



Oil Companies International Marine Forum

Safety, Health, Environmental Issues and Recommendations for Shipboard Handling of Elevated Mercury Crude Cargoes

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The OCIMF mission is to be the foremost authority on the safe and environmentally responsible operation of oil tankers, terminals and offshore support vessels, promoting continuous improvement in standards of design and operation.

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1 Introduction

1.1 General

Many crude oils and condensates are known to contain elevated levels of mercury. Mercury concentrations can vary considerably depending on the producing region and the depth of the reserve. Concentrations in excess of 10 ppb can be found in many wells around the world and in some regions (e.g. Asia Pacific) crude oils may have concentrations in excess of 100 ppb.

This paper provides information on the potential hazards, issues, and a concern associated with mercury in crude oil cargoes and contains advice to assist tanker operators to establish procedures aimed at minimising health, safety and environmental impacts.

1.2 Properties of Mercury

Metallic (elemental) mercury appears as a liquid metal at ambient temperature. It has high specific gravity (13.6 gm/cc), relatively high electro-conductivity and significant chemical stability. It freezes at a temperature of -38.89°C and has a boiling point of 357°C. At ordinary atmospheric and industrial environmental temperatures, it has a significant partial vapour pressure, thereby releasing vapours freely.

Mercury will enter into combinations with most metals forming alloys known as amalgams.

Mercury may settle to the bottom of a cargo tank as compound mercury (such as mercury sulphide) which may accumulate in the residual sludge and sediment. Mercury may also bond with the cargo tank bulkheads, pipelines, cargo pumps, and uncoated steel structures associated with the cargo containment system. Elemental mercury may also be present in suspension in oil cargoes and may be found in the vapour spaces of the cargo tanks.

Inorganic mercury and elemental mercury are not soluble in water but can be present in suspension. Once suspended in water, bacterial organisms can convert the mercury to the more hazardous organic state, methyl mercury, through a metabolic process.

Heating of mercury, such as during hot work, increases the release of toxic mercury vapours. Any hot work on mercury-impacted steel must be properly planned and strictly controlled to help ensure the safety of the workers, as detailed in Section 13.

2 Training of Personnel

Those involved in work where mercury may be present should be fully trained in the safe work practices necessary for the activities being performed.

Training should be company and task specific, but may include the following topics aimed at improving awareness:

- review of the relevant MSDS(s) for mercury or mercury-containing materials including physical properties and potential health effects
- exposure guidelines and limits
- locations where mercury exposure risks may occur
- identification of the presence of mercury
- techniques for measuring mercury vapour (e.g. passive diffusion samplers, sorbent tubes, portable mercury analyser)
- control measures which may include the selection and use of personal protective equipment (PPE)
- signage and warning labels identifying potential mercury and associated compounds exposure risk areas
- basic chemistry of mercury (e.g. propensity to form amalgams with other metals; liquid at room temperature with high vapour pressure that can result in significant airborne vapour concentrations; vapour pressure increase with temperature increase)
- personal hygiene and safety (e.g. proper hand washing and decontamination),
- and mercury exposure toxicity
- special precautions to minimise exposure including spill prevention techniques, proper spill clean-up procedures

In addition to awareness level training, more in-depth training for individuals enrolled in a mercury medical surveillance programme may include the following:

- medical screening requirements

- detailed use of Respiratory Protective Equipment (RPE) including respirator cartridge procedures specific for mercury exposure
- potential for mercury vapour concentrations to quickly increase after work begins and during confined space entry, hot work, mucking out sludge and other similar tasks
- waste handling and decontamination procedures.

3 Health and Environmental Impacts of Mercury

3.1 Health Impact

The human body can be exposed to mercury by the following means:

- inhalation
- absorption
- ingestion.

Mercury is hazardous to health when it is repeatedly absorbed by the body over an extended period (chronic exposure) or following sudden exposure to high concentrations (acute exposure). The toxic effects of principle concern relate to the impacts on the central nervous system and to kidney damage.

Chronic Exposure Effects - Repeated exposure by inhaling mercury vapour can affect vital organs including the brain, spinal cord, eyes, and kidneys. It may cause mood changes; inability to concentrate; memory loss, a slight shaking, tingling, or loss of feeling of the hand and also kidney disease.

