforms of offshore oil and gas operation in the Gulf of Thailand during 1993-1999. The results showed that total mercury levels were higher than those of the reference site, the Pranburi River. Total mercury concentrations in some samples were higher than the standard of Food Containing Contaminant. The mercury concentrations ranged from 0.001 to 1.18  $\mu\text{g/g}$  (wet weight). During 1997 - 1998, Tetra Tech, Inc. was assigned to monitor total mercury concentrations in fish collected at remote wellhead platforms (reference site) comparing to those in fish collected from the vicinity of the central production platforms (CPPs), in the Gulf of Thailand. It appeared that the concentrations of total mercury in fish from CPPs were significantly increased compared to mercury concentrations from fish collected at the reference site. (Tetra Tech, 1998, cited in PCD. 2001). Menasveta et al. (1995, cited in PCD. 2001) collected fish from the vicinity of oil and gas operations in the Gulf of Thailand during 1994 to 1995, and found that mercury concentrations ranged from less than 0.01 to 1.27  $\mu\text{g/g}$  (dry weight) compared with the samples taken from the reference site, Bangsare, with the range of 0.02-0.99  $\mu\text{g/g}$  (dry weight).

## **2.4.2 Sources of release of mercury to the environment and current production and use patterns in Thailand**

### **2.4.2.1 Amount of mercury imported**

In 1999, Thailand imported pure mercury from Algeria, Germany, the Netherlands, Spain, and the United Kingdom with amount of 13,064 kilograms and the year of 2000 mercury were imported from Germany, Japan, the Netherlands, Poland, Spain, the United Kingdom, and the United States in quantity of 12,080 kilograms. In 2001 during January to July, 13,110 kgs of mercury were imported from the same sources as in 1999 (www.customs.go.th, cited in PCD. 2001).

### **2.4.2.2 Sources of release of mercury to the environment and current production**

#### **1) Offshore oil and gas exploration and exploitation**

The exploration concession in Thailand for oil companies was awarded in 1962. By 1982, Thailand's first gas field started (Unocal, 1995, cited in PCD. 2001). And it was in 1985 at the Platong field in the Gulf of Thailand where Unocal first found mercury as a trace contaminant in natural gas and condensate. Since then, produced waters discharged from the process platforms to the sea, which contain mercury that has been scrubbed from natural gas and the gas condensate, have become significantly of concern. Three years later, that is, in 1988, mercury was first found at the Erawan field, the first gas field to come on stream in the Gulf of Thailand (Unocal, 1996, cited in PCD. 2001).

The amount of mercury discharged into the Gulf from oil and gas operations during 1991-1996 was estimated monthly sampling of the produced waters at four different platforms (Erawan, Platong, Satun, and Funan operated by Unocal Thailand, Ltd.). These values ranged between 40

and 330 kgs per year, the average value over this period of time was 187 kgs per year (Tetrattech, 1997, cited in PCD. 2001).

Thailand is currently producing natural gas and condensate from 1,225 wells (DMR, 2001, cited in PCD. 2001). In May 2001, Thailand natural gas production averaged 1,950 million cubic feet per day while accompanying condensate production averaged 55,830 barrels per day. Produced water is the highest volume waste source in the offshore oil and gas industries. The total volume of produced water being discharged by the oil and gas industries in 2000 is estimated to be 56,340 barrels per day, some of which is reinjected back into depleted wells ([www.dmr.go.th](http://www.dmr.go.th), cited in PCD. 2001). A long term reinjection test of produced water began in June 1996 with a capacity of 3,000 barrels per day at the Erawan field, which up to the present day can conduct zero discharge up to approximately 70%. Apart from Erawan, Bongkot platform operated by the Petroleum Authority of Thailand Exploration and Production has also conducted zero discharge policy with the capacity of 99% (DMR, 2001, cited in PCD. 2001). Characterisation of the produced water shows that mercury in the aquatic environment is present in elemental form ( $\text{Hg}^0$ ), including particulate mercury sulfide ( $\text{HgS}$ ), inorganic mercury ( $\text{Hg}^{2+}$ ), and methylated forms, such as monomethyl mercury ( $\text{CH}_3\text{Hg}$ ) which is readily absorbed by aquatic organisms, and other contaminants are present in water soluble forms.

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 2-8. Some gas is flared off at the central process platforms, which would allow some mercury to enter the atmosphere.

**Table 2-8** Mercury in Offshore Petroleum Activities (Unocal Thailand Water Treatment System, 1998, cited in PCD. 2001).

Sources of Mercury	Concentrations
Natural gas	10-25 µg /m <sup>3</sup>
Condensate	500-800 µg/l
Produced Water	30-800 µg/l

## 2) Gold Refining

Mercury is one of the most important raw materials for gold refining. The use pattern of mercury in gold refining in Thailand had declined in the last decade. There is a production report of gold mining in Narathiwat Province (South of Thailand) during the year 1994 - 1996 (www.dmr.go.th, cited in PCD. 2001), the quantity of gold produced was 95,680, 102,700 and 31,790 grams per year, respectively. However, the gold mining was closed in 1997. There is no report of the amount of mercury used for the extraction of gold in Thailand, since the amount of mercury used in domestic scale has never been recorded.

## 3) Pharmaceutical Products

The food and Drug Administration in Thailand (FDA) reported that there is no use of mercury in pharmaceutical and cosmetics products (FDA, 2001: Correspondence No.2, cited in PCD. 2001).

## 4) Battery and Tanning

Mercury has been generally used in battery manufacturing, but the Battery Organization and the Tanning Organization in Thailand reported that there is no mercury used in the process. (The Battery Organization, 2001: Correspondence No.3 and the Tanning Organization, Ministry of Defense, 2001: Correspondence No.4, cited in PCD. 2001).



### 5) Hospital

Medical facilities may encounter liquid mercury in the gauges found in monometers or vacuum gauges, mercury thermostat probes, also known as flame sensors or gas safety valves. Electron microscope might be used in some hospitals where mercury was used as vibration damper (Chulalongkorn Hospital, pers.com, cited in PCD. 2001). According to the information obtained from some hospitals in Bangkok, it was found that some medical facilities such as thermometers which contain liquid mercury are wrapped up and separated as a hazardous waste and disposed of accordingly by Bangkok Metropolitan Authority (Chulalongkorn Hospital, pers.com, cited in PCD. 2001).

### 6) Dentistry

Thai dentistry is using amalgam, which contains mercury compound, mixed with alloy powder in the proportion of 1:1. The dentists, dentist assistants, and patients are likewise exposed to mercury through this application. The use pattern of amalgam in Thai dentistry is of concern. Nevertheless, there is no record of the amount of mercury used. However, there is other free mercury material being used to substitute amalgam.

### 7) Paint Industry

There are less than 25% of the factories in Thailand that are still using mercury as an additive in the process and controlling the quantity to not more than 0.5% of mercury by total weight (Paisit, pers. com., cited in PCD. 2001). However, some paint industries have no mercury involved in processes since 1991 (Apichai, pers. com., cited in PCD. 2001), since the factory is certified with a green label as non-mercury used in the process.

### 8) Fluorescence Production

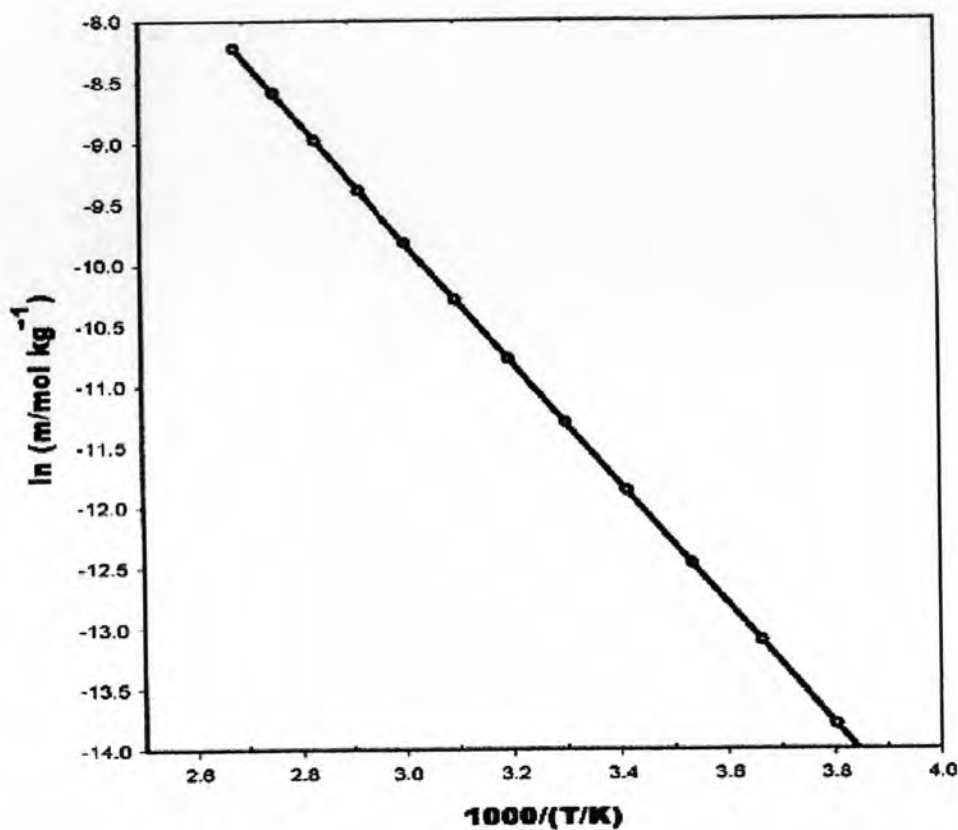
The lamp industries in Thailand are using mercury as an electrode and the processes are carried out in a close system. Therefore, the mercury will not be discharged during the process (Thunwa, pers.com., cited in PCD. 2001).

