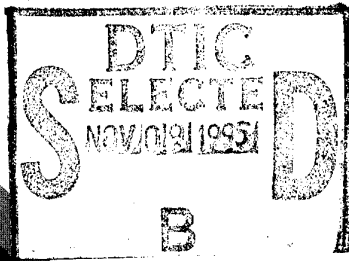


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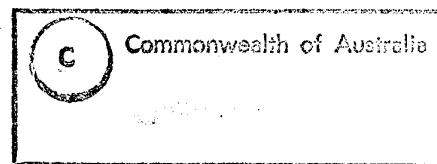
D.K.C. Hodgeman, F.J. Upsher
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Hydrogen Sulfide Generation in Shipboard Oily-water Waste: Part 1. Origin of the Hydrogen Sulfide

D.K.C. Hodgeman, F.J. Upsher and L.E. Fletcher

**Ship Structures and Materials Division
Aeronautical and Maritime Research Laboratory**

DSTO-TR-0053

ABSTRACT

This paper, the first in a series of four reports, provides an overview of the recurring problem of hydrogen sulfide generation in oily-water wastes in ships of the Royal Australian Navy. In the DSTO-AMRL investigation into this problem, we examined the physical and microbiological factors influencing the process under simulated storage conditions and related the findings to the shipboard situation. Sulfate from sea-water was the source of the sulfur for hydrogen sulfide formation. The sulfate was reduced to sulfide by anaerobic sulfate-reducing bacteria (eg *Desulfovibrio*) in concert with other bacteria. Physical and chemical conditions in the shipboard oily-water waste environment were generally conducive to this bacterial process. In addition to the need for sulfate, the other important requirement was for a supply of organic nutrient for the bacteria. Detergents used in cleaning are identified as significant nutrient sources.

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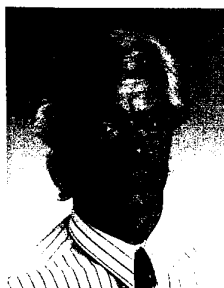
Ship Structures and Materials Division



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John Upsher, BSc Hons (Bath), MSc (La Trobe), joined Aeronautical and Maritime Research Laboratory as a microbiologist in 1966 then for 20 years investigated different problems associated with microbial deterioration of materials and equipment in storage and in the tropical environment. Responding to increasing concern within Defence on environmental matters, he has more recently investigated the bacterial generation of hydrogen sulfide in naval oily water wastes and the disposal of wastes including sewage and plastics.

L.E. Fletcher

Ship Structures and Materials Division



Lyn Fletcher, BAppSc (Chem.) (RMIT) joined Aeronautical and Maritime Research Laboratory in 1985 and worked for three years on research into polymer and solvent interactions. She then joined a small multidisciplinary group investigating some environmental problems encountered by the Royal Australian Navy. In support of this work, Lyn is currently studying for a MEnvSc at Monash University.

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1. Introduction

Hydrogen sulfide gas has been generated in oily-water waste in ships of the Royal Australian Navy. These wastes include the oily-water wastes in bilges and those moved from bilges and ballast to holding tanks to await disposal in an environmentally acceptable manner. Hydrogen sulfide is not always present in these wastes, but can become particularly noticeable when the wastes have remained stagnant in the bilge or holding tank for several days or more. The gas usually makes its presence known by its foul odour of "rotten eggs." This smell can occasionally be encountered in engine rooms, boiler rooms and other enclosed machinery spaces. Hydrogen sulfide is also found about the external vents to oily-water holding tanks, where it can enter the occupied part of the ship through the ventilation system. Problems with hydrogen sulfide formation in oily-water wastes are also well known in submarines.

Hydrogen sulfide is a toxic gas (Sax & Lewis, 1989), so its presence in confined spaces of ships or submarines is of some concern. It is also a very common gas, one which we encounter frequently in our everyday environment. Mostly, however, these encounters result in little more than a comment on the smell. This is because hydrogen sulfide is only toxic at high concentrations and has usually been well diluted in the air before it reaches our noses. In confined spaces, however, hydrogen sulfide presents a serious safety hazard and the gas has claimed many lives, particularly in sewers and utility access holes (Suruda & Agnew, 1989). Although the hazards arising from hydrogen sulfide generation in shipboard sewage treatment and storage systems are known (Lardis & Geger, 1978), oily-water wastes are not such an obvious source of this toxic gas.

The potential for formation of a toxic atmosphere in a ship through hydrogen sulfide generation in oily-water waste was brought to light by a tragic accident on HMAS Stalwart in 1985 (Royal Australian Navy, 1986). In this accident a large amount of stored oily-water waste was suddenly and unexpectedly released from a holding tank into the tiller flat area. Hydrogen sulfide, which had formed in the waste during storage, was rapidly released into the air in the compartment. The rate of release from the spillage exceeded the rate at which it could be removed by the ventilation system, and the resulting toxic atmosphere caused the deaths of three sailors and incapacitated many more (Royal Australian Navy, 1986).

Since the HMAS Stalwart accident, ships' crews justifiably have become very sensitive to the presence of hydrogen sulfide in their working environment, and express concern for their safety on smelling "rotten eggs". The Navy therefore introduced a program for investigation and management of toxic gas formation in oily-water wastes. An understanding of the factors present in the oily-water waste environment which contribute to hydrogen sulfide formation is an important aspect of this program, and the assistance of AMRL was sought in conducting this study. The objectives of the investigation were to:

- (a) Establish whether hydrogen sulfide is formed either by microbial or chemical processes, or by a combination of these processes.
- (b) Identify the principal sources of sulfur in the oily-water wastes, and establish which of these sulfur sources contribute significantly to the production of hydrogen sulfide.
- (c) Establish the role of detergents in the production of hydrogen sulfide.
- (d) Investigate the possibility of eliminating or inhibiting the formation of hydrogen sulfide in these wastes through the use of biocides and other chemical agents.

Hydrogen sulfide formation in industrial wastes and oil storage facilities is a common problem. In some wastes the hydrogen sulfide results from chemical reaction, but mostly it is a by-product of the growth of sulfate-reducing bacteria (Postgate, 1984). The oil industry experiences many problems with hydrogen sulfide generation by sulfate-reducing bacteria, particularly in offshore operations (Hill et al., 1987). The similarity between these and the shipboard environment would suggest a microbiological source for hydrogen sulfide generated in oily-water wastes.

This report, the first in a series of four which present the results of our investigation, introduces the background to the problem and addresses the origin of the hydrogen sulfide. In particular, evidence for a microbiological mechanism for generation of the hydrogen sulfide is presented, and the effect of some shipboard environmental factors on laboratory experiments is addressed.

