Qa³ On - site Chemistry

Information Sheets

Reference	**INF-016**
TITLE	Mercury Contamination in Oil and Gas Infrastructure Destined for Decommissioning

SUMMARY

During production of oil and gas, mercury is known to accumulate on the internal surfaces of process infrastructure. Aged facilities that have reached the end of their operational life and are selected for decommissioning may pose a serious risk to health and the environment. This applies to equipment destined to be left in-situ as well as equipment that is going for recycling via smelting .

Background

As oil and gas fields reach the end of their production life, they must be decommissioned. This is a complex task involving wells being plugged in preparation for abandonment and topside infrastructure being safely and efficiently dismantled and removed. With a large number of offshore rigs expected to reach the end of their production cycle over the next ten years, the annual global budget of decommissioning is expected to be in the tens of billions of dollars.
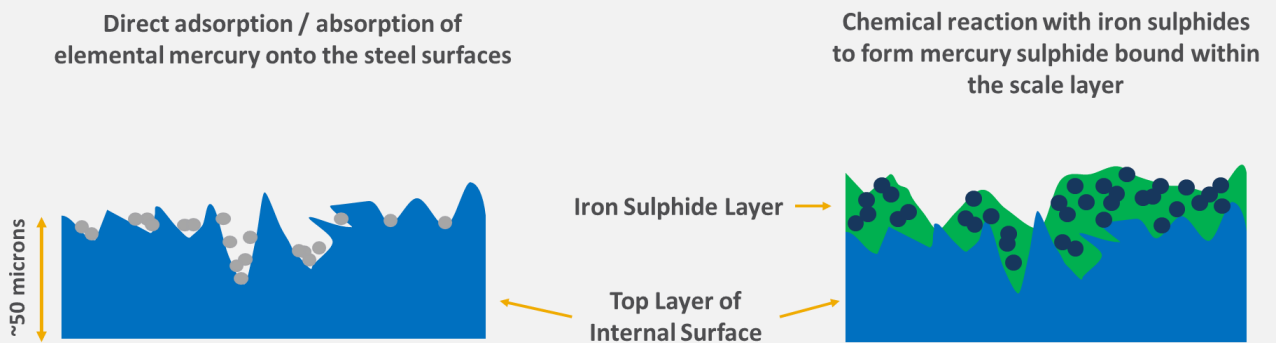
Decommissioning offshore assets is an exhaustive process that encompasses;

- Platform preparation
- Well plugging and abandonment
- Removal of subsea assets
- Topside removal of rig / platform
- Pipeline and power cable removal
- Material disposal / recycling

The entire process needs to be sustainable with minimal impact on the environment and as much recycling of the materials as is practically possible.

With regard to future decommissioning, the highest research priority is for the assessment of impacts of contaminants, including mercury and NORM, and to derive acceptable environmental limits to reduce potential for ecological harm [1].

Mercury is ubiquitous in oil and gas reservoirs with a wide variety of concentrations across the globe. It is well documented that where mercury is present in the produced oil and gas, it will deposit onto the internal process infrastructure via several mechanisms including chemisorption, adsorption [2], and most notably the reaction with iron sulphide scales [3] to form mercury sulphide, which becomes part of the scale layer. Thus, aged facilities that have reached the end of their operational life and are selected for decommissioning may pose a serious risk to health and the environment.

Direct adsorption / absorption of elemental mercury onto the steel surfaces

Chemical reaction with iron sulphides to form mercury sulphide bound within the scale layer

~50 microns

Iron Sulphide Layer →

← Top Layer of Internal Surface →

Qa^3 has conducted mercury measurements on hundreds of steel coupons taken from dozens of decommissioned oil and gas asset process equipment, both topside and subsea, and have found **mercury concentrations, expressed in whole steel, ranging from 0.004 mg/kg up to 1510 mg/kg**.

Whilst mercury concentrations at the parts per million level may sound low it has been shown that these concentrations can both exceed recommended levels for leaving *in situ* on the seabed, and in the case of recycling, can result in large masses of mercury released to the environment as well as the potential for worker exposure at steel smelters.