### 9) Power Plant

There are four major thermal - power plants; Mae Moh, South Bangkok, Wang Noi, Bang Par Kong reported by Environmental Officials of Electricity Generating Authority of Thailand (EGAT). Monitoring of airborne emission of mercury has not been carried out as there was no mercury in the lignite or in the fly ash left over from combustion.

## 2.5 Mercury in Petroleum

Elemental mercury and several mercury compounds occur naturally in geologic hydrocarbons. At ambient temperature, elemental mercury ( $Hg^0$ ) is soluble in liquid aliphatic hydrocarbons to a few (1 - 3 ppm) per Figure 2-1, which is several times greater than its 0.05 ppm solubility in water. Elemental mercury is highly adsorptive and adsorbs on metallic surfaces and on solid materials such as sand suspended in liquids.  $Hg^0$  reacts with iron oxide corrosion products on pipe and equipment walls. The solubility of  $Hg^0$  in produced hydrocarbons depends strongly on temperature, hence, when saturated liquids are cooled,  $Hg^0$  can precipitate in equipment.



**Figure 2-1** Solubility of elemental mercury in normal alkanes as a function of temperature.

**Table 2-9** Boiling points of volatile mercury compounds

Hg Compound	Boiling point ( $^{\circ}\text{C}$ )
$\text{Hg}^0$	357
$(\text{CH}_3)_2\text{Hg}$	96
$(\text{C}_2\text{H}_5)_2\text{Hg}$	170
$(\text{C}_3\text{H}_7)_2\text{Hg}$	190
$(\text{C}_4\text{H}_9)_2\text{Hg}$	206

Organic mercury compounds ( $\text{RHgR}$  and  $\text{RHgCl}$ , where  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ , etc.) are highly soluble in crude oil and gas condensate. Dialkylmercury compounds partition to hydrocarbon liquids in separations and to distillation fractions according to their boiling points (see Table 2-9). Monomethylmercury halides partition preferentially to water in primary separations. The natural

abundance of dialkylmercury compounds in produced hydrocarbons is a matter of some debate. The existence of organic mercury compounds is inferred when analysis for total mercury in a liquid matrix does not mass balance with operationally speciated forms. Dialkylmercury compounds have been detected in gas condensate and crude oil using chromatographic techniques, but typically at low concentrations.

Mercuric halides ( $\text{HgCl}_2$ ) are about 10 times more soluble than  $\text{Hg}^0$  (see Table 2-10) in 2 gas condensate and oil but partition to the water phase hydrocarbon water separations. The degree to which  $\text{HgCl}_2$  distributes between water and the liquid hydrocarbon in 2 primary separations depends on the salinity of the produced brine and its pH. The natural abundance of ionic compounds is uncertain because  $\text{Hg}^0$  has been found to oxidize in hydrocarbon liquid samples exposed to oxygen, thus casting doubt on some published speciation data.

Mercury (sulfur) complexes ( $\text{HgK}$  where K is an organic sulfide, thiol, thiophene or mercaptan) are postulated to exist in some crude oils and condensates. The existence of such compounds in produced hydrocarbons is speculative at present. Specific complexes of mercury have not been identified with certainty, but their existence is inferred in some chromatographic and operational speciation experiments. Unprocessed hydrocarbon liquids and many process streams contain suspended mercury compounds. The most common example is mercuric sulfide ( $\text{HgS}$ ), which is insoluble in water and oil. Particle sizes are typically small. Elemental mercury can also be suspended in liquids that become saturated due to cooling such as in cryogenic liquid separations. Also included in this category are mercury compounds that are not dissolved, but rather adsorbed on inert particles, such as formation fines.

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 points of organic compounds (Table 2-9) assist prediction of the distribution of compounds in distillations of crude oil. The solubilities of some mercury compounds in hexane are compiled in Table 2-10 and are useful to predict the distribution of compounds in phase separations. The solubility of elemental mercury in alkanes as a function of temperature is shown in Figure 2-1.

**Table 2-10** Solubility of some mercury compounds in hexane

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

### 2.5.1 Mercury Compounds in Hydrocarbon

Because of its volatility, elemental mercury vapor is the dominant species in natural gas. Dialkylmercury may also be present in gas, especially close to the wellhead where the gas is hot. The organic mercury compounds in gas partition to separated hydrocarbon liquids as the gas is cooled. The trapping process for determination of total Hg in gas precludes any speciation of volatile mercury components.

Crude oil and gas condensate, when sampled soon after primary separation of water and gas, typically contain significant amounts of suspended mercury compounds and/or mercury adsorbed on suspended solids. The suspended compounds are mostly HgS but include mercury adsorbed on silicates and other suspended solid material. The amount of

suspended mercury is determined by difference of total mercury in agitated/filtered (0.8 micron) samples and agitated samples. Mild extraction of the filtered solids yields the adsorbed/suspended fraction and the HgS in filtered solids is quantified by X-ray methods. The amount of suspended mercury can be a substantial percentage of the total concentration of mercury in liquid samples of produced hydrocarbons and they must be separated prior to any speciation of dissolved forms.

Gas condensate samples originate at several locations in a gas processing scheme (see Figure 2-2). A generic unprocessed condensate is the hydrocarbon liquid that separates in the primary separator, either at the wellhead or at the gas plant. Processed condensate is the C5+ fraction that is a product from a gas separation plant. Naphthas typically originate from the primary distillation of oil in the range of 50 °C to 150 °C (see Figure 2-3). The distribution of hydrocarbon compounds in both condensates and naphthas are similar and mostly in the range C4 to C10. Processed condensate and naphthas typically do not contain suspended mercury compounds.

Published Hg concentrations in condensate, naphthas and crude oil often do not fully disclose sampling procedures or analytical processing steps (filtration, centrifugation and exposure to air). For these reasons, some data are suspect in that the total mercury concentrations reported could include a contribution from suspended forms or the distribution of compounds could reflect species conversion. Aerobic processing of samples is suspected to promote oxidation of Hg<sup>0</sup> to ionic forms and thus to alter the distribution of species.

The total Hg concentration reported in hydrocarbons varies widely. Some condensates and crude oils are close to saturation with Hg<sup>0</sup> at concentrations of 1 – 4 ppm as determined by sparging of fresh, filtered samples. Adding suspended, ionic and organic forms, total mercury concentrations in crude oil exceeding over 5 ppm are known. Gas

condensates in SE Asia have dissolved total Hg concentrations in the 10 – 800 ppb range. Most crude oils in the US have relatively low mercury concentrations.

Musa *et al.* (1995, cited in Wilhelm and Bloom, 2000) reported total mercury in Libyan crude oils to be in the range of 0.1 to 12 ppb. Bloom (Bloom, 1999, cited in Wilhelm, S.M., Bloom, N. 2000) found total Hg in unfiltered crude oils ranging between sub-ppb levels to over saturation (see Table 2-11). The mean for crude oil (1.5 ppm, N= 76) likely is skewed high due to samples with some suspended mercury. The mean of the lower 38 samples was close to 1 ppb. Data for crude oils are compiled in Table 2-11 and Figure 2-4.

**Table 2-11** Total Hg in liquids (Bloom, 1999, cited in Wilhelm and Bloom, 2000)

Oil Type	N	[Hg] (ng/g)	
		Mean	SD
Crude oil (all)	76	1,505	3,278
Crude oil (highest half)	39	3,009	4,140
Crude oil (lowest half)	37	1.20	1.49
Condensate (all)	18	3,964	11,665
Condensate (highest half)	10	7,113	15,240
Condensate (lowest half)	8	20.4	19.7
Light distillates	14	1.32	2.81
Utility fuel oil	32	0.67	0.96
Asphalt	10	0.27	0.32

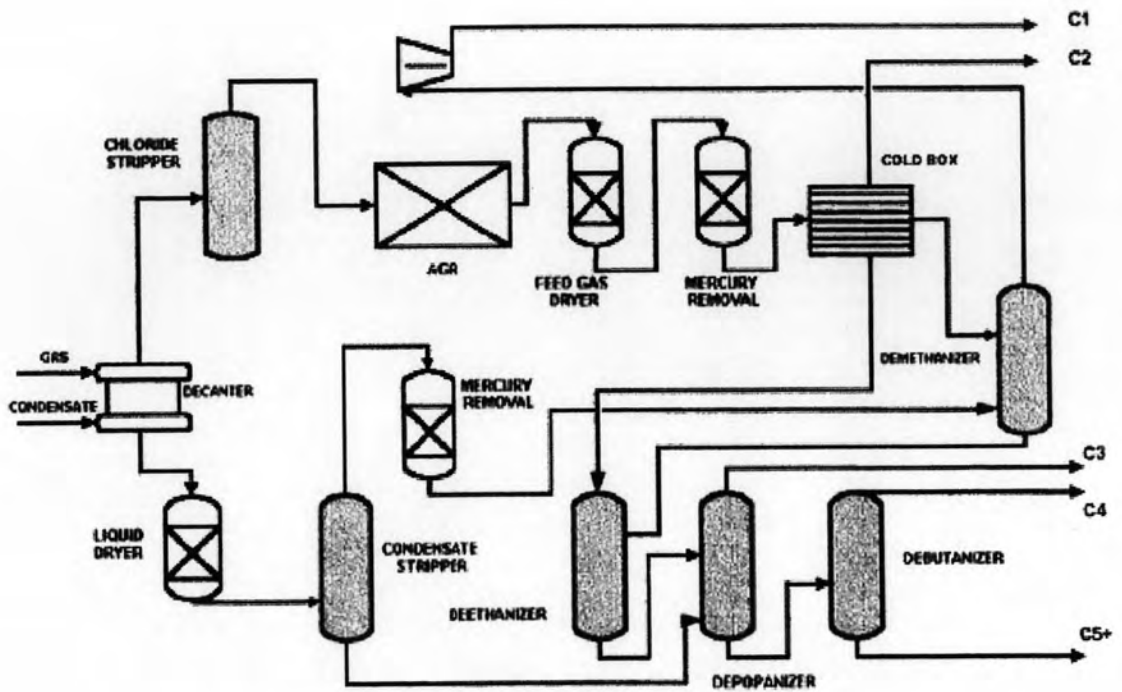


Figure 2-2 Gas plant liquid processing.