Subsequent reports will describe in greater detail the microbiological aspects of the formation of the hydrogen sulfide (Upsher et al., 1995), and the factors in the actual ship environment which lead to hydrogen sulfide formation (Hodgeman et al., 1995 a). Finally, some approaches to minimizing the danger from formation of hydrogen sulfide in the oily-water wastes will be discussed (Hodgeman et al., 1995 b).

2. Background

2.1 Oily-water Wastes in Ships

Ships generate oily-water waste in routine engine room, boiler room, ballast and tank cleaning procedures. Since large quantities of these wastes are usually formed their removal from bilges and other locations forms an important part of day-to-day routine. The largest component of the oily-water waste is usually water, and a mixture consisting of 95% water and 5% oil would be fairly typical. The water is a mixture of varying quantities of fresh water and sea-water. Components, such as detergents and other cleaning agents, may also be present in the water layer. A mixture of this composition would appear to be a relatively harmless industrial waste

which would not require any special storage precautions. As we have seen this is not so, as these wastes have the potential to produce dangerous quantities of hydrogen sulfide.

In times when there was little concern for protection of the natural environment, oily-water wastes were pumped overboard into the surrounding sea or waterway. This kept the quantities of waste stored in the bilges and tanks low, and the time for which they were stored relatively short. Such practices resulted, however, in severe and unsightly oil slicks in harbours and sea lanes. With increasing concern for protection of the marine environment from all types of pollution, regulations have been imposed by local and international authorities to restrict the oil content of discharged waste waters. Thus, the International Maritime Organisation (IMO) limits the oil content of water discharged into environmentally sensitive regions to 15 parts per million (ppm) (IMO, 1985), while a higher content (100 ppm) is allowed in less sensitive locations. Regulations imposed by local authorities for restricted and coastal waters may be even more severe than those imposed by the IMO, and it can be expected that this will reflect the trend for the future.

Meeting the present environmental regulations can cause difficulties to ships' operators. In particular, storage of oily-water wastes is wasteful of valuable space, especially when most of this waste is just water! Oil and water do not mix, so that storage could be greatly reduced by separation of the two components, provided the water fraction produced is acceptable for discharge. Many ships have been equipped with plate separators or centrifuge filters to achieve this aim, so that onboard storage of the smaller oil fraction for later disposal in an acceptable manner is all that is required. International guidelines for the effective operation of these separators are available (IMO, 1978).

Unfortunately, complete separation often fails due to the presence of emulsified oil which cannot be removed from the water layer. Such emulsions, which usually result from the use of detergents in machinery space or tank cleaning operations, do not meet the regulations for discharge overboard. Fifteen parts per million of oil in water is a very low level - it corresponds to about one tablespoon of oil in one tonne of water! Thus, when emulsions are formed the only option is to retain the waste until it can be discharged into a shore-based facility. It is not unusual, therefore, for a ship to be carrying several tonne or more of the unprocessed oily-water waste in holding tanks installed for this purpose. A destroyer, for example, could be carrying from 5 to 10 tonne of oily-water waste. The holding tank on HMAS Stalwart had a capacity of 90 tonne and was holding 82 tonne at the time of the 1985 accident. Formation of emulsions in the oily-water waste thus requires longer-term storage of the waste onboard. As often happens when industrial wastes are stored for extended periods, unexpected hazards arise.

2.2 Sulfate-Reducing Bacteria

Hydrogen sulfide generation in waste liquids is a common industrial problem which is usually attributable to growth of sulfate-reducing bacteria (Postgate, 1984). These bacteria are widely distributed in nature (Postgate, 1988). They are very common in the marine environment, where they are responsible for the sulfurous odour of estuaries at low tide (Widdel, 1988; Pfennig et al., 1981; Pfennig & Widdel, 1981) and have been identified in sludge collected from fuel tanks on naval ships (Neihof & May, 1983). The sulfate-reducing bacteria are a heterogeneous group of bacteria typified by the genera Desulfovibrio and Desulfotomaculum. These strictly anaerobic bacteria grow only in an environment depleted of oxygen, provided sulfate and organic nutrients are also available. Under these conditions the bacteria perform a process termed "dissimilatory sulfate reduction" (Postgate, 1984) in which inorganic sulfate is used as the terminal electron acceptor in the respiration process; this results in energy production for the bacterial cell and is accompanied by the reduction of sulfate to inorganic sulfide (the source of the hydrogen sulfide gas). Although few references relating specifically to hydrogen sulfide generation in shipboard oily-water waste appear in the scientific literature, the bacterial formation of hydrogen sulfide in closely related environments, such as on offshore oil platforms (Hill et al., 1987), has been well documented.

Shipboard oily-water waste consists mainly of diluted sea-water, a layer of waste oil, and varying quantities of biodegradable detergents which have been used in machinery space and tank cleaning activities. The extensive use of sea-water (sulfate content approx. 0.27% w/w (Riley & Skirrow, 1975)) in washing operations will ensure both inoculation of the oily-water waste environment with sulfate-reducing bacteria and the presence of large quantities of inorganic sulfate essential to their growth. Additional sulfur is present in the oil layer as organosulfur compounds and in some detergents as organic sulfonates and may contribute to the sulfate load of the waste after oxidative breakdown.

Besides sulfate, the bacteria also require a source of organic nutrient for growth and are known to utilise only a limited range of organic compounds including lactate, pyruvate and malate (Postgate, 1984). Although these compounds are unlikely to find their way directly into the oily-water wastes, they are common metabolic by-products of the growth of other widely distributed types of bacteria, and would most likely arise from bacterial breakdown of biodegradable detergents present in the waste. Biodegradation of the oil component may also contribute to the organic nutrient level (Nazina et al., 1985; Jobson et al., 1979) although this would be expected to be a slower process.

In locations where the waste has become anaerobic, through consumption of oxygen by aerobic bacteria or corrosion reactions, an environment will be established which is very favourable to growth of the sulfate-reducing bacteria and subsequent hydrogen sulfide production. With excess organic nutrient present in the waste, the ultimate yield of hydrogen sulfide will be limited only by the amount of sulfur available to the sulfate-reducing bacteria. Moreover, insoluble sulfides (which result from the reaction of dissolved sulfide with metal salts) can precipitate and collect in the sludge at the bottom of the bilge or holding tank.

