Removal of mercury from water in the petroleum industry

Darrell L. Gallup

Thermochem, Inc., Santa Rosa, CA, USA

Corresponding author:

Darrell L. Gallup, Thermochem, Inc., 554 E. Pasacana St., Meridian, ID, USA

Tel: +1.707.480.5508

Fax: +1.707.575.7932

e-mail: Darrell@thermochem.com

Abstract

Mercury is present in some oilfield produced waters and refinery wastewater at low concentrations, but above regulatory discharge limits. The solubility of mercury is governed by elemental mercury (~60 ppb at 25°C). If water is oxidized, the concentration of mercury exceeds that predicted for the solubility of elemental mercury due to the formation of ionic species. Mercury in produced water, refinery wastewater and glycol solutions may be removed to trace concentrations by adsorption, filtration and precipitation processes. Results of studies of mercury removal from petroleum industry waters are provided. Removal of mercury from water prior to discharge into the environment reduces the risk of contamination and biotic methylation of mercury.

1   INTRODUCTION

Co-produced water from oil and gas fields varies widely in physico-chemical properties. In fields producing mercury in hydrocarbons, produced water may be significantly contaminated with this element. Produced water separated from mercury-laden hydrocarbon phases in the field must be handled and disposed of carefully to prevent contamination of personnel and the environment [1]. Upon processing mercury-contaminated hydrocarbons at gas plants, oil refineries, and petrochemical plants, wastewaters may also become polluted with mercury and other heavy metals or metalloids.

As awareness increases in the petroleum industry, the concentration of mercury in waters is under scrutiny. Legislation limiting discharge to the environment is being imposed and enforced to mitigate toxicity to flora and fauna. Re-injection of mercury-contaminated produced water is the simplest method to dispose of water in order to prevent environmental discharge. When re-injection is not feasible, mercury in discharge waters must be removed to regulated limits. Primary removal methods for soluble mercury in produced or oily wastewaters are adsorption and precipitation. Particulate mercury may be removed by filtration. Ion exchange and membrane processes are rarely used to remove mercury in the petroleum industry due to fouling by dispersed oil or water soluble organics [2].

2   Geochemistry and Origin of Mercury in Produced Water

Several oilfield basins around world have mercury associated with gas, oil and water. These basins are often associated with the earth's mercuriferous and volcanic belts. Mercury ores usually occur in very young orogenic belts where rocks of high density are forced to the crust of Earth, often in hot springs or other volcanic regions [3]. Figure 1 is a world map of mercuriferous belts.
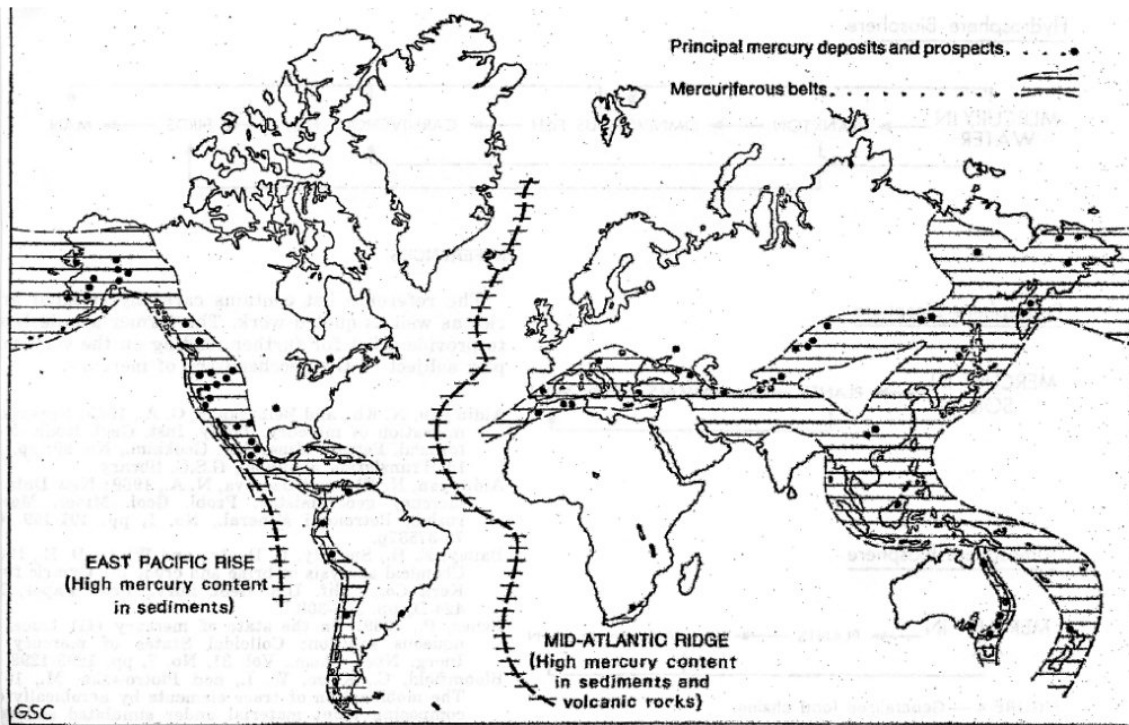

Figure 1: Mercuiferous belts of the earth

Fields producing elevated mercury concentrations in hydrocarbons typically exhibit characteristics such as low hydrogen sulfide, elevated carbon dioxide, abnormally high geothermal gradients, coaly or I-type tin granite or carbonate source rocks. Thermal degradation of carbonate source rocks often leads to fluid contamination with elevated mercury and carbon dioxide concentrations [4,5]. In sweet reservoirs, elemental mercury (Hg^0) and compounds may be present in gas, crude oil, condensate and produced water, whilst in sour reservoirs, mercury will almost always be present as m-cinnabar (HgS) or polysulfide complexes, HgS_x^{y-} [6].

Bedded coals tend to concentrate mercury and arsenic. As mercury-in-coal concentrations increase, the rank levels of these coals decrease. It is postulated that certain coal-forming land plants act as concentrators of mercury present in soils upon which they grow. Co-occurrence and correlations of mercury concentrations and total organic carbon (TOC) content in sedimentary rocks are referred to as "genetic origin." Mineral origin of mercury in hydrocarbons and water is explained by volatilization of mercury in rock at high temperature followed by dissolution in liquids devoid of significant sulfur [7]. That Hg° is soluble in both hydrocarbons and water results in contamination of natural gas, condensate, crude oil and water within a reservoir.

