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FAST BREAKING DETERGENTS: THEIR ROLE IN
THE GENERATION OF HYDROGEN SULFIDE IN
OILY-WATER WASTES

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JANE FLETCHER AND JOHN W. SHORR

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Fast Breaking Detergents: Their Role in the Generation of Hydrogen Sulfide in Oily-Water Wastes

Lyn E. Fletcher and F. John Upsher

MRL Technical Report
MRL-TR-93-11

Abstract

Fast breaking detergents (FBD) have recently been commissioned for use in naval ships to facilitate separation of oily-water wastes (OWW). They replaced the earlier emulsifying detergents which were known to contribute to the bacterial generation of hydrogen sulfide in OWW. The present investigation was undertaken to determine whether FBD would also contribute to hydrogen sulfide generation. The formulations of the FBD indicated that they would be biodegraded by bacteria and thus power the production of hydrogen sulfide. This was demonstrated for two of the products; the third supported a large bacterial population but did not consistently cause significant hydrogen sulfide production. The potential for hydrogen sulfide production with the FBD examined was found to be less than with the earlier emulsifying detergents.

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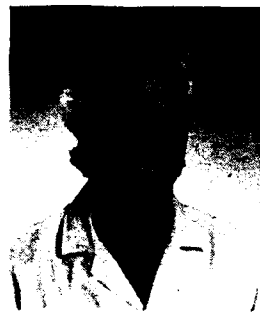
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Lyn Fletcher, BAppSc (Chem.) (RMIT) joined Materials Research Laboratory in 1985 and worked for three years on research into polymer and solvent interactions. She then joined a small multidisciplinary group investigating some environmental problems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

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Contents

1. INTRODUCTION	7
2. METHODS	8
2.1 <i>Materials</i>	8
2.2 <i>Methods of Analysis</i>	9
2.3 <i>Preparation of Inocula</i>	9
2.3.1 <i>Inoculum A</i>	9
2.3.2 <i>Inoculum B</i>	9
2.3.3 <i>Inoculum C</i>	9
2.4 <i>Comparison of Detergents</i>	10
2.4.1 <i>Sulfate Reduction</i>	10
2.4.2 <i>Bacterial Growth</i>	10
2.5 <i>Effect of Detergent Concentration</i>	11
3. RESULTS	11
3.1 <i>Comparison of Different Detergents</i>	11
3.2 <i>Effect of Detergent Concentrations</i>	15
4. DISCUSSION	16
4.1 <i>Biodegradation of Detergents</i>	16
4.2 <i>Biodegradation of Ethoxylate Detergents in OWW</i>	17
5. CONCLUSIONS	19
6. ACKNOWLEDGEMENTS	19
7. REFERENCES	19
APPENDIX 1 - <i>Description and Composition of the Detergents</i>	22

Fast Breaking Detergents: Their Role in the Generation of Hydrogen Sulfide in Oily-Water Wastes

1. Introduction

Detergents are extensively used in the engine and machinery rooms in Royal Australian Navy (RAN) vessels mainly for cleaning and removal of oil and grease deposits. "Comprox" and "Gamosol", representative of the earlier detergents used, are emulsifiers and classified as biodegradable. However, MARPOL 73/78 (International Maritime Organization, 1992) regulations limit the hydrocarbon content of waste water discharged to the sea to less than 15 parts per million of oil in effluent. Those emulsifying detergents did not facilitate efficient separation of the hydrocarbon component and were consequently no longer compatible with oily-water waste (OWW) disposal. Fast breaking detergents (FBD), with a major hydrocarbon component and lower surfactant concentrations, are consequently being introduced.

Hydrogen sulfide generation by anaerobic sulfate-reducing bacteria (SRB) is a concern for the RAN because it can occur in OWW, where it causes an unpleasant smell and can reach lethal concentrations in poorly ventilated areas. SRB carry out this process in aqueous environments in the absence of oxygen and where both sulfate and organic nutrients are available. These conditions often persist in OWW on RAN vessels (Hodgeman, Fletcher & Upsher, 1993) where the sulfate is provided by sea-water and the organic nutrients are provided by detergents and other wastes (Hodgeman, Upsher & Fletcher, 1993).

