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Hydrogen Sulfide Generation in Shipboard Oily-water Waste: Part 3. Ship Factors

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

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ABSTRACT

The chemical and microbiological composition of bilge-water in ships of the Royal Australian Navy has been investigated in relation to the formation of hydrogen sulfide by sulfate-reducing bacteria. Sulfate-reducing bacteria were found in most ships in populations up to 800,000 per mL. Sulfate in the wastes is provided by sea-water. Sea-water constitutes up to 60% (median 20%) of the wastes analysed. Evidence for generation of hydrogen sulfide in the ships was found directly as sulfide or indirectly as depressed sulfate concentrations. The low levels of sulfide found in bilge-water from machinery spaces suggested the ventilation systems were effectively removing the gas from the working area. The effect of storage of the wastes under conditions which simulated the oily-water holding tanks of ships were also investigated. Some wastes were found to produce large quantities of hydrogen sulfide on storage. The wastes that failed to produce hydrogen sulfide were investigated to identify any specific nutritional deficiencies. Some organic substances present in bilge-water, such as lactate or biodegradable cleaning agents, and phosphate strongly influenced the generation of hydrogen sulfide in stored oily-water wastes.

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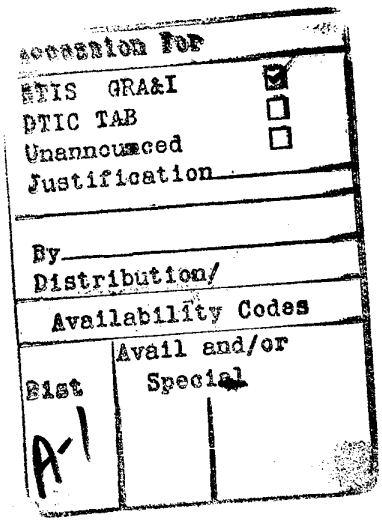

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Daryl Hodgeman, PhD (Adelaide), joined Aeronautical and Maritime Research Laboratory in 1973. He worked on the chemistry of polymer degradation and stabilization and the physical chemistry of polmer-solvent interactions prior to commencing the investigation of hydrogen sulfide formation in oily-water wastes for Navy. Current research interests are related to improving air quality in submarines and, in particular, the interaction of volatile organic compounds with materials in the submarine and adsorbents used for air purification.

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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.

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1. Introduction

The Royal Australian Navy has been experiencing problems with hydrogen sulfide forming in oily-water wastes in its ships and submarines. This gas, which is both unpleasant at low concentrations and toxic at high concentrations, is formed by sulfate-reducing bacteria (Hodgeman et al., 1995a). High concentrations of hydrogen sulfide in a ship present a serious hazard to the crew, and fatalities have occurred (Royal Australian Navy, 1986). Overcoming this problem requires a detailed understanding of the mechanism of production of the gas in the oily-water waste environment. DSTO-AMRL has investigated both the chemical and microbiological aspects of this problem and it is expected the results will help in developing straightforward methods for eliminating the hazard.

The first two reports in this series have described our work on the origin of the hydrogen sulfide (Hodgeman et al., 1995a) and the microbiological aspects of the problem (Upsher et al., 1995). A final article (Hodgeman et al., 1995b) discusses approaches for minimising formation of hydrogen sulfide in this waste. In this report we address three topics related to the development of a potential toxic hazard in the shipboard environment.

First, we investigated the composition of oily-water wastes from several ships and present the results of a small survey of the chemical and microbiological content of bilge-water. This survey was conducted to gauge the breadth and magnitude of the hydrogen sulfide problem in the RAN fleet. Samples of oily-water wastes were collected from most classes of surface ship in the fleet (Table 1), and examined in the laboratory. Ships of different age, size and engine type are all represented in the survey. We collected data on these specimens which would show if the bilge of each machinery space investigated was a suitable environment for growth of sulfate-reducing bacteria. We also sought evidence for generation of hydrogen sulfide in the ship's bilge before collection of the sample. Besides the Australian ships, we also collected bilge specimens from some foreign naval vessels (Table 2) which visited Melbourne. The results of their analysis are included in this survey for comparison.

Secondly, we examined the changes in composition of some oily-water waste specimens from RAN ships during long term storage in the laboratory. This experiment was conducted in an environment which simulated the holding tank of a ship and was undertaken to show the potential for formation of a hazardous mixture during storage of oily-water waste.

Finally, we investigated the type of nutrient additions necessary to start the generation of hydrogen sulfide in some bilge specimens. Not all bilge specimens contained hydrogen sulfide, or produced this gas during storage, even when the basic conditions for sulfate-reduction were met. An experiment was therefore undertaken to identify the missing components in these specimens. A knowledge of the specific deficiencies will identify nutrient substances which should be avoided in the oily-water waste environment. This information could also point to methods of control which do not require toxic additives or installation of additional plant in the ship.

One observation which warrants early mention, is that it was unusual to find measurable quantities of sulfide in bilge-water collected in working machinery spaces. The environment necessary for hydrogen sulfide generation was, however, provided in many bilges and evidence for formation of the gas was frequently found. This suggests that the forced air ventilation systems in the ships are efficiently exhausting the gas as it is formed in the bilge. Hazardous concentrations of hydrogen sulfide would, therefore, be unlikely to be found in well ventilated working areas during the normal operation of a surface ship.

2. Background

Oily-water wastes collect as bilge water in substantial quantities in engine rooms and boiler rooms of ships. International regulations (IMO, 1985), introduced to protect the marine environment from oil pollution, prohibit discharge of these wastes in coastal and restricted waters if more than 15 ppm oil is present. Many ships have been fitted with oily-water separators for handling these wastes in compliance with the regulations. Physical separation of the oil and water should allow discharge of an oil-free water component from the ship. Unfortunately, surfactant substances are often present in these wastes and cause formation of oil-in-water emulsions. These emulsions cannot be separated by the equipment currently available so the waste must be stored on the ship until it can be disposed of later in an environmentally acceptable manner. Thus, it is not unusual for a ship operating in regulated regions to be carrying several tonne of oily-water wastes in holding tanks for periods of several weeks. The main components of these wastes are oil, diluted sea-water, and surfactant-containing cleaning agents, most of which are biodegradable. Other substances, both organic and inorganic, also find their way into the oily-water waste handling system of a ship, but in much smaller quantities than those listed above. The bulk of the liquid is usually the aqueous phase which contains dissolved salts and organic nutrients. Such a mixture would not seem likely to present a toxic hazard in a ship. However, the mixture is ideal for growth of bacteria and, specifically, the sulfate-reducing bacteria (Postgate, 1984).

3. Results and Discussion

3.1 Survey of Composition of Oily-water Waste

Results of the chemical and microbiological analyses of oily-water waste specimens obtained from Royal Australian Navy ships are shown in Appendixes 1 to 5. Each specimen is identified by its source (ship and the collection site) and the date on which

it was collected. Thirty-six specimens were examined: 24 from engine rooms, four from boiler rooms and eight from auxiliary machinery spaces.

Background data used for the investigations were also collected. These included bilge temperature, the cleaning agents used in the machinery space, and the length of time the liquid had remained in the bilge since last being pumped out. Bilge temperatures were in the range 14-22°C for ships berthed in Sydney and Melbourne and the cleaning agents most often reported used were Gamosol D5, Sea-Clean and Comprox F46. Sixteen of the specimens had remained in the bilge for five days or more, and nine of these had come from bilges which had not been pumped out for at least 10 days. Experiments in our laboratory (Hodgeman et al., 1995a) have shown that, if all environmental conditions are favourable, a model oily-water waste produces hydrogen sulfide within a few days of inoculation by a bilge specimen. Details of the ship's recent movements were also obtained for some specimens, but this factor was not significant.

Microbiological analysis was restricted to enumerating the sulfate-reducing bacteria, total aerobic bacteria and the presumptive coliform bacteria populations in the specimens. The total aerobic bacteria counts were obtained to gain an indication of the bacterial load supported by the bilge. Coliform bacteria were measured because they produce lactate, a common nutrient for sulfate-reducing bacteria, in environments similar to those in which sulfate-reducing bacteria grow. Estimates of sulfate-reducing bacteria populations of the bilge specimens varied from effectively zero to 800,000 per mL using a "most probable number" method. As discussed previously (Upsher et al., 1995), this method can underestimate the population of sulfate-reducing bacteria by several orders of magnitude. Thus, the actual sulfate-reducing bacteria populations in the oily-water waste specimens may have been significantly higher than those measured. Total aerobe populations were all more than one million per mL. Presumptive coliform bacteria populations were usually around one thousand per mL or less, although a few specimens did show high populations of these bacteria (HMAS Perth, AC-2, 10,000 per mL; HMAS Warrnambool, engine room, 100,000 per mL; HMAS Cook, engine room, 10,000 per mL). The presumptive coliform bacteria, which are not necessarily Escherichia coli of intestinal origin, do not suggest any particular form of contamination of the bilge.