Hg Contaminated Equipment to be Left *in situ* on the Seabed

There is a good argument for some equipment (typically long distances pipelines) to be left *in situ* on the seabed since it often supports a diverse set of marine life and thus removal may actually cause significant negative impact; however, the transfer of the mercury into the local ecosystem during decay of the pipeline needs to be taken into consideration as part of the environmental impact assessment. Decomposition of the pipe and transference of mercury to sediment and subsequently marine organisms becomes significant when it gives rise to a concentration in the sediment above single parts per million[3]. Therefore, there only needs to be parts per million concentrations of mercury in the steel for a high chance of mercury affecting the local environment during the decay process.
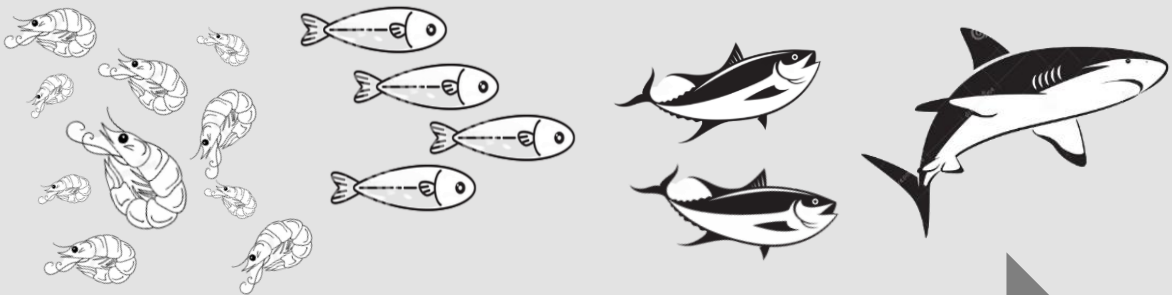
Biomagnification of Mercury

Hg Contaminated Equipment Sent for Smelting

In many regions there is no set legislation or regulations governing the maximum concentration of mercury in steel sent for smelting to be recycled; Some regions state that *'zero'* mercury is allowed although often no measurements are made to verify the steel is mercury free. In Thailand, for example, there is no limit set for smelters and the closest applicable specification limit (at the time of writing) is that set by the MOI for the maximum allowable mercury in landfill waste (Industry Waste Disposal B.E. 2548 specification), which is 20 mg/kg. The U.S. EPA set a limit for mercury in the smelting of scrap cars that potentially have mercury-containing electronic switches, at 0.5 grams mercury per 1.4 metric tons of steel (0.36 mg/kg), but there is no specific limit for mercury contaminated equipment from the oil and gas industry.

Whilst concentrations in the parts per million range may sound like low concentrations, due to the potentially large masses of steel that may be smelted over a relatively short period of time, rapid releases of significant masses of mercury may occur as all forms of mercury will be released as elemental mercury vapour at the temperature used during smelting. Without suitable controls, there may not be sufficient protection for workers involved in the smelting of steel originating from the oil and gas industry.

Predicting the level of worker exposure is not straightforward as there are a number of variables and unknowns. The figures provided in this document are theoretical and are provided to (i) highlight the potential for the release of significant masses of mercury even though the concentration in steel is in the parts per million range and (ii) to further the industry's understanding of the issue and promote further investigation and work.

Calculated Prediction for Mercury Released and Potential Worker Exposure

The potential for harm from smelting steel contaminated with ppm concentrations of mercury can be gauged by calculating potential theoretical mercury emission and worker exposure during smelting operations. In order to make this calculation a number of assumptions about the smelting process need to be made.

- Concentration of mercury in steel
- Mass of steel smelted
- Time for mercury to be released
- Area into which mercury diffuses

Batch sizes during smelting generally fall in the range 10 – 30 tonnes with a smelting time of approximately one hour. Thus, if a batch of steel with a mercury concentration of just 20 mg/kg was placed in an open smelter system within an enclosed building volume of 36,000 m³ (60 m x 30 m x 20 m), and as is normal practice during smelting, some workers are standing in close proximity (within 20 m) of the smelting pot in an effective space volume of 8000 m³ (assuming dimensions of 20 m x 20 m x 20 m), the potential mercury concentration in the whole building and in the atmosphere in close proximity to the smelting pot liberated from the steel can be calculated. Again, some assumptions need to be made on how quickly the mercury released at the beginning of each smelting process is diluted by air to a zero level, for the purposes of this calculation a 10 minute exposure time has been used.

