West of England

Loss Prevention Bulletin

The Dangers of Hydrogen Sulphide in Marine Bunkers

Introduction

Personnel working in the oil tanker industry are generally familiar with the hazards associated with the presence of hydrogen sulphide (H_2S) in hydrocarbon products carried as cargo. However, the possibility that marine bunkers may also produce H_2S gas is not always recognised so widely.

Marine bunkers can contain H_2S, but in varying concentrations depending on how it is manufactured. The gas itself is pungent, colourless, highly toxic and flammable. Exposure to high levels of H_2S gas can be fatal and inhalation has resulted in seafarers' lives being lost.

Prior to taking bunkers, SOLAS Regulation VI/5-1 requires the vessel to be provided with a Material Safety Data Sheet (MSDS). This became mandatory on 1 January 2011. The MSDS will contain information regarding the composition of the fuel including the concentration of H_2S, the effects of exposure to the gas and the first aid measures to be taken in such an event. In addition, the MSDS will often include guidance on the handling and storage of the product and exposure limits for each of its component parts.

Whenever bunkers are received, there is always a risk that they may produce H_2S gas. It is important to recognise that there is no direct correlation between the concentration of H_2S in the bunker oil on board in a bunker tank and the amount of gas that may be generated or the speed at which it may develop. These issues cannot be predicted with accuracy as they depend on many factors including the chemical properties of the oil, temperature, viscosity, heating, storage time, agitation, tank shape and ventilation.

When H_2S is present in a bunker fuel, the concentration of gas inside a bunker compartment will exceed the declared H_2S content of the bunkers by a significant margin as the latter is recorded as its liquid phase concentration, particularly in tanks with limited natural ventilation or within closed systems.

Toxicity

H_2S gas is highly toxic and has a distinctive odour of rotten eggs. The smell intensifies as the gas concentration increases, and above 30 parts per million (ppm) the odour becomes sickeningly sweet. However, concentrations exceeding 100 ppm paralyse the olfactory nerves in the nose resulting in loss of smell. This characteristic makes H_2S gas extremely hazardous.

Breathing difficulties may be experienced above 320 ppm, and exposure to concentrations beyond this level may be lethal. A single breath of H_2S gas at 1,000 ppm may result in immediate collapse and suffocation.

The table on the following page details the effect on humans of different concentrations of H_2S gas. Crewmembers should be made aware of the various symptoms of H_2S poisoning.

Many national authorities have also established long and short term exposure limits which should not be exceeded. In the United Kingdom a Workplace Exposure Limit (WEL) applies which sets a Time Weighted Average (TWA) regarding exposure to permitted concentrations of H_2S gas. Two time periods are specified; a long term exposure limit with an 8 hour TWA of 5 ppm, and a short term exposure limit with a 15 minute TWA of 10 ppm.

Flag state requirements regarding H_2S exposure limits may also apply, and checks should be made in this respect.

Other Hazards

Although the toxicity of H_2S gas remains the primary hazard, lesser risks in the longer term may include corrosion within bunker tanks and pipelines, and damage to other system components.

If the amount of H_2S gas inside a tank exceeds the oxygen content, H_2S may react with rust to form pyrophoric iron sulphide. Pyrophoric iron sulphide deposits may emit considerable heat when in contact with air and can be a source of ignition. As a by product of this reaction, hydrogen and water are produced. If this continues for some time and the tank atmosphere is humid, prolonged exposure to hydrogen may lead to fractures developing in the steelwork (known as hydrogen induced cracking) in areas subject to repeated tension and compression such as tank tops and floors.

Recommendations

International Standards Organisation (ISO) Fuel Standard ISO 8217:2010 limits the H_2S content of residual and distillate marine fuels to 2 ppm (mg/kg) by weight in the liquid and not as vapour or gas concentration. Although the H_2S limit does not apply until 1 July 2012, Members in the meantime may wish to stipulate ISO 8217:2010 with a maximum H_2S content of 2 mg/kg when ordering bunkers in case such product is available. However, it should be borne in mind that tanks containing such bunkers may still produce H_2S gas in concentrations which will be hazardous.

H_2S Concentration	Effects
0.0047 ppm	The recognition threshold of human smell and the concentration at which 50% of humans can detect the odour of rotten eggs.
2 ppm	Long term exposure may result in headaches, dizziness, fatigue, loss of appetite and irritability.
5 ppm	The maximum exposure limit for an 8 hour period.
10 ppm	The maximum exposure limit for a 15 minute period.
10-20 ppm	The borderline concentration for eye irritation.
50-100 ppm	Can lead to eye damage.
100-150 ppm	The olfactory nerve in the nose is paralysed after a few inhalations and sense of smell disappears, often together with an awareness of danger.
320-530 ppm	Leads to pulmonary oedema (fluid in the lungs) with the associated symptoms of shortness of breath or difficulty breathing, anxiety, apprehension, sweating with the possibility of death.
530-1000 ppm	Causes strong stimulation of the central nervous system and rapid breathing, leading to loss of breathing.
800 ppm	Lethal to 50% of humans after 5 minutes exposure.
>1000 pm	Can cause immediate collapse with loss of breathing, even after a single breath.

Concentrations and Effects of Hydrogen Sulphide Gas on Humans

Other recommendations include adding suitable guidance on the dangers of H_2S in marine bunkers to the Safety Management System (SMS), providing vessels with a correctly calibrated H_2S gas detector and personal monitors and training appropriate personnel in their use.

Should it be necessary to enter a tank which has carried bunkers, it will be necessary to follow SMS procedures regarding enclosed space entry and test the atmosphere for oxygen and hydrocarbons beforehand. Safety may be further improved by carrying out a series of checks using the H_2S gas detector. Since H_2S is heavier than air, the tank atmosphere should be sampled at various heights to ensure that an accurate assessment of H_2S gas can be made.

Within the engine room fuel oils will be treated (purified), handled and heated to very much higher temperatures, which in turn will cause greater evolution of this gas. Notwithstanding the forced ventilation in this area, H_2S being heavier than air will cause it to accumulate in the machinery space bilges and below the lower engine room plates. Under such circumstances access to these areas of the engine room should be treated in the same way as an entry into an enclosed space.

If the odour of rotten eggs emerges from a tank when it is opened or if the gas detector indicates that H_2S gas is present in quantities which exceed national or flag state exposure limits (typically 10 ppm), personnel should replace the tank lid immediately, evacuate the area and seek fresh air to breathe.

If the smell of H_2S gas is found to be coming from a bunker tank vent, the crew should be alerted immediately to this danger. All accommodation openings (doors and portholes) should be kept closed at all times with clear notices posted in these locations as to the presence of H_2S gas.

Storage tanks that contain residual dirty oil should be emptied periodically to ensure there is no build up of H_2S gas over time. Such tanks should also be tested regularly for the presence of H_2S gas.

Wherever possible, bunker storage tanks in machinery spaces that have sounding pipes that terminate within the space should be fitted with side level gauges so that the tank contents can be determined without opening the sounding pipe cap. As an additional safety measure, such sounding pipes may also be fitted with a gravity dead weight closing device to minimise the possibly of them being left open inadvertently.

Suitable notices should be posted to warn crewmembers that marine bunker tanks and residual dirty oil tanks may contain H_2S gas, and of the associated symptoms and hazards.

Members requiring further guidance should contact the Loss Prevention Department.

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