Chemical analysis was limited to measuring redox potential, pH and the concentrations of sulfide, sulfate, phosphate and chloride ions. These show if the waste is suitable for growth of sulfate-reducing bacteria and if hydrogen sulfide has been generated in the bilge before the sample was removed. Redox potential of bilge specimens from the RAN ships ranged from as high as 256 mV (aerobic) to as low as -390 mV (anaerobic) and the pH varied from 4.3 to 9.0 (mean, 7.1, standard deviation, 0.8). We also measured phosphate concentrations and these were, as expected, very low since this inorganic component is taken up by the microorganisms in the waste. Only one specimen contained a measurable quantity of phosphate (HMAS Canberra, 2 ppm).

Few instances of measurable concentrations of sulfide were found in the bilge specimens we examined. Sulfide was found in traces in some samples, and indirect

evidence was obtained for its formation in others. Thus, of 36 specimens measured, only five had more than trace quantities of sulfide and in only three of these were quantities significant (HMAS Sydney, 16 and 27 ppm; HMAS Bayonet, 133 ppm). Trace quantities of sulfide (<1 ppm) were found in a further four bilge specimens. Sulfate, the precursor of sulfide, was found in all specimens in which it was measured. Concentrations ranged from 2 ppm to 2,110 ppm (cf. sea-water, which has 2,712 ppm sulfate (Riley & Skirrow, 1975)).

The chloride concentration was measured for many specimens and enabled us to estimate the sea-water content of the bilge (assuming sea-water was the sole source of chloride). Using 19,344 ppm as the typical concentration of chloride in sea-water (Riley & Skirrow, 1975), the sea-water content of eighteen bilge specimens ranged from 1% to 60%.

An estimate of the sea-water content of the bilge can also be made from the measured sulfate concentrations. Values in the range 0% to 78% sea-water were obtained from 28 specimens. Sulfate, however, is consumed by sulfate-reducing bacteria or produced by the aerobic biodegradation of sulfonated detergents (Swisher, 1987), so its concentration may differ from that of diluted sea-water. We see evidence for occurrence of both of these processes when the two estimates of sea-water content are compared. Of the 18 specimens where both chloride and sulfate concentrations were available, in eight the two methods gave similar estimates of the sea-water content. However, for seven specimens (HMAS Sydney, HMAS Parramatta, HMAS Cook and four from HMAS Perth) the sea-water content estimated from sulfate concentration was significantly below that estimated from chloride. Three specimens (HMAS Adelaide, and two from HMAS Success) showed elevated sulfate concentrations. The depressed sulfate concentrations are usually associated with high sulfate-reducing bacteria populations, low redox potential and detectable quantities of sulfide and are consistent with prior hydrogen sulfide generation in the bilge of the ship. Figure 1 shows a plot of the ratios of sulfate and chloride for waste specimens containing Gamosol D5 or Comprox (the straight line represents the ratio in diluted sea-water). These data show that Gamosol D5 is frequently associated with depressed sulfate concentrations in the bilge and suggests Gamosol is acting as a nutrient for the sulfate-reducing bacteria in these wastes. For wastes containing Comprox, on the other hand, two of the three specimens examined showed elevated sulfate concentrations suggesting that Comprox (a linear alkylbenzenesulfonate-based detergent) has undergone an aerobic breakdown to produce sulfate. Formation of the excess sulfate for the highest Comprox data point in Fig. 1 would require complete aerobic breakdown of approximately seven litres of Comprox F46 concentrate (approx. 33% v/v sodium C-12 alkylbenzenesulfonate) per tonne of bilge. Alternatively, there could be other sources of sulfate in this bilge.

Figure 2 shows an overview of the results of the survey of the Australian ships. In this diagram the data obtained from individual specimens are overlaid, as would occur when these wastes are mixed in a holding tank. As Fig. 2 shows, most of the Australian ships in the survey had sulfate-reducing bacteria present in the bilge in at least some sites examined. This would ensure the presence of these bacteria in the holding tanks of these ships. The bacterial population distribution (Fig. 3) shows that

the highest populations of these bacteria are generally found in engine rooms and auxiliary machinery spaces where use of cleaning agents would be highest. Sea-water was present in the oily-water waste of all ships (Fig. 4). The median sea-water content of these specimens was approximately 20%. The final concentration of sea-water in a holding tank will depend on the relative quantities entering the tank from different locations in the ship. However, if 20% sea-water can be taken as typical for a holding tank, then the tank will contain sufficient reducible sulfur to produce 192 ppm hydrogen sulfide in the liquid if the sulfate reduction is complete. The hydrogen sulfide concentration in the bilge of a ventilated machinery space would not reach the maximum since the gas would be exhausted on diffusion into the air. The specimen obtained from Bayonet (133 ppm sulfide), however, shows that very high concentrations of sulfide can be reached in machinery space bilges. Consequently, caution should be taken on entering machinery compartments of ships which have been closed for some time without ventilation.

Sulfate-reduction requires an anaerobic environment with a redox potential below -100 mV (Postage, 1984). Figure 2 shows that about half the Australian ships surveyed had at least some environments which were sufficiently anaerobic for sulfide generation. The distribution of redox potential (Fig. 5) shows that well over half the specimens examined had redox potentials below zero millivolts and could support sulfate-reduction without much further change to the environment. The pH of the waste specimens also falls in the range required for growth of sulfate-reducing bacteria. Thus, the pH distribution (Fig. 6) shows only three specimens falling outside the preferred range of pH 6 to 9 (Widdell, 1988).

The results of this survey show that the oily-water wastes on RAN ships are often well suited to generation of hydrogen sulfide by sulfate-reducing bacteria. In such an environment the ultimate yields of hydrogen sulfide are limited by the quantity of sulfate available or by the amount of readily biodegradable organic nutrient in the bilge. Since we know the typical sulfate content of a bilge, it is possible to make an estimate of the quantity of biodegradable material required to completely reduce this sulfate to sulfide. With 20% sea-water as typical, sulfate would be present in the bilge at a concentration of 5.6 mmol/L. Reduction of this sulfate would require 11.2 mmol/L (or 1.0 g/L) of lactate, a substrate readily oxidised by the sulfate-reducing bacteria (Postgate, 1984). Thus, reduction of the sulfate would require approximately one kilogram of readily biodegradable organic matter per tonne of oily-water waste. This quantity could easily be provided by the biodegradable cleaning agents used in machinery spaces. Comprox F46, for example, contains approximately 33% biodegradable material so that approximately three litres of the concentrate would be sufficient to reduce all the sulfate in a tonne of typical oily-water waste. Bilge and the contents of the oily-water holding tank are, of course, continually changing environments and many different types of bacteria contribute to the breakdown of the biodegradable material. Discussion of the quantitative aspects of sulfate reduction in such an environment can only be made in very broad terms. However, it is obvious that sufficient biodegradable material could enter a typical bilge during routine operations to enable much of the sulfate present to be reduced to hydrogen sulfide.

The results of the analysis of bilge specimens from the foreign ships included in this survey are shown in Appendix 6. Although the data is limited it is useful to compare with those from Australian ships since the engineers of the foreign ships claimed hydrogen sulfide did not form in their oily-water wastes. An overview of the results (Fig. 7) shows sulfate-reducing bacteria were found in these ships along with a significant sea-water content in the bilge. The samples were, however, aerobic and unsuited to sulfate reduction by the bacteria. No sulfide was found in any of these specimens. It is significant that, except for the engine room of the New Zealand ship "Waikato", biodegradable detergents were not routinely used for machinery space cleaning. The total organic carbon analysis of these waste samples of approximately 15 ppm was consistent with the absence, or very low level, of detergent in the water layer of the bilge. The engine room sample from "Waikato" gave a total organic carbon reading of 40 ppm.

3.2 Simulated Storage of Oily-water Waste from RAN Ships

The changes which occurred during simulated storage of oily-water waste specimens from several Australian ships are shown in Tables 3 to 12. These experiments were designed to show whether the individual bilge specimens could produce potentially hazardous quantities of hydrogen sulfide on storage in a holding tank. Tall glass tubes were used which allowed the liquid only limited access to air, an environment similar to that of a deep stagnant bilge or holding tank. The temperature of the simulated storage, 31°C, was higher than that of bilge temperatures encountered in temperate waters but is realistic for a ship operating in tropical waters. Changes in sulfate and sulfide concentration were recorded throughout the experiment. Since the surface of the liquid was open to the air, sulfide would be lost to the atmosphere as hydrogen sulfide and sulfate consumption gave a more accurate measure of the amount of hydrogen sulfide generated in the waste. The redox potential and pH were also measured to monitor the suitability of the contents of each tube for growth of sulfate-reducing bacteria. Each test ran for approximately two months, which covers the length of time oily-water waste would be likely to remain in the holding tank of a ship.

