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## Potential Explosive Hazards from Hydrogen Sulfide Production in Ship Ballast and Sewage Tanks

Lyn E. Fletcher

DSTO-TR-0750

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**Maritime Platforms Division  
Aeronautical and Maritime Research Laboratory**

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## ABSTRACT

Hydrogen sulfide produced by sulfate-reducing bacteria is a well recognised toxic hazard in storage tanks on HMA Ships, however, it also has the potential to be an explosive hazard. Hydrogen sulfide can cause explosions when its concentration exceeds 4% in air. A number of storage tanks on HMA Ships theoretically have the potential to produce enough hydrogen sulfide to exceed this figure. This report assesses the likelihood of this occurring in ballast and sewage holding tanks. Sewage tanks pose the greatest risk of an explosive hazard occurring and this situation is exacerbated when seawater is used for flushing or a concentrated sewage is produced due to reduced flushing volumes, as is the situation with EVAC systems. Ballast tanks that contain only seawater and Deiso F76 pose minimal risk, but any contamination of the tanks with biodegradable material would increase this risk considerably.

19990308167

## RELEASE LIMITATION

*Approved for public release*

DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

DTIC QUALITY INSPECTED 1

AQF 99-06-1127

*Published by*

*DSTO Aeronautical and Maritime Research Laboratory  
PO Box 4331  
Melbourne Victoria 3001 Australia*

*Telephone: (03) 9626 7000*

*Fax: (03) 9626 7999*

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*AR-010-683*

*December 1998*

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# Potential Explosive Hazards from Hydrogen Sulfide Production in Ship Ballast and Sewage Tanks

## Executive Summary

Hydrogen sulfide produced from the action of sulfate-reducing bacteria is a well documented hazard on ships and has resulted in a number of fatalities on ships of the Royal Australian Navy (HMA Ships). What has not been as well documented is the potential of hydrogen sulfide in the headspace of storage tanks to reach potentially explosive concentrations. Hydrogen sulfide has a lower explosive limit of 4% in air and an upper explosive limit of 46%. Therefore, at concentrations between 4 and 46% an explosive hazard exists.

For sulfate-reducing bacteria to produce hydrogen sulfide at such high concentrations a number of conditions must be met. They include a high sulfate concentration, the presence of sufficient biodegradable organic materials and nutrients, time, absence of oxygen, and reducing conditions. A number of storage tanks exist on HMA Ships that could meet these conditions and theoretically produce hydrogen sulfide at high concentrations. These typically include tanks that store wastes or other liquids for at least a week or longer and contain mixtures of seawater and biodegradable organic materials. Sewage and seawater Dieso F76 slops and ballast tanks are typical candidates.

An assessment of sewage storage tanks shows that if a breakdown in tank aeration were to occur for a period of around 1 week then in most sewage systems on HMA Ships sufficient sulfate and biodegradable material would be present to produce the required hydrogen sulfide concentration. The risk is further increased in systems that use seawater flushing. In addition to hydrogen sulfide, stored oxygen depleted sewage can produce other flammable gases in the tank headspace that will increase the fuel load. Another factor that will alter the explosive hazard is the likely oxygen depletion that would occur under these conditions. Consequently, the greatest risk may occur when air is subsequently mixed into the oxygen deficient tank.

For seawater ballast and slops tanks analysis demonstrates that, while there is ample sulfate to theoretically produce explosive concentrations of hydrogen, there exists insufficient readily biodegradable material to support the required growth of sulfate-reducing bacteria. Consequently, for these tanks the risk of an explosion caused by hydrogen sulfide is minimal. However, the volatile components of Dieso F76 are flammable. Care should be taken to avoid any contamination of these tanks with biodegradable material, since the presence of these substances will greatly increase the risk of hydrogen sulfide production.

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# 1. Introduction

Hydrogen sulfide is produced in a number of holding tanks on ships of the Royal Australian Navy (HMA Ships) by the action of sulfate-reducing bacteria. These bacteria grow in oxygen deficient environments and convert sulfate to hydrogen sulfide. The microbial production of hydrogen sulfide gas in sewage systems and oily water waste holding tanks, has been the cause of a number of fatalities (Hodgeman *et al.* 1995a). Consequently, the ability of stored wastes to produce hydrogen sulfide is well documented and the RAN has developed a policy for controlling the production of this gas in oily water waste and sewage holding tanks DI(N) LOG 34-5 "Control of hydrogen sulfide in sewage and oily waste systems".

However, while the toxic risk that hydrogen sulfide poses is well recognised, the explosive hazard that hydrogen sulfide could pose has not been as well documented. Hydrogen sulfide can form explosive mixtures at concentrations above 4% in air. This is quite a high concentration for microbial produced gases and it is substantially higher than the concentration required to produce toxic hazards. However, it is feasible that a number of holding tanks on Royal Australian Navy (RAN) vessels are of such a size that they have the capacity to produce hydrogen sulfide at these explosive concentrations. While the RAN is aware of possible explosive conditions being present in storage tanks, there is a need for a detailed analysis of the potential for explosive concentrations to be produced through the action of sulfate-reducing bacteria. This report addresses the potential of stored ballast and sewage to produce explosive concentrations of hydrogen sulfide. This report does not seek to address and identify all potential explosive hazards in these tanks.