3. Results & Discussion

3.1 Collection of Oily-water Waste Specimens

As discussed above, the sulfate-reducing bacteria are a class of strictly anaerobic bacteria which grow only in environments depleted of oxygen. Such a situation can arise in oily-water waste through activity of aerobic bacteria, which use oxygen in their respiration processes, or by corrosion of steel plates, by which oxygen is consumed and converted into insoluble iron oxides. If the oxygen is removed by these biological and chemical processes at a rate faster than it diffuses in from the air at the surface of the liquid, then the waste becomes anaerobic and suitable for growth of sulfate-reducing bacteria. This will occur most readily in lower levels, particularly if the waste remains undisturbed for some time.

Although the sulfate-reducing bacteria are anaerobic they are not killed by an oxygen-containing environment, but they do cease to grow. These bacteria are very susceptible to oxygen shock which can present difficulties in collection of oily-water waste for return to the laboratory. For us to be confident in our experimental results, it was essential to establish reliable and reproducible sampling procedures. We therefore used considerable care in taking our early bilge samples to ensure that the specimens used in the laboratory typified those in a bilge.

For oily-water waste containing sulfate-reducing bacteria, this meant collecting samples without allowing them to be subjected to sudden and large changes in oxygen concentration. Collection by scooping from the surface of a bilge was considered unsuitable since, in a stagnant bilge, the oxygen concentration in the liquid is highest at the surface and the sulfate-reducing bacteria population would be expected to be low. For a bilge which had been mixed by recent pumping or ship movement, oxygen concentration profiles in the liquid would be different from those of a stagnant bilge. To gain some idea of the distribution of bacteria and hydrogen sulfide in the waste we initially took samples from different measured levels of the liquid and from deep stagnant corners of the bilges. The latter regions were expected to provide the most favourable conditions for growth of sulfate-reducing bacteria and were expected to provide the largest populations of these bacteria.

Sampling was initially conducted with hypodermic syringes, a technique used in collection of sensitive anaerobic bacteria from hot springs. Using syringes fitted with a long sampling tube, specimens were drawn from various levels of the bilge without contact with air. To avoid contamination, this apparatus was sterilized before use. Specimens collected in this way were sealed in the syringe (to prevent any subsequent contact with air during transit) and stored in ice for return to the laboratory. This procedure was found satisfactory and we were able, in our early experiments, to establish the presence of sulfate-reducing bacteria in bilge specimens taken from the engine rooms of HMAS Bayonet and HMAS Fremantle. Hydrogen sulfide

production in various nutrient-containing media inoculated with these wastes was also examined in the laboratory.

To provide a source of oily-water waste for laboratory experiments, a laboratory scale "holding tank" (see Plate 1) was established using the waste samples collected from the above ships and from the holding tank of HMAS Stalwart. This laboratory "holding tank", in which hydrogen sulfide was produced continuously, was maintained in an active state by the occasional addition of organic nutrient and inorganic sulfate. Inoculant specimens of oily-water waste for experiments were taken from this tank.

After several field trips to ships, we found that a hand-operated peristaltic pump (see Plate 2) was more convenient for collection of larger quantities of bilge-water from the machinery spaces of the ship. Using this method, oily-water waste samples of any required volume could easily be taken from any desired depth in the bilge.

3.2 Enumeration of Sulfate-reducing Bacteria

The presence of sulfate-reducing bacteria in oily-water waste specimens was confirmed by conventional microbiological methods (Clesceri et al., 1989). Inclusion of iron salts in the growth medium resulted in the precipitation of black iron sulfide in the region of sulfate-reducing bacteria colonies.

Enumeration of sulfate-reducing bacteria populations in the waste samples was found to be very difficult. This was because we were possibly not dealing with a single species of bacterium producing the hydrogen sulfide, but with several species, each with their own specialised nutrient requirements. The sulfate-reducing bacteria also form clumps, so that it is difficult to know whether a colony of cells arises from a single sulfate-reducing bacteria cell or from a clump containing many individual cells. After some experimentation we found a growth medium which enabled us to rank the population size of sulfate-reducing bacteria present in oily-water waste specimens collected from ships. This method was found to provide a good guide to the population levels of sulfate-reducing bacteria present in the waste samples and was used to obtain the results listed in Tables 1 and 2. The frequent high populations of sulfate-reducing bacteria found in oily-water waste specimens from RAN ships (Table 1) should be noted. Full experimental details of the methods used for enumeration of sulfate-reducing bacteria in oily-water waste specimens are presented in the second report in this series (Upsher et al., 1995).



Plate 1. A laboratory oily-water waste "holding tank".