Unless dynamic reactions occur in un-drilled reservoirs, one expects Hg° to achieve vapor-liquid-liquid equilibrium (VLLE) solubility. After penetration of the reservoir with the drill bit and eventual production, Hg° is expected to co-migrate to the surface with petroleum either in aqueous solution or as a solute in hydrocarbons. The loss of VLLE during migration of fluids to the surface likely re-distributes Hg° in the phases. Fluid cooling from the wellhead to surface allows Hg° to condense as liquid droplets, which may adsorb onto sand, clays and waxes. Oxidation during fluid flow may convert Hg° to mercurous ion, Hg^+, and/or mercuric ion, Hg^{2+}. The ions would, of course, prefer to partition to the aqueous phase.

Arsenic (As) is often present with mercury in southeast Asian oil and gas fields. The form, origin and behavior of arsenic tend to be quite different from mercury. For example, in a gas-condensate field (no produced water) trimethylarsine predominated in both phases [8]. In another well, only a trace of arsine was detected in gas, but the condensate contained significant triphenylarsine, together with a little triethylarsine and several unidentified species [9]. In subsequent tests of condensate containing dissolved Hg°, primarily arsenate was detected, with only 10% unidentified species believed to be triphenyl- or trialkylarsines [10]. Arsenic present in produced water is usually a mixture of arsenite and arsenate species.

3   Forms of Mercury in Produced Water

A number of forms of mercury may exist in produced water and wastewater depending on a variety of conditions. The most common species encountered in these waters are shown in Table 1 and Figure 2. The solubility of Hg° in pure water at 25°C is ~60 μg/L (ppb). Droplets of Hg° may settle out of water, be dispersed or may float on the surface (attached to dispersed or floating oil, encapsulated in wax, or bound to asphaltenes). Fortunately, very toxic dimethyl mercury, $(CH_3)_2Hg$, is nearly absent in petroleum systems. Through methylation reactions, however, Hg° can be converted into methyl mercury cation, CH_3Hg+, where the counter ion is usually chloride, Cl^-. Solid forms of mercury that may be present in water include precipitated Hg solids or produced formation flour in the forms of mercuric sulfide (cinnabar, HgS) and oxide (montroydite, HgO). When Hg° is oxidized, it may form rather insoluble mercurous salts or soluble mercuric salts; *e.g.,* Hg_2Cl_2 and $HgCl_2$, whose solubilities in pure water at 25°C are ~2 and ~70 g/L, respectively. Soluble complexes of Hg may also be present in produced water and wastewater.

Table 1. Common Hg species in water

Elemental	$Hg°$
Organic	$(CH_3)_2Hg$; $CH_3Hg^+X^-$
Inorganic	$HgCl_2$
Thiol complexes	C-S-Hg-S-C
Particulate sulfide and oxide	HgS; HgO
Suspended forms	Wax encapsulated; asphaltinic

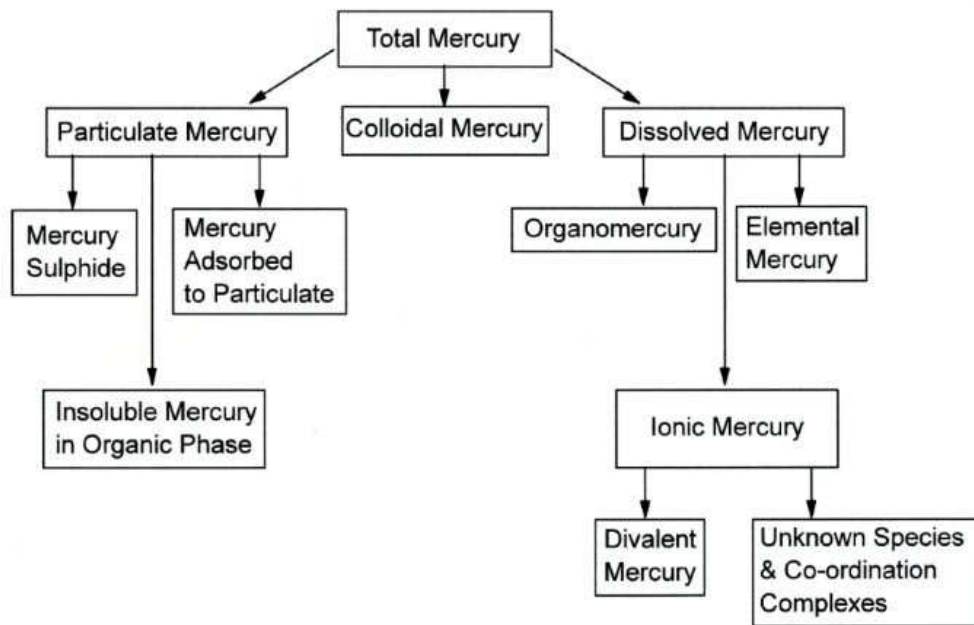# Chemistry of Mercury in Liquid Hydrocarbons

Figure 2. Mercury species

Wilhelm et al., [11] and Salvá and Gallup [12] have divided forms of Hg into basic categories. The simplest categorization is dissolved vs. insoluble. Dissolved Hg is that passing through a pressure filter with a pore size usually ranging between 0.2 and 0.8 μ, whilst insoluble Hg is that which will not pass through the filter. Insoluble Hg is termed, "particulate Hg" because there are several Hg compounds that are soluble and several that are insoluble in water. Further categorization includes:

4

Organic Hg (dissolved). Species are usually very soluble in hydrocarbons. The Hg atom is bound to a carbon atom: R-Hg, R-Hg-R, and R-Hg-X where R = CH_3, C_2H_5, etc. and X = Cl or another anion. Organic Hg is usually more toxic than the other forms. They are found in metabolites of micro-organisms, and some are relatively volatile. Methyl mercury cation is very soluble in water.

