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Unconsidered Mercury Emissions from the Oil and Gas Industry

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General Background

Mercury in any of its three forms (elemental mercury, inorganic salts, and organic compounds) is a highly toxic element that is found both naturally and as a globally dispersed contaminant in the environment.

Natural sources of atmospheric mercury include volcanoes, geologic deposits of mercury, and volatilisation from the ocean. Concentrations in rocks, sediments, water, and soils are generally low, although naturally high levels have been found in some mineral formations and thermal springs.

Widely recognised sources of anthropogenic mercury emissions and releases to both air and water include coal burning, mining, smelting, the production of iron and non-ferrous metals, cement production, the incineration of medical waste, the chlor-alkali industry, dental amalgam, waste from consumer products, and various mining activities. Once in the atmosphere, mercury is dispersed and can circulate for years leading to widespread distribution. On contact with surface water, mercury may be converted from one form to another. Some will enter the food chain, generally through a variety of bacterial mechanisms that involve the conversion of inorganic mercury to the considerably more toxic methylmercury.

Mercury toxicity most commonly affects the neurologic, gastrointestinal and renal organ systems. Poisoning can result from mercury vapour inhalation, mercury ingestion and absorption of mercury through the skin. Thus, mercury can be a threat to the health of people and wildlife in many environments with the overall risk being determined by (i) the likelihood of exposure (ii) the form of mercury present, as some forms are more toxic than others, and (iii) the geochemical and ecological factors that influence how mercury moves and changes form within the environment.

Mercury in the Oil and Gas Industry

Mercury is found in almost all oil and gas reservoirs, principally produced in the elemental (metallic) form but can react to form mercuric sulphide and soluble ionic mercury during production and processing.

Although there is some potential for worker exposure to toxic mercury at plants that process oil and gas, the concentrations found in such fluids are generally too low for any serious health risk to be generated from direct exposure to the gas or fluid. The biggest potential risk to workers arises during plant shutdowns or during service/maintenance work when mercury that has accumulated into the internal surface of processing equipment via adsorption can be released to the atmosphere after depressurisation of the system. This process is accelerated if any hot work is carried out (e.g. cutting or welding) and can be particularly problematic in confined spaces where the mercury concentration could potentially be above the occupational exposure limit (OEL). The OEL for mercury varies from region to region but is typically in the range 20 - 50 µg/m^3.

If not monitored and controlled correctly a plant contaminated with mercury can lead, not only to worker exposure during planned plant shutdowns, but also release of mercury to the environment and subsequent entry into the food chain via biotransformation into organic mercury.

Previous studies designed to evaluate mercury emissions from the oil and gas industry have either taken into consideration the mercury in the stabilised oil only or have made the assumption that gas plants equipped with mercury removal units (MRUs) capture all of the mercury present, resulting in no environmental release.

Qa^3 studies at gas separations plants and oil refineries have shown that, within such facilities, mercury may be released to the environment via a number of process outlets that are generally not recognised or considered by the oil and gas industry as sources of environmental mercury emission. This article describes the outlets and presents data from real world examples in order to highlight a potentially large problem that requires attention and perhaps, in some plants and refineries, modifications to current practices.