Ingested mercury may cause burning of the mouth and pharynx, abdominal pain, vomiting, corrosive ulceration and diarrhoea.

Elemental mercury can be absorbed through the skin and may cause allergic reactions. Repeated skin contact can cause the skin to turn grey in colour. Mercury absorbed through the skin may produce symptoms similar to ingestion.

Acute Exposure Effects - Inhalation of high levels of mercury vapour can cause the sudden onset of symptoms such as cough, chest pain, nausea, vomiting, diarrhoea, fever and a metallic taste in the mouth and other symptoms associated with heavy metal poisoning.

The ingestion of large amounts of mercury may cause severe inflammation of the digestive tract and renal failure, potentially leading to death. Elemental mercury vapour has produced both non-allergic dermatitic reactions in exposed individuals. Divalent mercury compounds have also produced skin sensitisation.

Due to the levels of mercury contained within crude cargoes, and the speed with which it becomes bound with other substances, the likelihood of acute exposure is low: however, it should always be considered as a threat, especially if conducting hot work in confined spaces or pipelines.

3.2 Environmental Impact

Mercury exists in the environment in its elemental form and in a range of organic (carbon containing) and inorganic (not containing carbon) compounds that vary in toxicity and persistence in living organisms. In the environment, mercuric compounds are formed through complex biogeochemical interactions that affect environmental and biological forms and concentrations. Some mercury compounds are more easily absorbed by living organisms than elemental mercury. When airborne mercury falls to earth or is introduced to eco-systems, it may be altered by bacterial or chemical action into an organic form known as methyl-mercury.

Methyl-mercury is much more toxic than the original metal molecules, and has the ability to migrate through cell membranes and "bio accumulate" within living tissue. Bioaccumulation is the process by which a substance builds up in a living organism from the surrounding air or water, or through the consumption of contaminated food. Bioaccumulation of persistent substances such as methyl-mercury will increase in concentration as it passes through the food chain from microorganisms, to fish, and then to fish-eating predators including humans. Elevated methyl-mercury levels may lead to the decline of affected wildlife populations and may affect human health when people consume significant quantities of fish or other contaminated foods.

On board tankers, levels of mercury may be present in suspension in slop water following the washing of cargo tanks that may have contained elevated mercury crude. This mercury will settle to the bottom of the slop tank over a period of time. It is therefore recommended that slop water which is required to be discharged with little settling time is analyzed for potential mercury content.

4 Occupational Exposure Limits of Mercury

'Occupational Exposure Limit' (OEL) is a generic term for the limits which many countries set to protect the health of workers from the adverse health effects of hazardous substances in the workplace. The most widely used limits, called Threshold Limit Values (TLVs), are those issued in the USA by the American Conference of Governmental Industrial Hygienists (ACGIH). The following table shows the current* TLVs for mercury (it should be noted that these limits may be subject to review and amendment):

	8-Hour Time Weighted Average (TWA) * mg/m ³	Short Term Exposure Limit (STEL) * mg/m ³
Mercury – Alkyl Compounds	0.01	0.03
Mercury – Elemental and Inorganic Forms	0.025	

*2011 Threshold Limit Values (TLVs) defined by the American Conference of Governmental Industrial Hygienists (ACGIH). TLVs refer to airborne concentrations of chemical substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, over a working lifetime, without adverse health effects.

It is recommended that the ACGIH TLVs should be followed where there is an absence of country specific legally enforceable Occupational Exposure Limits for mercury. Operations in countries which do have their own legally enforceable Occupational Exposure Limits for mercury should follow the country limits for OELs.