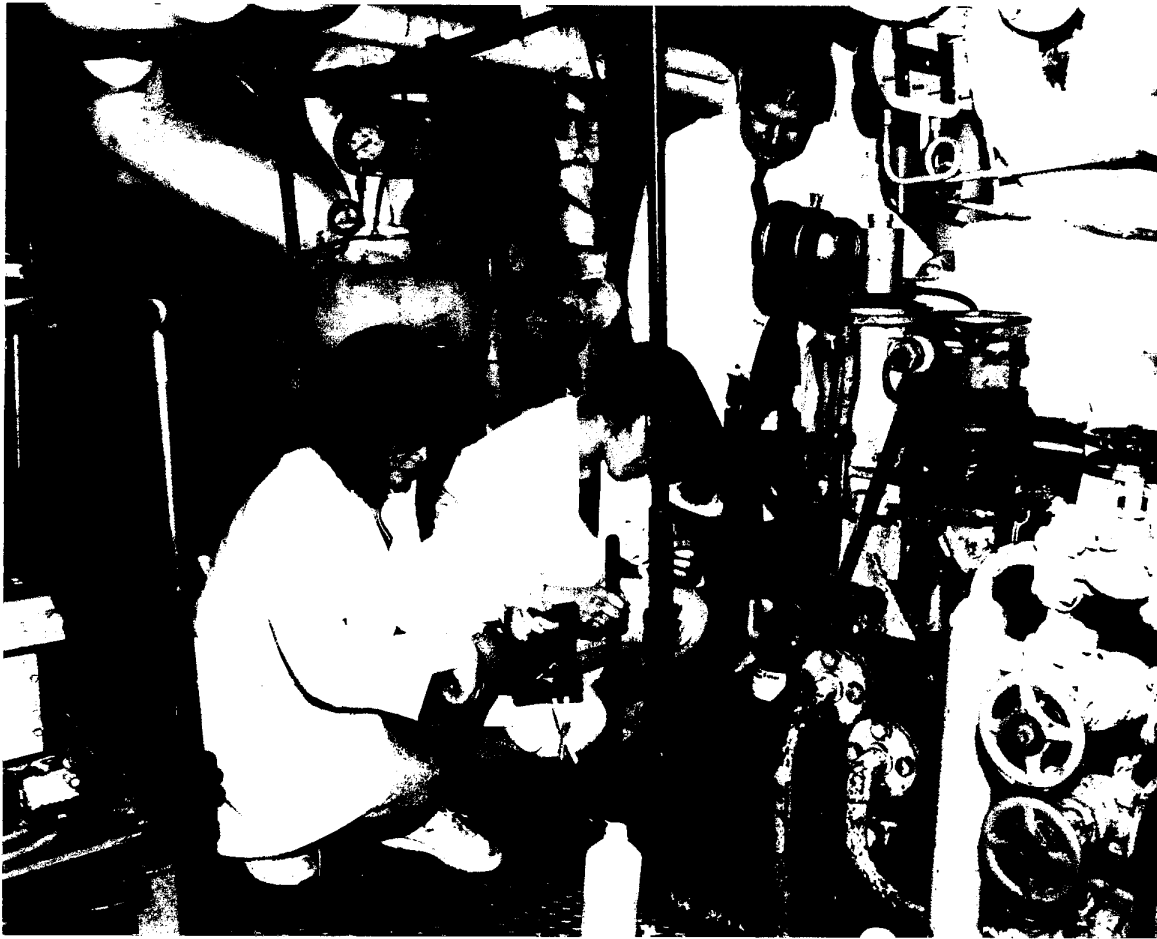


Plate 2: Pumping oily-water waste from the bottom of a bilge using a peristaltic pump.

Table 1: Sulfate-reducing bacteria populations in some samples of oily-water waste from Royal Australian Navy ships

Ship	Source	count/ml	Assessment
<i>HMAS Bayonet</i>	Engine Room	100	low
	Sludge	5,000	high
<i>HMAS Stalwart</i>	Engine Room	>1,000	average
<i>HMAS Success</i>	Engine Room	<10	clean
<i>HMAS Sydney</i>	Engine Room	>10,000	high
	Aux.Mach.Rm. 1	>10,000	high
	Aux.Mach.Rm. 2	<10	clean
<i>HMAS Success</i>	Engine Room	100	low
	Unknown	10,000	high

Table 2: Sulfate-reducing bacteria populations in some samples of oily-water waste from foreign vessels

Ship	Source	SRB count/ml	Assessment
<i>Aris</i> (Greece)	Engine Room	<10	clean
<i>Godavari</i> (India)	Boiler Room	1,000	average
<i>Colbert</i> (France)	Engine Room	<10	clean
<i>Caio Duilio</i> (Italy)	Engine Room	10,000	high
	Boiler Room	100	low
<i>Waikato</i> (N.Z.)	Engine Room	100	low
	Boiler Room	<10	clean

3.3 Analytical Procedures

To determine the important factors which contribute to production of the hydrogen sulfide, we required several methods for chemical analysis of the components of the oily-water waste. The bacteria present take the organic and inorganic matter available in the waste and use this either directly or indirectly as nutrient. We therefore measured the consumption of various chemical components used for their growth, and the formation of the by-products of growth, one of which is hydrogen sulfide.

Initially we concentrated on looking at the shift in oxygenation level of the waste from aerobic to anaerobic, the formation of hydrogen sulfide and the change in acidity of the waste. Using results of these analyses, we could then define the broad factors contributing to formation of hydrogen sulfide in the waste.

The techniques used throughout this investigation for chemical analysis of oily-water wastes and experiments with these wastes were ion-selective electrodes, ion chromatography (IC) and high performance liquid chromatography (HPLC). Thus, oxidation-reduction (redox) potentials and pH of specimens were obtained with electrodes and provided a measure of whether or not the waste had become anaerobic and its ability to release hydrogen sulfide gas if sulfide was present. Sulfate, phosphate and chloride ion concentrations could all be satisfactorily found by IC after extensive pretreatment of the specimen to remove interfering substances. Attempts were made to determine sulfide concentrations in these specimens by IC and HPLC methods but the results obtained were not reliable, possibly due to the presence of interfering substances. Satisfactory sulfide concentrations were obtained by using a sulfide specific electrode (Al-Hitti et al., 1983). Attempts were also made in some experiments to determine the concentration of significant organic nutrients for the sulfate-reducing bacteria by HPLC. However, due to the mixed population of bacteria present in the waste the concentrations of these organic nutrients often did not reach measurable levels. Experimental details of the procedures used for chemical analyses in this investigation are presented in the third report in this series (Hodgeman et al., 1995a).

3.4 Experiments

Having established the presence of sulfate-reducing bacteria in shipboard oily-water waste, and developed our basic methods of chemical analysis for these specimens, we then determined the main factors present in the shipboard environment which contribute to hydrogen sulfide production. We carried out a series of experiments with different growth media for the bacteria. These liquid media were intended to model the composition of an oily-water waste, except we could add or leave out components of the waste to establish the effects of composition changes on hydrogen sulfide production.

We prepared a basic liquid medium consisting of diluted synthetic sea-water (Riley & Skirrow, 1975), an organic nutrient which could be readily used by sulfate-reducing bacteria for growth (lactate (Postgate, 1984)), and smaller amounts of other substances essential to growth. The medium was then divided into individual 200 mL bottles which were sterilized and inoculated with a specimen from our laboratory "holding tank". The sealed bottles were then incubated at 30°C and, at selected intervals, were removed for chemical analysis. We measured sulfide concentration, redox potential and pH as a function of incubation time. The results, presented in Figs 1 - 5, are the average of the analytical measurements taken for three replicates removed at each sampling interval. Since this method only required many containers, and no specialized apparatus (except the analytical instruments), it enabled us to examine the effects of several factors concurrently. The method does, however, suffer from some scatter as seen from the size of some error bars shown in the plots of the results. This scatter results from each bottle really being a separate experiment and small differences in the contents of individual bottles at the time of inoculation were magnified by the time the analyses were made. However, the trends are obvious and, usually, the scatter was quite small showing that the behaviour we have observed is reproducible.

A selection of our experiments are discussed below, which specifically illustrate the need for sulfate and for live bacteria for the generation of hydrogen sulfide in oily-water waste. The effects of addition of two detergents used by the Australian Navy for machinery space cleaning are also shown. Details of the compositions of the media used in the experiments are presented in the Appendix.