## 2. Physical Properties of Hydrogen Sulfide

### 2.1 General Properties

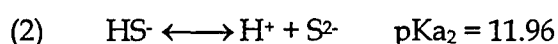
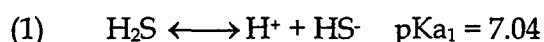
Hydrogen sulfide is a toxic gas with the distinctive odour of rotten eggs. It is commonly encountered in the natural environment in oxygen deficient situations. Hydrogen sulfide is a significant occupational hazard and numerous deaths have been attributed to it in the petrochemical (Hill *et al.*, 1987) and waste treatment industries (Saruda and Agnew, 1989). Table 1 lists some of the physical properties of hydrogen sulfide.

Table 1. Properties of pure hydrogen sulfide (H<sub>2</sub>S)

Property	Value	Reference
UN no.	1053	1
Hazchem	2WE	1
D.G. Class	2.1 (Flammable gas)	1
D.G. Sub risk	2.3 (Poison gas)	1
Molecular weight	34.08 g/mole	2
Melting point	-85.5 °C	2
Boiling point	-60.4 °C	2
Specific Gravity at 0°C	1.539 g/l	2
Vapour Density (air =1)	1.175	3
Lower Explosive Limit (LEL)	4.0%	2
Upper Explosive Limit (UEL)	46.0%	2
Ignition temperature	260 °C	2
OSHA TLV (ceiling)	20 ppm	3
Immediately Dangerous to Life and Health	100 ppm	3

References: 1 Infosafe MSDS; 2. Sax and Lewis (1989); 3. Vincolli (1996)

Hydrogen sulfide is moderately soluble in water and highly soluble in alcohols and other petrochemicals. The solubility of hydrogen sulfide in cold water is 437 ml/100 ml at 0°C and 186 ml/100 at 40°C. This equates to 6.72 g/l and 2.86 g/l, respectively. At 20 °C the solubility is 4.46 g/l (Beauchamp *et al.*, 1984). Hydrogen sulfide will, depending on pH and temperature, dissociate in water to HS<sup>-</sup> and S<sup>2-</sup> ions. The extent of the dissociation is measured by dissociation constants (pK<sub>a</sub> values). Equations 1 and 2 show the chemical reactions of hydrogen sulfide in water and the relevant dissociation constants at 18°C.



Consequently, at neutral pH approximately half of the sulfide will be present as the volatile H<sub>2</sub>S. If the solution is open to air, the volatile H<sub>2</sub>S will partition into the air above the solution (headspace) and shift the chemical equilibrium of the solution to produce more H<sub>2</sub>S. This over time, will reduce the total concentration of sulfide in the solution and alter the pH, until an equilibrium concentration of hydrogen sulfide is established between the solution and the headspace.

## 2.2 Conditions Required for Hydrogen Sulfide to Cause an Explosion

An explosion occurs when a fuel source ignites. The rapid increase in gas volume that results from generated heat and gases produces a shockwave that can result in significant damage to physical structures and, of course, life. Flammable gases, such as hydrogen sulfide, tend to explode when ignited. The important properties to be



considered when assessing the explosive hazard of a substance are its Lower Explosive Limit (LEL) and Upper Explosive Limit (UEL).

For an explosion to occur three basic conditions have to be met. Firstly a fuel or flammable material must be present, secondly an oxidising material that can react with the fuel must also be present (commonly oxygen present in air) and finally an energy or ignition source is required. Below the LEL, the concentration of the fuel (hydrogen sulfide) in the mixture is not at a sufficient concentration to support an explosion. Conversely above the UEL the concentration of the fuel is too rich and there is insufficient oxidant present (oxygen in air) to react with the fuel and produce an explosion. Consequently any mixture of air and hydrogen sulfide between these two values has the potential to produce an explosion if ignited. It is also pertinent that hydrogen sulfide is heavier than air and will be at higher vapour concentrations at the bottom of tanks.

The LEL of hydrogen sulfide is 4 % v/v and the UEL is 46% v/v. This corresponds to a concentration of hydrogen sulfide in air of 40,000 ppm (0.062 g/l) and 460,000 ppm (0.71 g/l), respectively, well above the acutely toxic concentration.

The autoignition temperature is the temperature at which an additional ignition source is not required for a fuel mixture to ignite. At this temperature and above a mixture of hydrogen sulfide within the LEL and UEL could spontaneously ignite and explode. The autoignition temperature for hydrogen sulfide, 260°C, is quite high and in most situations an additional ignition source would be required to ignite the fuel mixture. Additional ignition sources commonly include electrical sparks from electrical equipment or static electricity, naked flames, friction, impact energy or hot surfaces.