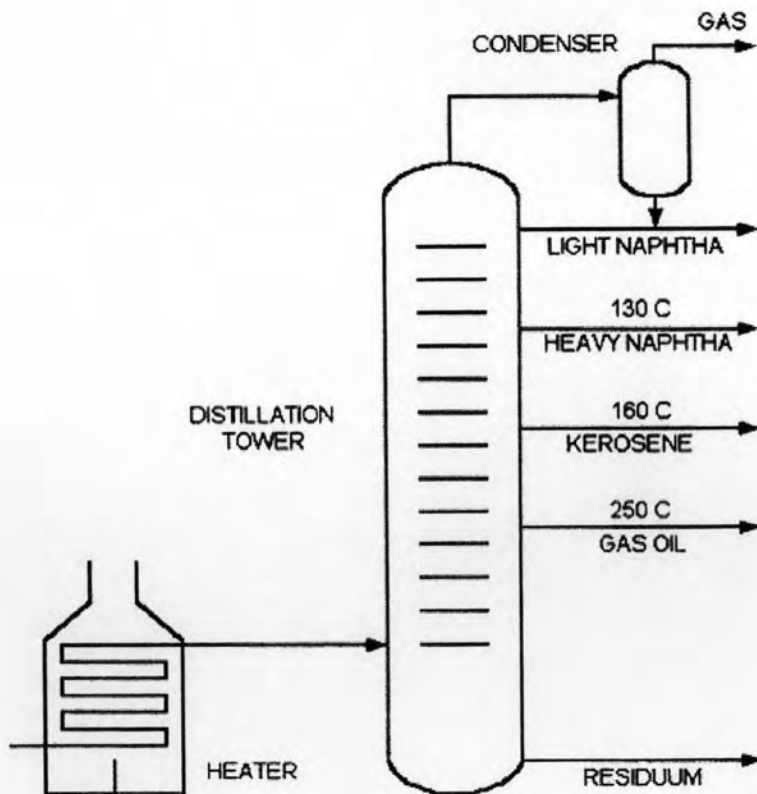


Figure 2-3 Primary distillation products.



Total mercury concentrations in gas condensates (Schickling and Broekaert 1995, Snell *et al.*, 1996, Zettlitzer *et al.*, 1997, Tao *et al.*, 1998, cited in Wilhelm and Bloom, 2000) are shown in Figure 2-5. Zettlitzer analyzed condensates from the Rottliegend formation in Germany and found total mercury in liquids in the range 3 – 6 mg/l and corresponding to mercury concentrations in gas of 1000 to 4400 ug/Nm<sup>3</sup>. It is not known if the liquid samples were filtered prior to analysis and thus, may have contained some suspended compounds. These concentrations are in the very high end of the range of total Hg concentration in condensate. Tao' s data for total mercury in condensates are included in Figure 2-5 and range between 10 and 200 ug/l (Note: data in the figures have been converted to g/g for uniformity).

The presently published data for total Hg in naphthas (Figure 2-6) are similar to condensates and range approximately between 5 and 200 ppb. High concentrations have not been reported in the limited published data. Naphthas originating from distillations would be expected to have lower concentrations than the raw produced liquids from which they originate.

Only limited data are available that allow examination of the distribution of concentrations of mercury compounds in hydrocarbon liquids. Of interest are the natural abundance of mercury compounds, the relative distribution of compounds in liquid samples, the partitioning of compounds in separations and distillations and transformation of species during processing.

The data of Tao *et al.* (1998, cited in Wilhelm and Bloom, 2000) on gas condensates, naphthas and a crude oil, are compiled in Table 2-12 and graphically depicted in Figure 2-6. The origin (process location) of samples analyzed by Tao was not disclosed. Tao' s data indicate that ionic mercury was the dominant species in the condensates examined. Hg<sup>0</sup> did not exceed 25% of the total in any of the condensate samples. The dialkyl species was detected (>10%) in some condensates. The monoalkyl species was detected

but at very low concentrations.  $\text{Hg}^0$  was not seen in naphthas as would be expected assuming a normal distillation profile.

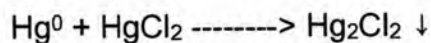
The more volatile  $\text{Hg}^0$  would be expected to partition to the lighter gas fraction.  $\text{RHgR}$  appeared to be the dominant species in one naphtha sample. Ionic forms of mercury were seen in all of the samples.

Zettlitzer *et al.* (1997) used two methods to measure concentrations of mercury species. The method for monoalkylmercury (HPLC-UV-PCO-CVAA) provided suitable detection limits. The concentrations of monoalkylmercury in the condensate analyzed by Zettlitzer were low and generally agree with the data of Tao. GC-MS was used to examine  $\text{RHgR}$  but the detection limit was high and the methodology suspect. Extracting condensate with HCl was postulated to remove ionic and organic forms. The concentration of acid-extractable mercury was operationally defined as the difference between the total amount extracted using HCl and the sum of ionic and monoalkylmercury determined independently.

Zettlitzer' s distributions of compounds, using operationally defined values for extracted mercury, are compiled in Table 2-13. The unprocessed condensate sample exhibited a 2 ppm concentration of  $\text{Hg}^0$  which is close to the saturation value for elemental mercury in hydrocarbon liquids. These data do not show the dominance of ionic species seen in the data of Tao.

Snell *et al.* (1996, cited in Wilhelm and Bloom, 2000) analyzed two condensates and found most of the total mercury in ionic form. The dialkyl form accounted for approximately 10% and the monoalkyl form less than 1%. Similarly, Schickling and Broekaert (1995, cited in Wilhelm and Bloom, 2000) analyzed two condensates and found mostly ionic compounds. Bloom' s operationally defined speciation (Table 2-14) data account for the majority of total dissolved mercury as either  $\text{Hg}^0$  or KCl extractable (mostly ionic).

In spite of the fact that dialkylmercury has been detected in some samples, the concentrations found for this class of compounds (see Table 2-12) are very low (<10 ppb) except for one naphtha in which it was found at a concentration of approximately 50 ppb. Based on the limited data, it is by no means apparent at this point in time that dialkylmercury is prevalent in petroleum. Stability of mercury species in synthetic gas condensate was examined by Snell et al. (1998, cited in Wilhelm and Bloom, 2000) who demonstrated conclusively that  $\text{Hg}^0$  and  $\text{HgCl}$  react to form  $\text{Hg}_2\text{Cl}_2$  that is insoluble in hydrocarbons and precipitates.



The reaction exhibited a half-life on the order of about 10 days at ambient temperature. The reaction of  $\text{Hg}^0$  and ionic forms suggests that reservoirs may contain solid  $\text{Hg}_2\text{Cl}_2$  and that, in the reservoir, equilibrium is maintained that allows the coexistence of both species. Production of liquids from reservoir conditions disrupts the equilibrium and allows  $\text{Hg}^0$  to decay. Most condensate samples contain both species thus implying, given the clearly defined observations of Snell, that species conversion is likely in gas condensate samples.

Bloom (1999, cited in Wilhelm and Bloom, 2000) likewise, examined sample stability and found standard solutions of  $\text{Hg}^0$ ,  $\text{HgCH}_3^+$  and  $\text{Hg}(\text{CH}_3)_2$  stable in paraffin oil stored in glass.  $\text{HgCl}$  was not stable in paraffin oil and  $\text{Hg}^0$  and  $\text{HgCl}$  were unstable in natural crude oil. Bloom's data generally support those of Snell's.

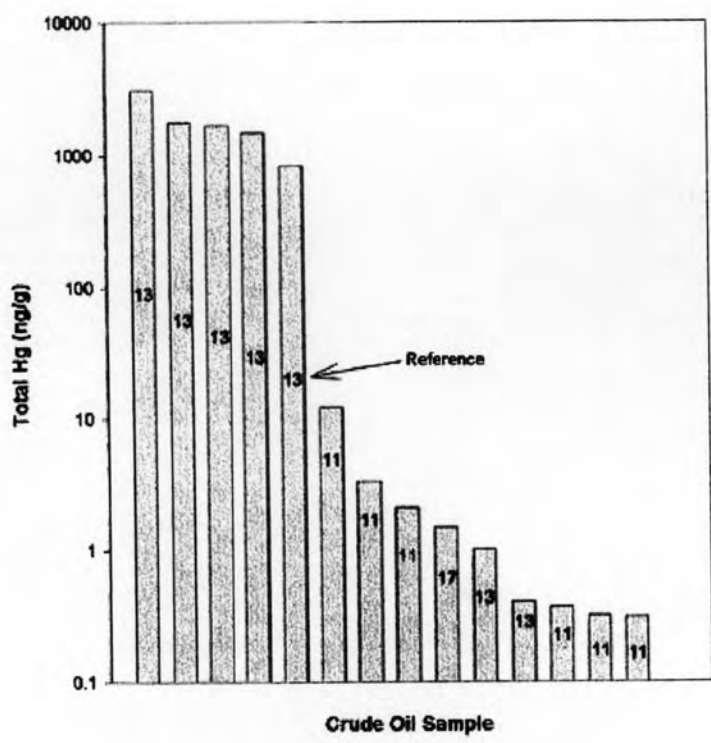


Figure 2- 4 Total mercury in crude oil.