Sources of Unconsidered Emission

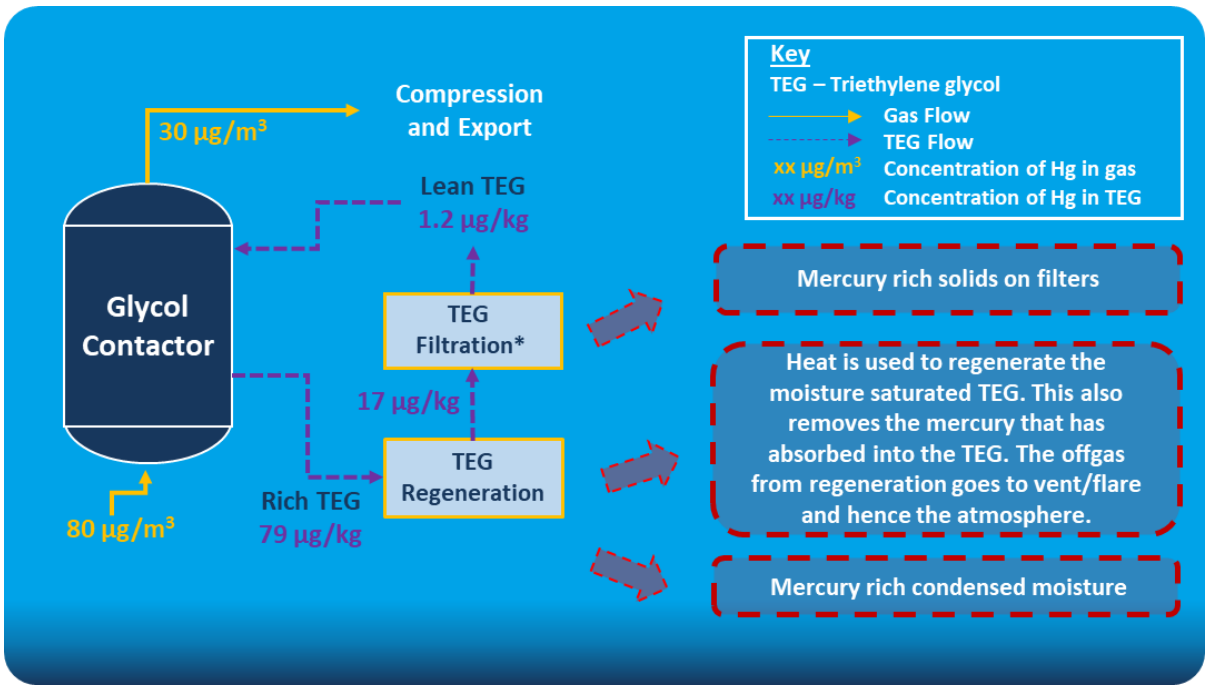
It is estimated that annual global mercury emissions from the oil and gas industry could be:

~ 90 tonnes

There are a number of potential sources of unintentional mercury release to the environment which are discussed in this document.

Molecular Sieve and Glycol Regeneration Cycles: Molecular sieves and glycols are designed to remove moisture from hydrocarbon gas; however, they also have the secondary effect of absorbing mercury from the gas. During the absorption cycle the moisture, together with a proportion of any elemental mercury present is continually removed from the gas. After the absorption cycle, the molecular sieve or glycol enters a regeneration mode, where the dehydration material is heated to drive off moisture. As the system is heated, in addition to the water, mercury is also desorbed from the molecular sieve / glycol. This spike in mercury

concentration in the offgas from regeneration, depending on the process design, will either re-enter production (most commonly for molecular sieve driers) or be vented to atmosphere (most common for glycol driers) or sent to flare as an unconsidered, unintentional emission to the environment.

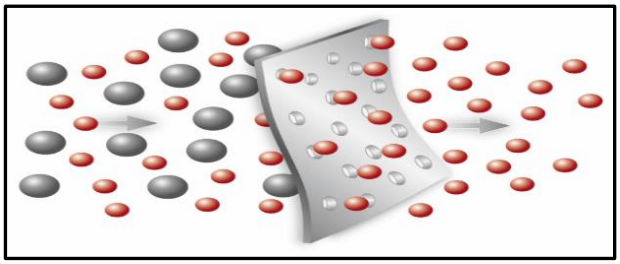


Gas to Flare: Flaring operations are very common throughout exploration and production of hydrocarbons. Flaring during exploration and appraisal well testing is performed due to the inability to reinject the flow of fluids back into the reservoir or feed product into existing production systems. Testing of such wells can last anywhere from a few hours to several weeks and generally, for the entirety of the test, all of the produced oil and gas is sent to flare during which time all trace non-hydrocarbon contaminants, including mercury, will be released to the environment.

In production systems, where gas isn't sent to sales pipelines or into a national grid-based network, it is normally flared within a license agreement with local governance. This will occur, for example, when there is no infrastructure in the region to accept the gas and economically it is not viable to put in the infrastructure but it is still desirable and economical to produced crude oil.