### **3. Physical Requirements for the Microbiological Production of Hydrogen Sulfide**

Hydrogen sulfide is often naturally produced in the environment by the action of sulfate-reducing bacteria (SRB). These bacteria are active in oxygen deficient conditions and reduce sulfate ions to hydrogen sulfide gas. This process can produce substantial hydrogen sulfide and is the source of the distinctive odours that develop in many low oxygen environments (low tide marine sediments, marshes, thermal pools, intestinal gases etc). Sulfate-reducing bacteria can be dormant in oxygenated water and sediments for a considerable length of time and can commence growth when conditions become favourable. Consequently, sulfate-reducing bacteria may be present in either a dormant or active form in many natural waters.

SRBs include a range of bacterial genera and species with differing nutritional and physical requirements. The unifying feature of this group is their ability to reduce sulfate. This diversity means that these microorganisms can become active over a fairly wide spectrum of conditions, although some conditions are more restrictive, for example the requirement for anaerobic conditions (no oxygen present) and the often

limited food sources for the various species. The most common SRBs encountered in natural waters are *Desulfovibrio* and *Desulfotamaculum* spp (Postgate, 1984; Kreig and Holt, 1984). Hodgeman *et al.* (1995b) when surveying HMA ships for SRBs in oily water waste, found that *Desulfovibrio* spp were the most commonly encountered.

However, before sulfate-reducing bacteria can grow they have a requirement for the following physical and chemical conditions.

### 3.1 Temperature

Sulfate-reducing bacteria have been isolated which are mesophilic (grow best between 20 and 45°C), thermophilic (grow at high temperatures, > 45°C) and psychrophilic (grow at low temperatures, <20°C). These have been isolated from distinctly different environments such as Antarctic hypersaline lakes (Franzmann *et al.*, 1985) and volcanic underwater thermal vents (Volikov *et al.*, 1983). Although on HMA Ships it is the mesophilic SRBs that are of interest, these microorganisms can grow between 10°C and 45°C (Postgate, 1984).

In a survey of SRBs in HMA Ships from oily-water waste Upsher *et al* (1995) observed growth of SRB up to 48°C. However, optimum growth was between 20°C and 38°C. In addition, growth rates of mesophilic SRB increase as the temperature increases within the range, ie SRBs grow significantly faster at 38°C than at 20°C (Upsher *et al.*, 1995). Consequently growth of SRBs is expected to be faster in the tropics than when the ship is in temperate waters.

The temperature of HMA ships' bilges and tanks appears to be suitable for growth of SRBs.

### 3.2 pH

Sulfate-reducing bacteria commonly grow within the pH range of 6-9. With the optimum growth being in pH neutral conditions of 7 (Postgate, 1984). In the survey of oily-water wastes Upsher *et al.* (1995) observed that SRB isolated from ship bilges followed this same growth pattern.

The pH of ballast water is expected to be close to neutral or slightly alkaline (pH range 7-8). This is because the ballast is seawater, which is often slightly alkaline due to dissolved carbonates. The chemistry of sewage is complex and pH of sewage will vary more widely depending on the type and quality of flush water, proportion of sewage to the volume of flush water and storage time.

### 3.3 Oxidation Reduction Potential

All sulfate-reducing bacteria require anaerobic conditions (the absence of oxygen). However, most SRBs also require that the conditions be reducing, that is a negative oxidation-reduction potential (ORP) is required. When reducing species are not

already present, growth is often not initiated until the ORP falls below -100mV (Postgate, 1984). The common method in the laboratory to achieve this is through seeding with a small amount of media that already contains growing SRBs and hydrogen sulfide (a strong reducing agent), or by adding another reducing agent. In nature this reducing environment can come about through the action of other microorganisms or a previous chemical reaction (for example corrosion products).

### 3.4 Salinity Requirements

Sulfate-reducing bacteria occur naturally over a range of environments and are frequently isolated from fresh water rivers, estuarine and marine waters and sediments. Consequently, there are SRBs that can survive and grow over a range of salinities. In addition some SRBs have a definite requirement for saline solutions.

### 3.5 Metabolic Requirements

For microorganisms to grow they need two things from their environment: energy, and substances necessary to reproduce and to repair their own cells. When the microorganism obtains energy it is called dissimilary metabolism and when the microorganism obtains chemical substances from the environment it is known as assimilary metabolism, due to the substances being incorporated into the cell. To achieve both of these requires energy to be released from a chemical reaction. In all organisms it requires two main reactants, that is an electron acceptor and an electron donor. In common aerobic organisms, like the higher mammals, the electron acceptor is oxygen that is derived by respiration, and electron donors are carbohydrates and fats obtained through the diet.