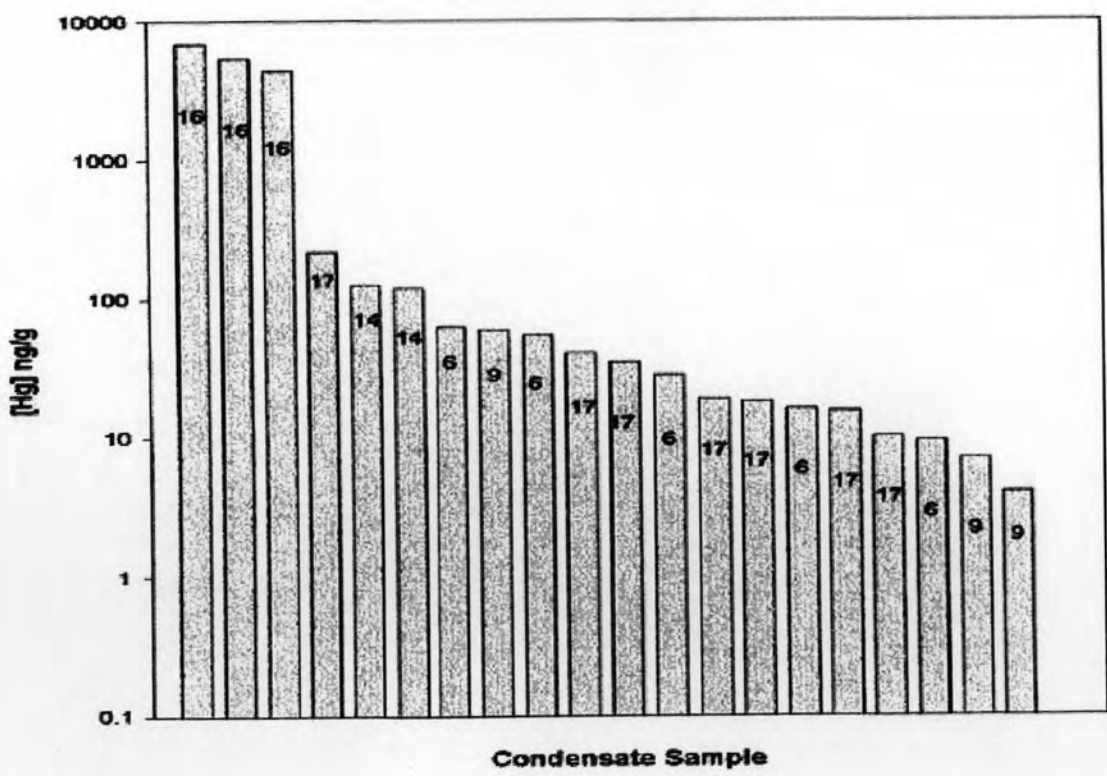


Figure 2-5 Total mercury in condensates.

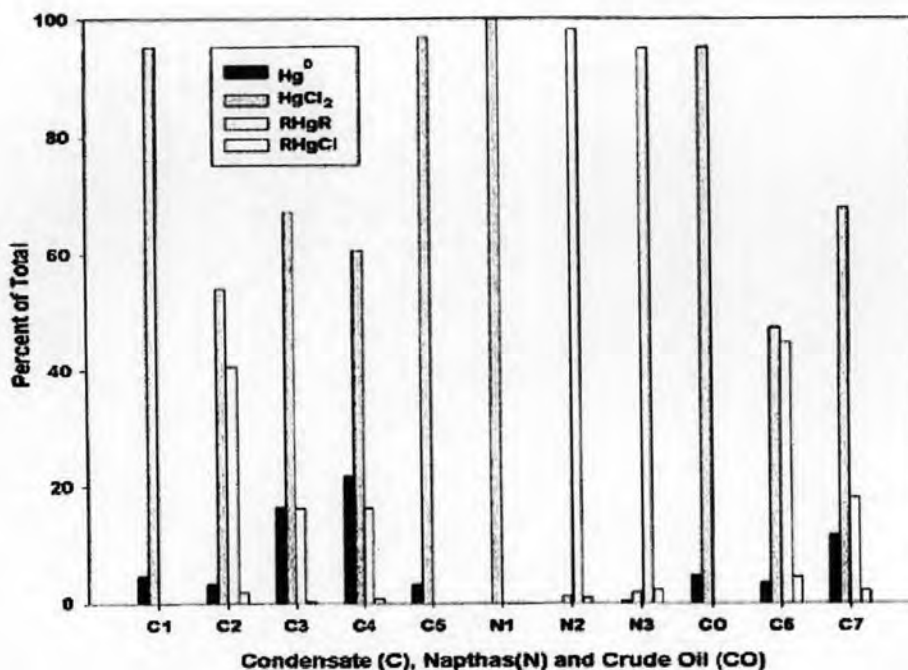
**Table 2-12** Analytical results for natural gas condensates, condensate naphthas and crude oil ( $\mu\text{g/l Hg}$ ) (Tao *et al.*, 1998, cited in Wilhelm and Bloom, 2000). The average values of both injection modes were adopted for DMeHg, MeEtHg and DEtHg; nd – not determined; < - below detection limit (J. Anal. At. Spectrom., 1998, 13, 1085).

Sample	Mode	Hg <sup>0</sup>	HgCl <sub>2</sub>	DMeHg	MeEtHg	DEtHg	MeHgCl
Condensate 1		1.5	3.09	< 0.0	<	<	<
	Percent	<b>4.6</b>	<b>95.4</b>				
Condensate 2		0.5	8.1	2.0	3.2	0.9	0.2
	Percent	<b>3.3</b>	<b>54.0</b>	<b>13.3</b>	<b>21.3</b>	<b>6.0</b>	<b>1.3</b>
Condensate 3		28.8	116	9.3	14.0	5.1	0.3
	Percent	<b>16.6</b>	<b>67.1</b>	<b>5.4</b>	<b>8.1</b>	<b>2.9</b>	<b>0.2</b>
Condensate 4		2.66	7.4	0.9	1.0	0.1	0.1
	Percent	<b>21.8</b>	<b>60.7</b>	<b>7.4</b>	<b>8.2</b>	<b>0.8</b>	<b>0.8</b>
Condensate 5		0.9	26.8	<	<	<	<
	Percent	<b>3.2</b>	<b>96.8</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>
Condensate naphtha 8		<	48.4	<	<	<	<
	Percent	<b>0.0</b>	<b>100.0</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>
Condensate naphtha 9		<	0.68	22.4	28.9	6.1	0.5
	Percent	<b>0.0</b>	<b>1.2</b>	<b>38.3</b>	<b>49.4</b>	<b>10.4</b>	<b>0.9</b>
Condensate naphtha 10		0.03	0.14	3.9	3.1	0.2	0.1
	Percent	<b>0.4</b>	<b>1.8</b>	<b>51.5</b>	<b>40.9</b>	<b>2.6</b>	<b>1.3</b>
Crude oil 11		0.03	0.60	<	<	<	<
	Percent	<b>4.8</b>	<b>95.2</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>
Condensate 6		0.3	3.8	2.6		1.0	0.3
	Percent	<b>3.7</b>	<b>46.9</b>	<b>32.1</b>		<b>12.3</b>	<b>3.7</b>
Condensate 7		1.7	9.8	2.3		0.3	0.2
	Percent	<b>11.8</b>	<b>67.8</b>	<b>16.1</b>		<b>2.1</b>	<b>1.4</b>

Table 2-12 (Cont.)

Sample	Mode	EtHgCl	Sum <sup>a</sup>	CV-AAS
Condensate 1		<	3.24	30.7
	Percent			
Condensate 2		0.05	15.0	12.1
	Percent	0.3		
Condensate 3			173	162
	Percent	0.0		
Condensate 4			12.2	12.6
	Percent	0.0		
Condensate 5		<	27.7	34.0
	Percent	0.0		
Condensate naphtha 8		<	48.4	nd
	Percent	0.0		
Condensate naphtha 9		<	58.5	nd
	Percent	0.0		
Condensate naphtha 10		0.07	7.58	8.49
	Percent	0.9		
Crude oil 11		<	0.63	1.50
	Percent	0.0		
Condensate 6		0.1	8.1	nd
	Percent	1.2		
Condensate 7		0.1	14.4	nd
	Percent	0.7		

<sup>a</sup> Sum = Hg<sup>0</sup> + HgCl + DMeHg + MeHg + DEtHg + MeHgCl + EtHgCl.



**Figure 2-6** Distribution of mercury compounds in liquid hydrocarbons (data of Tao *et al.*, 1998, cited in Wilhelm and Bloom, 2000).

Oxidative mechanisms may operate in hydrocarbon samples that are exposed to oxygen, that contact metal surfaces or that is treated with impure reagents as part of the analytical method. If this is the case, then the high concentrations of ionic forms in some samples may be an artifact of collection procedures, sample age and analytical processing methodologies. The author's experience with crude oils and gas condensate samples is that very fresh samples typically exhibit the dominance of the Hg<sup>0</sup> species. No reductive mechanisms are known that would account for generation of Hg<sup>0</sup> in samples of geologic hydrocarbons; hence, the transformation of ionic or organic species to elemental is not likely.

The primary separation of water in gas or oil production would be expected to segregate the majority of ionic species naturally present to the water phase. Produced water that has low dissolved mercury content is associated with co-produced hydrocarbon liquids containing high concentrations of ionic species analyzed days after collection. Such high

percentage concentrations of ionic species in the hydrocarbon liquid are not expected based upon the rationalization that the ionic species should partition to the separated water phase during primary separations.

If one compares the concentrations of  $Hg^0$  in co-produced hydrocarbon liquid and gas,  $Hg^0$  typically is dominant in both. This suggests that  $Hg^0$  is the dominant species in the reservoir fluids and the ionic forms are derived from it. Reaction mechanisms associated with sample stability certainly require further investigation. If the ionic content of liquid samples is merely an artifact of sample aging, then the distribution of mercury compounds previously cited is suspect. There is also considerable doubt that dialkylmercury exists abundantly in crude oil and condensate.

