



## Full Length Article

# The behavior of mercury in water, alcohols, monoethylene glycol and triethylene glycol



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## HIGHLIGHTS

- Solubility of mercury is reported for water, several alcohols, MEG and TEG.
- Elemental Hg may be stripped from MEG solution by petroleum gas.
- Hg partitions to the distillate phase during regeneration of MEG.
- Hg after inlet separators in rich MEG is particulate HgS.

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## ABSTRACT

The oil and gas industry is becoming aware of the effects of produced mercury on hydrocarbon processing systems, and that produced mercury contaminates processing equipment. The use of technical information is critical to planning for decommissioning, decontamination and waste minimization. To this end, the solubility of mercury in the polar solvents - water, alcohols, monoethylene glycol (MEG) and triethylene glycol (TEG) have been determined from approximately 243 to 373 K. Elemental mercury solubility in MEG and TEG is somewhat higher than that reported previously in the literature when a mass of mercury was agitated for several days in the respective solvent. Elemental mercury was nearly quantitatively stripped from water by natural gas in a small laboratory stripping column, and in a distillation experiment, about 75% of Hg<sup>0</sup> in 40 vol% MEG partitioned to the distillate phase. Elemental mercury is present in process inlet flow lines and can drop out. This is expected if the reservoir is both hot and saturated with elemental mercury (common), and the pipeline is colder (common). However, in the inlet separator, any dissolved mercury is removed by the drop in pressure and the flashing of C1-C4 hydrocarbons. These light hydrocarbons are very effective in stripping Hg<sup>0</sup> from the crude and condensate. What remains in the crude and condensate is particulate metacinnabar, β-HgS. In amine treaters and glycol dehydrators a portion of the Hg<sup>0</sup> in the gas can react with traces of oxygen to form heat-stable salts. These can further react to form Hg-rich sludges. The success of the experiments will be useful to the industry in understanding the behavior of mercury in polar solvents, gas hydrate inhibition and in glycol and amine contactors.

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## 1. Introduction

The awareness of toxic volatile metals such as mercury (Hg) in the petroleum industry is steadily increasing. Drilling into deeper and hotter reservoirs increases the probability of encountering Hg in produced fluids. Mercury is a naturally occurring trace constituent of crude oil, natural gas, and natural gas condensate, and virtually all geologic hydrocarbons contain measurable quantities. Recent shale gas and coal bed methane Hg detection from the

Americas to Australasia have impacted the hydrocarbons processing industry's risk to midstream and downstream processing. Trace metals including Hg are scavenged by carbon/stainless steel (adsorbed/chemisorbed) into interfacial surfaces and can complex into scale/metal grain boundaries, requiring special chemistry and chemical application methods for successful decontamination [1,2]. The Hg forms primarily on the interior surface of the scale of the pipe, not in grain boundaries. It forms by a reaction between Hg<sup>0</sup> and the scale oxides and sulfides. As the pipe corrodes and the scale gets thicker, the Hg layer stays on the interior surface. Since the reaction product, β-HgS is primarily on the interior, at least a portion can be removed by aggressive pigging [3].

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Hydrocarbons with elevated Hg levels traditionally have been associated with a limited number of regions around the world. The deep drilling now occurring is producing elevated Hg in hydrocarbons in regions that have not previously experienced the phenomenon [4]. Mercury impacts on the industry range from health and safety risks due to corrosion of aluminum and copper alloys (also known as liquid metal embrittlement), to toxicity to flora and fauna through emissions to the environment, to catalyst poisoning, and to contamination of process equipment that must be ultimately decommissioned [5].

Elemental mercury and its compounds are very toxic leading to severe poisoning symptoms in organisms, and sometimes death. Elemental mercury is a priority pollutant and as such is regulated in the United States due to toxicity, but the risk to personnel and the environment should be underscored by the overarching risk to processes, which can lead to catastrophic failure and explosion of cryogenic trains, which there have been ~10 in as many years. The presence of even trace levels of Hg in oil and gas feed stocks also can require additional environmental and health and safety controls that are well known throughout the industry, but have traditionally been implemented only in regions known to experience elevated Hg. Furthermore, elevated Hg-containing hydrocarbons frequently carry a significant price discount in world markets, since they must be processed using specialty equipment that is not common in most refineries.

The solubility of Hg in petroleum fluids has received much recent interest [6,7–10]. Several factors adversely affect the production, handling and processing of Hg-contaminated fluids. Therefore, it is important to understand the concentrations and forms of Hg that are present in not only produced fluids such as crude oil, natural gas, water and natural gas condensate, but also fluids that are used to process especially natural gas. Gas dehydration, acid gas removal, and chemical treatment processes, (for example, gas hydrate control using methanol or MEG), are all potentially impacted by Hg present in produced fluids. Several oil-field basins around world have Hg 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.