| Parameter		Units	Mercury Emission into Large Area (Building)	Mercury Emission into Small Area (vicinity around smelter that workers may enter)
Mercury Content of Scrap Steel		ppm m/m (mg/kg)	20	20
Mass of Steel placed in Smelter		(Tonnes)	20	20
Area into which Mercury is Emitted	Length	(m)	60	20
	Width	(m)	30	20
	Height	(m)	20	20
	Volume	(m^3)	36000	8000
Occupational Exposure Limit for Mercury (8 hour TWA)		(mg/m^3)	< 0.020, < 0.025 (depending on region)	
Mercury Concentration in Atmosphere when Mercury Initially Released		(mg/m^3)	11.1	50
Number of Smelting Operations Per Day		(per 8 hours)	5	5
Time of Exposure for Each Smelting Operation		(minutes)	10	10
Occuptaional Exposure for 8 Hour Period		(mg/m^3)	1.2	5.2
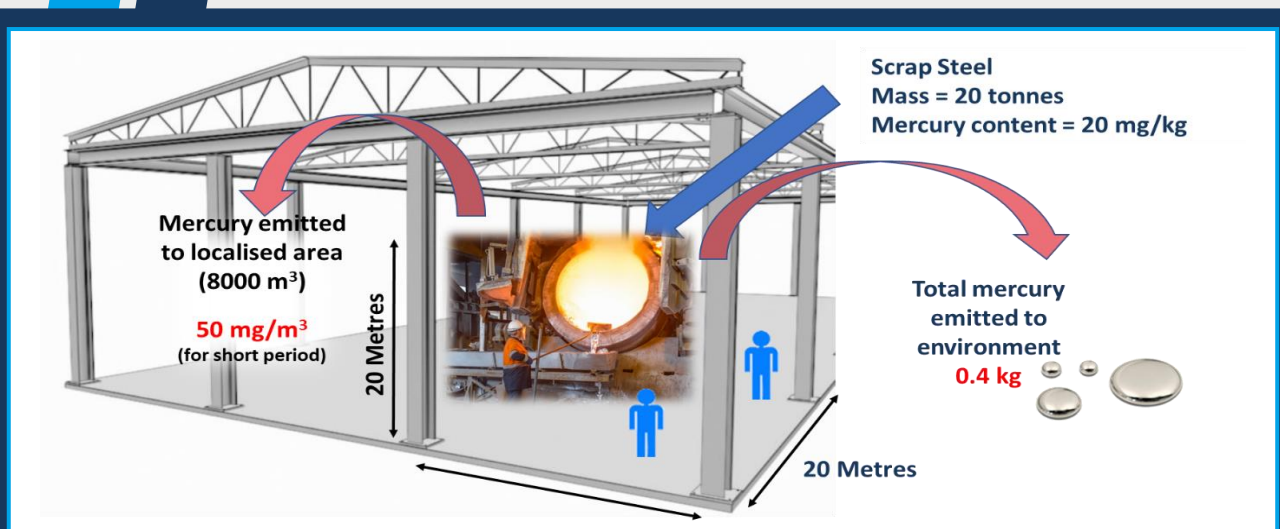
In the case of close proximity and indeed the whole building, the potential mercury concentration in the atmosphere would exceed the OEL (≤0.020, ≤0.025 mg/m^3) for mercury; however, it should also be taken into consideration that there will be some natural air dilution within the building so workers would not be exposed to this concentration for the duration of an 8-hour working day (the OEL is a time weighted average for an 8-hour period). It should also be noted that, according to NIOSH, a concentration of 10 mg/m^3 of mercury is immediately dangerous to health (even for short periods).

Due to the number of variables, in order to fully evaluate the potential for worker exposure, controlled experiments would need to be carried out at the smelting site to measure the mercury released during the smelting operation.

Based simply on this theoretical calculation, with the assumptions already discussed, the appropriate concentration of mercury in steel to give a TWA exposure at half the OEL would be approximately 0.05 mg/kg.

Some, but not all smelters have extraction systems built into the design of the smelting works.
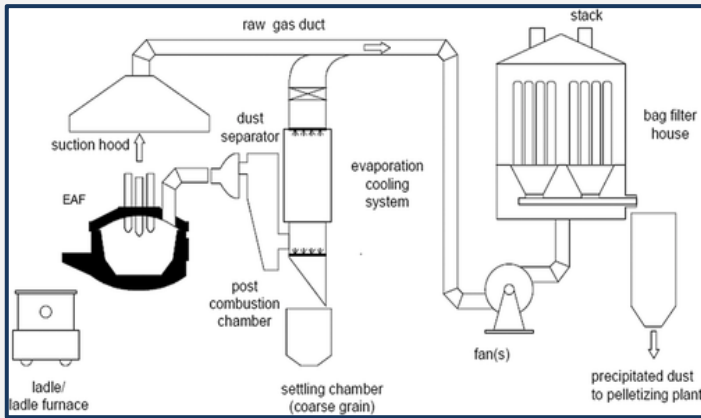
It is possible theses extraction systems will reduce or eliminate the potential for worker exposure, depending on how efficient they are at capturing the released mercury vapour. Confirmation of how effective each system is can be gained only from direct monitoring.