Inorganic mercury salts. These compounds may be insoluble, or both oil and water-soluble; *viz.,* (HgX)+ or HgX_2, where X is usually the chloride ion. Water-soluble species behave like ionic mercury. Some mercuric halides remain somewhat un-ionized in aqueous and organic solutions; *viz.* $HgCl_2{}^0$, which is also soluble in oil, alcohols and glycols. The most common insoluble forms are HgS and HgO. Meta-cinnabar, β-HgS, is often present as a formation mineral or a precipitate due to the reaction with H_2S in oil fields exhibiting high total mercury, THg. Particles of HgS and HgO may be adsorbed on solids such as paraffin, clay or sand.

Elemental mercury (Hg^0). Hg° consists of vapors, dissolved or particulate forms of metallic mercury, and is usually the predominant specie in most hydrocarbon matrices, primarily as small drops. It is often the main specie in "particulate" mercury, PHg. Hg^0 is soluble in water and other polar solvents up to several hundred ppb. Hg^0 is soluble in hydrocarbons (paraffins and aromatics) up to 2,500 ppb at 25°C. Dissolved mercury (DHg) tends to be stable in hydrocarbon solvents and it exhibits some vapor pressure above the solvent [13]. Volatile Hg is determined by sparging samples with a gas and then analyzing the gas for THg.

The study of amounts and forms which Hg is present in petroleum is important when analyzing and risking health, environmental and safety issues, and when selecting removal technologies. For Hg in liquid samples, operational speciation is used in simple sequences to identify/quantify the most important species according to the following equation:

$$THg = Hg^0 + (R\text{-}Hg\text{-}R + Hg\text{-}K) + (HgCl_2 + RHgCl) + PHg \qquad \text{(Eq. 1)}$$

(1) = (2) + (3) + (4) + (5) where,

(1)   THg = Total Mercury, measured in original matrix (unfiltered).

(2) Hg^0 = Dissolved elemental mercury. Specie can be assessed by sparging inert gas (normally helium) in the cooled matrix. Then, elemental mercury is measured when a gold trap is intercepted in the helium flow stream, or by measuring residual value of mercury in the matrix. Dissolved Hg^0 is often measured directly in samples after filtration.

(3)   (R-Hg-R + Hg-K) = The total addition of organic mercury and complexed mercury.

(4)   ($HgCl_2$ + RHgCl) = Corresponding to ionic mercury, measured in the lab by a technique where the hydrocarbon sample makes contact with a solution of L-cysteine in water; this allows selective and quantitative extraction of ionic species into the water phase.

(5)   PHg = THg – DHg   (Eq. 2)

Dissolved mercury, DHg, is determined by filtering with 0.45 µm pore size membrane; then PHg can be estimated. Sometimes PHg is measured gravimetrically, and speciated by special analytical techniques.

Values of (1), (2), (4) and (5) may be relatively easy to acquire or estimate in oil field laboratories. Usually, values of organic Hg (3) are extremely low and estimated by closing the balance presented in Eq. 2. To ensure all species are identified, and if organic Hg is present, specialty contract laboratories perform very careful separations under controlled conditions to completely close the balance of the equations.

4 Mercury Cycle in the Environment

Prior to discussing analytical and removal issues of mercury in water, it is important to understand the reaction chemistry, health and environment of mercury, also known as the mercury cycle. Figure 3 shows a representation of this cycle. Reactions of mercury in water, and especially in the benthic zone, include oxidation, reduction, methylation, demethylation, volatilization, and sedimentation. When the end product of the mercury cycle is biotic methylation, CH_3Hg^+ often becomes assimilated in organisms and begins to bioaccumulate in the environment. Ultimately, methyl mercury is biomagnified in flora and fauna, especially in fish. Mammals eating mercury-contaminated fish or plants risk toxification.
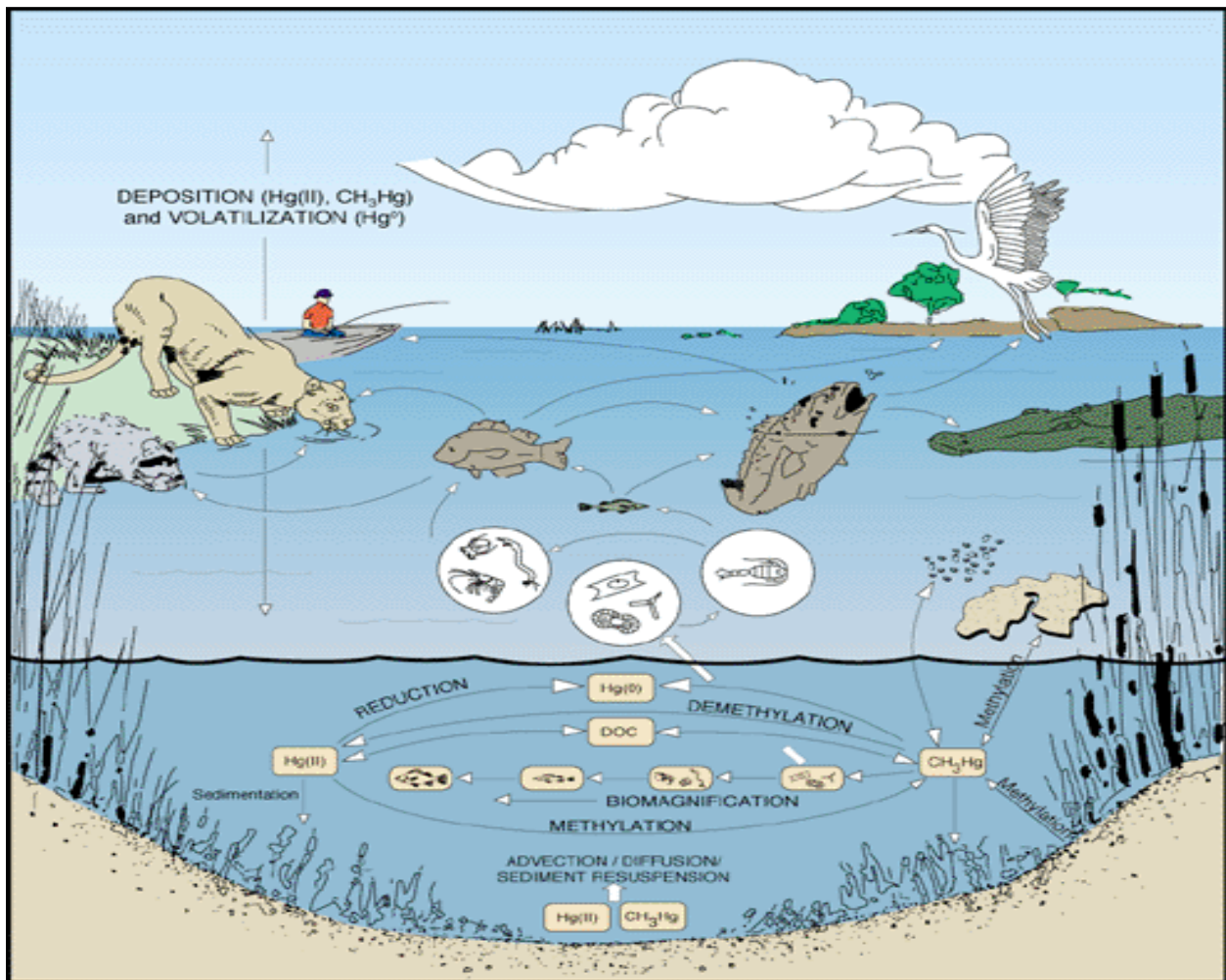