The data in Tables 3 to 12 show that at some stage of the experiment all specimens were sufficiently anaerobic (redox potential below -100 mV) for growth of sulfate-reducing bacteria to occur. Two specimens (HMAS Brisbane and HMAS Perth) required adjustment of the pH to bring them within the preferred range for sulfate-reducing bacteria.

Although all specimens superficially appeared suitable for growth of sulfate-reducing bacteria, not all exhibited formation of sulfide or a corresponding loss of sulfate during the experiment. Thus, the specimens from HMAS Canberra, HMAS Adelaide, HMAS Brisbane, HMAS Perth (engine room, 12-May-90), HMAS Success and HMAS Tobruk showed neither significant hydrogen sulfide generation nor change in sulfate concentration with time. The specimens which failed to produce hydrogen sulfide in the laboratory showed neither detectable quantities of sulfide on

arrival nor, where data was available, any indication of hydrogen sulfide generation in the ship's bilge. The specimen from HMAS Brisbane had a pH reading of 4.3 which is below the preferred range for sulfate-reducing bacteria. All specimens, except those from HMAS Adelaide, HMAS Brisbane and HMAS Tobruk (which was not measured), had populations of sulfate-reducing bacteria of one thousand per mL or more and contained sulfate when received at the laboratory. However, the specimens from HMAS Adelaide, HMAS Brisbane and HMAS Success had no detectable population of sulfate-reducing bacteria at the end of the experiment, showing that the sulfate-reducing bacteria had died.

The remaining four specimens all showed evidence of hydrogen sulfide generation during storage. The specimen from HMAS Parramatta, which had trace quantities of sulfide on arrival, rapidly produced hydrogen sulfide during the first nine days of storage (Table 9). This was consistent with the high sulfate-reducing bacteria population (800,000 per mL) and depressed sulfate content on arrival which showed prior sulfide generation in the ship's bilge. However, generation of hydrogen sulfide by this specimen was not sustained beyond the initial stages of the experiment, and the hydrogen sulfide formed was either oxidised back to sulfate or lost by diffusion from the liquid.

The specimen from HMAS Sydney was very low in sulfate when received, but came from a bilge containing only 2% sea-water. With a sulfate-reducing bacteria population of over 10,000 per mL, this specimen showed evidence of hydrogen sulfide generation in the ship which was sustained in the laboratory (Table 4). The ability of this bilge specimen to produce large quantities of hydrogen sulfide during storage was confirmed by continued sulfide generation after additional sulfate was introduced during the experiment. Similar behaviour would be expected in the ship if bilge water containing significant quantities of sea-water sulfate was pumped into the holding tank.

The second specimen from HMAS Perth (engine room, 26-May-90) also showed the behaviour of an oily-water waste which actively produced large quantities of hydrogen sulfide on storage (Table 8). The specimen, on arrival, showed evidence of prior hydrogen sulfide generation in the ship's bilge. Thus, it was highly anaerobic (-317 mV) and supported a sulfate-reducing bacteria population of 20,000 per mL. The sulfate content of the bilge was depressed and a small amount of sulfide (1 ppm) was present on arrival. During storage in the laboratory the sulfate was completely consumed in the first 37 days. The behaviour after the addition of more sulfate on day 38 was consistent with sustained generation of hydrogen sulfide and suggested an excess of bulk organic nutrient in the bilge. This is another instance where continued hydrogen sulfide generation would be expected on addition of further quantities of bilge water to the holding tank. Addition of molybdate, a specific inhibitor for sulfate-reduction, on day 54 of the experiment (with adjustment of pH) completely inhibited the generation of hydrogen sulfide. This observation provides direct evidence for sulfate-reducing bacteria being responsible for the hydrogen sulfide generation.

The specimen from HMAS Cook, which came from a bilge showing evidence of prior hydrogen sulfide generation, produced some hydrogen sulfide during simulated storage (Table 12). However, the process was not sustained long enough to consume all the sulfate. This suggests that one or more nutrients had become limiting during the storage experiment. The nutrient deficiencies in this specimen are examined in detail in the following section.

Of the four waste specimens which produced hydrogen sulfide on simulated storage in the laboratory, three (HMAS Sydney, HMAS Perth and HMAS Parramatta) came from bilges where Gamosol D5 was used. No data was available on the cleaning agent used on HMAS Cook. However, in a sampling of HMAS Cook six months earlier, Comprox had been used in the same location.

3.3 Investigation of Nutritional Deficiencies

The bilge specimens in the previous experiment which failed to begin, or to sustain, hydrogen sulfide generation were deemed to lack ingredients essential for bacterial reduction of sulfate. We therefore examined these specimens to identify the missing ingredients since this might offer a method of controlling the problem.

The specimens from HMAS Adelaide, HMAS Brisbane and HMAS Success had no viable population of sulfate-reducing bacteria at the end of the storage experiment. Although it is uncertain at what stage the sulfate-reducing bacteria died in these experiments, their absence would account for the lack of hydrogen sulfide generation. Since no reason for the death of the bacteria is obvious, these specimens do not appear to point to any reliable method of control.

The remaining specimens all contained viable populations of sulfate-reducing bacteria at the end of the storage experiment. They were therefore subjected to a series of batch experiments to identify those nutrients or nutrient combinations which were deficient in the medium. Various additions of bulk organics (lactate or a cleaning agent), inorganic salts (phosphate and iron) and trace organics (tryptone and yeast extract) were made. The subsequent generation of hydrogen sulfide was followed both visually (by estimating the degree of darkening of the medium by iron sulfide (FeS)) and by measuring sulfate concentration. The results of these experiments are presented in Tables 13 to 17, where sulfate concentration is expressed as the fraction of the initial sulfate consumed. The data in Tables 13 to 17 are ordered to reflect the amount of sulfate consumed so that the cultures showing the greatest yield of hydrogen sulfide are at the top of the table. The data show that the visual assessments of hydrogen sulfide formation and sulfate consumption were only approximately correlated. Since sulfate consumption is a more reliable estimate of hydrogen sulfide generation in the medium, all subsequent assessments were based on this method. Yields of hydrogen sulfide are expressed as the percentage of sulfate consumed.

The bilge specimens from HMAS Parramatta and HMAS Cook showed evidence of hydrogen sulfide generation in the ship and produced hydrogen sulfide on simulated

storage in the laboratory. Both specimens, however, failed to sustain the process long enough for complete conversion of the sulfate to hydrogen sulfide. The data in Tables 15 and 17 show that both environments were inadequate for growth of the bacteria. Thus, the specimen from HMAS Parramatta (Table 15) gave the highest yields of hydrogen sulfide (32-50%) when composite additions of bulk organics, minerals and trace organics were made. Addition of the separate components, lactate, Gamosol or phosphate, resulted in lower yields of hydrogen sulfide (approx. 10%). The addition of iron alone had little effect (2%), while the more complete medium obtained by combined addition of tryptone and yeast extracts resulted in 35% yields of hydrogen sulfide. Similar behaviour was observed with the specimen from HMAS Cook (Table 17), although the influence of phosphate was more pronounced. Addition of bulk organics alone again resulted in low yields of hydrogen sulfide (most below 10%), while composite additions gave yields as high as 62%. Again, iron had little effect (3%), and the tryptone/yeast extract addition yielded 30% hydrogen sulfide.

The results from HMAS Parramatta and HMAS Cook suggest that reduced use of cleaning agents, and control of phosphate, would reduce hydrogen sulfide generation in these ships. If the cleaning agent cannot be eliminated entirely, the yield of hydrogen sulfide arising from it can be greatly reduced by preventing unnecessary additions of phosphate to the bilge. In addition, the relative high yields of hydrogen sulfide obtained on addition of tryptone and yeast extracts show that the disposal of food scraps and other organic waste in the bilge should be avoided.

The cultures from HMAS Canberra, HMAS Perth (engine room No. 1, 12-May-90) and HMAS Tobruk all failed to produce hydrogen sulfide during simulated storage in the laboratory. The results of addition of nutrients to these cultures (Tables 13, 14 and 16, respectively) show that they could produce hydrogen sulfide if given suitable conditions. The waste specimens from HMAS Canberra and HMAS Perth were mainly deficient in the bulk organic component. Thus, addition of lactate resulted in a 100% yield of hydrogen sulfide in the waste from HMAS Canberra (Table 13), while the addition of Gamosol alone resulted in a yield of approx. 50%. Phosphate also affected the yield of hydrogen sulfide. However, the high yields of hydrogen sulfide obtained on adding Gamosol alone would suggest that both components should be controlled to reduce hydrogen sulfide production in this waste. Iron was also deficient in this culture, but it would be impractical to attempt to control this component in a steel ship. The culture from HMAS Perth (Table 14) behaved in a similar way to that from HMAS Canberra, although the effect of phosphate additions was diminished. Control of cleaning agent and phosphate levels would be necessary to reduce hydrogen sulfide formation in the waste from HMAS Perth. The data in Table 16 show that for HMAS Tobruk the addition of Gamosol (with iron, which had no influence by itself) resulted in only 3% yields of hydrogen sulfide. On the other hand, Gamosol, in the presence of phosphate and other components, resulted in a 20% hydrogen sulfide yield. This waste specimen was deficient in both bulk organic and phosphate, so control of the phosphate level would greatly reduce the yield of hydrogen sulfide produced in this bilge specimen.