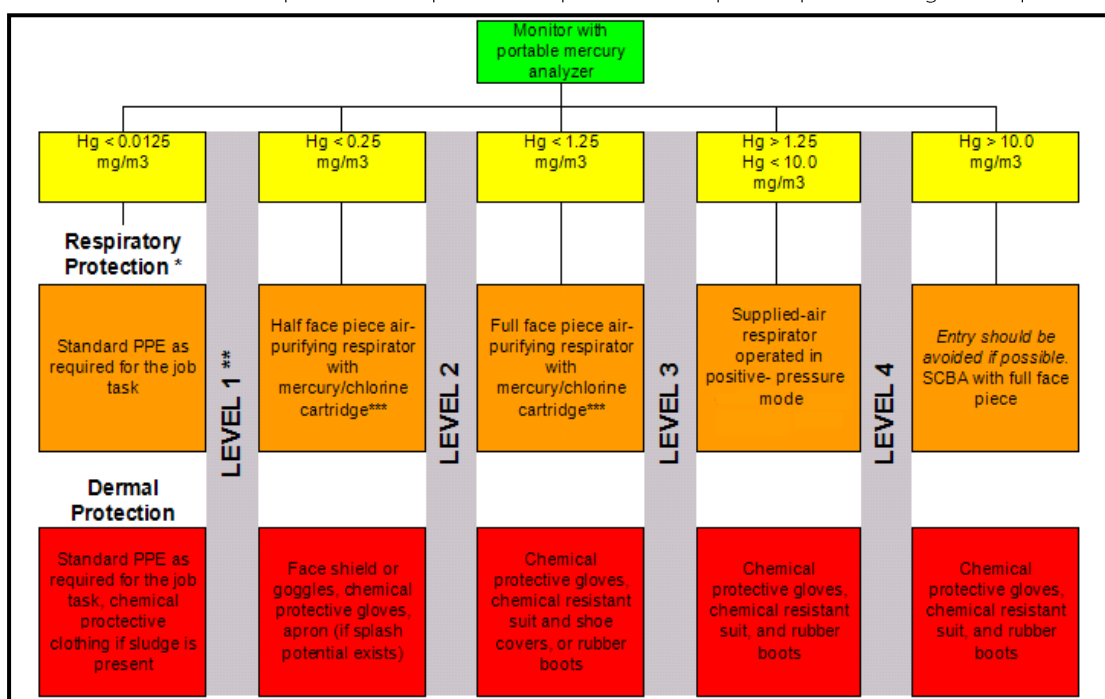
The OEL is often the trigger level at which respiratory protective equipment (RPE) must be worn. Many organisations set Action Levels of half the OEL value to factor in an additional level of safety.

In addition, mercury is assigned the 'Skin' Notation, indicating that mercury can be absorbed through the skin.

5 Exposure Protection and Monitoring

5.1 Personal Protective Equipment

The following respiratory protection and Personal Protective Equipment (PPE) action levels are provided as an example of how risks of workforce exposure may be controlled when work is being undertaken in close proximity to mercury vapour or when handling mercury-contaminated materials. It is recommended that companies develop their own procedures to protect personnel against exposure



EXAMPLE PPE MATRIX TO PROTECT AGAINST MERCURY EXPOSURE

5.2 Monitoring for Mercury

Direct Reading Instrumentation

Real-time mercury monitoring can be carried out using a mercury direct reading instrument. Examples of such instruments are the NIC (Nippon Instrument Corporation) EMP-1A Mercury Gas Monitor and the Jerome 405 Mercury Vapour Analyser but others are available. These instruments have a variable measuring range which can be less than 0.01mg/m³ to over 2mg/m³ depending on the instrument type. However, it should be noted that they are not usually approved for operation in a potentially explosive atmosphere and a hot work permit (or equivalent) will normally be required for their use.

Determining Mercury Levels in Samples

Measurement of mercury in crude oil, oil products, aqueous and solid samples can be done by accredited external laboratories and typically uses specialist pyrolysis and hydride generation techniques.

Air Sampling

If a direct reading analyser is not available, the following alternative methods are available :

- Collection of sample into a gas sample bag, such as a Tedlar bag, followed by introduction into gold-coated cartridges
- Direct collection of the sample onto the gold-plated cartridges
- Draeger or alternative Chemical Discolouration Tubes

Tedlar bag sampling offers a simple, relatively cost-effective and yet precise method to determine the mercury (and arsine concentration) in dry natural gas and LPG. The dry gas is extracted from the liquid phase of the sample vessel or sample pipe line through a pressure reduction valve or heating manifold into a Tedlar bag.

The gold-plated cartridges are used to collect the mercury in the sample which is subsequently released and measured in the analyser.

Chemical Discolouration tubes, such as Draeger tubes, can provide an inexpensive and reliable method of monitoring using existing technology already available. It must be noted however that detection levels are sometimes in excess of exposure limits which should be factored into safety plans when using this method.