Figure 3. The mercury cycle

For this and similar reasons, the World Health Organization has set 2 µg/L (ppb) mercury as its drinking water standard. The USEPA Toxicity Characterization Leach Procedure (TCLP) defines solid waste or soil has hazardous when the acetate buffer lixiviant contains ≥ 0.2 mg/kg (ppmw) total mercury. Produced water and wastewater discharge limits in the petroleum industry vary significantly around the world from <0.1 to as high as 100 µg/L. The more stringent limits set for overboard discharge from offshore production platforms are typically ≤ 5 µg/L. One of the tightest limits for mercury discharge is from refinery wastewater in the state of California (USA). A monthly average of 0.079 ppb must be met, although a maximum discharge of 0.2 ppb in a single episode is allowed, provided it is quickly corrected. The tightest limit for any water discharge is 0.0013 ppb into the Great Lakes of the United States and Canada. The primary reason for limiting mercury in water discharged to the environment is to protect against Minimata disease [14].

Biotic methylation reactions are most commonly responsible for the production of CH_3Hg^+. However, Bloom and Chu [15] recently reported that abiotic methylation may also occur in the presence of hydrocarbons. Abiotic methylation of Hg was found to occur in both acidic and alkaline conditions and/or in presence of clays. The reaction involves the intermediate formation of radicals and the production of alcohols. In a system that is supposed to be free of alcohols, the by-product appearance in solution can be an indicator of the aboitic methylation of mercury:.

- $RCH_3 \rightarrow R^* + CH_3^*$ (Eq. 3)

- $CH_3^* + Hg(OH)_2 \rightarrow CH_3HgOH + OH^- \ R^* + OH^- \rightarrow ROH$ (Eq. 4)

5 Analysis of Mercury in Produced Water

Several protocols for sampling with the intent to analyze mercury in produced and waste waters in the petroleum industry have been developed [16]. It is important to obtain representative water samples because "it is not just the analysis, but what one analyzes." Sampling is perhaps more crucial than the analysis. When mercury analyses include not only the total concentration, but the forms of mercury present, sample collection must assure proper handling, extraction and sample conditioning, the latter being critical when speciation is to be conducted. It may be necessary to collect water samples using "clean hands/dirty hands" methods (USEPA 1669) to ensure that samples are not compromised when collected.

The objective of sampling must be to always obtain representative samples of water as they exist in a pipeline or vessel at the sample point, without allowing phase changes, aeration or oxidation of $Hg^0 \rightarrow Hg^{2+}$, and loss of volatile Hg species. Where mixed phases are present in pipelines, we recommend obtaining relatively organic-free water by sampling through isokinetic probes and mini-separators in a fashion similar to that found in ASTM (American Society for Testing and Materials) E-1675. Water samples to be sent to the laboratory for mercury analysis are best collected following ASTM D7482 using amber borosilicate VOA-type vials with Teflon®-coated septa or lined screw caps. The use of clear glass, plastic or metal containers must be avoided, together with paper, rubber or other linings in screw caps due to adsorption of un-recoverable mercury thereon. VOA (volatile organic analysis) vials should be filled to the brim to limit air bubbles as a means of preserving specie oxidation state and limiting "degassing" of mercury from the water or other aqueous solution. At ambient temperature, for example, the concentration of Hg° vapor that may partition to the headspace of an aqueous solution containing dissolved Hg°, according to the Henry's constant, $[Hg°]_{air}/[Hg°]_{aq}$, is approximately 0.3 at 25°C [13].

ASTM and USEPA (United States Environmental Protection Agency) have developed standard methods for analyzing water and other aqueous solutions for mercury [16]. Most total mercury analyses in water rely on stannous ion reduction and cold-vapor atomic absorption (CVAAS) or atomic fluorescence spectroscopy (AFS) as called for in USEPA Methods 245.1, 245.7 and 1631 [17]. Elemental mercury dissolved in water is measured by sparging with an inert gas (such as nitrogen, helium or argon) and trapping the mercury vapor on gold-coated substrates. Other forms of mercury can be speciated by filtration, *vide supra*, and by chromatography, ion exchange, trapping, redox reactions, etc. In certain instances, especially in water containing dispersed oil or high concentrations of water-soluble organics, mercury which sticks to glass walls or Teflon® linings may be washed and recovered using BrCl, L-cysteine or HNO_3 solutions. Mercury detected in wall washings is added to that measured in the bulk liquid to yield an accurate total mercury concentration. Unfortunately, wall washings cannot be speciated. However, we have found that Hg in aqueous phases adhering to glass surfaces consists of di- and tri-mercury oxide species; *i.e.,* Hg_2O and Hg_3O^+. Sometimes the mercury which adheres to glass is minor compared to the total in the bulk solution, but other times, it may constitute the major fraction of mercury collected in a glass container.

A number of mercury-specific analyzers are available to allow water to be analyzed for mercury with high accuracy and precision. Table 2 lists many of these analyzers that have been utilized by the petroleum industry to monitor mercury concentrations in aqueous solutions. Some use direct injection, while others utilize attachments to reduce or oxidize mercury for improved detection. In addition to the primary CVAAS and AFS mercury detectors used in analytical instruments for water analyses, UV absorption, inductively-coupled plasma / mass spectrometry, etc., may be used as detectors in the various analytical instruments.