(1) A model oily-water waste

In this experiment a layer of Dieso fuel oil was included in the medium to approximate a complete oily-water waste. Two separate experiments were conducted: one in which sulfate was present (Fig. 1a), and the other in which sulfate was omitted (Fig. 1b). In each case the medium became anaerobic, as shown by the decrease in redox potential over the first few days. Sulfide, however, was only produced in the medium containing sulfate and only after the medium had become anaerobic. No significant quantities of hydrogen sulfide were produced in the sulfate-containing medium during the first four days or in the sulfate-free medium over the duration of the experiment. Details of these experiments are covered in the third report in this series (Hodgeman et al., 1995).

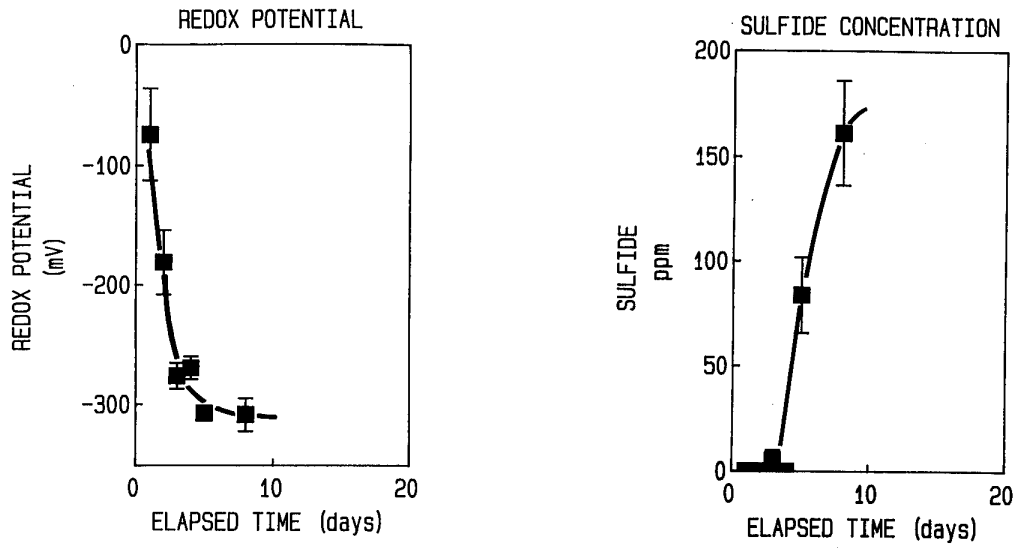


Figure 1a: Inoculation of a model oily-water waste containing sulfate with a specimen of shipboard oily-water waste.

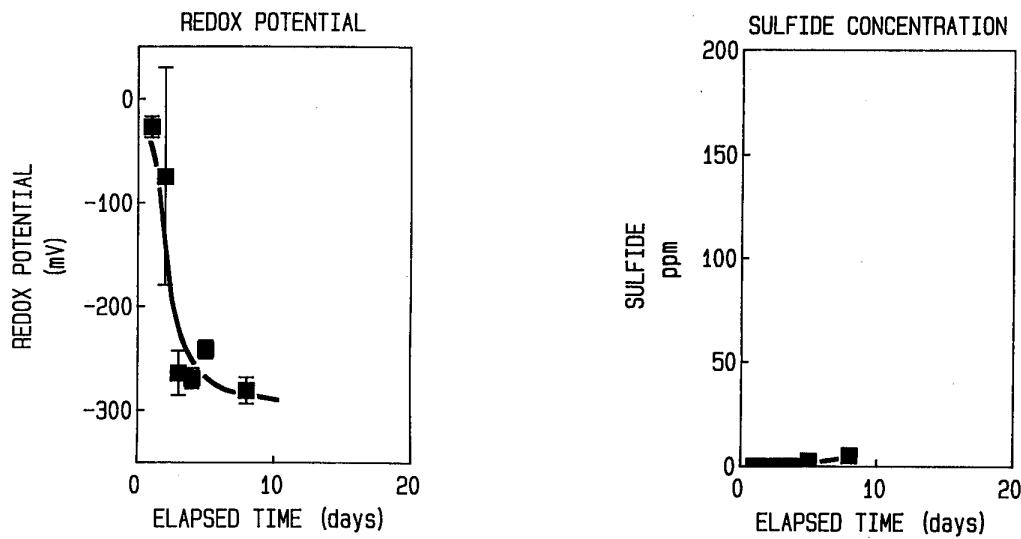


Figure 1b: Inoculation of a model oily-water waste from which sulfate was omitted with a specimen of shipboard oily-water waste.

This experiment showed that a model oily-water waste inoculated with a genuine oily-water waste was capable of producing hydrogen sulfide gas, provided sulfate was present. After a period of about four days, during which the medium became anaerobic, the hydrogen sulfide concentration increased rapidly.

This is the behaviour which might be expected if oily-water waste is collected in a bilge or holding tank and allowed to stand undisturbed. Thus, if the waste is discharged from the ship within the first few days and not allowed to accumulate (as was probably the case before introduction of regulations prohibiting discharge of these wastes from ships), no significant quantities of hydrogen sulfide would be expected to form. A cause of the hydrogen sulfide problem in shipboard oily-water waste would appear, therefore, to be the need to store the waste for extended periods in the ship.

(2) A model without oil

Figs. 2a and 2b show the results of an experiment similar to that above but in which the oil was omitted. Essentially the same behaviour was observed, i.e., hydrogen sulfide was only produced in the medium containing sulfate and only after the media became anaerobic.

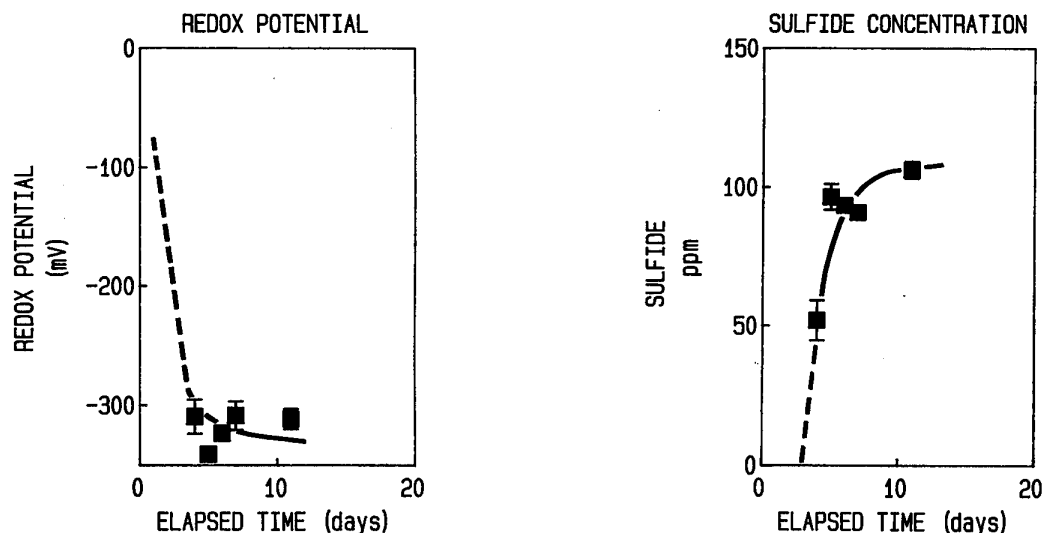


Figure 2a: Inoculation of a model bilge-water containing sulfate but no oil with a specimen of shipboard oily-water waste.