In sulfate-reducing bacteria the electron acceptor is most commonly sulfate and the electron donors include a limited number of small organic substances. As well as reducing sulfate, some SRBs are also capable of reducing sulfite, thiosulfate and elemental sulfur to hydrogen sulfide and in some species nitrate reduction to ammonia can also occur (Postgate, 1984).

The types of compounds that can be used by sulfate-reducing bacteria as electron donors (or food sources) are much more complex. Individual species often have a very limited number of substrates they can use. Of the known species, the most common organic compounds used are lactate and pyruvate. Other compounds that are used by some *Desulfovibrio* species include malate, choline, palmitate, acetate and butyrate. Other genera of SRBs can utilise propionate, higher fatty acids, ethanol and benzoate and other aromatic compounds (Kreig and Holt, 1984).

Most of these compounds are not abundant or common in natural waters. Consequently, for SRB to thrive, a consortium of bacteria is required. Many of the organic compounds mentioned above are the products or intermediary products of other microbiological metabolic processes. For example, fermentative bacteria that can also grow in anaerobic conditions can produce as an end product many of the above

mentioned compounds. Therefore, in an environment where many different microorganisms are active, the range of substrates is effectively increased. Consequently, the growth of SRB is dependent on the environment's ability to provide a readily biodegradable substrate that can be used by other microorganism to produce the substrates required by the SRB. In other words, if all other conditions are optimal, the level of SRB growth will depend on the concentration of readily biodegradable materials present in the mixtures.

### **3.6 Nutrients**

In addition to the main metabolic requirement a number of nutrients are also required. The common ones are phosphorus, nitrogen, calcium and magnesium. The main source of phosphorus is dissolved phosphate ion, which can often be in low concentrations in natural waters (0-90 ppb, Kennish, 1994). The nitrogen source most often used by SRB is ammonia, due to the anaerobic conditions in which SRBs grow. Calcium and magnesium are commonly found as dissolved salts. In addition, SRBs have a requirement for trace levels of numerous other elements. However, in situations where substantial biodegradation is occurring, it can be assumed that these environments are providing sufficient nutrients to support SRB.

## **4. Potential for Explosive Concentrations to Develop in Sewage Tanks**

A number of conditions must exist before an explosion can occur in sewage systems from the accumulation of hydrogen sulfide. Firstly, hydrogen sulfide must be produced from SRB. This requires all of the conditions listed in Section 3 to be achieved. Secondly, it must occur to the extent that hydrogen sulfide will degas from the sewage and accumulate to a very high concentration of at least 40,000 ppm in the headspace.

Hydrogen sulfide can be produced from anaerobic sewage in substantial concentrations. Sewage provides a very biologically active environment where much biodegradable matter is available for metabolism, as well as the nutrients required to support growth. Anaerobic degradation of the organic components of sewage follows a number of stages. Firstly, the proteins, polysaccharides and fats present are converted to long chain fatty acids, peptides, amino acids, glycerol and monosaccharide. The second stage involves the production of a range of low molecular weight compounds including hydrogen, formic and acetic acids, ketones (acetone) and alcohols. The final step involves the complete conversion of the above precursors to methane and carbon dioxide (Harrison, 1990).

Unfortunately there have been numerous instances where hydrogen sulfide has been produced at sufficient concentrations to result in fatalities on ships. However, for fatalities to occur the concentration of hydrogen sulfide in the air above the waste needs to be greater than 600 ppm. This is well below the lower explosive limit and

does not indicate that in these situations an explosive hazard would also have been present. However, considering the high concentration of biodegradable organic material in ships' sewage and the abundance of nutrients available it could potentially produce much higher concentrations of hydrogen sulfide during storage if left anaerobic. In addition, some of the intermediates of biodegradation that occur in sewage are also flammable compounds that could contribute to the fuel load in the head space, exacerbating the risk of explosive conditions occurring.

#### **4.1 Shipboard Sewage System Characteristics**

A number of different sewage systems operate in the RAN fleet. These include seawater flush with electrocatalytic chlorination of waste, chemical toilets, fresh water flush with collection and holding tanks. This discussion will be based on a collection and holding system where the large volumes of held waste could create a substantial problem.

The RAN FFGs use a Collection, Holding and Transfer (CHT) system. This system relies on being able to collect and hold wastes for a sufficient length of time to reach port facilities or waters where discharge can occur. The WCs are flushed with 1.5 litres of fresh water with an EVAC vacuum transport system (the FFGs were previously flushed with seawater). The sewage is then collected in CHT tanks with a total volume of 3600 US Gallons (Ferrier, pers comm., 1997). The working range of the tank is up to 3300 US Gallons.