There is no documented evidence that SRB can derive energy by their own catabolism of surfactant molecules. However, they have been observed to proliferate and produce hydrogen sulfide when oils and detergents are present (Guynes & Bennett, 1959; Isenberg & Bennett, 1959; Jobson, Cook & Westlake, 1979; Nazina, Rozanova & Kuznetsov, 1985). The process is dependent on the presence of other bacteria, with enzymes able to biodegrade the surfactant and hydrocarbon molecules to smaller molecules that the SRB can utilise. The main pathways for aerobic biodegradation of alkylethoxylate, the most common type of surfactant encountered in OWW, are well documented and include: (a) central fission, which produces a free acid and polyethylene glycol; (b) ω -oxidation followed by β -oxidation, which results in acetic acid being removed

from the alkyl chain and (c) E-chain hydrolysis or oxidation, which results in ethylene glycol or glycolic acid being removed from the ethoxylate chain (Swisher, 1987). These reactions ultimately produce small organic molecules which can be oxidised to carbon dioxide and water or incorporated into bacterial cell material.

Under anaerobic conditions it is expected that hydrolytic pathways will dominate because ω -oxidation of alkyl chains require oxygen. Thus, the products of E-chain hydrolysis will be more prevalent. The polyethylene glycol moiety removed through central fission can be metabolised under anaerobic conditions by *Pelobacter propionicus* to produce acetic and propionic acids (Wagener & Schink, 1988), a methanogenic consortium to produce ethanol and acetic acid (Dwyer & Tiedje, 1983) and *Desulfovibrio desulfuricans* to produce ethanol and acetic acid (Dwyer & Tiedje, 1986). Under anaerobic conditions, the necessary oxygen is obtained from water molecules and in the process, large amounts of H₂ are formed that can also be utilised by the SRB (Sørensen, Christensen & Jørgensen, 1981).

Thus, the main metabolites available for the SRB are hydrogen, acetic acid and ethylene glycol, all of which can be utilized by SRB, together with other partially metabolised intermediates.

This investigation was undertaken to determine whether fast breaking detergents (FBD) can support SRB growth and hydrogen sulfide production under the conditions encountered in OWW. As the compositions of the detergents were not fully disclosed by the manufacturers, this work was restricted to examining the effects of the complete detergent formulations on hydrogen sulfide production, without examining the impact of individual components.

Five commercial detergents were selected for this investigation: "Comprox", a general purpose emulsifying detergent which has been in use on RAN vessels for some time; "Gamosol", an emulsifying detergent extensively used in the engine and machinery rooms of RAN vessels; and "Ameroid", "Cleanphase" and "Vecom", which are fast breaking detergents, and candidate replacements for "Gamosol".

2. Methods

2.1 Materials

The following detergents were obtained from commercial suppliers: concentrated "Comprox F46" from BP Australasia, Melbourne, Vic.; "Gamosol D5" and "Cleanphase II" from Gamlen Australasia, Lane Cove, N.S.W.; "Vecom" from Port Marine Services, Port Melbourne, Vic.; and "Ameroid" from Drew Ameroid Australasia, Annandale, N.S.W. Appendix 1 lists the composition of the detergents and the structure of the major surfactant. All other chemicals used were laboratory reagent grade or better, and obtained from commercial suppliers.

2.2 Methods of Analysis

The redox potential and pH were determined using an Orion model 96-78 platinum redox electrode and model 81-72 Ross sure-flow pH electrode, with an Orion model 720 pH/ISE meter.

Sulfate was determined using a Dionex 2000i/SP Chromatograph with an Ionpac AS4A analytical column and Ionpac AS4G, NG1 and MFC-1 precolumns and detected by conductivity.

Samples were pretreated before chromatography analysis using 0.45 micron filters and the Dionex solid phase extraction cartridges Oguard-RP and Oguard-H, to remove particulate matter, organic compounds and metal ions respectively.