Personal Air Monitoring

Personal air monitoring devices are available such as mercury specific diffusive badges, for example the SKC Inorganic Mercury Passive Sampler (for full shift monitoring), or low flow sampling pumps fitted with tubes.

6 Cargo Planning and Operations

Cargo operations should be conducted in accordance with the recommendations of ISGOTT. Additionally, all planning of cargo operations and carriage of elevated mercury cargoes should take a risk-based approach and should include controls or precautions to manage the associated additional hazards.

The following additional controls / precautions should be amongst those considered when planning operations:

- Hazard Awareness - Prior to loading the cargo, a meeting should be conducted to discuss the hazards and necessary precautions relating to elevated mercury cargoes. All shore personnel who will be performing work (e.g., surveyors) should be given advance notice of the mercury content of the cargo.
- Exposure Control - Before connecting or disconnecting cargo hoses or loading arms, manifolds should be thoroughly drained. All tank lids, purge pipes, valve glands and other apertures where leakage may occur should be inspected and monitored before arrival to ensure integrity.
- Personnel Protection - PPE should be used appropriate to the potential exposure level and in accordance with established recommendations, as described in Section 5.1.

7 Cargo Tank Venting

In line with safe operations, if the tank pressure is approaching higher levels and requires venting to atmosphere, special consideration should be given to the presence of mercury. All venting should be conducted in accordance with the recommendations contained in ISGOTT with additional consideration

given to the following:

- Personnel Management - All personnel not required for the operation should remain in safe areas away from the likely path of the vented vapours.
- Personnel Protection – If the IG mast riser valve is locally operated, the operator should wear PPE appropriate to the potential exposure and in accordance with established recommendations.
- Exposure Control – When considering pressure reduction, the aim should be to reduce the pressure by the minimum amount required, while minimising the number and frequency of venting operations. Due consideration should be given to factors that include the time of day, ambient temperature and vessel movement.

8 Tank Washing and Preparation

Mercury, when introduced into the cargo system and spaces may remain present through:

- collection in existing sediment within the cargo spaces as a result of drop out from suspension within the crude oil
- bonding to the exposed steel surfaces of the tank, which can result in a surface coating of compound mercury along with absorption within the steel
- collection of condensed elemental mercury from the vapour space on horizontal surfaces of the cargo tank.

Once a high or elevated mercury cargo is carried onboard a vessel, the containment system and associated equipment may be impacted. Prior to any ship repair period requiring tank cleaning, plans should be discussed to develop procedures aimed at minimising the exposure to personnel working within the cargo tanks.

Although scientific studies regarding in-tank mercury impacts are not fully complete, sufficient information exists to indicate that attempts to dilute the presence of mercury through the carriage of additional low mercury cargoes is not effective. As the mercury cannot be easily removed prior to the repair period, measures should be developed to minimise the volume of in-tank waste through full crude oil washing cycles for at least the two previous cargoes.

Mercury bound to the steel surfaces of cargo tanks cannot be removed with crude oil or by water washing.

Efforts should be made to eliminate the potential vapours present in the work area. This includes (and could be a combination of):

- sludge removal
- venting vapours away from the work area with mechanical forced ventilation fans
- use of general and local exhaust ventilation fans
- use of chemical suppressants.

On-site assessments should be made to determine which is the safest and most effective option for the task.

Repeated monitoring of the concentration of mercury vapour in the work area should be performed, and applicable PPE requirements should be adhered to.

Ventilation, both forced and extraction, will help ensure that any mercury vapour generated is properly dispersed and will also assist in providing a more comfortable working environment for personnel whilst wearing the additional PPE.

The ventilation plan should consist of extraction ventilation along with forced supply ducting at the local work site. For extraction ventilation, it is important to ensure that strong non-collapsible ducting is used to channel the extracted atmosphere away from the work site. This should act to minimise workforce exposure on deck.

All individuals performing tank cleaning or de-mucking operations where there is a potential for mercury exposure should be briefed on the hazards of mercury exposure, methods of exposure control and environmental protection requirements.

Worker exposure may be reduced by the implementation of a work rotation schedule aimed at reducing the length of work shifts. A plan should be agreed with the attending superintendent as to the schedule and deployment of the workforce.