Monoalkylmercury does not appear to be a dominant species in petroleum. If dialkylmercury were abundant then the monoalkyl species would be expected to be similarly abundant. Given the low concentrations of  $HgCH_4$  in condensate, it is unlikely that discharges of produced water to the ocean would contain significant amounts and thus would not have a major, direct contribution to monomethylmercury levels in fish in proximity to platforms.

**Table 2-13** Concentrations of mercury compounds in natural gas condensates ( $\mu g/l$  Hg) (Zettlitzer *et al.*, 1997)

Sample	$Hg^0$	$HgCl_2$	Other	$RHgCl$	Sum <sup>a</sup>	Total	HgS
Low temperature separator (Percent)	250	400	644	6	1300	3500	2200
	19.2	30.8	49.5	0.5	100.0		
Ambient temperature separator (Percent)	2000	400	2600	100	5100	5500	400
	39.2	7.8	51.0	2.0	100.0		
Storage tank (Percent)	200	200	1250	50	1700	4300	2600
	11.8	11.8	73.5	2.9	100.0		

<sup>a</sup>sum =  $Hg^0$  +  $HgCl_2$  +  $RHgCl$  + Other = acid extracted –  $HgCl_2$ ; Total – sum.



**Table 2-14** Operational Hg speciation in petroleum samples (Bloom, 1999)

Sample ID	Unfilterate Hg (ng/g)		0.8 $\mu$ filtered Hg (ng/g)		
	Total	Hg <sup>0</sup>	Dissolved total	Hg(II)	CH <sub>3</sub> Hg
Condensate #1	20,700	3060	5210	2150	3.74
Condensate #2	49,400	34,500*	36,800	2370	6.24
Crude oil #1	1990	408	821	291	0.25
Crude oil #2	4750	1120	1470	433	0.26
Crude oil #3	4610	536	1680	377	0.27
Crude oil #4	4100	1250	1770	506	0.62
Crude oil #5	15,200	2930	3110	489	0.45
Crude oil #6	1.51	0.09	1.01	0.39	0.15
Crude oil #7	0.42	0.17	0.41	0.02	0.11

## 2.6 Mercury Adsorption on Metal Surface

### 2.6.1 Metal Surface Structure

In most technological applications, metals are used either in a finely divided form (e.g. supported metal catalysts) or in a massive, polycrystalline form (e.g. electrodes, mechanical fabrications).

At the microscopic level, most materials, with the notable exception of a few truly amorphous specimens, can be considered as a collection or aggregate of single crystallites. The surface chemistry of the material as a whole is therefore crucially dependent upon the nature and type of surfaces exposed on these crystallites. In principle, therefore, we can understand the surface properties of any material if we know the amount of each type of surface exposed, and have detailed knowledge of the properties of each and every type of surface plane.

It is therefore vitally important that we can independently study different, well-defined surfaces. The most commonly employed technique, is to prepare macroscopic (i.e. size ~ cm) single crystals of metals and then to deliberately cut them in a way which exposes a large area of the specific surface of interest.

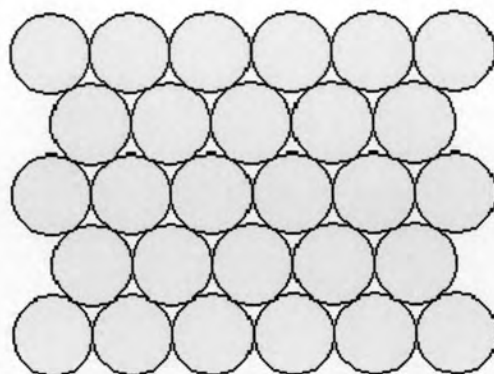
Most metals only exist in one bulk structural form the most common metallic crystal structures being:

- 1) bcc: body centered cubic
- 2) fcc: face centered cubic
- 3) hcp: hexagonal close packed

For each of these crystal systems, there are in principle an infinite number of possible surfaces which can be exposed. In practice, however, only a limited number of planes (predominantly the so-called "low-index" surfaces) are found to exist in any significant amount and we can concentrate our attention on these surfaces. Furthermore, it is possible to predict the ideal atomic arrangement at a given surface of a particular metal by considering how the bulk structure is intersected by the surface. Firstly, however, we need to look in detail at the bulk crystal structures.

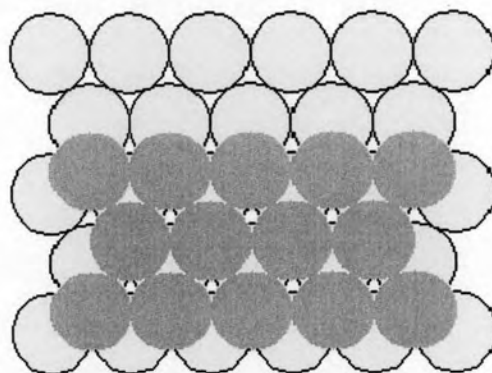
#### 2.6.1.1 The hcp and fcc structures

The hcp and fcc structures are closely related: they are both based upon stacking layers of atoms, where the atoms are arranged in a close-packed hexagonal manner within the individual layer.



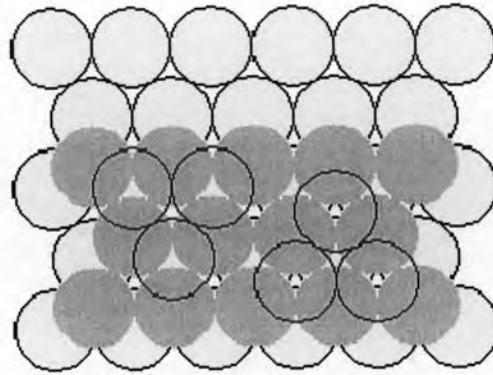
**Figure 2-7** The hcp and fcc structures – first layer

The atoms of the next layer of the structure will preferentially sit in some of the hollows in the first layer - this gives the closest approach of atoms in the two layers and thereby maximizes the cohesive interaction.



**Figure 2-8** The hcp and fcc structures – second layer

When it comes to deciding where the next layer of atoms should be positioned there are two choices - these differ only in the relative positions of atoms in the 1st and 3rd layers.



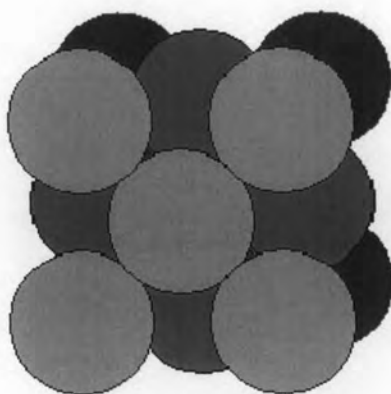
**Figure 2-9** The hcp and fcc structures – next layer

In the structure on the left the atoms of the 3rd layer sit directly above those in the 1st layer - this gives rise to the characteristic ABABA packing sequence of the hcp structure.

In the structure on the right the atoms of the 3rd layer are laterally offset from those in both the 1st and 2nd layers, and it is not until the 4th layer that the sequence begins to repeat. This is the ABCABC packing sequence of the fcc structure. Because of their common origin, both of these structures share common features: a) the atoms are close packed b) Each atom has 12 nearest neighbours ( i.e. CN = 12 ).

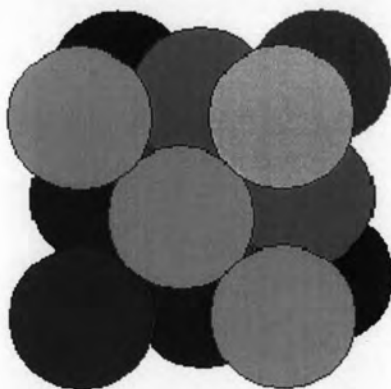
#### 2.6.1.2 fcc structure

Although it is not immediately obvious, the ABCABC packing sequence of the fcc structure gives rise to a three-dimensional structure with cubic symmetry.



**Figure 2-10** fcc structure

It is the cubic unit cell that is commonly used to illustrate this structure - but the fact that the origin of the structure lies in the packing of layers of hexagonal symmetry should not be forgotten.

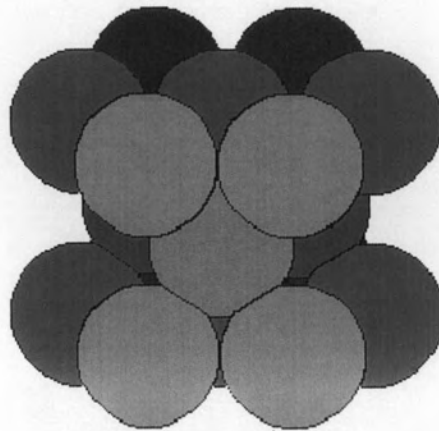


**Figure 2-11** Hexagonal closed-packed layers

The above diagram shows the atoms of one of the hexagonal close-packed layers highlighted in shades of red, and the atoms of another highlighted in shades of green.

### 2.6.1.3 hcp structure

The ABABA packing sequence of the hcp structure gives rise to a three-dimensional unit cell structure whose symmetry is more immediately related to that of the hexagonally-close packed layers from which it is built, as illustrated in the diagram below:



**Figure 2-12** hcp structure

#### 2.6.1.4 bcc structure

The bcc structure has very little in common with the fcc structure except the cubic nature of the unit cell. Most importantly, it differs from the hcp and fcc structures in that it is not a close-packed structure.



**Figure 2-13** bcc structure

## 2.6.2 Molecular Adsorption

The adsorption of molecules on to a surface is a necessary prerequisite to any surface mediated chemical process. For example, in the case of a surface catalyzed reaction it is possible to break down the whole continuously-cycling process into the following five basic steps:

- Diffusion of reactants to the active surface
- Adsorption of one or more reactants onto the surface
- Surface reaction
- Desorption of products from the surface
- Diffusion of products away from the surface

The above scheme not only emphasizes the importance of the adsorption process but also its reverse - namely desorption.