Table 17 shows the influence of additions of several other cleaning agents found in machinery spaces. These are Alfloc 707, HDE 777 and Nalfleet 9111. Alfloc 707 and

HDE 777, contain phosphate as polyphosphates and a phosphate ester respectively, with other organic material. The yields of hydrogen sulfide of 6 to 9% are consistent with the addition of both phosphate and bulk organics. However, the amount of hydrogen sulfide produced is not as high as with phosphate and either Gamosol or Comprox. Nalfleet 9111, which consists mainly of sodium nitrate, had no influence on hydrogen sulfide formation on its own, and depressed the effect of Alfloc 707. These observations are probably consistent with the oxidising potential of nitrate (Postgate, 1984).

4. Conclusions

The bilge-water environment of RAN ships is generally well suited to generation of hydrogen sulfide by sulfate-reducing bacteria. These bacteria probably occur in all ships of the fleet in bilges, oily-water holding tanks, and any other locations where their growth requirements are met. However, the presence of these bacteria in the RAN ships cannot be considered unusual as they are also found in foreign naval vessels which do not have problems with hydrogen sulfide. The combination of large quantities of sea-water sulfate and biodegradable cleaning agents, together with the need to store the oily-water wastes for extended periods, contribute to development of potential toxic hazards in RAN ships. These hazards would appear to be confined mainly to stored wastes, as machinery spaces are generally well ventilated and hydrogen sulfide gas is removed as it diffuses into the air. Poorly ventilated bilge areas could present a danger. A detailed understanding of the chemical composition of all commercial substances used in machinery spaces, and a policy for control of their selection and use, could significantly reduce the problem. Importantly, the quantities of biodegradable material, such as cleaning agents and general organic rubbish, entering the bilge should be kept to a minimum. If possible, substances containing phosphates should be completely avoided.

5. Experimental Section

5.1 Materials

All samples were collected in new poly(ethylene) or poly(propylene) containers, and new food grade Tygon or C-flex tubing (Masterflex) was used when the oily-water waste was pumped from the bilge.

All reference compounds for ion chromatography and high performance liquid chromatography were of reagent grade or better.

Cleaning agents used in the experiments were Gamosol D5 (Gamlen Australasia, Lane Cove, NSW), Comprox F46 (BP Australasia, Melbourne, VIC), Sea-Clean (Gamlen Australasia, Lane Cove, NSW), Alfloc 707 (Catoleum Pty. Ltd., Botany, NSW), HDE-777 (Drew Ameroid Australasia, Annandale, NSW) and Nalfleet (Nalfloc Ltd., Norwich, UK).

5.2 Collection of Bilge Specimens

Oily-water waste specimens were collected from accessible bilges of naval vessels which visited Melbourne, or were berthed at Garden Island Dockyard, Sydney. Sampling in Melbourne was conducted by laboratory staff while specimens collected in Sydney were obtained by Navy personnel.

Bilge specimens collected in Melbourne were usually recovered from the bilge using a hand-operated peristaltic pump (Masterflex) which enabled some control over the location and depth from which the sample was collected. Specimens collected in Sydney were "grab" samples taken from near the surface of the bilge. Sample containers were filled to the top before tightly capping to reduce the effects of air and prevent loss of volatile substances from the sample. Oily-water waste specimens collected in Sydney were packed in ice and transported to the laboratory by overnight airfreight and stored under refrigeration (4°C) until tested. Chemical and microbiological analyses of the bilge specimens were conducted within one to three days of collection.

5.3 Microbiological Analysis

Full details of the microbiological analysis of oily-water waste specimens have been described previously (Upsher et al., 1995).

5.4 pH and Redox Potential

The pH of oily-water waste was measured using an Orion 81-35 epoxy flat bed pH electrode calibrated with buffers at pH 4.00 and 7.01. Oxidation-reduction (Redox) potential of oily-water waste specimens were measured with an Orion 96-78 redox electrode.

5.5 Sulfide Analysis

Sulfide was measured using an Orion 94-16 Ag^+/S^{2-} ion selective electrode with an Orion 90-02 reference electrode. The oily-water waste sample (1 mL diluted to 50 mL

with de-ionised water) was added to 50 mL of sulfide antioxidant buffer (2M NaOH, 0.2M L-ascorbic acid, 0.2M EDTA di-sodium salt) for sulfide measurement. The electrode was calibrated with two reference sulfide solutions which bracketed the oily-water waste sulfide concentration. The sulfide reference solutions were prepared by dilution of a 1000 ppm stock solution standardised by iodine titration (APHA, 1975).

5.6 Analysis of Other Inorganic Anions

Sulfate, chloride and phosphate concentrations were measured using a Dionex model 2000i/SP ion chromatograph with a Dionex HPIC-AS4A anion separation column and conductivity detection. The anions were eluted with a mixture of sodium carbonate (0.0018M) and sodium bicarbonate (0.0017M) flowing at 2 mL/min. Samples required extensive pretreatment to prevent damage to the anion separation column by oil and precipitated metal sulfides. In-line pretreatment consisted of a particle filter, an organics trap (Dionex MPIC-NG1), a metal cation trap (Dionex MFC-1), and a guard column (Dionex HPIC-AG4A). Diluted oily-water waste samples were injected into the ion chromatograph through a Millipore Millex HV filter (0.45 micron), a Dionex OnGuard-RP cartridge (to remove oil and surfactants), and a Dionex OnGuard-H cartridge (to remove metal salts). Anion concentrations were determined by external calibration.

5.7 Simulated Storage of Oily-water Waste

Simulated storage of oily-water waste specimens was carried out in vertical glass cylinders (7 x 140 cm) open to the air at the top. Each cylinder contained several sampling ports along its length for removal by syringe of specimens from different depths. The cylinders were maintained at 31°C by water circulated from a constant temperature bath. Before adding the oily-water waste specimen, each tube was thoroughly cleaned, sampling port fittings renewed, and the cylinder sterilised with ethanol. The ethanol was allowed to evaporate before the waste specimen was added.

5.8 Determination of Additional Nutrient Requirements

Possible nutrient deficiencies were investigated by incubating the oily-water waste specimen in sealed 100 or 200 mL bottles at 31°C after addition of the selected nutrient substances. The various additions were: sodium lactate (Ajax) (4 mM), cleaning agents (0.5% v/v), potassium dihydrogen phosphate (May & Baker) (50 ppm), iron (as two small mild steel nails), tryptone (Difco) and yeast extract (Oxoid) (each 0.1 g/L). Ascorbic acid (Ajax) (0.2 g/L) was added to all specimens as a redox poising agent.

6. Acknowledgments

The authors are grateful to Sub-Lieutenant David Peake of Fleet Intermediate Maintenance Authority (FIMA, HMAS Kuttabul) for collection of the oily-water waste specimens from ships berthed at Garden Island Dockyard. The authors are also grateful to the Commanding Officers of the foreign ships for allowing us to collect specimens of oily-water waste from their ships' bilges.

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Table 1: Details of Royal Australian Navy ships from which bilge-water specimens were collected.

Ship	Class	Launched	Displ. (tons)	Engines
Darwin	Frigate	1982	3,680	Gas turbine
Canberra	Frigate	1981	3,680	Gas turbine
Sydney	Frigate	1980	3,680	Gas turbine
Adelaide	Frigate	1978	3,680	Gas turbine
Brisbane	Destroyer	1966	4,720	Steam turbine
Perth	Destroyer	1963	4,720	Steam turbine
Parramatta	Destr. Escort	1959	2,750	Steam turbine
Success	Fleet Oiler	1984	17,933	Diesel
Tobruk	Landing Ship	1980	5,800	Diesel
Warrnambool	Patrol Boat	1980	220	Diesel
Cook	Survey Ship	1977	2,550	Diesel
Bayonet	Patrol Boat	1968	149	Diesel

Source: "Navy Today", Defence Public Relations.

Table 2: Details of foreign ships from which bilge-water specimens were collected during September and October 1988.

Ship	Country	Class	Launched	Displ. (tons)	Engines
Aris	Greece	Training	1978	2,630	Diesel
Godavari	India	Frigate	1980	3,850	Gas turbine
Colbert	France	Cruiser	1956	11,300	Steam turbine
Caio Duilio	Italy	Cruiser	1962	6,500	Steam turbine
Waikato	New Zealand	Frigate	1965	3,035	Steam turbine

Source: "Janes Fighting Ships"

Table 3. Changes in chemical composition of an oily-water waste specimen from HMAS Canberra (a) during simulated storage at 31°C.