Consideration should be given to the following:

- use of additional ventilation units and the utilisation of exhaust vent hoses to vent vapours away from the work area
- implementation of site control and barricading to form a secure control zone to keep all unnecessary personnel away from work areas
- keeping all impacted equipment within the control zone
- adherence to basic personal hygiene procedures, e.g. no eating, drinking, chewing gum/tobacco, or smoking within the work area
- provision of a wash station for workers to use after removing their PPE and prior to any food or drink consumption.

Decontamination procedures should be used to ensure that impacted equipment and clothing are not removed from the controlled area (see Section 11).

9 In-Tank Work

When working within the cargo tank it is important to conduct an efficient and effective clean up while at the same time minimising the potential exposure to the workforce. To enable such an operation a plan should be developed which allows adequate rest periods for the workforce.

The recommendations and procedures contained in ISGOTT regarding working in enclosed spaces should be closely followed, particularly with regard to the monitoring of atmospheres. A risk assessment should be undertaken and a work plan developed. The plan should include the process for measuring and assessing mercury and toxic hazards using appropriate measuring instruments, as well as methods to contain the mercury in designated areas.

Measurement of mercury concentrations (elemental and inorganic forms) above the Action Level of 0.0125 mg/m³ will indicate that additional safety precautions should be considered/implemented.

10 On-Deck Work during Mucking Operations

Prior to work commencing, a hazardous zone should be established and the area around the tanks being cleaned should be cordoned off. The number of persons operating within the hazardous zone should be limited to those essential to the operation. Persons within the zone should wear the required mercury exposure PPE.

ISGOTT recommendations regarding safeguards for enclosed space entry should be strictly followed.

Mercury containing sludge should be removed and handled whenever possible within sealed double lined bags to avoid human exposure and to minimise any cross contamination. The bags should be placed directly into approved containers which should be sealed once full.

11 Decontamination

Measures should be taken to ensure that the safe decontamination of the workforce is managed inside the cordoned off hazardous zones. Within these zones all impacted PPE should be removed, cleaned or decontaminated before re-use or approved disposal. Disposable PPE that has been impacted with sludge should be put into plastic bags which should be sealed and labelled as containing mercury waste prior to sending for disposal.

As mercury is not water soluble, it is difficult to remove from equipment by conventional means and, in many cases, safe disposal of the equipment is the preferred option.

12 Sediment and Sludge Handling and Storage

12.1 Generation Source

Sediment and sludge removed from cargo tanks that have regularly carried mercury crudes can contain elevated levels of mercury that might require specific precautions for handling, storage and disposal, in a similar manner to those in place for materials containing asbestos. Apart from sediment and sludge, the waste may also comprise of used personal protective equipment such as gloves, masks, overalls, etc. and other associated solid wastes accumulated during the tank cleaning activity. It is recommended that the waste removal is performed only by approved companies operating in compliance with applicable regulatory regimes.

12.2 Segregation

The segregation of mercury impacted PPE and solid waste, such as sediment and sludge is critical to control exposure and cross contamination of wastes. The following precautions should be taken:

- segregate mercury impacted wastes in dedicated containers without mixing with other types of waste or material
- segregate mercury impacted wastes from softer metals such as gold, silver and aluminium since elemental mercury tends to form amalgams or to corrode these types of metals.

12.3 Storage Containers

The following precautions should be taken for containers used for the storage of mercury waste:

- mercury impacted PPE and solid waste should be placed into plastic bags that are strong, leak proof and puncture resistant. These bags should be impervious to the elemental mercury and completely surround the contents preventing them from escaping from the package, irrespective of their position or orientation;
- bags should be sealed so that mercury vapour is contained. The bags should be put into a second bag which should also be sealed;
- double-bagged containers should be placed into plastic drums. The drums should be of a UN-standard, suitable for the storage and transportation of toxic waste;
- plastic drums should be equipped with full top covers which should be securely closed before moving or shipping;

The use of metal drums is not recommended due to the propensity of mercury to form amalgams which tends to corrode softer metals. In addition, metal drums may be subject to deterioration during transit and storage which could result in leakage of material.