## 2.6.3 Adsorption Modes

There are two principal modes of adsorption of molecules on surfaces as follows:

### 2.6.3.1 Physical Adsorption

The only bonding is by weak Van der Waals - type forces. There is no significant redistribution of electron density in either the molecule or at the substrate surface.

### 2.3.6.2 Chemisorption

A chemical bond, involving substantial rearrangement of electron density, is formed between the adsorbate and substrate. The nature

of this bond may lie anywhere between the extremes of virtually complete ionic or complete covalent character.

**Table 2-15** Typical Characteristics of Adsorption Processes

Descriptions	Chemisorption	Physisorption
Temperature Range (over which adsorption occurs)	Virtually unlimited (but a given molecule may effectively adsorb only over a small range)	Near or below the condensation point of the gas (e.g. Xe < 100 K, CO <sub>2</sub> < 200 K)
Adsorption Enthalpy	Wide range (related to the chemical bond strength) - typically 40 - 800 kJ mol <sup>-1</sup>	Related to factors like molecular mass and polarity but typically 5-40 kJ mol <sup>-1</sup> (i.e. ~ heat of liquefaction)
Crystallographic Specificity (variation between different surface planes of the same crystal)	Marked variation between crystal planes	Virtually independent of surface atomic geometry
Nature of Adsorption	Often dissociative May be irreversible	Non-dissociative Reversible
Saturation Uptake	Limited to one monolayer	Multilayer uptake possible
Kinetics of Adsorption	Very variable - often an activated process	Fast - since it is a non-activated process

The most definitive method for establishing the formation of a chemical bond between the adsorbing molecule and the substrate ( i.e. chemisorption ) is to use an appropriate spectroscopic technique, for example:

1) IR (infrared) - to observe the vibrational frequency of the substrate/ adsorbate bond.

2) UPS - to monitor intensity & energy shifts in the valence orbitals of the adsorbate and substrate.



#### 2.6.4 Mercury Adsorption

Currently, investigation on mercury adsorption on metal surface; especially those of offshore oil and gas production in presence of mercury in the process, is very limited. Therefore, factors contributing to scale and extent of mercury adsorption on metal surface are not well perceived by taking into account the various process conditions including the matrix (e.g. hydrocarbon stream, gas, water) that equipment and material is servicing, temperature, flow, pressure and etc.

An investigation undertaken to identify factors affecting Hg adsorption on various carbon materials found the following: a) the mercury capturing capacity of all carbon samples decreased when carbon bed temperature increased. This is consistent with the physisorption theory; b) Origin of carbon affects its adsorption capacity; carbon from various sources shows entirely different performance; c) all carbon samples indicate faster capturing rates at high inlet Hg concentration.

Another similar investigation on experimental and kinetic studies of mercury adsorption on various mercury and various activated carbons show similar results and findings. These include the factors affecting the adsorption efficiency include the type of activated carbon, the adsorption temperature, the inlet mercury concentration, and the gas flow rate.

A study conducted to identify the effect of porous structure and surface functionality on the mercury capacity of fly ash carbon show that oxygen functionality and the presence of halogen species on the surface of fly ash carbons may promote mercury adsorption, while the surface area does not seem to have a significant impact on their mercury capacity. Moreover, it has previously been reported that pre-treating activated carbon with HCl leads to higher capacity for Hg<sup>0</sup> adsorption in fixed bed capture tests.

It was reported from an investigation of mercury adsorption on fly ash that adsorption of elemental mercury or mercury vapors follows Langmuir isotherm behavior which is characterized as monolayer adsorption.

In order to better understand the mechanism of mercury adsorption on metal surface, surface characteristics or profiles play a vital role. For example a number of important metals (e.g. Fe, W, Mo) have the bcc structure. As a result of the low packing density of the bulk structure, the surfaces also tend to be of a rather open nature with surface atoms often exhibiting rather low coordination numbers, which shows high potential of deposition or adsorption of mercury on the surface.

### **2.6.5 Mercury Contamination on Steel**

A study was conducted to assess scales, extents and forms of mercury in steel used for natural gas production from Rotliegend formation in North Germany (Zettlizer, 1997). Analyses of steel samples for mercury contamination in the past have shown that mercury deposit can occur in the following forms:

- 1) Mercury is in the form of insoluble sulphides.
- 2) Penetration of mercury into the surface deposit, such as rust layers, scales, or salt precipitates.
- 3) Mercury at previously damaged sites of the steel component, such as corrosion pits or open stress cracks.
- 4) Mercury in pores in the steel, which communicate with the surface by way of channels.
- 5) Mercury in the grain boundary zone as a result of transcrystalline diffusion.

The type and extent of the occurrence of mercury in pipelines or risers therefore depend on the steel quality, the pressure and temperature conditions, the gas quality, the composition of the water present, the duration of exposure and of course, the mercury concentration in the gas or liquid phase. On the contaminated surfaces, mercury is detected in elemental metallic forms as well as in its compounds. The results of analysis of mercury contaminated steel samples collected from different wellhead platforms (N, O) of the field are presented below:

**Table 2-16** Mercury distribution in an extremely severely contaminated and in a contaminated steel sample

Well	N		O	
	Content per unit area g/m	Mass concentration mg Hg/kg steel	Content per unit area g/m	Mass concentration mg Hg/kg steel
Rust layer	11	163	0.7	10
0 – 1 mm	5	75	0.09	1.3
1 – 2 mm	0.019	0.32	0.016	0.26
2 – 3 mm	0.005	0.09	0.008	0.14

## 2.7 Review Current Mercury Decontamination Techniques

### 2.7.1 Mechanical decontamination

While mechanical decontamination has typically referred to manually applied, physical contaminant removal techniques, like wet or dry abrasive blasting, surface grinding, and spalling, it now includes such supplementary activities as washing, foaming, wet-wiping, or the application of removable or tie-down coatings. These techniques are applied to either clean surfaces of contamination or to remove the contaminated surface itself. When contaminants are located on or at near surface levels, surface cleaning is usually effective, depending upon the contaminants involved and the nature of

the surface material. Contamination at deeper levels may require surface removal techniques and depending upon the type of surface material may be of limited practicality (e.g., activated metal structures).

The following is a list of mechanical decontamination methods, ranging from the mildest surface cleaning types to the most aggressive surface removal types:

- Flushing with water
- Dusting/Vacuuming/Wiping/Scrubbing
- Fixative/Stabilizer Coatings
- Turbulator (recirculating cleaning tank)
- Paint Removal (removal solvents, scraping, detergent scrubbing)
- Strippable Coatings
- Steam Cleaning
- Sponge Blasting
- Carbon Dioxide Blasting
- Wet Ice Blasting
- Hydro-blasting
- Ultrahigh-Pressure Water
- Shot Blasting
- Wet Abrasive Cleaning
- Grit Blasting

- Grinding
- Scarification
- Milling
- Drill and Spall
- Paving Breaker/Chipping Hammer
- Expansive Grout.

### **2.7.2 Chemical decontamination**

In chemical decontamination, chemical reagents are applied to remove fixed contaminants from the surfaces of facility structures, fixtures, and equipment. This process can be carried out manually or remotely, reaching inaccessible surfaces, with few airborne hazards. Some disadvantages exist, however, including minimal effectiveness on porous surfaces, the generation of moderate volumes of secondary waste that require additional treatment, and corrosion and safety problems if carried out improperly.

Chemical decontamination may utilize dilute or concentrated reagents to chemically dislodge the contaminant. Typical chemical reaction sequences include the following:

- High-pH oxidation with dissolution
- High-pH oxidation followed by low-pH dissolution
- Low-pH oxidation with dissolution
- Low-pH oxidation followed by low-pH dissolution
- Low-pH dissolution

- Low-pH reduction with dissolution.

The following is a list of decontamination reagent systems typically applied separately or in sequence:

- Water/Steam
- Strong Mineral Acids
- Acid Salts
- Organic/Weak Acids
- Alkaline Salts
- Complexing Agents
- Oxidizing and Reducing Agents
- Detergents and Surfactants
- Organic Solvents
- Alkaline Permanganate
- Chemical Foam
- Chemical Gel

### **2.7.3 Decontamination Problems specific to mercury Contaminated Surface**

Decontamination of mercury from mercury-contaminated surfaces of metals and porous materials deserves special considerations because of the unique properties of elemental mercury, which is supposed to be the main species in the mercury-containing contaminants. Elemental mercury is a liquid and is volatile at room temperature. It may transfer from one area to another

very easily and quickly. Raising the temperature during manipulation will increase this relocation process dramatically.

On the other hand, elemental mercury forms amalgams with many metals, such as copper, zinc, nickel, tin, cadmium, and gold. The formation of amalgams, instead of surface absorption, makes the decontamination process more complicated. Elemental mercury has very low solubility in water and in many mineral acids. Procedures involving mobilization of mercury by washing with steam water are not appropriate and efficient techniques. Application of strong mineral acids directly on the surface of metals and porous materials is also a bad choice because of the low efficiency for removing elemental mercury and the potential damage of the surfaces.

#### **2.7.4 Potential Modified Mercury Decontamination Methods**

Taking the unique properties of mercury into consideration, several processes have been identified as potential techniques for decontamination of mercury-contaminated metal and porous surfaces. Their potential merits and applicability are summarized here.

##### **2.7.4.1 Reactive strippable coatings**

Strippable or temporary coatings are innovative technologies for decontamination that effectively reduce loose contamination at low cost (Ebadian *et al.*, 1999, cited in Ebadian *et al.*, 2001). These coatings have become a viable option during the deactivation and decommissioning (D&D) of both DOE and commercial nuclear facilities to remove or fix loose contamination on both vertical and horizontal surfaces.