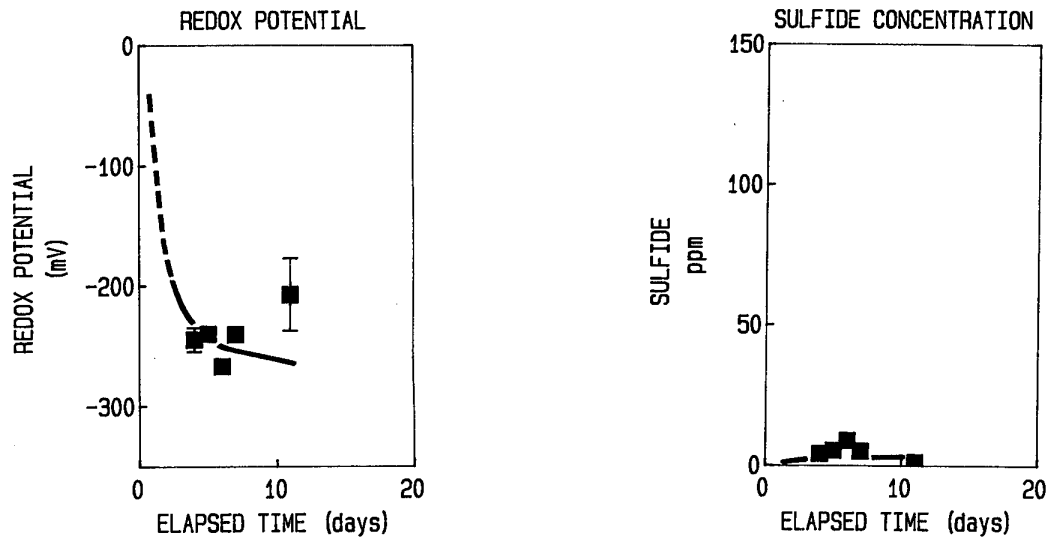


Figure 2b: Inoculation of a model bilge-water containing neither sulfate nor oil with a specimen of shipboard oily-water waste.

(3) The need for live bacteria

The need for live bacteria for hydrogen sulfide production was demonstrated by taking a medium containing sulfate, as used above, and heat sterilizing immediately after inoculation with the genuine oily-water waste specimen. This procedure killed any bacteria introduced with the waste specimen. The results (Fig. 3) show that no hydrogen sulfide was produced after this treatment and are consistent with the requirement for live sulfate-reducing bacteria for formation of the hydrogen sulfide. The increase in redox potential in this medium during incubation was probably due to diffusion of oxygen through the bottle seal.

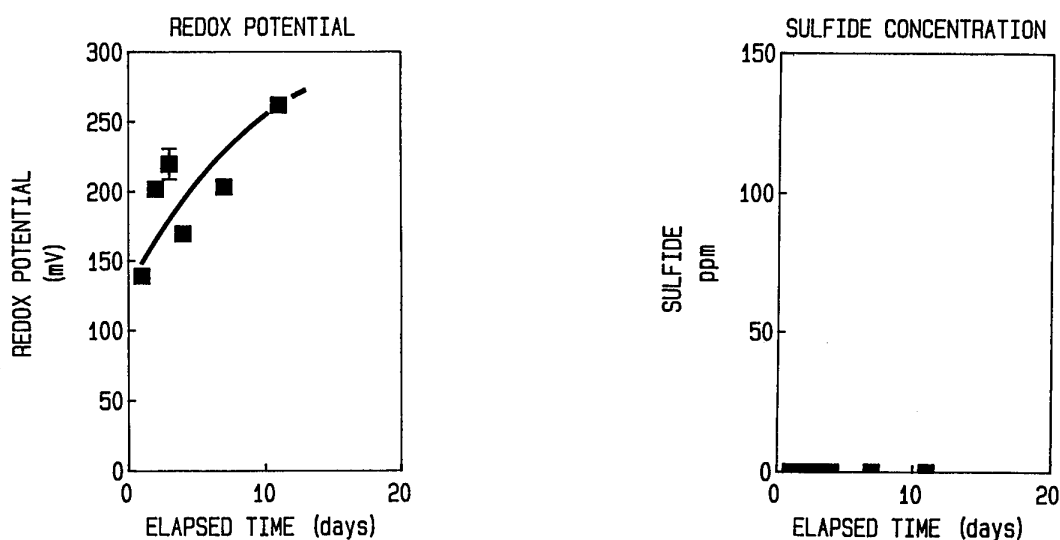


Figure 3: The effect observed when bacteria were destroyed by heat-sterilization after inoculation of the model oily-water waste with shipboard oily-water waste. Sulfate included.

(4) The effects of detergents

The effects of adding two detergents used by Navy, "Gamosol D5" (Gamlen Australasia, Lane Cove, NSW) and "Comprox F-46" (BP Australasia, Melbourne, VIC), are illustrated in Fig. 4 and Figs. 5a and 5b, respectively. When sulfate is present in the medium containing the detergents, sulfide is rapidly produced after an induction period during which the medium became anaerobic. With "Gamosol D5" present, the induction period was approximately the same as that observed in the presence of lactate (see Fig. 1a). The induction period observed in the presence of "Comprox F-46" (Fig. 5a) is greater than that observed in the presence of lactate (Fig. 1a) suggesting that this detergent is inhibiting sulfide formation. Since the induction period was only increased by a few days, this inhibition is insufficient to form the basis of a method of controlling hydrogen sulfide generation.