Table 2. Some mercury-specific instruments for aqueous media analysis

Manufacturer	Name	Detection Method
Nippon Instruments	SP-3D, WA-4, MA-3000	CVAAS[a]
PS Analytical	Sir Gallahad, Millenium	AFS[b]
Lumex	RA915+	Zeeman CVAAS
Milestone	DMA-80	CVAAS
Leco	AMA254	Direct combustion
Teledyne Leeman	Hydra	CVAFS
CETAC	Quicktrace	CVAAS
Mercury Instruments	LA254	CVAAS
Hitachi	HG-400	CVAAS
Perkin Elmer	FIMS	AAS, ICP, ICP-MS[c]
BrooksRand	MERX, Model III	CVAAS, AFS
AntonPaar	Asher	Acid Digestion + AFS
Tekran	2600	AFS

a. Cold vapor atomic absorption spectroscopy; b. atomic fluorescence spectroscopy; c. inductively-coupled plasma and mass spectrometry

In our experience, some laboratories periodically encounter difficulty in calibrating or operating instruments. As a result, we recommend that labs incorporate good quality control and assurance (QA/QC) to ensure accurate and precise mercury analyses. Laboratories are encouraged to use internal control charts, and to participate in round robin and performance (blind standard) evaluations.

6   Mercury Removal from Aqueous Solution

Mercury removal from natural gas, condensate and naphtha are very mature technologies with a number of successfully installed units (mercury removal units – MRU). In contrast, MRUs installed for crude oil treatment are almost non-existent [12]. There are several produced (oily) water treatment technologies available, but not very many installed. Treatment technologies applied to water and aqueous solution technologies in the petroleum industry are neither highly diverse nor particularly mature. Whereas the removal of mercury from drinking or agricultural water by ion exchange and membranes is well studied and applied, these technologies are not very useful in oily produced water or wastewater due to fouling by organics.

The most common method for disposing of mercury-containing waters that have been in contact with petroleum hydrocarbons is re-injection. In many oilfield, it is advantageous to dispose of water by injecting back into the producing formation so as to sweep more oil to producing wells (waterflooding or secondary recovery), and/or for reservoir pressure support. In this manner, mercury is returned to the reservoir from whence it was originally produced.

In some gas fields, oilfields and at refineries or other process plants, water re-injection is not practiced for a variety of reasons (usually the lack of nearby injection wells). In these instances, water is usually disposed to the environment. When mercury is present in produced waters or aqueous solutions it should be removed prior to discharge, re-use or recycling. The primary methods that have proven successful in these applications are adsorption and precipitation (including flocculation and sedimentation). Biotreating wastewater, as practiced at many refineries, can also remove some forms of mercury. However, bio-oxidation often simply converts elemental mercury to ionic mercury, Hg^{2+}, which is very soluble in water. Unless sour water is available for mixing with water streams containing Hg^{2+} to allow precipitation of HgS, dissolved mercury may not be removed in bioreactors. A similar effect is observed for arsenic in produced water.

6.1 Adsorption

The vast majority of adsorbents used to remove mercury species from aqueous solutions in petroleum operations rely on sulfur capture of mercury in the form of HgS. Sulfur impregnation or incorporation of thiol and mercapto groups on inert, but high surface area substrates comprise the vast majority of adsorption processes. The high affinity of mercury for sulfur normally results in adequate removal efficiencies. Table 3 summarizes some of the adsorbent systems that have been developed to remove mercury from oily produced water, wastewater and other aqueous solutions, *e.g.,* glycol and amine solutions used in natural gas processing plants for dehydration and acid gas removal, respectively. Many of these adsorbents are similar in composition, but vary enough to have been separately patented.

Table 3. Some mercury-specific removal adsorbents

Sulfur-impregnated carbon
Metal sulfide-coated alumina or carbon
Oil-bath silica gel
Thiol-templated clay
Thiol-templated mesoporous silica
Thiol-templated amended silicate
Thiol-templated mesoporous polymer

Some examples of adsorbent deployment by the author are:

Example 1. Sulfur-impregnated carbon columns have been used for several years on an offshore platform. The inlet Hg concentration typically ranges from 30 – 60 ppb. Mercury speciation in the water includes elemental micro-droplets and mercuric ion, Hg^{2+}. The effluent Hg concentration remains below 10 ppb until such time that the absorbent is replaced. The adsorbent is susceptible to fouling when excess dosing of flotation polymer occurs in an upstream induced gas flotation (IGF) unit.

Example 2. A thiol-templated bentonite clay pellet bed was pilot tested on offshore produced water and refinery wastewater. Again, due to carryover of IGF polymer on the platform, the cartridge filters installed upstream of the clay bed prematurely plugged. At the refinery dissolved air flotation (DAF) unit, the cartridge filters prematurely plugged with solids and polymer. Thus, the operator was unable to determine the mercury removal efficiency of the template clay adsorbent.

Example 3. Thiol-templated mesoporous silica was bench-scale tested on a produced water stream. Although the adsorbent appeared to initially remove dissolved mercury, the fine nature of the product became plugged with solids. Essentially, the adsorbent behaved like a media filter. In order to utilize this product, it will be necessary to pelletize it.

Example 4. Thiol-templated mesoporous polymer was also bench-scale tested on a produced water stream. In this test, the polymer became coated with dispersed oil resulting in fouling and premature termination of the test before mercury removal efficiency could be quantified.

Example 5. In a small-scale laboratory test, a column of thiol-templated amended silicate was examined for removal of Hg from an aged monoethylene glycol (MEG) solution obtained from a gas processing plant. Unfortunately, the adsorbent plugged quickly by what appeared to be adhesion of MEG to the adsorbent pellets precluding collection of treated solution for Hg analysis. Flow was severely restricted compared to water alone.

The author's experience with adsorbents for mercury removal from aqueous solutions has indicated that the technology is only effective when upstream water is relatively free of solids and excess chemicals. This requires operator attention to water stream quality being sent to adsorption units for polishing mercury therein. Whether adsorption can be applied to aqueous glycol or amine solutions remains to be determined. In order for ion exchange or membrane processes to effectively remove mercury from petroleum industry aqueous solutions will also require careful pre-treatment and attention to water quality and process conditions.