It is worth noting, that where extraction hoods are fitted, they are commonly positioned several metres above the furnace and so may not extract all mercury evolved.

These systems incorporate a *'bag filter'*, 'however, these are designed to capture dust particulate and will not capture any of the released mercury vapour, which will be emitted to the environment.

The example given in this document is a simplified calculation designed to raise awareness of the potential for steel, with apparently very low mercury concentrations, to result in localised atmospheres that may be hazardous to health during smelting. Many other factors including the design of the smelters, the total mass of steel smelted over a given time period, the rate at which the steel is smelted, the ventilation afforded, the availability of appropriate PPE, the proximity of the workers to the smelters and the length of exposure of workers to the most hazardous areas would all need to be taken into consideration in order to evaluate an accurate risk to health; however, there is sufficient evidence that, without suitable controls, the specification limits being applied in some regions for smelting that were originally designed for landfill applications, where a slow release of mercury over an extended period of time may be expected, may not afford sufficient protection to workers involved in smelting contaminated steel, where considerable masses of mercury may be released over a short period.

In addition to the potential for workplace air to be above OEL levels, consideration also needs to be given to the overall emissions of mercury to air from the smelting of mercury contaminated steel. For example, consider a pipeline with a 219 mm diameter and 11 mm wall thickness that contained just 20 mg/kg (parts per million) of mercury. If 10 km was sent for smelting, this would be 569 tonnes of steel which would give rise to the emission of 11.4 kg of mercury.

10 km of Decommissioned Pipeline Mercury Content = 20 mg/kg (ppm)

Smelted in Arc Furnace

Total Mercury Emitted to the Environment
11.4 kg

As already stated, due to the number of variables, in order to fully evaluate the potential for worker exposure, controlled experiments would need to be conducted at the smelting site to measure the mercury released during the smelting of steel with known mercury concentrations.

Semi-quantification of mercury in steel is most conveniently carried out *in-situ* using a portable XRF analyser (a portable easy-to-use analytical instrument). This technique measures mercury only at the surface and cannot be used to gain an accurate concentration in whole steel, it is, however, a useful tool for establishing the extent of mercury contamination and also assessing the effectiveness of any decontamination treatment applied. In order to be able to convert a surface measurement in mg/kg to a whole steel measurement an assumption must be made on the depth of the mercury/scale layer. Hence, this technique can only ever provide semi-quantitative data in terms of mercury in whole steel. These instruments also have sensitivity limitations; Qa[3] has experience of portable XRF's from three separate manufactures and have observed detection limits for the measurement of surface mercury on steel in the range 80 - 300 mg/kg.

A calculation is then required to express the surface measurement yielded by XRF into a *'semi-quantitative total mercury in steel'* concentration, taking into account the dilution factor exerted by the main body of steel. Research work carried out by the Qa[3] laboratories involving comparison of data obtained by portable XRF with that obtained by acid digestion and quantification by AAS on hundreds of coupons allows for the estimation of a suitable factor, such that a surface measurement by pXRF of 1000 mg/kg equates to approximately 2.7 mg/kg for a section of steel with a thickness of 13 mm. Therefore, the lowest limit of detection of the pXRF (80 mg/kg) when expressed in whole steel terms for 13 mm steel is 0.24 mg/kg. For thinner steel this value would increase proportionally.


Therefore, whilst pXRF is a convenient tool to assess the extent of mercury contamination, based on the theoretical calculations and assumptions made for emission of mercury during smelting, the pXRF instruments may not be able to measure sufficiently low enough to quantify a safe level for the purposes of sending steel for smelting; thus, accurate measurement by acid digestion followed by Atomic Absorption Spectrometry is recommended.

Acid Digestion
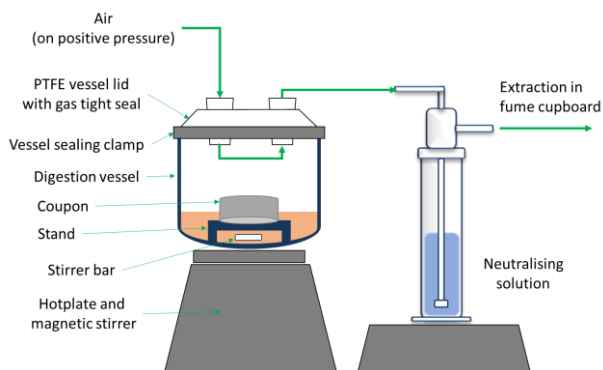
Atomic Absorption Spectroscopy (AAS)
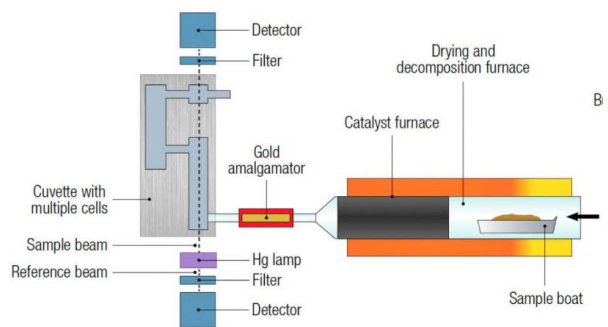
Solutions for the Oil and Gas Industry

