H2S – exposure, toxicity, and good practices to adopt.

Introduction

In our Maritime FEEBACK issue 57 we published a report relating to an incident that involved the dangerous exposure of three persons to hydrogen sulphide (H_2S), aboard an oil tanker.

This paper follows up on that report. It focuses on human exposure to H_2S by inhalation and highlights safe work practices that, if adopted, will greatly reduce the likelihood of dangerous exposure to H_2S on board. Special attention will be given to operations on oil tankers as the above-mentioned incident report concerned an oil tanker.

Toxicity of hydrogen sulphide

Hydrogen sulphide is absorbed into the body by inhalation. H_2S is an extremely toxic colourless gas at ambient pressure and temperature. It has a distinctive odour of rotten eggs. The gas is 1.189 times heavier than air and therefore has a tendency to first sink to the lower parts of a compartment, deck or space. A widely recognized occupational exposure limit for airborne concentrations has been established by the American Conference of Governmental Industrial Hygienists (ACGIH), and the definitions of the terms they use are shown in figure 1.

ACGIH currently recommends a Threshold Limit Value – Time Weighted Average (TLV-TWA) of 1 ppm and a Threshold Limit Value – Short-Term Exposure Limit (TLV-STEL) of 5 ppm for hydrogen sulphide.

Threshold Limit Value *(TLV®) refers to an airborne concentration of the chemical substance 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.*

Threshold Limit Value–Time-Weighted Average (TLV–TWA)
The TWA concentration for a conventional 8-hour workday and a 40-hour workweek, to which it is believed that nearly all workers may be repeatedly exposed, day after day, for a working lifetime without adverse effect.

Threshold Limit Value–Short-Term Exposure Limit (TLV–STEL)
A 15-minute TWA exposure that should not be exceeded at any time during a workday, even if the 8-hour TWA is within the TLV–TWA.

Threshold Limit Value–Ceiling (TLV–C)
The concentration that should not be exceeded during any part of the working exposure.

Refer to **https://www.acgih.org/tlv-bei-guidelines/tlv-chemical-substances-introduction** for a detailed ACGIH definition of TLVs.

Figure 1 – Threshold Limit Value Definitions

The odour threshold for hydrogen sulphide is extremely low. In the air, the gas can be smelled at concentrations of 0.01 ppm (when the rotten egg smell is first noticeable to some). For a toxic gas, this should be considered as a positive attribute.

In the case of H_2S, at concentrations of around 100 ppm, the victim can have olfactory fatigue and soon cease to smell the gas, so after initially smelling H_2S the subsequent absence of smell does not indicate that the atmosphere is safe. Although most people can smell very low concentrations of H_2S, it is dangerous to assume that the odour provides adequate warning. At concentrations of around 150 ppm paralysis of the olfactory nerve has been observed, so sense of smell is totally deadened. Progressively higher concentrations of hydrogen sulphide have even more harmful effects, and exposure to very high concentrations causes immediate death. Also, death or permanent injury may occur after very short exposure to small quantities. The gas acts directly upon the nervous system resulting in paralysis of respiratory centres.

The following table summarises the negative health effects of inhalation of hydrogen sulphide:

HUMAN HEALTH EFFECTS OF HYDROGEN SULPHIDE AT VARIOUS CONCENTRATIONS - EXPOSURE VIA INHALATION	
H_2S Concentration (ppm vol. in air)	**Physiological Effects**
0.00011-0.00033	Typical background concentrations
0.01-1.5	Odour threshold (when rotten egg smell is first noticeable to some). The odour becomes more offensive at 3-5 ppm. Above 30 ppm, odour described as sweet or sickeningly sweet.
2-5	Prolonged exposure may cause nausea, tearing of the eyes, headaches or loss of sleep. Airway problems (bronchial constriction) in some asthma patients.
20	Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.
50-100	Slight conjunctivitis ("gas eye") and respiratory tract irritation after 1 hour. May cause digestive upset and loss of appetite.
100	Coughing, eye irritation, loss of smell after 2-15 minutes (olfactory fatigue). Altered breathing, drowsiness after 15-30 minutes. Throat irritation after 1 hour. A gradual increase in severity of symptoms over several hours. Death may occur after 48 hours.
100-150	Loss of smell (olfactory fatigue or paralysis).
200-300	Marked conjunctivitis and respiratory tract irritation after 1 hour. Pulmonary oedema may occur from prolonged exposure.
500-700	Causes staggering collapse in 5 minutes. Serious damage to the eyes in 30 minutes. Death after 30-60 minutes.
700-1000	Rapid unconsciousness, "knockdown" or immediate collapse within 1 to 2 breaths, breathing stops, death within minutes.
1000-2000	Nearly instant death
Developed from the table provided in the US Department of Labor website: *https://www.osha.gov/SLTC/hydrogensulfide/hazards.html*	

Figure 2 - Human Health Effects of Exposure to H_2S by Inhalation.