These technologies are thought to be suitable for removal of mercury from large or medium surfaces, such as mercury-contaminated equipment or laboratory walls. They are not appropriate, however, for treatment of small debris.

Strippable coatings are polymer mixtures, such as water-based organic polymers, that are applied to the surface by paintbrush, roller, or spray applicator (Ebadian *et al.*, 1999, cited in Ebadian *et al.*, 2001). Upon applying to the surface, these polymers can absorb, attract, and chemically bind the contaminants. Then during the curing process, they mechanically lock the contaminants into the polymer matrix.

Incorporating fiber reinforcement, such as a cotton scrim, into the coating may enhance the strength of these coatings. Once the coating dries, it can be stripped manually from the surface.

In the case of auto-release coating, the mixture cracks, flakes, and is collected by vacuuming (Ebadian *et al.*, 1999, cited in Ebadian *et al.*, 2001). Nevertheless, once the strippable coating is removed, the loose surface contaminants are removed with the coating, producing a dry and clean surface.

Florida International University's Hemispheric Center for Environmental Technology (FIUHCET) recently conducted a comprehensive study to evaluate the physical properties of some commercially-available coating materials. The capability of these coatings on removing contaminant elements, Cesium (Cs), Thorium (Th), and Uranium (U), from stainless steel disks was evaluated (Ebadian *et al.*, 1999, cited in Ebadian *et al.*, 2001). The decontamination factors (DF = initial contamination/final contamination) calculated ranged from 1.53 to 4.35, which reflects 34.8 to 77.0% removal. These results indicated the effective removal of contaminants could be achieved.

Mercury presented on the surface of metal and porous materials can exist in different forms depending on the sources of mercury and the environmental conditions, although elemental mercury is expected to be the major form. Elemental mercury may form alloys with metals, consequently prohibiting the removal by these strippable coating processes. However,



mercury in other forms and free elemental mercury may be removed by appropriate coatings. Since mercury binds sulfur strongly, sulfur modified coating materials may be a good alternative. The commercial availability of such coatings, however, is not known. Surface pretreatment before applying coatings may also improve the mercury removal efficiency. Oxidation of elemental mercury to  $\text{Hg}^{2+}$  (see section 5.3.2) followed by strippable coating may significantly increase the efficiency of mercury removal.

The secondary wastes generated by the coating process are expected to be a relatively small amount. Since the coating materials are usually made of organic compounds, incineration/combustion would be a good choice to recover the mercury from the coatings. It is also possible, given the significant insolubility of any mercury sulfide compounds formed in the coating, that the coating wastes would pass the TCLP and thus LDR.

#### 2.7.4.2 Chemisorbing surface wipes

##### 1) Foraging sponge adsorption

Details of using forager sponge adsorption for mercury decontamination from mercury contaminated waters have been given in section 3.2.2.4. The sponge, an open-celled cellulose with an amine-containing polymer is reported to have a selective affinity for aqueous heavy metals, in both cationic and anionic states, including mercury ion ( $\text{Hg}^{2+}$ ) (USEPA 1997a, cited in Ebadian *et al.*, 2001). The polymer is reported to form complexes with ions of heavy metals, providing ligand sites that surround the metal and form a coordination complex. The sponge can be used in different configurations such as in columns, fishnet-type enclosures, or rotating drums. Adsorbed ions can be eluted from the sponge using techniques typically employed to regenerate ion exchange resins and activated carbons. Following elution, the sponge can be reused in the next adsorption cycle.

The number of useful cycles is reported to depend on the nature of the adsorbed ions and the elution technique used. Alternatively, the metal saturated sponge could be incinerated. Metal volatilization would be of concern. The sponge may be dried and reduced in volume to facilitate disposal.

It is important to note that a single technology may not be adequate to address all the decontamination needs of mercury-contaminated metal and porous materials. Rather, strategies will often be required that combine several technologies for removing the various forms of mercury from varying materials. Using forager sponge for cleaning mercury from the surfaces of metal and porous material requires pretreatment of the surfaces to convert different forms of mercury to "active" mercury ion ( $\text{Hg}^{2+}$ ). The oxidation/complexing procedure using iodine/iodide lixiviant (Section 5.3.2) could be modified and used for this purpose. Once the different forms of mercury are converted to  $\text{Hg}^{2+}$ , it could be wiped out from the surfaces with the forager sponge.

## 2) Grafted cotton

Sulfhydryl cotton fiber has been synthesized and used for mercury preconcentration from aqueous solutions (Lee and Mowrer 1989, Cai *et al.*, 1996, cited in Ebadian *et al.*, 2001). The thiol (-SH) group introduced onto the cotton fiber has very strong capability for binding mercury ion ( $\text{Hg}^{2+}$ ). The binding capability for elemental mercury has not been reported but is supposed to be weak. Again, an oxidation pretreatment would be first used to convert different forms of mercury to  $\text{Hg}^{2+}$ . However, sulfhydryl cotton fiber is not stable in strong oxidative solution. The oxidation of the thiol group will dramatically reduce the absorption capability. Anyway, the possibility of using the grafted cotton for wiping out mercury from surfaces of the contaminated metal and porous material remains to be studied.

#### 2.7.4.3 Surface/Pore fixation through amalgamation or stabilization

Stabilization technologies may be used for mercury-contaminated small debris with high porous surface. Mercury contained in these materials is not readily accessible to strippable coating, leaching agents, or thermal desorption. Mercury may be chemically bound to a matrix constituent or trapped in the matrix. Thus, it is more practical to stabilize mercury in those materials to comply with regulations rather than extracting or removing the mercury. These techniques have been summarized in previous sections.

### 2.8 Mercury Decontamination by Using Iodine and Potassium Iodide Lixiviant

Processes leaching or dissolving mercury species away from a solid matrix must contend with peculiar mercury chemistry (Perona and Brown 1993). Most mercuric salts are only moderately to slightly soluble in water. Elemental mercury is not soluble in water and many mineral acids.

However, as discussed in the previous sections, mercuric halides form anionic soluble complexes, which are soluble in excess of the corresponding halide,  $\text{HgX}_4^{2-}$ .

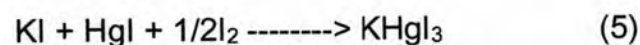
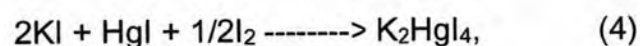
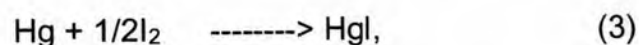
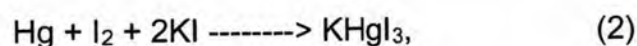
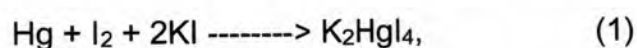
The use of solutions containing active chlorine or elemental chlorine to produce soluble mercury chloride anionic complexes was established in two patents. In another patented process developed by Foust (1993, cited in Ebadian *et al.*, 2001), mobilization/removal of mercury from solid wastes was conducted using a lixiviant consisting of an aqueous solution of potassium iodide/iodine ( $\text{KI}/\text{I}_2$ ). This process utilizes solutions consisting of  $\text{I}_2$  (0.001 to 0.5 M) as the oxidizing agent and the iodide ion (0.1 to 1.0 M) as a complexing ligand. Mercury in contaminated solid wastes in the form of oxides, sulfides, elemental, and adsorbed phases is mobilized by the  $\text{KI}/\text{I}_2$

lixiviant through oxidation and complex-forming reactions (Foust 1993, Mattigod *et al.*, 1999, Cox *et al.*, 1996, cited in Ebadian *et al.*, 2001).

Iodine, an oxidizing agent, is capable of oxidizing the various species of mercury, including elemental mercury, to mercuric iodide. Potassium iodide, a complexing agent or solubilizing agent, reacts with mercuric iodide to form a water-soluble compound having the formula  $K_2HgI_4$ .

After such mobilization, the dissolved and strongly complexed mercury can be removed, and the lixiviant is recycled. Techniques have been developed to recover mercury from the spent lixiviant (Mattigod *et al.*, 1999).

The chemical reactions are illustrated in equation bellows:



The potential mercury contaminated porous and metal surfaces found in the DOE sites are:

- Porous
- Brick wall – uncoated
- Concrete floor, wall, or ceiling – uncoated
- Wood – scrap lumber
- Metal/Nonporous

- Cable
- Carbon steel plate – coated and uncoated
- Chain link fencing
- Galvanized metal plate and posts
- I-beams – coated and uncoated
- Lead brick
- Stainless steel plate – coated and uncoated
- Plastic pipes and posts
- Wood, metal and glass debris

Since chemical-cleaning processes, such as the iodine/iodide lixiviant, involve transfer of the mercury contaminant to a liquid phase, it is essential that the contaminated solid material be in a form suitable for washing. Liquid phase containing the decontamination reactants, are passed or percolated through the particulate solid materials, thereby contacting the contaminant, which is generally in solid form with the reactants. This process seems to be efficient for surface decontamination. Preferred oxidizing agents are those, which are characterized as being mild, and which do not strongly react with any of the varied components of the metal and porous materials to form oxidation products, which complicate the decontamination process. With these criteria in mind, iodine is the most preferred oxidant (Foust 1993, cited in Ebadian *et al.*, 2001).

In the same patented procedure, Foust (1993, cited in Ebadian *et al.*, 2001) reported an electrochemical procedure to recover the extracted mercury in the form of elemental mercury, which can be utilized and handled in accordance with established procedures and techniques. The

electrochemical regeneration cell consists of an anode, a cathode separated by a cation exchange membrane. The cell is provided with a reference electrode, which controls the potential between the anode and cathode and prevents electrolysis of water at cathode. Mercury will deposit at the cathode, while iodine will be formed at the anode.