In some circumstances, if there is a problem with the processing system, for example, failure of a gas compressor, then the gas will be sent to flare until such a time as the wells can be shut in. If the gas contains mercury and has not been pre-treated by passing through an MRU beforehand, then this mercury will be released to atmosphere as an unconsidered, unintentional emission.

CO_2 and N_2 Removal: Many refineries around the world incorporate removal technologies to strip out chemical components that are considered undesirable contaminants or reduce the overall calorific value of the gas thus dropping the overall product value. In some instances, where CO_2 and/or N_2 removal is required, membrane technology may be employed.



It is well known that, in addition to the CO_2 and N_2, membrane technology will also remove mercury from the natural gas. This mercury will be released to the atmosphere as part of a continuous removal process and also when the membrane material is changed and replaced during maintenance.

Acid Gas Removal: Acid gas removal systems are a necessary tool used to remove corrosive and toxic acid gases such as H_2S and CO_2; however, they are known to also remove a proportion of the mercury from the gas. In amine-based systems as well as absorbing elemental mercury into solution, it is postulated that mercury removal by the amine solution is also based on the chemical reaction between sulphur and mercury forming mercury sulphide. The amine will react with H_2S to form stable soluble sulphides in solution and the sulphides, in turn, can react with elemental mercury to form mercury sulphide:

$$\mathbf{RNH_2 + H_2S \rightleftharpoons RNH_3 + SH^-}$$
$$\mathbf{SH^- + Hg^0 \rightleftharpoons HgS + H^+}$$

Mercury can be emitted to the environment via two mechanism:

1. The solid mercuric sulphide formed is removed from the amine by filtration within the amine regeneration system. When the filters are changed the spent filters may not be recognised as mercury contaminated and so may be disposed of through an inappropriate route resulting in mercury release to the environment.
2. The regeneration process that re-volatilises sour gases from the liquid amine will also drive off any absorbed elemental mercury from the liquid into the vapour phase which will mobilise with the gas fraction. This gas will then either be sent to flare, resulting in direct mercury release to the atmosphere, or be directed into a sulphur recovery unit where the mercury will react to reform mercury sulphide.

Pipework and Equipment: Elemental mercury may adsorb onto the internal surfaces of new pipework and process equipment. Additionally, overtime a mercury rich scale can develop on internal surfaces from the reaction of elemental mercury with iron sulphide to form mercury sulphide. The adsorption / chemisorption of mercury will continue over the active lifetime of the plant. Upon decommissioning, without careful consideration of the mercury content of the metal, the regimens employed to discard / abandon old pipes and process equipment, such as (i) abandonment *in situ* (e.g. for subsea pipelines) (ii) heating and cutting of the metal into smaller manageable sections or (iii) smelting of the steel back into a recycled reusable form, could inadvertently release mercury into the environment.

Waste Solids and Sludge: The processing of oil and gas generates some waste streams which may contain significant concentrations of mercury. For some of these, the presence of mercury is expected, for example, the mercury bed media at end of life will contain high percentage concentrations of mercury and should be disposed of through approved routes; however, for some wastes, it may not be recognised that these could potentially be high in mercury (sometimes % levels) and should be treated as mercury waste. Some examples of these are:

- Mercury rich particulates present in filters on amine, glycol, caustic and water systems.
- Mercury rich solids in filters used on heavy ends recovery systems (systems used to condense heavier hydrocarbons out of gas streams).
- Sludge from pigging activities and sludge accumulated in storage tanks.

Effluent Water: Most production platforms and refineries worldwide have strict regulations imposed on the maximum allowable concentration of trace contaminants in water that is discharged back into the environment; however, there are locations where local governance have yet to include controls on the maximum allowable mercury in discharge water. If this produced water contains mercury and is not treated, this will result in an unconsidered emission of mercury to the environment.

Atmospheric Venting of Oil Cargo Tanks: Atmospheric venting of oil cargo tanks to avoid pressure build, can result in mercury emissions with the LPG rich vent gas.

Estimations of Global Unconsidered Emissions from the Oil and Gas Industry

The tabulated data below shows annual production rates for Crude Oil, Natural Gas and LPG worldwide and estimated mercury concentrations in those products from across the seven largest hydrocarbon producing regions.