Where is hydrogen sulphide likely to occur on board?

On board ships there are several circumstances where personnel can be subject to H_2S exposure. Strict monitoring and detection methods along with appropriate use of personal protective equipment will greatly reduce the risk of hazardous exposure to H_2S. Following are some of the common sources of H_2S on board:

- H_2S can be generated by the decay of organic matter in the absence of air. Whenever there is:
  - a mixture of vegetable oils or animal oils with seawater.
  - a mixture of slops from drilling operations with seawater.
- shipboard sewage systems and piping are prone to release H_2S when opened without ensuring that they are isolated, cleared of all sewage, and ventilated/flushed to ensure safe atmospheres within them.
- cargo hold bilges and pumping systems containing residues of grain or similar cargoes which are exposed to seawater and allowed to decay are likely to generate H_2S.
- all enclosed spaces. Treat every enclosed space on board as a suspect for H_2S until proven otherwise by detection and monitoring device(s).

- H_2S can occur in the vapour space of tanks carrying bunker oils or petroleum oil cargoes (including crude oil) due to the inherent chemical composition of the oil. The concentration of H_2S in the liquid can be readily discovered by examining the quality certificate of the oil. The concentration of H_2S in the liquid is usually expressed in ppm by weight whereas the concentration of H_2S in the atmosphere is expressed in ppm by volume. Although it is not possible to predict the likely vapour concentration from any given liquid concentration, it is known that the H_2S concentration in the vapour can be higher - for example crude oil containing 70 ppm (by weight) H_2S has been shown on occasion to produce a concentration of as much as 7,000 ppm (by volume) in the gas stream leaving the tank vent. H_2S can be encountered in crude oils as well as refined products such as naphtha, fuel oil, bunker fuels, bitumens and gas oils. All precautions for H_2S should be taken for every oil bunker/cargo until the absence of H_2S has been confirmed through relevant cargo information (including Material Safety Data Sheets) and by onboard monitoring.

Training of shipboard personnel

The best way to prevent H_2S exposure, injury and death on board is through good planning, risk assessments, and targeted training of all seafarers. The following topics may be considered for inclusion in the training;

- identification of the characteristics, sources, and hazards of H_2S.
- symptoms of H_2S exposure.
- use and operation of the H_2S detection devices on board.
- recognition of, and proper response to, H2S warnings and alarms, including alarms of portable and personal H_2S gas detection devices.
- use and maintenance of PPE including Emergency Escape Breathing Device (EEBD) and Self-contained Compressed Air Breathing Apparatus (SCABA). Appropriate respiratory protection for normal and emergency use.
- rescue techniques and first-aid procedures to be used in an H_2S exposure incident.
- emergency response procedures, corrective actions, and shutdown procedures.
- general safe working practices to prevent accidental exposure to H_2S during routine work and maintenance procedures.
- enclosed space entry procedures.
- wind direction awareness; using it to advantage during operations on board.
- corrosion and metal fatigue to ship's systems and equipment caused by H_2S exposure. The corrosive nature of H_2S can adversely affect electronic H_2S gas detection devices over a period.

The training, focused upon H_2S hazards or potential hazards on board, should serve as a supplement to the shipboard familiarization training and all existing mandatory training and drills required by ISM.

In addition to the training mentioned above, shipboard personnel should include a task-specific risk assessment review of the likelihood of H_2S and additional precautions to be taken, in the toolbox meeting before any task.

Detection and monitoring of hydrogen sulphide

Sense of smell provides the earliest detection of H_2S. However, **sense of smell should never be relied upon as a warning device for H_2S** because the sense of smell will be deadened as the concentration of H_2S increases. The only reliable means for detection of hydrogen sulphide in the atmosphere is by using purpose-built gas detection devices.

Since there are several circumstances where personnel can be subject to H_2S exposure on board, the risk of H_2S exposure should always be considered during job / risk / hazard assessments. In all cases where exposure of personnel to H_2S is likely, the ship's safety management system should require that areas accessed by personnel are monitored by gas detection devices to establish that the area is free of harmful levels of H_2S and to establish the level of personal protective equipment needed in that area. Care should be taken to ensure that the measurement units of the gas detection device are in ppm to facilitate easy comparison with the published TLV of the gas.