Fields producing elevated mercury concentrations in hydrocarbons and water 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. High Hg crudes are not necessarily low sulfur crudes, however. They are low mercaptan crudes, and usually low H<sub>2</sub>S crudes. Mercaptans react with Hg<sup>0</sup> over time to form β-HgS which decorates the exterior of formation materials. The sulfur species that remain in the crude and do not react with the Hg<sup>0</sup> to form HgS are thiophenic. Thermal degradation of carbonate source rocks often leads to fluid contamination with elevated Hg and carbon dioxide concentrations [11]. In sweet reservoirs, Hg<sup>0</sup> and compounds may be present initially in gas, crude oil, condensate and produced water, whilst in sour reservoirs, Hg will almost always be present as β-HgS.

Bedded coals tend to concentrate Hg and arsenic. As Hg concentrations increase, the rank levels of these coals decrease. It is postulated that certain coal-forming land plants act as concentrators of Hg 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 Hg in hydrocarbons and water is explained by volatilization of Hg in rock at high temperature followed by dissolution in liquids devoid of significant sulfur [12]. That Hg<sup>0</sup> is soluble in both hydrocarbons and water results in contamination of natural gas, condensate, crude oil and water within a reservoir.

Elemental Hg<sup>0</sup> solubility in liquid hydrocarbons follows the general trend of increases with increasing carbon number. Solubility is generally higher in straight chain hydrocarbons than branched hydrocarbons or olefins. Recent work has been published that is designed to allow the prediction of the thermodynamic behavior of Hg<sup>0</sup> in a wide variety of solvents, solvent mixtures, and operating conditions where experimental data are unavailable [8,13,14]. Solubility is higher in aromatics than alkanes, and always increases with temperature [8]. It also follows the general order: alcohols > TEG > MEG > Amines > H<sub>2</sub>O for these pure polar solvents. When the temperature-dependent solubility of Hg<sup>0</sup> in natural gas or liquid hydrocarbons is exceeded, liquid Hg<sup>0</sup> may “precipitate”. Several upstream oil and gas facilities have had to install low point drain systems, such as low temperature separators, slug catchers and other dewpointing system's vessels (cold process where most of the Hg<sup>0</sup> will drop out) dedicated to drain off liquid Hg<sup>0</sup>. Mercury collection systems (Hg collection pots) may be drained manually or automatically. Liquid Hg<sup>0</sup> tends to drop out of gas at about 8.7 °C [15]. Operators drain from the aforementioned pots regularly (sometimes as often as weekly or biweekly basis) to remove the liquid Hg<sup>0</sup> from the system. The liquid Hg<sup>0</sup> is collected in Bethlehem flask containers dedicated for Hg disposal. After the Bethlehem container is full, it is sold, disposed in dedicated injection wells, or transported to local waste treatment company for further disposal/treatment [16].

The solubility of Hg in hydrocarbons is important in understanding its partitioning and distribution in various phases and process fluids. It is important to understand the behavior of Hg prior to decommissioning and plant turnarounds. Furthermore, it is relevant in the pre-planning decommissioning phase, since many operators have not performed any studies, and a last resort is to attempt to understand mercury behavior just before decontaminating production platforms, floating-production-storage units (FPSOs), and midstream processing plants. Although many new assets are constructed with an understanding that Hg mass flux and distribution affect asset risks and risks to process, personnel and the environment change as systems equilibrate and evolve, many assets are in the aforementioned state and close to cessation of production. At this point, obtaining precise quantification, distribution and mass loading data is imperative to develop accurate decontamination and waste minimization plans [17,18].

Unless dynamic reactions occur in un-drilled reservoirs, one expects Hg<sup>0</sup> to achieve vapor-liquid-liquid equilibrium (VLLE) solubility. After penetration of the reservoir with the drill bit and eventual production, Hg<sup>0</sup> is expected to co-migrate to the surface with petroleum either in aqueous solution, the gas phase or as a solute in liquid hydrocarbons. Mercury as β-HgS will accumulate on drill strings and production tubing, and therefore, will affect partitioning and distribution downstream of the wellhead. The change in temperature and pressure during migration of fluids to the surface likely re-distributes Hg<sup>0</sup> in the phases. Fluid cooling from the wellhead to surface allows Hg<sup>0</sup> to condense as liquid droplets, which may adsorb onto sand, clays and waxes. Much of the total mercury fraction, THg, in gas condensate is comprised of suspended particles in the 1–10 μm range. Dimethylmercury, although present in very low concentrations in condensate and produced water, but preferring those phases as the stream cools, requires measuring it upstream where the temperature is elevated (at first separation of the condensate). Note also that during the regeneration cycle of dehydrators, dimethylmercury can be measured in not only the gas phase, but also in the aqueous knockout vessel [6].

The speciation of Hg is critical to the development of methods to manage it. This is an active area of research. Elemental Hg can drop out if the temperature of the separator (or pipe) is less than the reservoir temperature (this is common). Prior to stabilization

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