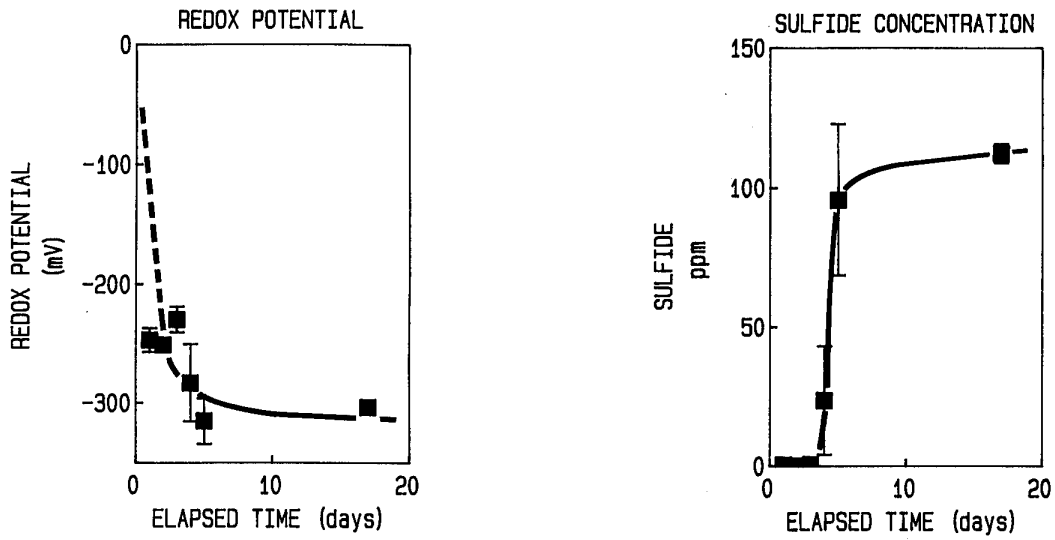


Figure 4: The effect of adding Gamcosol D5 to the model bilge-water inoculated with a specimen of shipboard oily-water waste. Sulfate included.

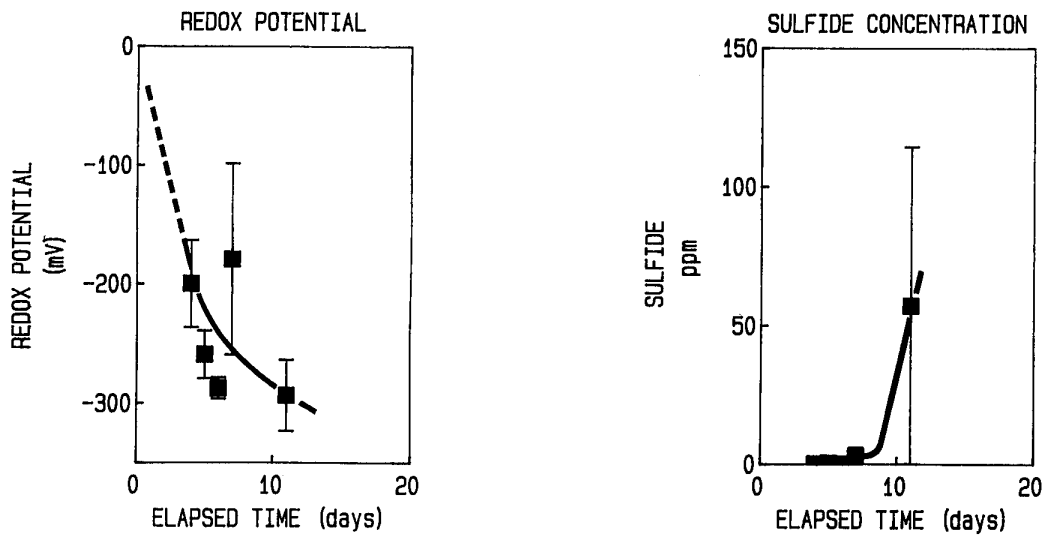


Figure 5a: The effect of adding Comprox F-46 to the model bilge-water inoculated with a specimen of shipboard oily-water waste. Sulfate included

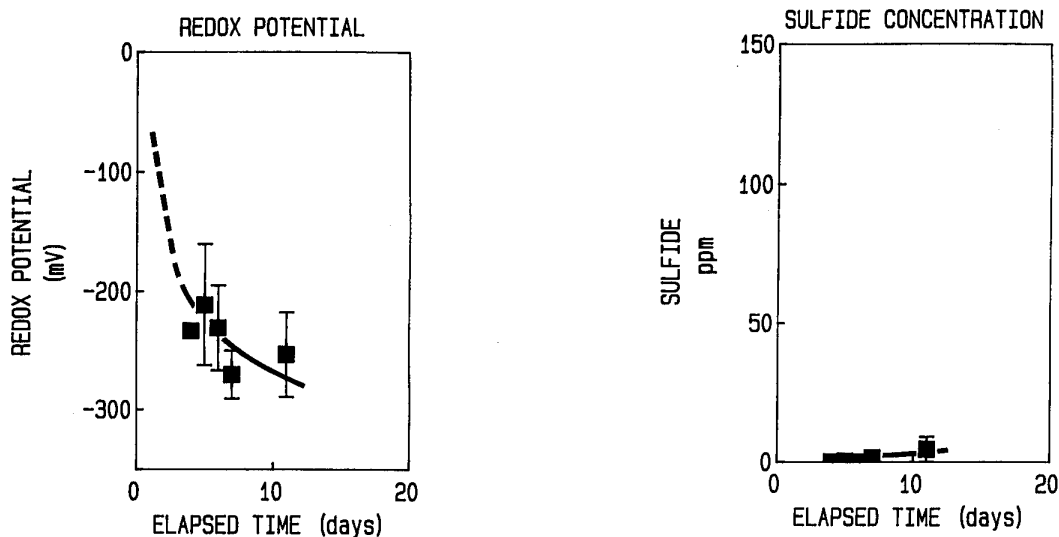


Figure 5b: The effect of adding Comprox F-46 to the model bilge-water inoculated with a specimen of shipboard oily-water waste. Sulfate omitted.

4. Conclusions

Hydrogen sulfide is formed in a medium which modelled the oily-water waste on a ship but only after inoculation with oily-water waste taken from a ship's bilge. Since no hydrogen sulfide was produced in the absence of sulfate, or after sterilizing the medium, the observations are consistent with the hydrogen sulfide being produced by bacterial reduction of the sulfate.

If sufficient organic nutrient and sulfate are present, the concentration of hydrogen sulfide increases rapidly after an induction period of a few days during which the medium becomes anaerobic. The amount of hydrogen sulfide produced will then be limited only by the availability of organic nutrient and sulfate.

Sulfate-reducing bacteria and sulfate both enter a ship in sea-water used in normal operating procedures. Thus, the potential for a toxic hazard arising by this means is probably widespread in ships storing oily-water waste to conform with environmental regulations.