6.2 Filtration

The application of cross-flow microfiltration to metal finishing waste treatment involves the addition of chemicals to the waste stream to effect precipitation and then continuous dewatering through the membrane filter which typically has a 0.1 micron pore size. The microfilter consists of a series of tubes measuring up to 2.5 cm in diameter. The polymeric membrane is designed to resist the pH range required to precipitate the heavy metals out of solution, as well as to withstand the abrasive effects of these suspended solids. The treated solution is pumped at turbulent velocities down the center of the tubes, and a downstream valve creates the necessary backpressure to force the clarified water through the microporous membrane.

Typically, the dewatered suspended solids (concentrate) are recycled to the feed tank in order to increase the concentration of the suspended solids up to 5 – 10%. A portion of this concentrate stream is continuously bled from the system, often to an inclined plate-type clarifier for further dewatering up to approximately 20% solids. If increased dewatering is justified, this slurry can be directed to a filter press to bring the solids concentration up to 60%.

Treatment of oilfield produced waters is becoming more necessary to meet environmental discharge standards for total hydrocarbons and suspended solids. The low concentrations now being mandated are unattainable when classical oil-water separation processes are used. To overcome the challenges posed by more stringent regulations, operators have turned to membrane filtration schemes which have the potential to minimize additional costs and disposal issues. The use of ceramic ultra- and nanofiltration membranes represents a relatively new approach to the treatment of produced water [18]. A drawback to the use of ceramic and membrane filters is fouling by waxes and asphaltenes.

Considering filtration as a means of removing heavy metals from metal finishing operations, and ceramic or other filters as a means of removing oil, a pilot test was conducted in an effort to remove mercury from produced water at a field in SE Asia. Polymeric and ceramic membrane filters in cross-flow microfiltration mode was examined for removal of mercury and oil from the produced water. Most of the oil in the produced water was initially removed by de-oiling hydrocyclones. At the start of the pilot test, dispersed oil and some mercury believed to be present as HgS and fine droplets of elemental Hg was removed. As the testing progressed the membrane filter became plugged. Plugging was observed in all tests with varying flow rates, membrane composition and membrane sizing. Post test examination of the filters showed that plugging was due to polymerized silica. The dissolved silica in the water was elevated to approximately 200 ppm due to the relatively high temperature of the reservoir (185°C). In the filters, the temperature of the water was only 26°C where the equilibrium solubility of amorphous silica is only about 125 ppm. Apparently, the silica became supersaturated with amorphous silica/silicate in the oilfield water causing "scaling" of the membranes.

Supported liquid membranes have found use in the extraction of metal ions from hydrometallurgical solutions [19]. An extension of this technology to remove heavy metal ions in water for decontamination involves extraction via hollow fiber supported liquid membranes (HFSLM). Pancharoen et al., [20] developed such a membrane to removed $HgCl_4^{2-}$ from water. The success of this extraction in the HFSLM led to the development of a synergistic mixture of Cyanex 471 and Aliquat 336 extractants in the hollow fiber membrane that simultaneously removes arsenic and mercury from water produced at a gas field in the Gulf of Thailand [21]. It is not known if this technology is currently operating commercially to treat produced water.

6.3 Precipitation

Frankiewicz and Gerlach [22] developed and deployed a precipitation process to remove mercury, arsenic and oil from produced water that was overboard discharged into the ocean. The process consists of (a) treating deoiler water with bleach to oxidize Hg° to Hg^{2+}, and As^{3+} to As^{5+}; (b) treating with ferric chloride ($FeCl_3$) to co-precipitate Hg^{2+} and As^{5+} with $Fe(OH)_3$, (c) treating with a flotation polymer at the inlet to an IGF unit, (d) skimming off the oily precipitate in the IGF, (e) sending the skimmings to a small clarifier, and (f) disposing of the Fe-Hg-As residuals, while reclaiming a little oil or condensate.

Early in the operating life of the process on a number of offshore processing platforms, it was discovered that Hg sometimes exceeded the water overboard discharge limit of 10 ppb. As a result, the process was improved by further optimizing the bleach dosage, and then adding a