Elapsed time (days)	Redox potential (mV)	Sulfate conc. (ppm)	Sulfide conc. (ppm)	pH
0	140	93	0	7.1
16		103		
33	-214		0	6.7
40	-261	98	trace	6.6
55	-121	112	0	6.6
62	-119	108	0	6.7
69	-116	100	0	6.7
97	-21	95	0	6.6
101		102		
111		102		
114		97		
121	-93	94	trace	6.6

(a) Engine room, 16-Jun-90.

Table 4: Changes in chemical composition of an oily-water waste specimen from HMAS Sydney (a) during simulated storage at 31°C.

Elapsed time (days)	Redox potential (mV)	Sulfate conc. (ppm)	Sulfide conc. (ppm)	pH
0		2		
9	-229	4	2	5.7
16	-208	7	2	5.8
26	-161	126 (b)	1	5.9
30	-172		1	5.8
36	-142			5.8
47		8		
Addition (day 50): Sulfate				
51	-208		2	5.8
54	-152		1	6.0
55		316		
57	-225	239		6.2
61	-216	146	74	6.6

(a) Engine room, 03-Mar-90.

(b) The sulfate reading of 126 ppm after 26 days is probably an experimental error.

Table 5: Changes in chemical composition of an oily-water waste specimen from HMAS Adelaide (a) during simulated storage at 31°C.

Elapsed time (days)	Redox potential (mV)	Sulfate conc. (ppm)	Sulfide conc. (ppm)	pH
0	-137	1,854	0	8.9
7	-142	2,216	0	8.8
14	-130	1,898	0	8.8
34	-66		0	8.6
42	53	1,970	0	8.5
46		2,061		
56		2,048		
59	32	2,523		8.4
66	-21	2,103	0	8.3
70		2,110		
76		2,134		
82		2,030		
91	-298	2,130	5	8.1
102	-298	1,957	trace	8.0
111		2,109		
117	-287	2,101	trace	7.9
119		2,148		
123	-314		0	8.0

(a) Engine room, 23-Jul-90.

Table 6. Changes in chemical composition of an oily-water waste specimen from HMAS Brisbane (a) during simulated storage at 31°C.

Elapsed time (days)	Redox potential (mV)	Sulfate conc. (ppm)	Sulfide conc. (ppm)	pH
0	-74		0	4.2
10	-57	317	0	4.1
14			0	4.0
20	251			3.9
31		361		
35	-186		0	3.8
38	72		0	3.8
39		314		
Addition: Alkali				
41	-38	298		7.3
45	53	310	0	7.4
75		371		
101		344		
115	-187		0	4.6

(a) Boiler room no. 1, 17-Mar-90.

Table 7. Changes in chemical composition of an oily-water waste specimen from HMAS Perth (a) during simulated storage at 31°C.

Elapsed time (days)	Redox potential (mV)	Sulfate conc. (ppm)	Sulfide conc. (ppm)	pH
0	-21	268	0	6.6
25		267	0	
51	-258	290	0	6.3
75	-287	253	trace	6.3
90	-215	256	0	6.3
97	-181	277	0	6.4
104	-166	275	0	6.3

(a) Engine room no. 1, 12-May-90.

Table 8. Changes in chemical composition of an oily-water waste specimen from HMAS Perth (a) during simulated storage at 31°C.

Elapsed time (days)	Redox potential (mV)	Sulfate conc. (ppm)	Sulfide conc. (ppm)	pH
0	-317	335	1	6.8
37		0		
Addition (day 38): Sulfate				
39		734		
41		728		
44		487		
46		341		
47		240	130	
54	-190			5.1
Addition (day 54): Molybdate				
61		228		
Addition (day 61): Alkali				
61	-199		23	7.9
76	-172	256	2	7.8
83	-155	278	4	8.0
90	-164	254	2	8.2

(a) Engine room no. 1, 26-May-90.

Table 9. Changes in chemical composition of an oily-water waste specimen from HMAS Parramatta (a) during simulated storage at 31°C.

Elapsed time (days)	Redox potential (mV)	Sulfate conc. (ppm)	Sulfide conc. (ppm)	pH
0	-360	238		7.6
9	-383	247	88	7.5
16	-328	260	31	7.5
26	-287	253	53	7.5
30	-317		42	7.5
31	-244			7.5
36		351		
47	-259		24	7.3
54	-217		20	7.3
55		333		
57	-263	311		7.6
61	-213	327	15	7.7
91		359	0	

(a) Engine room, 26-Jan-90.

Table 10. Changes in chemical composition of an oily-water waste specimen from HMAS Success (a) during simulated storage at 31°C.

Elapsed time (days)	Redox potential (mV)	Sulfate conc. (ppm)	Sulfide conc. (ppm)	pH
0	50	562	0	8.2
10	22	518	0	8.1
14		561		
24		571		
27	38	647		8.1
34	-33	598	0	8.0
45		574		
Addition (day 49): Ascorbic acid Addition (day 50): OWW from HMAS Perth				
59	-278	578	4	6.8
71	-262	530	0	6.8
79		568		
85	-258	556	trace	6.8
87		575		
100	-308	470	trace	6.9
115		553		
119	-179		0	7.0
122	-164			7.0

(a) Engine room, starboard, 03-Aug-90.

Table 11. Changes in chemical composition of an oily-water waste specimen from HMAS Tobruk (a) during simulated storage at 31°C.

Elapsed time (days)	Redox potential (mV)	Sulfate conc. (ppm)	Sulfide conc. (ppm)	pH
0	110	940	0	6.9
14		931		
24	-277	915	0	7.0
49	-316	966	0	6.9
56	-213		0	6.9
66	-140	898	0	6.9

(a) A mixture of specimens from HMAS Tobruk.

Table 12. Changes in chemical composition of an oily-water waste specimen from HMAS Cook (a) during simulated storage at 31°C.

Elapsed time (days)	Redox potential (mV)	Sulfate conc. (ppm)	Sulfide conc. (ppm)	pH
0		437		
3	-253	554	0	6.9
14		490		
21		470		
26		452	3	
35	-492	462	10	6.9
46	-520	385	18	6.9
56		441		
61	-492	459	2	6.8
63		470		
76	-450	395	trace	6.8

(a) Engine room no. 1, 31-Aug-90.

Table 13. Influence of added nutrients on sulfate consumption and sulfide production in an oily-water waste specimen from HMAS Canberra.

Sulfate Consumed (%)	BULK ORGANICS			MINERALS		TRACE ORGANICS	Assessed Sulfide Level (a)
	Lactate	Cleaning agent		Phosphate	Iron	Tryptone/Yeast	
100	Lactate	-		Phosphate	Iron	Tryptone/Yeast	+++
100	Lactate	-		Phosphate	Iron	-	+++
100	Lactate	-		Phosphate	-	Tryptone/Yeast	++
100	Lactate	-		-	-	-	++
80	Lactate	-		Phosphate	-	-	++
66	-	Gamosol	(b)	Phosphate	Iron	-	++
66	-	Gamosol	(b)	-	Iron	Tryptone/Yeast	++
62	Lactate	-		-	-	Tryptone/Yeast	+++
60	-	Gamosol	(b)	-	-	-	+
54	-	Gamosol		Phosphate	Iron	Tryptone/Yeast	.
49	-	-		Phosphate	-	-	+
43	-	Gamosol		Phosphate	Iron	-	.
41	-	-		Phosphate	Iron	-	+
40	-	Gamosol		-	-	-	.
37	-	-		-	-	-	+
35	-	-		-	Iron	-	+
20	-	-		-	-	Tryptone/Yeast	+
0	-	-		-	-	-	++

(a) FeS darkening: (.) none, (+) faint, (++) moderate, (+++) extensive.

(b) Surfactant only

Table 14. Influence of added nutrients on sulfate consumption and sulfide production in an oily-water waste specimen from HMAS Perth.

Sulfate Consumed	BULK ORGANICS			MINERALS		TRACE ORGANICS	Assessed Sulfide Level (a)
(%)	Lactate	Cleaning agent		Phosphate	Iron	Tryptone/Yeast	
82	Lactate	-		Phosphate	Iron	Tryptone/Yeast	+++
82	Lactate	-		Phosphate	Iron	-	+
81	Lactate	-		Phosphate	-	-	+
63	Lactate	-		-	-	-	.
60	-	Gamosol	(b)	Phosphate	Iron	-	+++
56	Lactate	-		Phosphate	-	Tryptone/Yeast	+
53	-	Gamosol	(b)	-	Iron	Tryptone/Yeast	+++
45	-	Gamosol	(b)	-	-	-	+
40	Lactate	-		-	-	Tryptone/Yeast-	+
39	-	Gamosol		Phosphate	Iron	-	.
35	-	Gamosol		Phosphate	Iron	Tryptone/Yeast	.
35		Gamosol		-	-	-	+
20	-	-		-	-	Tryptone/Yeast	.
19	-	-		Phosphate	-	-	.
9	-	-		-	Iron	-	.
3	-	-		Phosphate	Iron	-	.
0	-	-		-	-	-	.