The worst case scenario for this system would be a failure to aerate the stored sewage and the inability to pump or discharge the sewage. In this situation anaerobic conditions would occur and hydrogen sulfide generation would begin. In sewage large amounts of biodegradable material are present and this is not expected to be a limiting factor to SRB growth. Likewise ample nutrients should be available and conditions should be appropriate to support SRB growth. The extent of hydrogen sulfide production would depend on sufficient sulfate being available to the SRB, together with sufficient time for the SRB to grow to the extent required.

#### **4.2 Likelihood of Production of Explosive Concentrations of Hydrogen Sulfide**

A literature review was performed on marine accident reports to determine whether an explosion from shipboard sewage systems has been previously documented. No evidence was found.

One of the most significant factors that will influence the amount of hydrogen sulfide produced is the concentration of sulfate ions in the sewage. Unfortunately this figure will vary substantially depending on the composition of the sewage. For example, municipal sewage is much more dilute than shipboard sewage due to the presence of household and industrial wastes (storm water is often also a component). When only head wastes from WCs are present in sewage, the type and quality of water used for

flushing, together with flushing volumes will affect the sulfate concentration. Consequently, without exact concentration data from EVAC CHT sewage systems it is difficult to predict a representative sulfate concentration.

The EVAC systems use a fresh water flush so the concentration of sulfate won't be as high as instances where seawater is used. However, the sulfate concentration in fresh water varies, but the maximum permissible concentration for drinking water is 400 mg/l (ANZECC, 1992). For ships that use reverse osmosis to desalinate seawater, a typical sulfate concentration is around 14 mg/l (Ferrier, pers. comm., 1997). Consequently the concentration of sulfate in fresh water flushed sewage could vary substantially. Sewage will also contain sulfate from urine and faeces. In a David Taylor Research study into gas generation in CHT tanks, Lardis *et al.* (1978) measured sulfate in Head wastes at 420 mg/l. However, for systems that use sea water flush, the sulfate concentration can be up to 2,700 mg/l (Kennish, 1994). Consequently a figure of 400 mg/l appears to be a reasonable mid-level concentration and will be used for modelling purposes in this report.

If all sulfate in this model sewage is converted by SRBs, then 141 mg/l of hydrogen sulfide would be produced and dissolved in the water. A concentration of 141 mg/l is feasible. In the oily-water waste study Hodgeman *et al.* (1995b) observed hydrogen sulfide concentrations of 133 mg/l in an open bilge on HMAS BAYONET. This concentration is well below the solubility limit for hydrogen sulfide of 4.46 g/l at 20°C. This hydrogen sulfide would then partition between the sewage and the headspace in the tank. Since hydrogen sulfide is moderately soluble in water not all of the hydrogen sulfide will out gas.

The maximum working volume of the tank is 3300 US gallons (12,500 litres), which when full leaves a headspace of 300 US gallons (1,135 litres). This is 1/11<sup>th</sup> of the liquid volume. Consequently, the sewage in a full tank could contain a total 1,760 grams of hydrogen sulfide. To achieve the LEL of 0.062 g/l of hydrogen sulfide in the headspace volume, a total of 70.4 grams of hydrogen sulfide would be required. This constitutes a reduction of hydrogen sulfide in the liquid sewage phase of 4%. Consequently the concentration of hydrogen sulfide in the liquid sewage would drop to 135 mg/l. This appears to be well within the bounds of probability given that hydrogen sulfide is only moderately soluble and dissolved hydrogen sulfide will equilibrate with the headspace gases and partition between the liquid and gas phases. Consequently, it is feasible that stored sewage could produce enough hydrogen sulfide to reach the LEL.

This situation becomes more significant as the concentration of sulfate increases. When seawater flushing is used, if sufficient biodegradable material is present, the maximum hydrogen sulfide produced in a full tank of sewage could be up to 11,880 g. To achieve the LEL concentration of hydrogen sulfide in the headspace requires only 0.6% of this amount to out gas. Conversely when the sulfate concentration is low it becomes much more difficult to produce the LEL concentration. At 14 mg/l sulfate, the maximum hydrogen sulfide produced in a full tank would be only 61.6 g, which is not enough to produce the LEL.

Also, hydrogen sulfide is heavier than air and will concentrate at the bottom of the head space. So the concentration will not be uniform and could locally be higher in certain regions.

The other issue is time. Do the SRB have enough time to convert this much sulfate to hydrogen sulfide? Sewage is a very biologically active waste and should rapidly become anaerobic when aeration ceases. Consequently the lag time required for the conditions to become anaerobic to support SRB growth should be minimal. In addition Hodgeman *et al.* (1995b) observed that an oily-waste from HMAS PERTH that was given sufficient sulfate and optimum conditions converted approximately 500 mg/l of sulfate to hydrogen sulfide in 6 days. Consequently, given favourable conditions, sewage stored for one week without aeration should have ample time to produce high levels of hydrogen sulfide.