polymeric thiol compound to precipitate the last traces of mercury to < 10 ppb (see Fig. 4) [23]. The success of the modified process led to installation on a refinery wastewater stream. Due to the presence of ammonia in the water, oxidation by chlorine is not particularly effective due to formation of chloramines. Therefore, peroxide is used to replace the bleach in the oxidizing step (a), *vide supra*.
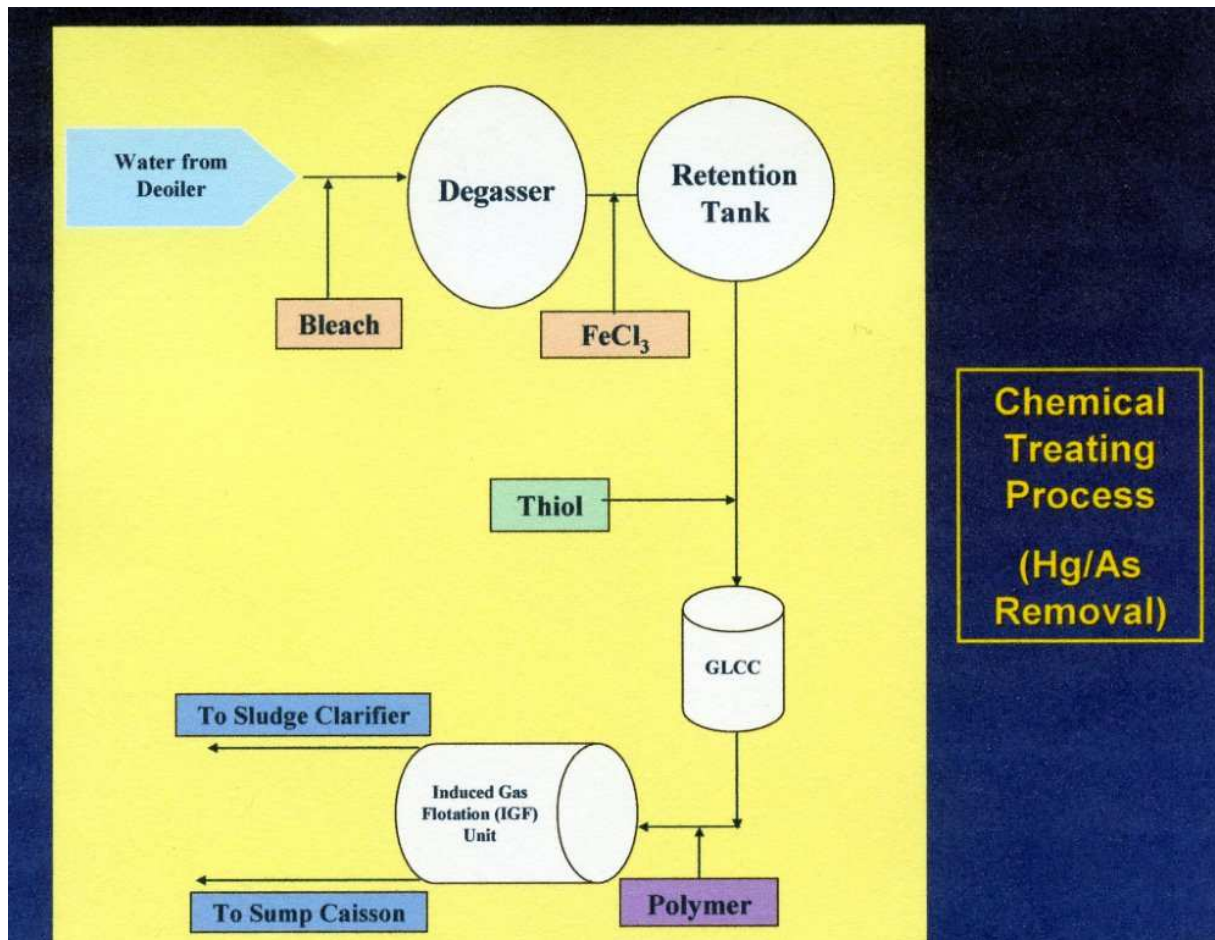

Figure 4. Precipitation process

In the absence of arsenic in water, simply treating the water with the polymeric thiol is sufficient to precipitate Hg. Although the original process used the IGF to separate the precipitate and oil/condensate from water, a settling process in a flocculated clarifier could also be employed. It is not surprising that a filter can also be used to separate the precipitates from the treated waters [24]. A filter preferred by the author for this process is an automatic backwash screen (sintered metal) type.

Another potentially useful method to remove mercury from water is hydroxide precipitation. The solubility of $Hg(OH)_2$ at 25°C reaches a minimum at pH ~11.5. (The precipitation product of Hg^{2+} treatment with caustic soda or lime is ultimately HgO.) However, the K_{sp} of HgO is considerably greater than HgS (10^{-26} vs. 10^{-52}). Furthermore, the solubility of $Hg(OH)_2$/HgO is highly pH dependent due to hydroxyl-complex formation. When the resulting pH of hydroxide treatment of

water to precipitate $Hg(OH)_2$ is < 8 or > 14, the concentration of Hg^{2+} in solution will exceed 10 ppb. Therefore, the resulting pH of water in the hydroxide precipitation of Hg process must be carefully monitored and controlled.

Yet another method to remove mercury from water is treatment with zero-valent iron, Fe°. The removal of mercury and other electroactive metals by zero-valent iron occurs as a consequence of reductive precipitation or co-precipitation reactions on the grain surfaces of the iron. The reactions have kinetic limitations, but generally occur at sufficiently rapid rates to have potential application in produced water flow through a series of zero-valent iron-packed columns [25].

An advantage of the precipitation processes is that glycol or methanol solutions containing mercury may be treated without the problem of fouling as in the case of certain adsorbents and filters. In this regard, glycol solutions containing up to 400 ppb of dissolved elemental mercury were treated with a polymeric thiol. The sulfide precipitate readily settled in these bench-scale tests leaving supernatant Hg-free water for decanting. The concentrations of Hg° resulting from these treatments were < 2 ppb.

A potential drawback to precipitation processes for mercury removal is the presence of complexes in aqueous solutions. Mercuric ion can complex with a number of anions causing its solubility to increase, and its removal efficiency to decrease. The strength of mercuric complexes is measured by formation constants. Table 4 lists a variety of complex formation constants at ambient temperature [26]. The strongest complex of Hg^{2+} is cyanide, CN^-. Therefore, if an aqueous solution contained significant CN^-, it will be more difficult to precipitate Hg^{2+} with thiol polymer or hydroxide. As a result, water chemistry should be well-characterized before attempting to use precipitation for Hg removal.

Table 4. Mercuric ion complex formation constants

$$Hg^{2+} + nL \rightarrow HgL_n^{(+, 0, -)}$$
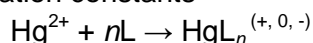
Ligand	Log K	Ligand	Log K	Ligand	Log K
Ammonia	19.3	Bromide	21.0	Chloride	15.1
Cyanide	41.4	Iodide	29.8	Acetate	8.4
Sulfite	22.7	Thiocyanate	17.5	Thiosulfate	33.2
EDTA	22.0	Pyridine	10.4	Tren/Trien	22 - 25
Glycine	19.2	NTA	12.7	Oxalate	7.0
Phenantholine	23.4	Thioglycolate	43.8	Thiourea	26.8

7 Conclusions

Oil/gas field produced waters typically contain < 100 ppb of total Hg. Re-injection of produced water returns Hg back into the reservoir. Discharge limits for produced water disposal to the environment range from about less than 10 ppb to 1 ppb. Petrochemical plant and oil refinery wastewaters contain much less Hg due to dilution with other process waters (primarily through the use of desalters.) The most stringent discharge limit for Hg from these plants and refineries is 0.079 ppb in the San Francisco Bay of California. Other aqueous solutions (glycols, amines, caustic washes, etc.) may contain several hundred ppb of mercury. The world drinking water standard is 2 ppb.

The most common forms of dissolved mercury in waters and solutions are elemental, Hg°, inorganic, Hg^{2+}, and methyl mercury cation, CH_3Hg^+, the latter resulting primarily from biotic methylation of the former. Abiotic methylation of Hg is also possible under certain conditions.