References

Al-Hitti, I.K., Moody, G.J., Thomas, J.D.R. (1983). "Determination of Sulphide Produced by Desulfovibrio Species of Sulphate-reducing Bacteria", *Analyst*, 108, 43-52.

Clesceri, L.S., Greenberg, A.R., and Trusse, R.R., (eds) (1989). "Standard Methods for the Determination of Water and Wastewater", 17th Edition. Alpha-AWWA-WPCF, Washington, D.C., p. 9-121.

Hill, E.C., Shennan, J.L. and Watkinson, R.J. (eds) (1987). "Microbial Problems in the Offshore Oil Industry", Institute of Petroleum, London.

Hodgeman, D.K.C., Fletcher, L.E., and Upsher, F.J. (1995a). "Hydrogen Sulfide Generation in Shipboard Oily-water Waste. Part 3. Ship Factors", DSTO-TR-0055.

Hodgeman, D.K.C., Upsher, F.J., and Fletcher, L.E. (1995b). "Hydrogen Sulfide Generation in Shipboard Oily-water Waste. Part 4. Minimization of the Problem", DSTO-TR-0056.

Inter-Governmental Maritime Consultative Organization (IMO) (1978). "Recommendation on International Performance and Test Specifications for Oily-water Separating Equipment and Oil Content Meters", Inter-Governmental Maritime Consultative Organization, London.

Inter-Governmental Maritime Consultative Organization (IMO) (1985). "International Convention for the Prevention of Pollution from Ships, 1973 as Amended by the 1978 Protocol and Amendments Adopted in 1984 and 1985. ANNEX 1: Regulations for the Prevention of Pollution by Oil", Inter-Governmental Maritime Consultative Organization, London.

Jobson, A.M., Cook, F.D., and Westlake, D.W.S. (1979). "Interaction of aerobic and anaerobic bacteria in petroleum biodegradation." *Chemical Geology*, 24, 355-365.

Lardis, A. E., and Geger, A. T. (1978). "Biodegradation of Shipboard Wastewater in Collection, Holding and Transfer Tanks." David W. Taylor Naval Ship Research and Development Center, Report No. DTNSRDC-78/041.

Nazina, T.N., Rozanova, E.P., and Kuznetsov, S.I. (1985). "Microbial oil transformation processes accompanied by methane and hydrogen sulfide formation." *Geomicrobiology Journal*, 4(2), 103-130.

Neihof, R., and May, M. (1983). "Microbial and particulate contamination in fuel tanks on naval ships", *Int. Biodeterior. Bull.*, 19, 59-68.

Pfennig, N. and Widdel, F. (1981). "Ecology and physiology of some anaerobic bacteria from the microbial sulfur cycle" in "Biology of Inorganic N and S", Boethe, H. and Trebst, A. (eds), Springer-Verlag, Berlin.

Pfennig, N., Widdel, F., and Truper, H.G. (1981). "The dissimilatory sulfate-reducing bacteria", in "The Prokaryotes.. Vol. 1. A Handbook on Habitats, Isolation and Identification of Bacteria", Starr, M.P., Stolp, H., Truper, H.G., Balows, A., and Scholgel, H.G. (eds), Springer-Verlag, Berlin, pp. 926-940.

Postgate, J.R. (1984). "The sulphate-reducing bacteria", 2nd edition, Cambridge University Press, Cambridge.

Postgate, J. (1988). "Bacterial worlds built on sulfur", *New Scientist*, 14 July, 58-62.

Riley, J.P., and Skirrow, G. (eds) (1975). "Chemical Oceanography", 2nd edition Academic Press, London, vol. 4, p. 320.

Royal Australian Navy (1986). Naval Board of Inquiry into HMAS Stalwart. HMAS Stalwart Toxic Gas Accident 22nd October 1985 - Summary of Board of Inquiry Report.

Sax and Lewis (1989). "Dangerous Properties of Industrial Materials", 7th Edition, Van Nostrand Reinhold.

Suruda, A., and Agnew, J. (1989). "Deaths from asphyxiation and poisoning at work in the United States 1984-6", *British Journal of Industrial Medicine*, Vol 46, 541.

Upsher, F.J., Fletcher, L.E., and Hodgeman, D.K.C. (1995). "Hydrogen Sulfide Generation in Shipboard Oily-water Waste. Part 2. Microbiological Aspects", DSTO-TR-0054.

Widdel, F. (1988). "Microbiology and ecology of sulfate- and sulfur-reducing bacteria." In "Biology of Anaerobic Microorganisms." Zehnder, G.F., and Alexander, J.B. (eds), Wiley, New York.

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Appendix: Composition of Media Used in the Experiments.

Component	Concentration
<u>1. Sea salts</u>	
NaCl	5.30 g/L
Mg Cl ₂ .6H ₂ O	1.00 g/L
Mg SO ₄ .7 H ₂ O (a)	0.66 g/L (a)
Ca Cl ₂ .2 H ₂ O	0.22 g/L
KCl	0.16 g/L
Na HCO ₃	0.04 g/L
Na Br	0.06 g/L
<u>2. Bacterial growth additives</u>	
Yeast extract	1.00 g/L
Tryptone	1.00 g/L
Ascorbic acid	0.10 g/L
K ₂ HPO ₄	0.50 g/L
Sodium lactate	5.00 g/L
<u>3. Further additions (as required)</u>	
Deiso (oil)	10.0 mL/200mL bottle
Gamosol D5	0.1% V/V
Comprox F-46	0.1% V/V

(a) Excluded from media for which sulfate was omitted

Hydrogen Sulfide Generation in Shipboard Oily-water Waste:
Part 1: Origin of the Hydrogen Sulfide

D.K.C. Hodgeman, F.J. Upsher and L.E. Fletcher

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ABSTRACT

This paper, the first in a series of four reports, provides an overview of the recurring problem of hydrogen sulfide generation in oily-water wastes in ships of the Royal Australian Navy. In the DSTO-AMRL investigation into this problem, we examined the physical and microbiological factors influencing the process under simulated storage conditions and related the findings to the shipboard situation. Sulfate from sea-water was the source of the sulfur for hydrogen sulfide formation. The sulfate was reduced to sulfide by anaerobic sulfate-reducing bacteria (eg *Desulfovibrio*) in concert with other bacteria. Physical and chemical conditions in the shipboard oily-water waste environment were generally conducive to this bacterial process. In addition to the need for sulfate, the other important requirement was for a supply of organic nutrient for the bacteria. Detergents used in cleaning are identified as significant nutrient sources.

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