(a) FeS darkening: (.) none, (+) faint, (++) moderate, (+++) extensive.

(b) Surfactant only

Table 15. Influence of added nutrients on sulfate consumption and sulfide production in an oily-water waste specimen from HMAS Parramatta.

Sulfate Consumed	BULK ORGANICS		MINERALS		TRACE ORGANICS	Assessed Sulfide Level (a)
(%)	Lactate	Cleaning agent	Phosphate	Iron	Tryptone/Yeast	
50	Lactate	-	Phosphate	Iron	-	+++
44	-	Gamosol	Phosphate	Iron	Tryptone/Yeast	+
35	-	-	-	-	Tryptone/Yeast	+
32	Lactate	-	Phosphate	Iron	Tryptone/Yeast	+
26	-	Gamosol	Phosphate	Iron	-	.
18	-	Gamosol	Phosphate	-	-	.
11	-	Gamosol	-	-	-	.
9	-	-	Phosphate	Iron	-	.
9	Lactate	-	-	-	-	.
8	-	-	Phosphate	-	-	.
2	-	-	-	Iron	-	.
0	-	-	-	-	-	.

(a) FeS darkening: (.) none, (+) faint, (++) moderate, (+++) extensive.

Table 16. Influence of added nutrients on sulfate consumption and sulfide production in an oily-water waste specimen from HMAS Tobruk.

Sulfate Consumed	BULK ORGANICS		MINERALS		TRACE ORGANICS	Assessed Sulfide Level (a)
(%)	Lactate	Cleaning agent	Phosphate	Iron	Tryptone/Yeast	
20	-	Gamosol	Phosphate	Iron	Tryptone/Yeast	+++
7	Lactate	-	Phosphate	Iron	-	++
6	Lactate	-	Phosphate	-	-	+
3	-	Gamosol	-	Iron	-	.
1	-	-	-	-	Tryptone/Yeast	+++
1	Lactate	-	Phosphate	-	Tryptone/Yeast	+++
0	Lactate	-	-	-	-	.
0	-	-	-	-	-	.
0	-	-	-	Iron	-	.
0	-	-	Phosphate	-	-	.
0	-	-	Phosphate	Iron	-	+

(a) FeS darkening: (.) none, (+) faint, (++) moderate, (+++) extensive.

Table 17. Influence of added nutrients on sulfate consumption and sulfide production in an oily-water waste specimen from HMAS Cook.

Sulfate Consumed	BULK ORGANICS		MINERALS		TRACE ORGANICS	Assessed Sulfide Level (a)
(%)	Lactate	Cleaning agent	Phosphate	Iron	Tryptone/Yeast	
62	Lactate	-	Phosphate	Iron	Tryptone/Yeast	+++
62	Lactate	-	Phosphate	-	Tryptone/Yeast	+++
49	Lactate	-	Phosphate	Iron	-	+++
41	Lactate	-	Phosphate	-	-	++
33	Lactate	-	-	-	Tryptone/Yeast	+
31	-	Comprox	Phosphate	Iron	-	+++
30	-	-	-	-	Tryptone/Yeast	+
17	-	Gamosol	Phosphate	Iron	-	++
16	-	-	Phosphate	-	-	+
15	-	Gamosol	-	-	-	.
10	-	-	Phosphate	Iron	-	+
10	-	Sea-clean	Phosphate	Iron	-	+
9	-	Alfloc 707	-	-	-	++
7	-	HDE 777	-	-	-	.
6	-	Alfloc/HDE	-	-	-	+
5	-	Sea-clean	-	-	-	.
3	Lactate	-	-	-	-	.
3	-	-	-	Iron	-	.
3	-	-	-	-	-	.
2	-	Comprox	-	-	-	.
2	-	Alfloc/Nalfleet	-	-	-	.
0	-	Nalfleet 9111	-	-	-	.
0	-	-	-	-	-	.

(a) FeS darkening: (.) none, (+) faint, (++) moderate, (+++) extensive.

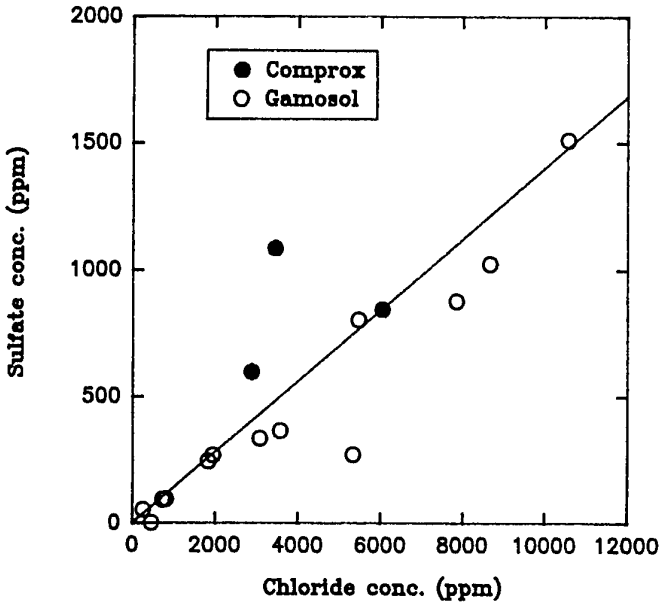

Figure 1: Scatter plot of sulfate concentration vs. chloride concentration for oily-water waste specimens from bilges of RAN ships using Gamosol and Comprox detergents. (The straight line shows the ratio of sulfate to chloride in diluted sea-water).

Overview of Bilge Composition
RAN Ships

	SRB population	Sea-water content	Redox potential	Highest sulfide conc. (ppm)
Darwin	++	+++	---	0
Canberra	++	.	--	0
Sydney	++++	.	+++	27
Adelaide	++++	++++	+++++	0
Brisbane	+	.	----	0
Perth	+++	+++	+	1
Parramatta	++++++	++	++++++	1
Success	+++	+++	-	1
Tobruk	(no data)	+++	--	0
Warrnambool	+	++++	++	0
Cook	++++	+++	+	1
Bayonet	++	(no data)	++++++	133

Figure 2: Tabular bar chart showing estimated levels of SRB populations, sea-water concentrations and anaerobic conditions in combined specimens of oily-water waste for each of the RAN ships surveyed. (An increasing number of '+' signs indicates increasingly favourable conditions for growth of SRB and production of hydrogen sulfide). The highest single sulfide reading for each ship is also shown.

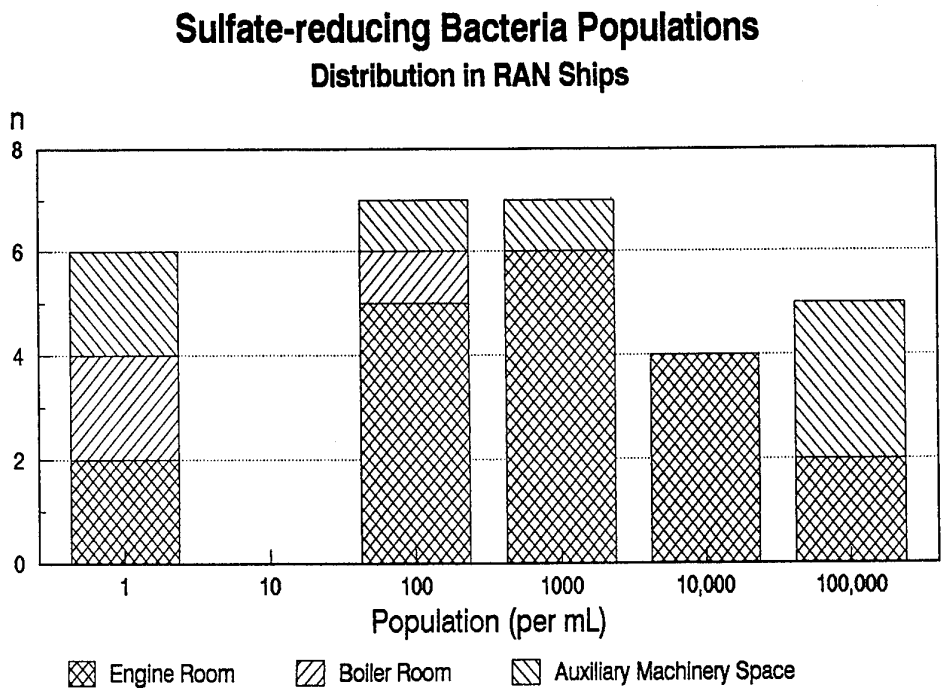

Figure 3: SRB population distribution for oily-water waste specimens collected from different locations in RAN ships. (n is the number of specimens, total 29).