Monitoring of H_2S in an enclosed space before and during enclosed space entry is mandated by international regulations. Regulation 7 of SOLAS Chapter XI-1 states *"Every ship to which chapter I applies shall carry an* *appropriate portable atmosphere testing instrument or instruments. As a minimum, these shall be capable of measuring concentrations of oxygen, flammable gases or vapours, hydrogen sulphide and carbon monoxide prior to entry into enclosed spaces. Instruments carried under other requirements may satisfy this regulation. Suitable means shall be provided for the calibration of all such instruments."*

Whenever risk assessment establishes a risk of H_2S exposure, personnel should wear personal H_2S gas detection devices in addition to appropriate personal protective equipment. H_2S gas detection devices should be set to alarm at an airborne concentration of hydrogen sulphide at TLV-TWA. If there is more than one alarm provided in the device the first alarm (LOW) should be set at TLV-TWA and the second alarm (HIGH) should be set at TLV-STEL.

Persons responsible for use and calibration of these devices should be fully familiar with the contents of the equipment manual and capable of operating/calibrating the devices in accordance with the guidance provided in the manual.

Personnel involved in gauging, sampling, cleaning filters, entering a pumproom, connecting and disconnecting loading lines, draining to open containments and mopping up spills of bunkers or petroleum cargoes which may release harmful concentrations of H_2S should also wear personal H_2S gas detection devices. Personal sampling badges should not be used as a means of detection of H_2S.

An H_2S gas detection device based upon an electrochemical sensor is the most practical type of H_2S detector because it responds in seconds to gas exposure. When selecting an H_2S gas detection device it is extremely important to ensure it has the sensitivity and accuracy needed to measure airborne concentrations of H_2S from below TLV-TWA through to extremely high concentrations that may be operationally encountered. Ideally, the device should be:

- conveniently small and portable;
- intrinsically safe for use in areas where a combustible atmosphere may exist;
- response time of 15 seconds or less;
- a lower detection limit (sensitivity) of no more than 0.5 ppm;
- ppm resolution (smallest detectable change);
- an accuracy of ± 5% over its calibrated range of at least 0-100 ppm;
- an accuracy of ± 0.05 ppm at 1 ppm (± 5%) to meet the requirement of a reliable alarm;
- a built-in data-logging function for data collection and analysis;
- a low probability of false alarms. Generally, this requires a design with low-temperature drift (typically, less than 0.1 ppm for the zero reading) and high selectivity for H_2S in the presence of interfering gases, such as sulphur dioxide, nitrogen dioxide, and hydrocarbons. Reliable H_2S measurements at sub-ppm levels and selectivity to discriminate H_2S from interfering materials in the work environment are crucial elements of a monitoring device.

If reliable electronic H_2S gas detection devices are not available, due to breakdown or defect, detector tubes should be used to monitor H_2S.

PPE for hydrogen sulphide

- Filter respirators should not be used as inhalation protection against H_2S because airborne concentrations of the gas may exceed the operational capability of the respirator being used. This situation could prove fatal.
- Although measurements may not reveal hazardous levels of H_2S, whenever there is a known H_2S hazard in an area, all persons working in that area should be equipped with Emergency Escape Breathing Devices (EEBD) in addition to personal H_2S gas detection devices. These persons should have been trained to respond to the personal H_2S gas detection device alarm when it activates. In particular, when the first alarm activates (TLV-TWA alarm or LOW alarm), they should don the EEBD and immediately leave the area and report to the predetermined muster location and staying, as far as practicable, upwind of the H_2S gas source.
- When the atmosphere in an area is known to be at TLV-TWA for H_2S concentrations or higher, all persons entering that area must don SCABA and be equipped with personal H_2S gas detection devices. These persons must have been trained to respond to the personal H_2S gas detection device

alarm when it activates. In particular, when the second alarm activates (TLV-STEL alarm or HIGH alarm), they should immediately leave the area and report to the predetermined muster location while staying, as far as practicable, upwind of the H_2S gas source. This degree of breathing protection should also be adopted in all spaces/areas where the nature of the atmosphere is unknown. In addition, a "buddy system" is recommended – i.e. two persons must make a coordinated entry into the space/area together. The breathing protection should be reduced to EEBD only when it is confirmed by repeated measurement that the H_2S concentration in the atmosphere is below TLV-TWA.