### **4.3 Additional Factors that Impact on the Risk of Explosion**

While the discussion has so far been addressing hydrogen sulfide generation, other explosive gases can also be produced by the anaerobic decomposition of sewage. Methane is often produced from the action of methanogenic bacteria. Methane has a LEL of 5% and a UEL of 15%. Ammonia can also be produced which has a LEL of 15%. Also, some of the intermediaries in the anaerobic degradation of sewage are volatile flammable compounds. For example, hydrogen has a LEL of 4.1%, acetone has a LEL of 2.5%, ethanol has a LEL of 3.3% and acetic acid has a LEL of 5.4% (Vincolli, 1996). Table 2 lists some of the properties of these gases based on increasing ignition temperature. This list is not an exhaustive list as the decomposition of sewage is extremely complex and a cocktail of organic compounds will be formed. However, the following table lists some common and representative compounds.

Table 2. Properties of compounds commonly found during the decomposition of sewage.

Compound	Boiling Point (°C)	Vapour Pressure (mm Hg)	LEL (%)	UEL (%)	Ignition Temperature (°C)	OSHA TLV (ppm)	Vapour Density (Air=1)
Hydrogen sulfide	-60	Gas	4	44	260	20	1.175
Ethanol	78	44	3.3	19	363	1000	1.59
Hydrogen	-252	Gas	4.1	74.2	400	-	0.07
Acetone	56	180	2.5	12.8	465	1000	2.0
Acetic acid	118	11.4	5.4	16.	465	10	2.07
Methane	-167	Gas	5	15	537	-	0.6
Ammonia	-3.5	Gas	15	28	650	35	0.6
Carbon dioxide	-78.5	Gas	Nil	Nil	Not flammable	5000	1.53

Comparing the compounds listed in table 2, the compounds have vastly different vapour densities and will partition somewhat in the headspace. Generally the organic compounds that are not gases at room temperature are heavier than air and will partition between the sewage and headspace depending on the vapour pressure of individual compounds. Sewage will produce many longer chain organic compounds, some of which will be volatile and also partition into the headspace. Generally, the larger the compound, the less volatile it is and less will partition into the headspace. Consequently, the headspace gases above anaerobic sewage will be a very complex mixture and will contain more flammable gases than just hydrogen sulfide.

The presence of any additional flammable gases in the gas phase can constitute a component of the total fuel load in the headspace. The concentration of flammable gases can be combined to indicate the total concentration of flammable gases present. Consequently, when a mixture of any of these gases reaches around 3-5 % an explosive hazard must be assumed to exist. For example a gas containing 1.5 % hydrogen sulfide, 1.5 % methane, 1 % volatile organic compounds (VOC) and a small amount of hydrogen and ammonia could be an explosive hazard if oxygen was present.

One aspect that may help to reduce the risk is the probable absence or depletion of oxygen in the headspace when aeration has ceased. During anaerobic conditions most of the oxygen present in the headspace will be in equilibrium with the dissolved oxygen in the sewage and should be consumed by the biodegradation process occurring in the wastes. For oxygen to be present it must continually be replenished by ventilation which would also act to dilute the concentration of flammable gases in the headspace. For the worst case scenario, when ventilation and aeration has ceased, the risk is greatest when the tank is opened to the air or at the vent outlets. At these points air and fuel rich gas will mix and an explosion is possible. However, if air is required to mix with the gases before enough oxygen is present, then dilution of these flammable gases will occur. Consequently, under these conditions the concentration of flammable gases will have to be greater than the LEL to account for dilution. However, it cannot be assumed that these conditions could not be met in stored anaerobic sewage.

Also in an EVAC system minimal flushing volumes are used (1.7 litres). Therefore, the stored waste will be more concentrated than either municipal or other shipboard systems that use traditional flushing WCs. Traditional flush volumes vary but can be



around 7 litre/flush. Consequently the amount of sulfate and biodegradable organic compounds will be much greater in the EVAC system; up to 5 times more concentrated. Consequently the ability of this sewage to produce flammable sewage gases is increased significantly.

Considering all of the above variables, it is feasible that CHT tanks containing EVAC delivered sewage could produce flammable gases at a concentration that could constitute an explosive hazard. It is also noted that the concentration of sulfate present in the sewage has a large effect on this risk. Using a high quality fresh water flush would reduce this risk.

## **5. Potential for Explosive Concentrations to Develop in Ballast Tanks**

Slop tanks that collect oil contaminated ballast waste and fuel compensated fuel tanks also contain large quantities of sulfate and an organic component. Consequently, the conditions could be favourable for the generation of hydrogen sulfide and other flammable gases in these tanks. This section will assess the potential of slop tanks and fuel compensated fuel tanks to generate explosive gases.