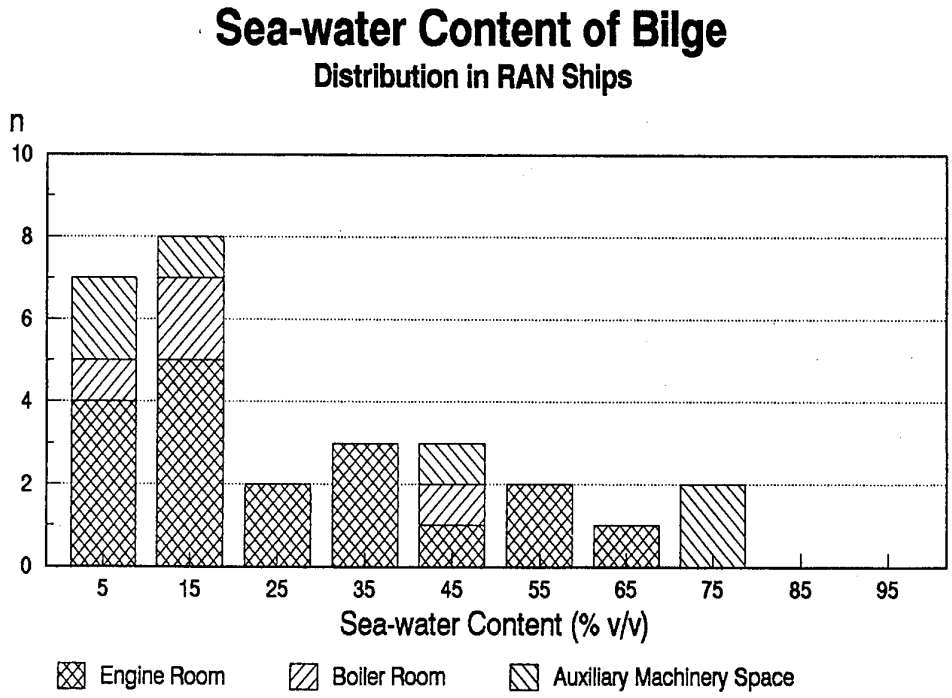

Figure 4: Sea-water content distribution for oily-water waste specimens collected from different locations in RAN ships. (n is the number of specimens, total 28).

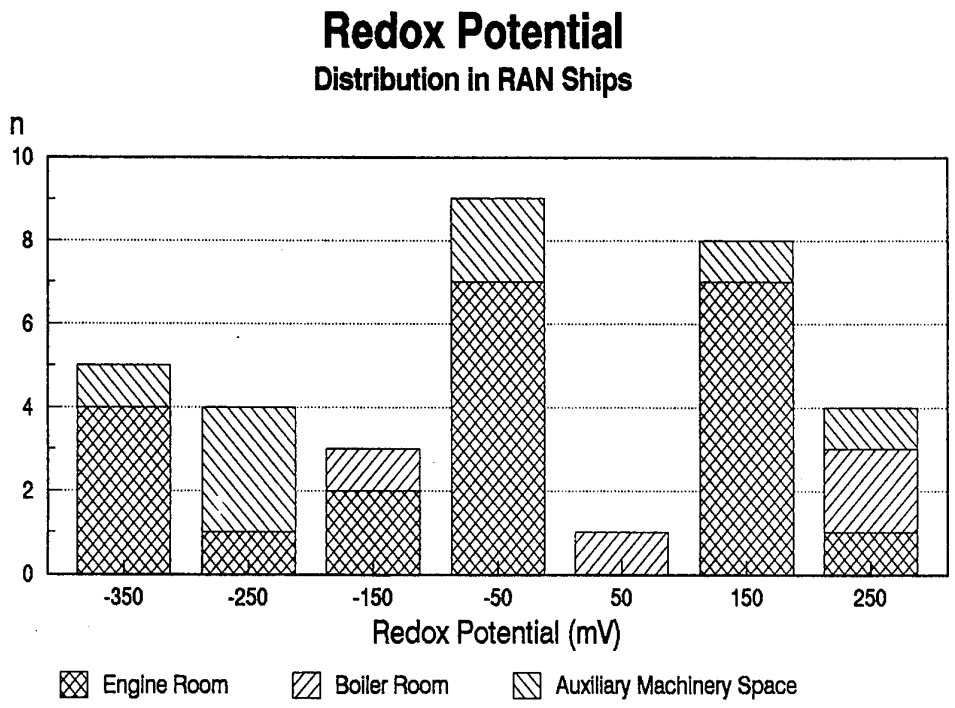

Figure 5: Redox potential distribution for oily-water waste specimens collected from different locations in RAN ships. (n is the number of specimens, total 34).

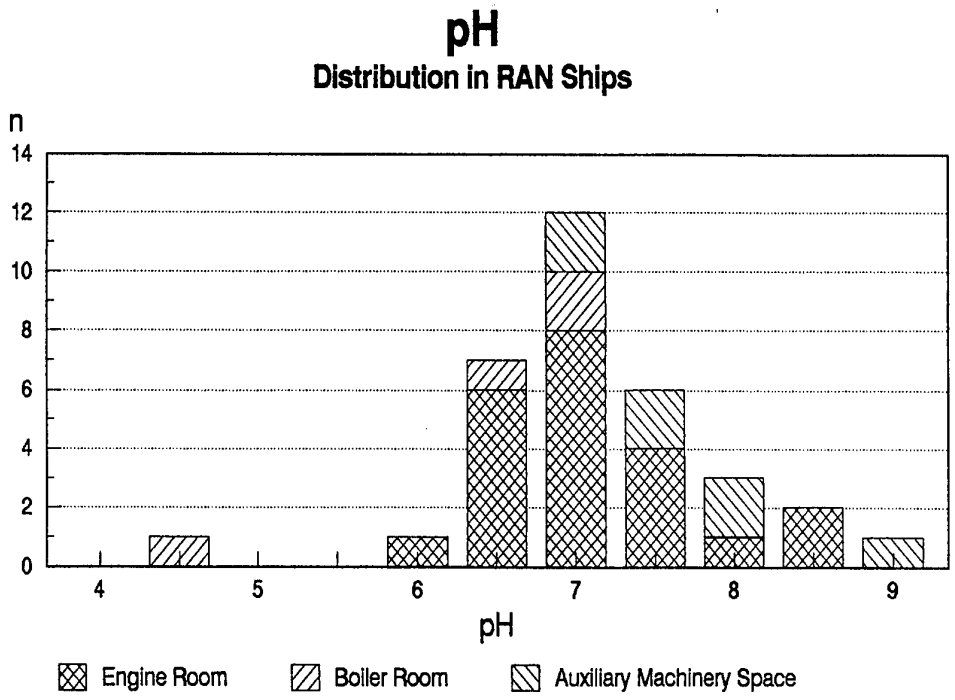

Figure 6: pH distribution for oily-water waste specimens collected from different locations in RAN ships. (n is the number of specimens, total 34).

Overview of Bilge Composition
Foreign Ships

	SRB population	Sea-water content	Redox potential	Highest sulfide conc. (ppm)
Aris	+	(no data)	+	0
Godavari	+ + +	+ + +	- - -	0
Colbert	+	+ + + + + +	- - -	0
Caio Duilio	+ + +	+ + + +	-	0
Waikato	+ +	+ + +	- -	0

Figure 7: Tabular bar chart showing levels of SRB populations, sea-water concentrations and anaerobic conditions in specimens of oily-water waste from foreign naval vessels. (See Figure 2 for an explanation of the symbols).

Appendix 1.

Results of chemical and microbiological analysis of oily-water waste specimens from HMA ships Darwin and Canberra.

	HMAS Darwin Engine Room	HMAS Darwin Aux. Machinery Room No. 2	HMAS Darwin Aux. Machinery Room No. 3	HMAS Canberra Engine Room	HMAS Canberra Aux. Machinery Room No. 2	HMAS Canberra Engine Room	HMAS Canberra Engine Room
	03-Dec-89	03-Dec-89	03-Dec-89	22-Sep-89	22-Sep-89	16-Jun-90	16-Jun-90
(1) Sample							
Bilge temperature (C)						14	14
Bilge stagnant (days)				2	2	5	5
Detergent(s) present				Gamosol	Gamosol	Gamosol	Gamosol
(2) Microbiological Analysis							
SRB (per mL)	>100	>100	<10			1,000	<10
Total aerobes (per mL)						5,400,000	1,500,000
Coliforms (per mL)	>100	>100	<10			<100	100
(3) Chemical Analysis							
pH	6.6	7.2	7.3			7.1	7.0
Redox potential (mV)	221	144	201			140	132
Phosphate (ppm)	0	0	0	2	0	0	0
Sulfide (ppm)	0	0	0	0	0	0	0
Chloride (ppm)						733	820
Sulfate (ppm)	827	1315	131	36	208	93	96
Sea-water content of bilge:							
Est. from chloride conc.						4%	4%
Est. from sulfate conc.	31%	49%	5%	1%	8%	3%	4%

Appendix 2.

Results of chemical and microbiological analysis of oily-water waste specimens from HMA ships Sydney, Adelaide and Brisbane.