12.4 Labelling

All containers containing mercury impacted wastes should be properly labelled in accordance with local regulations. The standard label requirements for such wastes should include the following:

- the UN number (UN2809) attached to the external side of the container
- hazard warning labels attached to the external side of the container, below the UN number.

12.5 Handling Instructions

Mercury impacted waste can be safely handled provided appropriate PPE is worn. The recommended PPE used for handling such material includes the following:

- approved respirator with the appropriate filters for the maximum-use concentrations and/or the potential exposure limits
- chemical goggles or, if there is a risk of splashing, a full-face shield or splashguard
- protective gloves, boots, aprons, gauntlets, etc. to prevent any contact with the skin
- emergency eyewash stations, washing facilities and quick-drench showers available in work areas.

Precautions for handling mercury impacted wastes should be strictly followed and should include:

- double packed containers for shipment
- a full face respirator with mercury filter should be worn along with rubber gloves, boots and apron or coveralls.
- adherence to basic personal hygiene procedures including no eating, drinking, or smoking in any working area where mercury vapour might be present
- restricting the use of contact lenses while working with the waste material
- restricting the wearing of rings, necklaces or earrings while working with the waste material since it could form amalgams with these materials

- removal of contaminated clothing with proper processing before wearing again
- separating work and street clothes, storing work clothes in special lockers and always showering before changing into street clothes

12.6 Transit Storage Arrangements

The transit storage of mercury impacted PPE and solid waste material should be within a specialised warehouse and the following precautions should be taken:

- containers should be transported as soon as practicable to a warehouse for storage until shipment to a disposal facility
- containers should be stored in a dry, well-ventilated (and if possible, cool) area in tightly closed unbreakable containers
- containers should be protected from physical damage
- storage areas should have smooth, hard, nonporous floors with no cracks or spaces
- containers should be segregated and stored separately from other waste and with limited access
- containers should be stored away from sources of ignition
- waste storage areas should have a high fire safety standard including provisions for fire extinguishing, smoke detection, fire walls, emergency shut-down doors etc.
- an inventory of stored materials should be maintained.

12.7 Disposal

Disposal of mercury impacted waste should always be conducted in accordance with the national legislative requirements of the country where the waste is to be disposed.

13 Repair Work in Tanks

If a vessel has uncoated tanks and has been regularly carrying mercury cargoes, the potential exists for mercury to be bound to the steel.

When this bound or compound mercury is heated, such as during hot work, it will vaporise back to its elemental form, therefore posing a potentially significant health hazard. During hot work, the following precautions should be taken:

13.1 PPE

Welders, cutters and fire watch personnel should utilise adequate PPE in line with the recommendations contained in Section 5.

13.2 Ventilation

Adequate ventilation should be provided to the spaces where hot work is to be conducted. The ventilation should include extraction from the site of the work and an adequate supply of fresh forced ventilation to the worker to move the fumes away from the workspace and towards the extraction location. The exhaust from the extraction ventilation should be managed so that it is discharging in a cleared zone away from the workforce.

13.3 During the Work

While work is being conducted, the atmosphere should be monitored at frequent intervals. All tank workers should wear personal monitoring devices.

14 Medical Surveillance

All personnel directly involved with mercury waste handling should undergo medical surveillance (including urine analysis) in line with their national regulatory requirements for Mercury Exposure. Where no such requirements exist or can be found the following may be used as reference:

Medical screening shall be conducted:

- if employees are, or may be, occupationally exposed to mercury at or above the Action Level (0.015

mg/m³) for 30 or more days a year; or

- if exposed to a single 8-hour time weighted average (TWA) exposure above the Exposure Limit (0.025 mg/m³); or
- upon notification by an employee that they have developed signs and symptoms commonly associated with toxic exposure to mercury and its associated compounds.

It should be noted that if there is a potential for personnel to be exposed to alkyl mercury compounds, a lower TWA should be set.

On completion of specific mercury-related work, a further analysis should be taken to ascertain quantifiable exposure levels.

After absorbing elevated levels of elemental mercury, the body excretes it fairly slowly, the mercury having a half-life of 40 to 60 days. Most elemental mercury is excreted in exhaled air and small amounts in the faeces and urine. If exposure is suspected, it is important that medical analysis is undertaken as soon as possible.