First aid measures for persons affected by H_2S

- persons overcome by H_2S gas should be removed to clean fresh air as soon as possible.
- if breathing, maintain the victim at rest and administer oxygen.
- keep the victim lying down, with soft padding under the neck and shoulders to keep the airway open.
- after the evacuation of the victim, even if heart and breathing seem normal, keep the victim under continuous observation for a period of at least 2 hours, or until medical assistance is available.
- if the victim is not breathing, start artificial respiration immediately and continue until oxygen can be made available at the site.
- if the eyes are affected by H_2S, wash them thoroughly with water.
- for eyes mildly inflamed due to H_2S, apply cold compresses.

Other precautions for hydrogen sulphide

When the risk of harmful H_2S exposure is likely to affect the atmosphere in accommodation and machinery spaces, the following measures should be adopted:

- every effort should be made to identify the source of H_2S and stop/control the release of the toxic gas. While at sea, consideration should be given to adjusting the course and speed of the vessel to ensure that the relative wind direction carries the gas away from the accommodation.
- bridge, control rooms, accommodation and machinery spaces should be monitored for airborne H_2S concentrations.
- routine access to the accommodation should be restricted to one or two locations.
- accommodation ventilation and the air-conditioning system should be operated on one hundred per cent recirculation with all external intakes fully closed to ensure that positive pressure is maintained within the accommodation – it may be necessary to consider stopping or minimising the number of forced exhaust vent fans serving the accommodation (e.g. sanitary space exhaust vent, galley exhaust vent).
- as far as practicable, machinery space ventilation systems should be operated in such a manner as to prevent H_2S vapour from entering the machinery space.
- the vapour space of bunker tanks should always be monitored for H_2S before, during and after bunkering.
- periodical monitoring of the vapour space of the bunker tank should be established as a routine until the tank is free of that parcel of bunkers and free of H_2S.
- ventilation to lower the concentration of H_2S in the vapour space should be carried out as soon as practicable. Care should be taken to ensure that such ventilation does not adversely affect the atmosphere in the accommodation and machinery spaces. Even after the tank has been ventilated to reduce the concentration to an acceptable level, subsequent transfer, heating and agitation of the fuel within a tank may cause the concentration to reappear.

Certain crude oil and refined petroleum cargoes on an oil tanker may contain hazardous concentrations of H_2S. The vapour space of such cargo tanks is likely to have H_2S concentrations in excess of 100 ppm.

These cargoes may be considered to be **high H_2S cargoes**. The following precautions should be taken when preparing for these cargoes:

- test and confirm that all cargo piping and valves are leak tight.
- ensure vent valves serving the cargo system operate according to design.
- tank openings should be ensured gastight.
- heating coils in cargo tanks should be tested to ensure leak tightness.
- fill liquid pressure vacuum breakers to correct levels, as per design.
- ensure that doors and ports leading to the cargo area and open deck are capable of being sealed shut without any possibility of gas or air leaking through.
- make a cargo operation plan having due regard to the hazardous nature of the cargo.
- conduct shipboard drills for a dangerous gas leak where the complete emergency response plan for H_2S hazards is exercised.
- rig a windsock or lightweight flag at a clear location above the cargo deck, so it can be easily observed from the cargo control room in order to monitor wind direction.

During the loading operation of high H_2S cargoes on an oil tanker:

- adopt a closed loading procedure.
- monitor H_2S concentrations on the cargo deck regularly.
- all venting of vapours from cargo tanks should be through a mast riser or high-velocity vent valve.
- H_2S vapour is heavier than air and will tend to sink to the cargo deck if there is low velocity at the point of egress;
- in ship-to-ship operations bear in mind the relative freeboard of the vessels when choosing the safer venting option.
- stop loading cargo if there is no wind, if vapour from the cargo tank does not disperse or if the wind direction takes cargo tank vapour towards the accommodation.
- only essential personnel with designated cargo and security duties should be permitted on the cargo deck.
- only essential shore personnel should be permitted on the cargo deck. They should be duly briefed of the prevalent H_2S hazard and escorted by responsible shipboard personnel.
- prohibit all maintenance activity in the cargo area and on all systems related to cargo operations except emergency maintenance.

The International Safety Guide for Oil Tankers and Terminals (ISGOTT) may be consulted for further information relating to H_2S properties and the good practices which should be adopted. See https://www.witherbyseamanship.com/isgott.html