Ballasting is done with seawater which contains up to 2,700 mg/l of sulfate ion (Kennish, 1994). This is adequate to support the production of the required concentration of hydrogen sulfide. However, the SRBs also require an ample organic food source and nutrients to grow. Diesel fuel consists of a mixture of aromatic and aliphatic hydrocarbons, and most hydrocarbons are slow to biodegrade. Slop tanks and fuel tanks are not expected to contain an appreciable amount of any additional organic substances, consequently, the amount of readily biodegradable material is expected to be small. Also, seawater and fuel are limited in the amount of major nutrients that they can supply. However, some sediments may be present in ballasting water and will subsequently, settle to the bottom of the tank. Therefore, the overriding issue when assessing the potential of ballast to generate explosive conditions through hydrogen sulfide production is the ability of these mixtures to provide conditions necessary for SRB growth, including the ability to readily become anaerobic.

### **5.1 Ballast Tanks and Ballasting System Characteristics**

HMAS SUCCESS is a large RAN tanker with a deep displacement of 17,900 tonnes and carries cargoes of distillate Dieso F76 and F44 AVCAT. To maintain stability when cargoes are offloaded, seawater ballast is loaded first into dedicated ballast tanks. When these are full, additional seawater ballast is added to empty Deiso F76 cargo fuel tanks. In extreme circumstances 4000 tonnes of seawater ballast could be stored in empty Dieso F76 tanks.

All tanks are routinely cleaned with in-tank nozzles and Butterworth hot seawater washing equipment. No foreign substances other than Dieso F76 are expected in these

tanks. After washing, the residue is stored in the slops tank before treatment by an oily-water separator prior to disposal. The slops tank on HMAS SUCCESS can contain 166 tonnes at 95 % capacity and is "L" shaped. In the worst case, where oil separators fail, a mixture of seawater and Dieso F76 may sit in the slops tank for up to 28 days (Ferrier, pers. comm., 1997).

## 5.2 Likelihood of Production of Explosive Concentrations of Hydrogen Sulfide

The first condition that must be met before SRBs can grow is the formation of anaerobic and reducing conditions with an oxidation reduction potential (ORP) of less than -100 mV. To achieve this, biological activity in the ballast water must consume all of the dissolved oxygen present in the seawater ballast. The concentration of dissolved oxygen in seawater at 35‰ salinity and 25 °C is approximately 4.7 ml/l, or 6.7 mg/l (Kennish, 1994). Consumption of this amount of dissolved oxygen through biological processes will require a commensurate amount of biodegradable organic material to be available.

Dieso F76 is a complex and variable mixture of hydrocarbons produced to meet certain specifications such as boiling range, cloud point and sulfur content etc. No range is stipulated for aromatic and non-aromatic fractions, and aromatic contents vary and can exceed 50%. Consequently, it is difficult to be specific about the biodegradability of the components of Dieso F76 since the components can vary with each batch. However, the components in Dieso F76 are not generally readily biodegradable, containing mostly mixtures of aromatic compounds and long chain straight and branched chain aliphatic hydrocarbons. Table 2 lists some typical biodegradation rates.

Also aromatic and non-aromatic hydrocarbons are not soluble in water, and the majority of the biological activity will be restricted to the water/oil interface.

*Table 3 Biodegradation rates for typical components of Dieso F76*

Compound	Aerobic half lives	anaerobic half lives
Benzene	5-16 days	2 years- 16 weeks
Naphthalene	480 hrs - 12 hrs	37 weeks - 3.5 weeks

Source: Howard et al., (1991)

Considering the low solubility of the components of Dieso F76 in water and the generally low biodegradation rates of the components, it is unlikely that enough material would be available for organisms to consume the dissolved oxygen.

To test this, a laboratory experiment was set-up to simulate stored ballast, 250 ml of Dieso F76 was added to 750 ml of seawater in an airtight container and continually stirred at 30°C for 2 months. To four samples various amounts of an active SRB inocula was added. One sample was also kept in the dark for the entire period. The inocula was obtained by isolating and enriching SRBs from a sediment core obtained from

Williamstown, Victoria, using AMRL SRB culture media (Upsher *et al.* 1995). The ORP levels at the start and end of the 2 month period are presented in Table 3.

Table 4. Laboratory results simulated slop tank

Sample	Original ORP (mV)	Final ORP (mV)	Final pH
Sample 1 No inocula	186	310	5.5
Sample 2, 1ml inocula	-98	330	6
sample 3, 5 ml inocula	-164	310	7
Sample 4, 1 ml inocula, dark	-100	210	7

No hydrogen sulfide was produced in any of the samples. The most relevant aspect of these results is that with time the oxidation-reduction potential increased in all samples. With the samples subject to light, photosynthetic organisms could account for this increase in ORP. However, the sample in the dark also increased or became more oxidative with time. This can partially be attributed to the action of oxygen in the headspace reacting with the reduced components in the inoculum. However, other microbiological processes cannot be ruled out.

This experiment demonstrates that the negative ORP required for SRB growth is difficult to produce or maintain in a situation where only seawater and Dieso F76 are present.