Continent / Region	Annual Production*			Estimated Average Mercury Concentration#			Estimated Annual Mass of Mercury Produced (tonnes)	Estimated Annual Mercury Emission Assuming 30% Losses (tonnes)
	NG (Bm^3)	CO (Mt)	LPG (Mt)	NG ($\mu g/m^3$)	CO (µg/kg)	LPG (µg/kg)		
Europe	236	149	13	6	12	60	4.0	1.2
North America	1128	927	188	15	15	90	48	14.3
Latin America	174	289	11	25	20	120	11	3.4
CIS	847	711	10	15	10	100	21	6.2
Asia Pacific	672	350	19	140	110	1000	152	45.6
Africa	238	394	15	30	25	150	19	5.8
Middle East	695	1321	119	20	15	90	44	13.3
TOTALS	***3989***	***4141***	***377***	-	-	-	***300***	***90***

** Based upon data collected by BP – 'Statistical Review of World Energy 2020, 69th edition'*
 # Based upon Qa³ project experience, observations and available literature
NG – Natural Gas, CO – Crude Oil, LPG – Liquefied Petroleum Gas

The estimation of the total mass of mercury in natural gas and LPG for each region has been calculated taking into account the annual production data (*Statistical Review of World Energy 2020, 69th edition*) and the average mercury concentrations found in these fractions by Qa³, supplemented where necessary by other available literature. The mass of mercury emitted through unconsidered emissions per year is estimated taking into account the routes for mercury emissions discussed in this document and Qa³'s experience in what this accounts for in terms of the overall mercury present in the feedstocks to the processing and refining facilities.

Conclusions

The percentage of mercury present in produced oil and gas that is released into the environment through unconsidered emissions can vary significantly from facility to facility and from one geographical location to another. Qa³ has monitored the concentration of mercury in oilfield products from numerous offshore and onshore production systems across the globe for many years and has witnessed that, despite improvements in process and refining technology, there is still a significant total mass of mercury unintentionally lost to the environment through unconsidered emissions. The most effective way to eliminate any unwanted unconsidered emission of mercury from an oil and gas facility to the environment is to install MRU systems as far upstream in the process as possible and where MRUs are not

installed, a full assessment of mercury within the process should be carried out to identify the mercury concentrations present and where losses are occurring.

The accuracy of the Qa^3 estimations of the unconsidered mercury emissions from the processing of oil and gas is of course a matter of contention as it is difficult to determine whether or not the data obtained by Qa^3 studies in each region is representative of the true average and also whether the estimate of 30% loss across the board is accurate, conservative or an overestimate. However, for natural gas alone, based on a current global annual production of four trillion cubic metres, Qa^3 estimate that the total mass of mercury generated from natural gas is 150 tonnes, which equates to a weighted average global mercury concentration of 37.6 µg/Nm^3. If this average concentration is applied to the 2015 global production of 3.59 trillion tonnes, then the total mass of mercury generated from natural gas would have been 135 tonnes. From communications with mercury reclamation companies, UNEP have estimated that the total mass of mercury captured from natural gas by mercury removal systems in 2015 was 30 – 100 tonnes. Clearly, there is a significant discrepancy between the respective estimations of mass of mercury produced and that captured, which suggests that a significant proportion of the mercury in natural gas is either lost to the environment or accumulates in pipework and process equipment. This accumulated mercury has the potential to enter the environment if decommissioning is not carried out in a considered manner.

The intention of this document is not to provide a wholly accurate quantification of such emissions, but rather to provoke thought and discussion and suggest the possibility that previously published figures may be a significant underestimate. The UNEP Global Mercury Assessment (2013) did not quantify mercury emissions and releases associated with the flaring, extraction and transport of oil and gas and estimated that in 2010 the total global emissions to the atmosphere resulting from oil and gas refining was in the range 7.3 - 26.4 tonnes, representing ~1% of the total anthropogenic emissions (1960 tonnes). Clearly, Qa^3 estimation of 90 tonnes of unconsidered mercury emissions, if anywhere near accurate, is an order of magnitude higher than previous estimates and would not only have a significant impact on the environment but would also require a radical rethink across the industry in the approach to identifying and controlling mercury issues which are currently largely unrecognised.

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