Methyl mercury cation bioaccumulates and biomagnifies in aquatic systems. Humans may become intoxicated with mercury via consumption of larger predator fish [14].

In the petroleum industry, the primary methods deployed for removal of Hg from waters and aqueous solutions are adsorption and precipitation. In the author's opinion, the latter removal technique is more robust than the former due to toleration of dispersed oil and treatment chemicals. Ion exchange and membrane filtration removal technologies may have application in the industry provided that dispersed oil and treatment chemicals are precluded to mitigate fouling. Removing the bulk of the Hg by thiol, hydroxide or zerovalent iron precipitation followed by polishing with the adsorbent removal technologies (again provided that oil and treatment chemicals do not adversely affect them) may ultimately prove to be the optimum treatment method. Removal of the Hg precipitates from produced water using sintered metal, automatic backwash filters have been tested in the field with encouraging results.

References

1. S.M. Wilhelm, N. Bloom N., Mercury in petroleum, Process Technol., 63 (2000) 1-27.

2. C.L. Hamann Jr., J.B. McEwen, A.G. Myers, In: F.W. Pontius, Water Quality and Treatment, McGraw-Hill, New York, 1990, pp. 157-187.

3. X. Feng, G. Qui, S. Wang, L. Sang, Distribution and speciation of mercury in surface waters in mercury mining areas in Wanshan, Southwestern China. J. Phys. IV France, 107 (2003) 455-458.

4. N.A. Ozerova, N.R. Mashyanov, V. Ryzhov, Yu.J. Pikovsky, Prediction of mercury-bearing gas deposits (theoretical and environmental aspects). Materials Geoenviron., 51 (2004) 181-185.

5. G. Li, Z. Yuan, Y. Zhuang, H. Jiang, Geological significance of mercury element in petroleum exploration. Watan Yu Huatan, 32 (2008) 143-145.

6. B. Bouyssiere, F. Baco, L. Savary, R. Lobinski, Speciation analysis for mercury in gas condensates by capillary gas chromatography with inductively coupled plasma mass spectrometric detection. J. Chromatogr.A 976 (2002) 431-439.

7. C. Brosset, Total airborne mercury and its possible origin. Water Air Soil Pollution, 17 (1982) 37-50.

8. E.M. Krupp, C. Johnson, C. Rechsteiner, M. Moir, D. Leong, J. Fledman, J., Investigation into the determination of trimethylarsine in natural gas and its partitioning into gas and condensate phases using (cryotrapping)/gas chromatography coupled to inductively coupled plasma mass spectrometry and liquid/solid sorption techniques. Spectrochemica Acta Part B: At. Spectrom., 62 (2007) 970-977.

9. B. Bouyssiere, F. Baco, L. Savary, H. Garraud, D.L. Gallup, Investigation of speciation of arsenic in gas condensates by capillary gas chromatography with ICP-MS detection. J. Anal. At. Spectrom., 16 (2001) 1329-1332.

10. G. Raber, K.A. Francesconi, D.L Gallup, Investigation of arsenic speciation in crude oil and natural gas condensate, (2014) manuscript in preparation.

11. S.M. Wilhelm, L. Liang, D. Kirchgessner, Identification and properties of mercury species in crude oil. Energy Fuels, 20 (2006) 180-186.

12. C.A. Salva, D.L. Gallup, Mercury removal process is applied to crude oil of Southern Argentina. Soc. Petrol. Eng. (2010) Paper SPE 138333.

13. N.S. Bloom, D.L. Gallup, On the solubility of mercury in hydrocarbons. *AIChE Spring Meeting 2010 Proc., (2010)* pp. 4.

14. A. Kudo, S. Miyahara, Predicted restoration of the surrounding marine environment after an artificial mercury decontamination at Minamata Bay, Japan - Economic values for natural and artificial processes. Water Sci. Tech., 25 (1992) 217-226.

15. N. Bloom, P. Chu, Abiotic methylation of mercury. 10th Intern. Conf. Merc. Glob. Poll. (2011) FS22-O3.

16. ASTM Method D7482, Standard practice for sampling, storage and handling of hydrocarbons for mercury analysis. 2008, pp. 4.

17. N.S. Bloom, Analysis and stability of mercury speciation in petroleum hydrocarbons. Fresenius J. Anal. Chem. 366 (2000) 438-443.

18. K.S. Ashaghi, M. Ebrahimi, P. Czermak, Ceramic ultra- and nanofiltration membranes for oilfield produced water treatment: A mini review. Open Environ. J. (2007) 1: 1-8.

19. P.K. Parhi, Supported liquid membrane principle and its practices: A short review, J. Chem., 2013 (2013): Article ID 618236, pp. 11.

20. U. Pancharoen, S. Somboonpanya, S. Chaturabul, A.W. Lothonkum, Selective removal of mercury as $HgCl_4^{2-}$ from natural gas well water by TOA via HFSLM. J. Alloys Compounds, 489 (2010): 72-79.

21. A.W. Lothonkum, S. Suren, S. Chaturabul, N. Thamphiphit, U. Pancharoen, Simultaneous removal of arsenic and mercury from natural-gas-co-produced water from the Gulf of Thailand using synergistic extractant via HFSLM. J. Membrane Sci., 369 (2011): 350-358.

22. T.C. Frankiewicz. J. Gerlach, Removal of hydrocarbons, mercury and arsenic from oil-field produced water, (2000) US Patent 6,117,333.

23. D.L. Gallup, J.B. Strong, Removal of mercury and arsenic from produced water. Proc. 13th Intern. Petrol. Environ. Conf. (2006) paper 91.

24. M.B. Gustafsson, B.K. Kaul, B.S. Fox, D.A. Masciola, B. Wanichkal, B. Wastewater mercury removal process. (2011) US Patent 8,034,246.

25. C.G. Weisener, K.S. Sale, D.J.A. Smyth, D.W. Blowes, Field column study using zerovalent iron for mercury removal from contaminated groundwater. Environ. Sci. Technol., 39 (2005) 6306-6312.

26, J.A. Dean, Lange's Handbook of Chemistry, McGraw-Hill, New York. 1985.