	HMAS Sydney Engine Room 09-Mar-89	HMAS Sydney Aux. Machinery Room No. 1 09-Mar-89	HMAS Sydney Aux. Machinery Room No. 2 09-Mar-89	HMAS Sydney Engine Room 03-Mar-90	HMAS Adelaide Aux. Machinery Room 23-Jul-90	HMAS Adelaide Engine Room 23-Jul-90	HMAS Brisbane Boiler Room (a) 17-Mar-90	HMAS Brisbane Boiler Room (b) 17-Mar-90
(1) Sample								
Bilge temperature (C)				18	16	16		
Bilge stagnant (days)				14	>14	>14	2	2
Detergent(s) present	Sea-clean	Sea-clean	Sea-clean	Gamosol Sea-clean	Sea-clean	Sea-clean Genesolve	Gamosol	Gamosol
(2) Microbiological Analysis								
SRB (per mL)	>100,000	>100,000	<10	>10,000	>100,000	100	<10	<10
Total aerobes (per mL)				2,600,000	11,300,000	6,000,000		
Coliforms (per mL)					10	<10	100	100
(3) Chemical Analysis								
pH	7.1	7.8	8.0	5.9	9.0	7.6	4.3	6.3
Redox potential (mV)	-368	-240	-34	-28	-261	-278	256	225
Phosphate (ppm)				0	0	0	0	0
Sulfide (ppm)	27	16	trace	0	0	0	0	0
Chloride (ppm)				460		11,606		259
Sulfate (ppm)				2	2,110	1,800	278	53
Sea-water content of bilge:								
Est. from chloride conc.				2%		60%		1%
Est. from sulfate conc.				0%	78%	66%	10%	2%

Appendix 3.

Results of chemical and microbiological analysis of oily-water waste specimens from HMAS Perth.

	HMAS Perth Engine Room No. 1 (a) 12-May-90	HMAS Perth Engine Room No. 1 (b) 12-May-90	HMAS Perth Engine Room No. 2 12-May-90	HMAS Perth AC-2 12-May-90	HMAS Perth Engine Room No. 2 26-May-90	HMAS Perth Boiler Room No. 2 26-May-90	HMAS Perth Boiler Room No. 1 26-May-90	HMAS Perth Engine Room No. 1 26-May-90
(1) Sample								
Bilge temperature (C)	22	22	22	22	17	17	17	17
Bilge stagnant (days)					5	5	5	5
Detergent(s) present	Gamosol	Gamosol	Gamosol	Gamosol	Gamosol	Gamosol	Gamosol	Gamosol
(2) Microbiological Analysis								
SRB (per mL)	10,000	<1,000	>1,000	3,000		400		20,000
Total aerobes (per mL)								
Coliforms (per mL)	100	1,000	<100	10,000		<100		100
(3) Chemical Analysis								
pH	6.6	6.5	6.8	7.7	6.9	7.1	6.8	6.8
Redox potential (mV)	-21	135	-37	-224	-141	-138	32	-317
Phosphate (ppm)	0	0	0	0	0	0	0	0
Sulfide (ppm)	0	0	0	0	0	0	0	1
Chloride (ppm)	1,952	10,565	5,464	3,566	7,848	8,664	1,840	3,072
Sulfate (ppm)	268	1,511	804	365	878	1,025	244	335
Sea-water content of bilge:								
Est. from chloride conc.	10%	55%	28%	18%	41%	45%	10%	16%
Est. from sulfate conc.	10%	56%	30%	13%	32%	38%	9%	12%

Appendix 4.

Results of chemical and microbiological analysis of oily-water waste specimens from HMA ships Parramatta, Success and Tobruk.

	HMAS Parramatta	HMAS Success	HMAS Success	HMAS Success	HMAS Success	HMAS Success	HMAS Tobruk
	Engine Room	Engine Room	Engine Room	(?)	Engine Room Port	Engine Room S'board	Engine Room
	26-Jan-90				03-Aug-90	03-Aug-90	13-Jan-90
(1) Sample							
Bilge temperature (C)	19				16	16	17
Bilge stagnant (days)	10				10	10	>14
Detergent(s) present	Gamosol	Nalfleet Comprox Sea-clean			Comprox	Comprox	Gamosol
(2) Microbiological Analysis							
SRB (per mL)	800,000		100	100,000	>1,000	>1,000	
Total aerobes (per mL)					5,600,000	2,200,000	
Coliforms (per mL)	>1,000				1,000	1,000	
(3) Chemical Analysis							
pH	7.7	8.5	6.4	6.5	7.5	8.3	6.9
Redox potential (mV)	-390	145	175	-48	-110	122	110
Phosphate (ppm)	0				0	0	0
Sulfide (ppm)	trace	0	0	1	0	0	0
Chloride (ppm)	5,340				3,443	2,876	
Sulfate (ppm)	271				1,085	597	940
Sea-water content of bilge:							
Est. from chloride conc.	28%				18%	15%	
Est. from sulfate conc.	10%				40%	22%	35%

Appendix 5.

Results of chemical and microbiological analysis of oily-water waste specimens from HMA ships Warrnambool, Cook and Bayonet.

	HMAS Warrnambool Engine Room 22-Nov-89	HMAS Cook Engine Room 10-Feb-90	HMAS Cook Aux. Machinery Room 10-Feb-90	HMAS Cook Engine Room No. 1 (a) 31-Aug-90	HMAS Cook Engine Room No. 1 (b) 31-Aug-90	HMAS Bayonet Engine Room
(1) Sample						
Bilge temperature (C)		22	22	18	18	
Bilge stagnant (days)	5	11	11			
Detergent(s) present	Eco-temp	Comprox	Comprox			
(2) Microbiological Analysis						
SRB (per mL)	<10	2,000	300,000	10,000	1,000	100
Total aerobes (per mL)	>1,000,000			1,600,000	1,200,000	
Coliforms (per mL)	<100,000	>100	>100	>10,000	1,000	
(3) Chemical Analysis						
pH	8.1	7.1	7.2	6.7	6.7	7.5
Redox potential (mV)	-97	-11	-67	-54	-47	-360
Phosphate (ppm)	0	0	0	0		
Sulfide (ppm)	0	0	0	trace	trace	133
Chloride (ppm)		6,046		3,724		
Sulfate (ppm)	1,390	845	2,060	383		
Sea-water content of bilge:						
Est. from chloride conc.		31%		19%		
Est. from sulfate conc.	51%	31%	76%	14%		

Appendix 6.

Results of chemical and microbiological analysis of oily-water waste specimens from the foreign ships.

	"Aris" Engine Room 20-Sep-88	"Godavari" Boiler Room (?) 20-Sep-88	"Colbert" Engine Room 14-Oct-88	"Caio Duilio" Boiler Room 14-Oct-88	"Caio Duilio" Engine Room 14-Oct-88	"Waikato" Boiler Room 14-Oct-88	"Waikato" Engine Room 14-Oct-88
(1) Sample							
Bilge temperature (C)							
Bilge stagnant (days)							
Detergent(s) present	none	none	Ravitol (a)	none	none		Klen 1808 (b) Klen 1702 (b)
(2) Microbiological Analysis							
SRB (per mL)	<10	1,000	<10	100	10,000	<10	100
Total aerobes (per mL)							
Coliforms (per mL)							
(3) Chemical Analysis							
pH	8.9	6.9	7.6	7.6	7.7	7.2	7.4
Redox potential (mV)	-42	157	165	107	-55	178	32
Phosphate (ppm)							
Sulfide (ppm)	0	0	0	0	0	0	0
Chloride (ppm)		7,390	25,000	21,000	1,380	9,530	1,870
Sulfate (ppm)							
Sea-water content of bilge:							
Est. from chloride conc.		38%	129%	109%	7%	49%	10%
Est. from sulfate conc.							

Hydrogen Sulfide Generation in Shipboard Oily-Water Waste: Part 3. Ship Factors

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ABSTRACT

The chemical and microbiological composition of bilge-water in ships of the Royal Australian Navy has been investigated in relation to the formation of hydrogen sulfide by sulfate-reducing bacteria. Sulfate-reducing bacteria were found in most ships in populations up to 800,000 per mL. Sulfate in the wastes is provided by sea-water. Sea-water constitutes up to 60% (median 20%) of the wastes analysed. Evidence for generation of hydrogen sulphide in the ships was found directly as sulfide or indirectly as depressed sulfate concentrations. The low levels of sulfide found in bilge-water from machinery spaces suggested the ventilation systems were effectively removing the gas from the working area. The effect of storage of the wastes under conditions which simulated the oily-water holding tanks of ships were also investigated. Some wastes were found to produce large quantities of hydrogen sulfide on storage. The wastes that failed to produce hydrogen sulfide were investigated to identify any specific nutritional deficiencies. Some organic substances present in bilge-water, such as lactate or biodegradable cleaning agents, and phosphate strongly influenced the generation of hydrogen sulfide in stored oily-water wastes.