There are proven technologies that allow process equipment and pipelines to be mercury decontaminated. These treatments will remove > 90% of the mercury contamination. The waste mercury waste generated in the decontamination procedure is collected, concentrated and then disposed of through approved routes that ensure the mercury is not put back into the environment.

Pipeline in Operation

80 µg/kg Hg

30 µg/kg Hg

10 µg/kg Hg
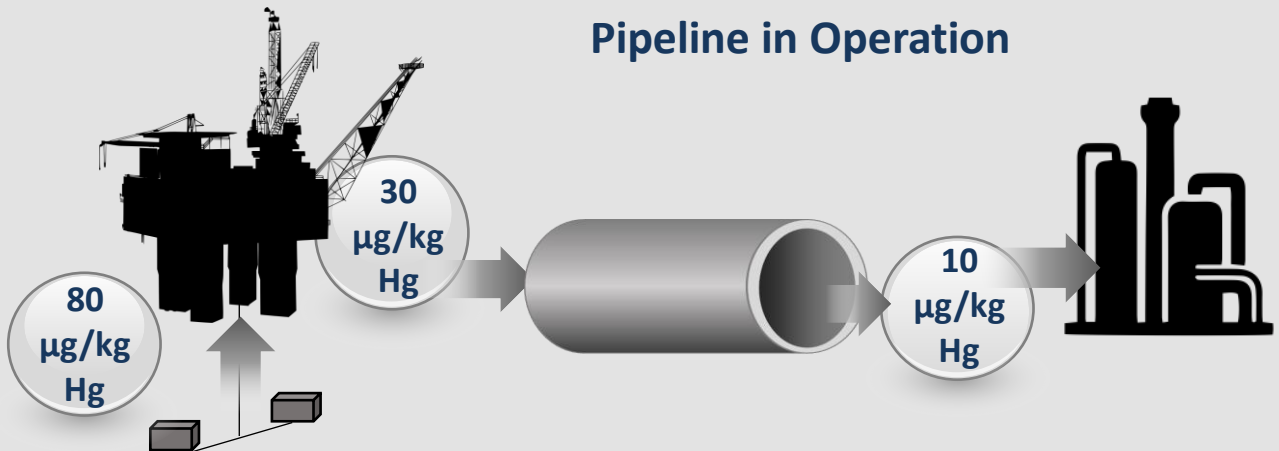
End of Life Options

Leave *in situ* on Seabed

no decontamination

decontamination undertaken

Release of mercury into aquatic ecosystems as the pipeline degrades over a long period of time

Minimal release of mercury. Mercury is removed in decontamination treatment and is safely disposed of

Recover for Smelting

no decontamination

decontamination undertaken

Potential release of mercury into the environment and possible worker exposure

Minimal release of mercury to the environment and within OEL

The assessment of mercury contamination as well as other trace contaminants like NORM and hence their potential impact on the environment should form an integral part of any oil and gas asset decommissioning plan. Since the long-term accumulation of mercury in process equipment is now well proven, even if mercury was only present at trace concentrations in the produced oil and gas and did not cause any production issues during the lifetime of the asset, it should not be excluded from the environmental impact assessment of decommissioning activities.

References

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(2) Lhiam Paton, Peter Crafts, David Clases, Thomas Lindsay, Andreas Zimmer, Henrik Siboni, Raquel Gonzalez de Vega, J¨org Feldmann. (2023) **The impact of corrosion on the adsorption of gaseous Hg0 onto the surface of steels: Implications for decommissioning in the oil and gas industry**; Journal of Hazardous Materials 458 (2023) 131975.

(3) Francesca Gissi, Darren Koppel, Alexandra Boyd, Fenny Kho, Rebecca von Hellfeld, Stuart Higgins, Simon Apte and Tom Cresswell. (2022) **A review of the potential risks associated with mercury in subsea oil and gas pipelines in Australia**; Environmental Chemistry 19(3 and 4), 210–227.