A literature review was also performed into accidents involving explosions in ballast tanks. No instances of explosion were found where a source of hydrocarbon gas was not identified as the source of flammable gas; for example, cracks in a bulk head leading to leaking of adjacent fuel stores (NTSB, 1992).

Consequently, it is considered to be highly unlikely that a slops tank or ballasted empty Dieso F76 cargo tank could produce explosive concentrations of hydrogen sulfide. However, if other contamination occurred that could increase the availability of readily biodegradable organic compounds to the bacteria, this situation could change substantially.

## 6. Conclusion

If aeration ceases, sewage stored in CHT tanks on HMA Ships could generate enough flammable gases, including hydrogen sulfide, to create a potentially explosive atmosphere in the headspace. Various factors will have an impact on the likelihood of this occurring, however, the most relevant factor is the amount of sulfate originally present in the sewage.

The EVAC flushing and sewage distribution system used on FFG results in a more concentrated sewage due to less dilution through lower flushing volumes. This will increase the amount of organic material available for biodegradation and will result in more volatile gases being produced. However, if good quality fresh water with a low sulfate concentration is used for flushing this could control the total amount of hydrogen sulfide that can be produced. In DDGs and other ships where seawater flushing is used, explosive concentrations of hydrogen sulfide could readily be produced if enough biodegradable material was present.

The amount of oxygen in the headspace will also probably be reduced due to the action of microorganisms and reaction of reduced compounds with oxygen. Consequently, in these situations some dilution with fresh air may be required before explosive conditions could exist, and a higher concentration of flammable gases will be required to compensate for this dilution.

The major risk factor identified for sewage is the initial concentration of sulfate. Consideration should therefore be given to controlling sulfate concentrations. To achieve this fresh water flushing should be the preferred option.

For ballast and slops tanks that contain only Deiso F76 and seawater the risk of an explosion hazard occurring through the action of SRBs is minimal. While seawater can supply enough sulfate to theoretically cause a potential problem, there appears to be insufficient readily biodegradable material present to consume the dissolved oxygen present and produce the anaerobic conditions required by the SRB. However, any contamination of the ballast or slops tank would increase this risk substantially.

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Lyn E. Fletcher

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DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION DOCUMENT CONTROL DATA				1. PRIVACY MARKING/CAVEAT (OF DOCUMENT)	
2. TITLE Potential Explosive Hazards from Hydrogen Sulfide Production in Ship Ballast and Sewage Tanks			3. SECURITY CLASSIFICATION (FOR UNCLASSIFIED REPORTS THAT ARE LIMITED RELEASE USE (L) NEXT TO DOCUMENT CLASSIFICATION)  Document (U) Title (U) Abstract (U)		
4. AUTHOR(S) Lyn E. Fletcher			5. CORPORATE AUTHOR Aeronautical and Maritime Research Laboratory PO Box 4331 Melbourne Vic 3001 Australia		
6a. DSTO NUMBER DSTO-TR-0750		6b. AR NUMBER AR-010-683		6c. TYPE OF REPORT Technical Report	
				7. DOCUMENT DATE December 1998	
8. FILE NUMBER 510/207/0983	9. TASK NUMBER NAV 96/078	10. TASK SPONSOR DNPSE	11. NO. OF PAGES 16		12. NO. OF REFERENCES 21
13. DOWNGRADING/DELIMITING INSTRUCTIONS			14. RELEASE AUTHORITY Chief, Maritime Platforms Division		
15. SECONDARY RELEASE STATEMENT OF THIS DOCUMENT  <i>Approved for public release</i>  OVERSEAS ENQUIRIES OUTSIDE STATED LIMITATIONS SHOULD BE REFERRED THROUGH DOCUMENT EXCHANGE CENTRE, DIS NETWORK OFFICE, DEPT OF DEFENCE, CAMPBELL PARK OFFICES, CANBERRA ACT 2600					
16. DELIBERATE ANNOUNCEMENT  No Limitations					
17. CASUAL ANNOUNCEMENT Yes					
18. DEFTEST DESCRIPTORS  Explosions, hazardous wastes, toxic hazards, hydrogen sulfide, ballast tanks, sewage disposal					
19. ABSTRACT Hydrogen sulfide produced by sulfate-reducing bacteria is a well recognised toxic hazard in storage tanks on HMA Ships, however, it also has the potential to be an explosive hazard. Hydrogen sulfide can cause explosions when its concentration exceeds 4% in air. A number of storage tanks on HMA Ships theoretically have the potential to produce enough hydrogen sulfide to exceed this figure. This report assesses the likelihood of this occurring in ballast and sewage holding tanks. Sewage tanks pose the greatest risk of an explosive hazard occurring and this situation is exacerbated when seawater is used for flushing or a concentrated sewage is produced due to reduced flushing volumes, as is the situation with EVAC systems. Ballast tanks that contain only seawater and Deiso F76 pose minimal risk, but any contamination of the tanks with biodegradable material would increase this risk considerably.					