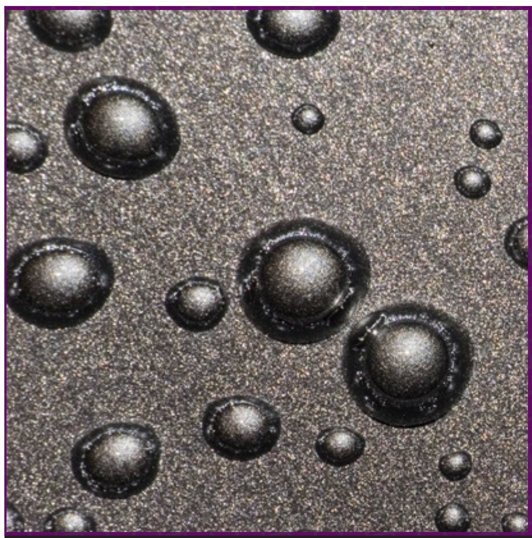


Unconsidered Mercury Emissions from the Oil and Gas Industry

Qa³ Ltd
Unit 3, The Calvert Centre, Woodmancott, Winchester, Hampshire SO21 3BN United Kingdom
Email enquiries@qa3.co.uk • Web www.qa3.co.uk • Tel + 44 (0) 1256 397390

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, mercury injection 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 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 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 to 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 (MRU) capture all of the mercury present resulting in no environmental release.

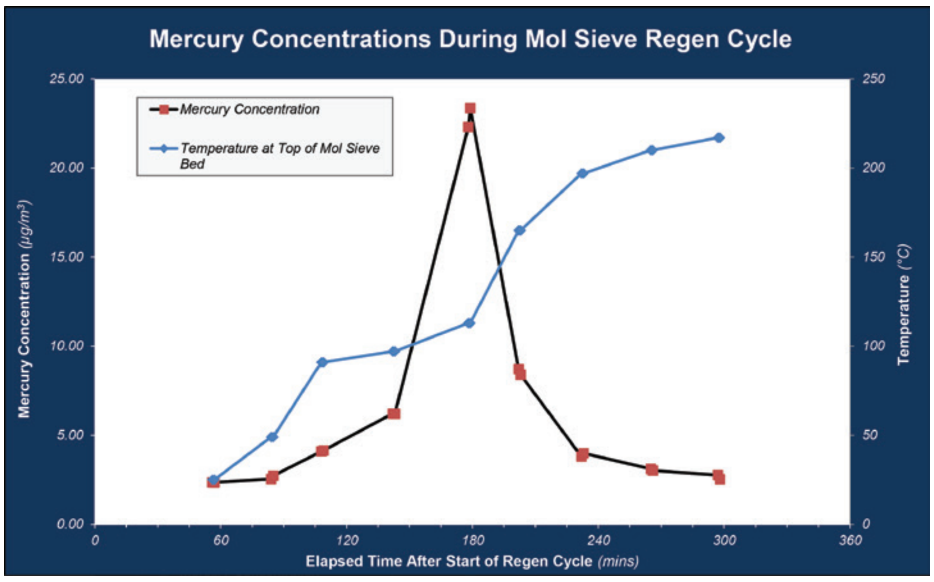
Our studies at gas separations plants and oil refineries have shown that mercury may enter the environment via a number of process outlets within such facilities that are generally not recognised or considered as sources of environmental mercury emission by the oil and gas industry or the United Nations Environment Programme (UNEP). 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 unconsidered global mercury emissions from the oil and gas industry couldrange from:

There are a number of potential sources of unintentional mercury release to the environment which shall be discussed.

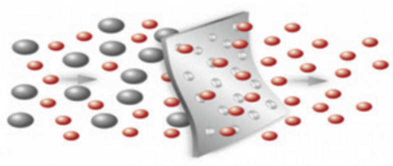
Molecular Sieve Regeneration Cycle: Molecular sieves are designed to remove moisture from hydrocarbon gas; however, they also have the secondary effect of adsorption mercury from the gas. During the adsorption cycle the moisture, together with any elemental mercury present is continually removed from the gas. After the absorption cycle, the molecular sieve enters a regeneration mode, where the system is heated to drive off moisture. As the system is heated mercury is also desorbed from the molecular sieve and as shown in the graph below, when the temperature of the heating cycle reaches approximately 100°C, nearly all of the adsorbed mercury is desorbed. This spike in mercury concentration, depending on the process design, will either re-enter production or be dispelled to atmosphere 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 off within a license agreement with local governance. In many circumstances, if the refining system experiences surges in production where the pressure increases too much or the gas : liquid ratio (GLR) increases such that the total volume of gas cannot be passed through the process, then a proportion of the gas will be sent to flare. 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.