Separation of complexed mercury from a lixiviant consisting of an aqueous solution of potassium iodide/iodine has been carried out with a novel adsorbent material consisting of self-assembled mercaptan groups on mesoporous silica (SAMMS) substrate (Feng *et al.*, 1997, cited in Ebadian *et al.*, 2001). This adsorbent has specifically designed functional groups that have very high specificity and adsorption capability for mercury and other soft cationic contaminants of concern. The pores in SAMMS have a very narrow, specifically tailored (15 to 400 Å) pore-site distribution, resulting in a very high surface area (>800 m<sup>2</sup>/g) (Mattigod *et al.*, 1999, cited in Ebadian *et al.*, 2001).

Mattigod *et al.* (1999, cited in Ebadian *et al.*, 2001) demonstrated recently the effectiveness of the SAMMS adsorber in removing strongly complexed mercury (II) from spent KI lixiviant. The adsorption density measurements indicated that SAMMS material can adsorb from 26 to 270 mg/g of strongly complexed mercury (as HgI<sub>4</sub><sup>2-</sup>) from potassium iodide/sulfate waste solutions. The adsorption density increased with decreasing iodide concentration. Dissolved mercury (II) has a higher affinity for thiol groups in SAMMS as compared to silanol groups in silica gel, affirming the nature of soft cation-soft base interaction expected between mercury and –SH groups. The kinetic data indicated that the adsorption reaction occurs very rapidly, independent of mercury (II) concentration and pH.

### 2.8.1 Effect of Potassium Iodide and Iodine

Previous literature reviews show that 87 to 96% of mercury removal can be achieved from the surface of various metals by using Iodine and Potassium iodide leaching at very low concentrations of the potassium iodide and iodine mixture. The results of the study are presented in the Table 2-17 below:

**Table 2-17** Effect of KI and I<sub>2</sub> Concentration on Removal of Mercury from Metal Surfaces

Metal Surfaces	Initial Hg concentrations (ng/squar)	Treatment Time (min)	% of Mercury Removal	
			0.05MKI/0.005MI <sub>2</sub>	0.01MKI/0.001MI <sub>2</sub>
Al	40-80	2	87	91
Fe	300-430	2	93	96
Stainless Steel	13-35	2	96	63

Source: Ebadian *et al.*, 2001

Based on the results presented in the table above, it reveals that there are no significant differences of percentage of mercury removal efficiency when concentrations of potassium iodide and iodine decreased. This is noted that the reported high removal efficiency can be achieved with a limited treatment interval of only 2 minutes.

Other investigation undertaken to identify effect of potassium iodide and iodine concentrations on removal of mercury from soil is undertaken under a United States registered patent. The results of the study are presented in the table below:

**Table 2-18** Effect of KI and I<sub>2</sub> Concentrations on Removal of Mercury from Soil

KI(M)	I <sub>2</sub> (M)	% Hg Removal	% HgO Removal
0.45	0.01	103	103
0.3	0.1	106	97
0.1	0.01	106	105
0.1	0.001	97	101
0.1	0.0001	42	94
0.1	0	38	86
0.09	0.01	110	100
0.05	0.01	99	103
0.05	0.001	101	105
0.005	0.001	105	101

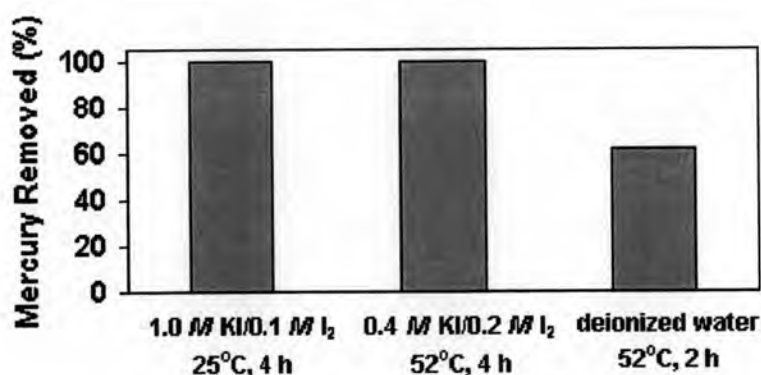
Source: United States Patent: 5226545; Extraction of mercury and mercury compounds from contaminated material and solution, 1993

Based on the results, it shows that generally, iodine concentration ranging 0.001 to 0.5 moles per liter and potassium iodide concentrations of from about 0.1 to 1 mole per liter are effective in removal of mercury from soil. (US Patent, 1993, cited in Ebadian *et al.*, 2001) However, based on the obtained information of the patent, the initial mercury concentrations and their ranges have not been included. In practice, it was reported that the concentration of oxidizing and complexing agents can be optimized based on the amounts of mercury and mercury compounds carried by the material to be treated.



It was also reported that iodine is generally employed in amounts of at least about twice the stoichiometric amount, based on the amount of mercury in the contaminated material. Higher concentrations can be used. In general, iodine concentrations of about one half molar in one molar potassium iodide have been found to be effective for extracting mercury from a wide range of contaminated materials. (US Patent, 1993, cited in Ebadian *et al.*, 2001)

Other studies undertaken to identify effects of potassium iodide and iodine on leaching of mercury show that a leaching solution consisting of 0.4 M KI and 0.2 M I<sub>2</sub> is very effective in removal of Hg compared against 1.0 M KI and 0.1 M I<sub>2</sub>. (K. Thomas *et al.*, 1997) The results are presented in a Figure 2-14 below:



**Figure 2-14** Effect of temperature and decontamination solution towards mercury removal

### 2.8.2 Effect of Treatment Time and Temperature

An investigation carried out to identify effect of treatment time of chemical leaching by employing potassium iodine and iodide on metal surface shows the effect of treatment time on mercury removal efficiency as presented in a table below:

**Table 2-19** Effect of Treatment Time on Hg Removal Efficiency

Materials	0.05M KI/0.005M I <sub>2</sub>	
	20 Seconds	2 Minutes
Copper	22.6±7.4%	34.6±71.6%
Aluminum	81.5±5.1%	87.34±6.5%
Steel	75.9±16.5%	92.9±5.1%
Stainless Steel	89.0±6.0%	96.2±2.0%
Grout	NA	41.9±6.9%

Source: Ebadian, *et al.*, 2001

Based on the table above, it shows that increased treatment time from 20 seconds to 2 minutes also increase mercury removal efficiency. However, it should be noted that the experiment was conducted in lab scale with small pieces of metal specimens, and thus high mercury removal efficiency can be achieved very rapidly.

An investigation carried out to identify effect of treatment time on efficiency of mercury removal from contaminated storm drain sediment by employing potassium iodide and iodine leaching process show the results as presented in a table below:

Evaluation of various leaching conditions for treatment of contaminated storm sewer sediments is presented below:

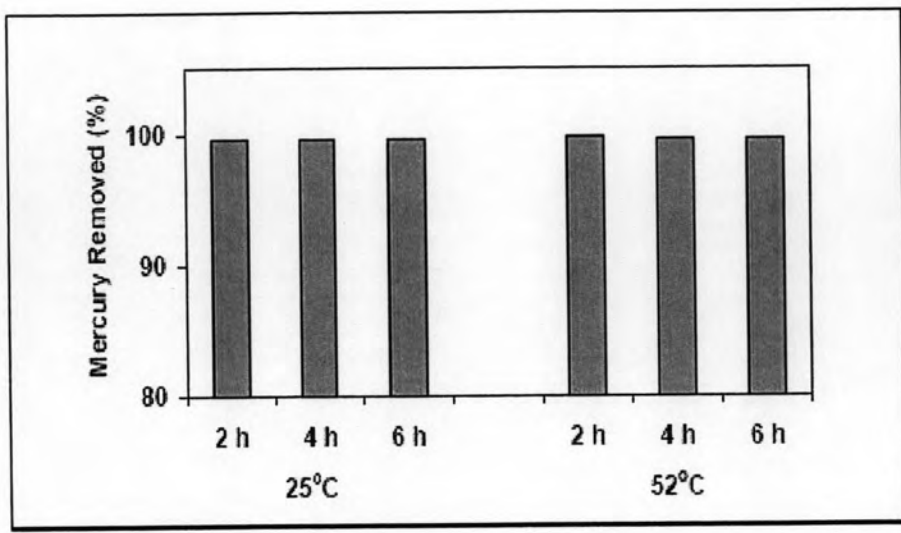
**Table 2-20** Mercury Removal by Using Iodine and Potassium Iodide in Sediment

Leaching solution	Treatment time (h)	Initial mercury concentration <sup>a</sup> (mg/kg)	Final mercury concentration (mg/kg)	Mercury removal (%)
DIW <sup>b</sup> control	2	34,900	20,600	41
DIW control	4	34,900	16,477	53
1.0 M KI/0.1 M I <sub>2</sub>	2	34,900	1,038	97
1.0 M KI/0.1 M I <sub>2</sub>	4	34,900	909	97
0.4 M KI/0.2 M I <sub>2</sub>	2	34,900	686	98
0.4 M KI/0.2 M I <sub>2</sub>	4	34,900	848	98

Source: Thomas *et al.*, 1997

From the table above shows increasing treatment time from 2 to 4 hours rendering no effect on mercury removal efficiency in all samples tested with considerably high concentrations of mercury of 34,900 mg/kg or about 3.5 percent.

Another similar experiment was undertaken to understand the effect of treatment time and temperature toward the percentage of mercury removal by using surrogate Hg contaminated storm sewer sediment by using 0.4 molar of KI and 0.2 Molar of Iodine. The results are presented in Figure 2-7 below:



**Figure 2-15** Effects of Temperature and Decontamination Periods on Percentage of Mercury Removal

The Figure above shows that increasing treatment time did not significant increase mercury removal efficiency of the surrogate samples analyzed.

The figure also shows that increasing temperature from ambient level of 25°C, does not significantly increase mercury removal efficiency at all treatment time intervals.