Flaring Operations



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 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 it is postulated that mercury absorption into the amine solution is based on the chemical reaction between sulphur and mercury forming mercuric 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 mercuric sulphide:

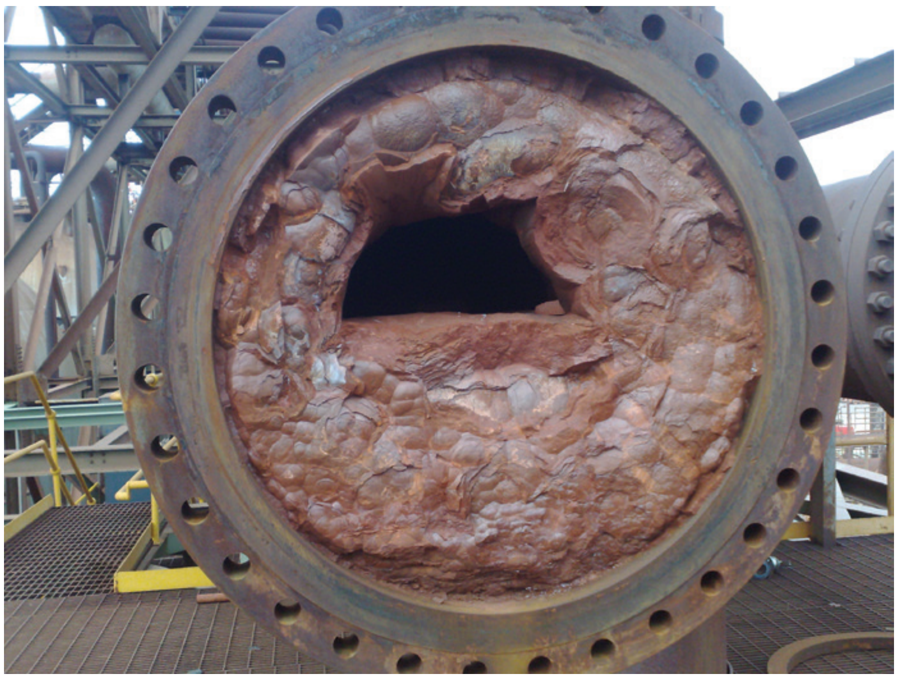
$$\mathbf{RHN_2 + H_2S \rightleftharpoons RNH_3 + SH^-}$$
$$\mathbf{SH^- + Hg^\circ \rightleftharpoons HgS + H^+}$$

Mercury can be emitted to the environment via two mechanism; (i) the formation of solid mercuric sulphide may remain in the amine column and, during maintenance shutdowns, could be discarded as waste that is incorrectly categorised and sent to normal refuse sites where the mercury can leach into the water table, (ii) the regeneration process that re volatilise sour gases from the liquid amine will also drive off any absorbed 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 mercuric sulphide.

Pipework and Equipment: The internal surfaces of new pipework and process equipment are populated with active sites to which mercury will adsorb. The adsorption 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 old pipes and process equipment, such as heating and cutting of the metal into smaller manageable sections or smelting of the steel back into a recycled reusable form, could inadvertently release mercury into the environment.

Equipment Decontamination

Waste Solids and Sludge: In many global locations solid waste is not correctly categorised and / or checked routinely for mercury as a contaminant. Some of the solid waste products may contain up to percentage concentrations of mercury and be disposed of in normal refuse sites where the mercury can potentially leach into the environment over time.



Pipeline Solid Waste

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 fed into surface waters, this will result in an unconsidered, unintentional emission of mercury to the environment.

Estimations of Global Unconsidered Emissions from the Oil and Gas Industry

The tabulated data below shows annual production rates for natural gas and LPG worldwide and mercury concentrations in those products from across the eight largest hydrocarbon producing regions.

Continent / Region	Annual Production*		Average Mercury Concentration#		Estimated Annual Mass of Mercury	
	NG	LPG	NG	LPG	Produced	Unconsidered Emisssions
	(Bm^3)	(Mt)	($\mu g/m^3$)	($\mu g/kg$)	(t)	(t)
Europe	**286**	**647**	**5**	**40**	**27**	**5**
North America	**845**	**955**	**10**	**60**	**66**	**13**
Latin America	**229**	**351**	**20**	**50**	**22**	**4**
CIS	**878**	**328**	**10**	**100**	**42**	**8**
Asia	**429**	**1262**	**350**	**1000**	**1412**	**282**
Pacific	**60**	**37**	**30**	**60**	**4**	**1**
Africa	**189**	**110**	**30**	**90**	**16**	**3**
Middle East	**561**	**399**	**20**	**80**	**43**	**9**
TOTALS	***3477***	***4089***	**-**	**-**	***1632***	***326***

** Based upon data collected by Enerdata – 'Global Energy Statistical Yearbook 2014 (2013 Figures)'*

 # Based upon Qa³ chemists project experience, observations and available literature

NG – Natural Gas, LPG – Liquefied Petroleum Gas

The estimation of the total mass of mercury in natural gas and LPG for each region has been calculated taking from the annual production data *(Enerdata – 'Global Energy Statistical Yearbook)* 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 on the assumption that processes that have the secondary effect of removing mercury from gas or LPG absorb / adsorb ~20% of the total mass of mercury from the product. The estimate that 20% of mercury may be lost to such refining process units or pipework is calculated based upon extensive Qa³ experience and measurements of mercury distribution within refining systems, however, in some instances the losses of mercury may be far greater than 20%.

Conclusion

The percentage of mercury emitted to the environment through unconsidered emissions can vary significantly from refinery to refinery 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 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.

The accuracy of the Qa³ estimations of the unconsidered mercury emissions from the processing of oil and gas is of course a matter of contention. 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 (1960 tonnes). Clearly, Qa³ estimations of 326 tonnes of unconsidered mercury emissions, if anywhere near accurate, would have a significant impact on the environment and 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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