2.3 Preparation of Inocula

2.3.1 Inoculum A

A composite oily-water waste, which included samples from several RAN ships, was held in a sealed 70 litre perspex tank at 30°C and agitated intermittently using a peristaltic pump. Sulfate levels were monitored and replenished with 35 g of Na₂SO₄ when depleted. To minimise carry over of nutrients, inocula for experiments were taken when sulfate oxidation had ceased, indicating nutrient depletion.

2.3.2 Inoculum B

Inoculum B was prepared by adding 2 litres of inoculum A to 38 litres of synthetic OWW medium (Na₂SO₄, 20.0 g; sodium lactate, 70%, 10.0 g; K₂HPO₄, 4.0 g; glucose, 4.0 g; ascorbic acid, 2.0 g; CaCl₂·2H₂O, 0.4 g; (NH₄)₂SO₄·FeSO₄·6H₂O, 0.2 g; yeast extract desiccated (Oxoid), 1.0 g; tap water, 32 l; sea water, 6 l) in a 70 litre perspex tank and kept at 30°C. Sulfate levels were monitored and replenished with 35 g of Na₂SO₄ when depleted. Inocula were taken for experiments when sulfate reduction had ceased.

2.3.3 Inoculum C

10.0 ml of inoculum B was reinforced with 1.0 ml suspensions of bacterial cells cultured in media containing each of the five detergents, so that inoculum C contained strains of bacteria that had been acclimated to each detergent. The suspension was diluted to a concentration of 50% with a 0.5% saline solution and shaken thoroughly.

2.4 Comparison of Detergents

2.4.1 Sulfate Reduction

The basal culture medium (NaCl, 5.3 g; MgCl₂, 0.5 g; MgSO₄·6H₂O, 0.66 g; CaCl₂·2H₂O, 0.22 g; K₂HPO₄, 0.2 g; KCl, 0.16 g; Na₂HCO₃, 0.04 g; NaBr, 0.06 g; ascorbic acid, 0.3 g; deionised water, 1.0 l) was prepared and 200 ml portions autoclaved in medical flat bottles. "Comprox", "Gamosol", "Cleanphase", "Ameroid" and "Vecom", 0.1% (w/v), were added after cooling. Test controls were (a) non-nutrient with no organic additive and (b) SRB-nutrient with 0.1% w/v sodium lactate added after sterilization. The pH of all media were 7.0 ± 0.5. Each series was conducted in triplicate. 10.0 ml of inoculum A was added to each and incubation was at 30°C ± 1°C for 14 days, after which the sulfate concentration and redox potential were determined. Two series were performed with inocula of different ages.

2.4.2 Bacterial Growth

A basal medium for assessing the influence of detergents on bacterial growth was prepared (NaCl, 5.0 g; MgSO₄·6H₂O, 0.5 g; CaCl₂·2H₂O, 0.2 g; K₂CO₃, 0.2 g; K₂HPO₄, 0.2 g; (NH₄)₂SO₄·FeSO₄·6H₂O, 0.1 g; yeast extract (Oxoid), 0.1 g; tryptone (Oxoid), 0.1 g; agar (Oxoid No. 4), 4.0 g; filtered tap water, 1.0 l; pH adjusted to 7.0). 98 ml portions were sterilized by autoclaving, in 100 ml medical flat bottles. Detergents were added, as indicated in Table 1. A nutrient control with glucose added and a non-nutrient blank, with water only added, were prepared as in Table 1. Each bottle was inoculated with 1.0 ml of inoculum C, sealed then shaken to mix the contents. Incubation was at 30°C ± 1°C. At daily intervals, 1.0 ml aliquots were taken aseptically by pipette and transferred to 9.0 ml of sterile diluting fluid (NaCl, 0.9% w/v; peptone, 0.1% w/v; in tap water) for serial decimal dilution. Selected dilutions were transferred to petri dishes for estimation of the total aerobic bacteria count, using Nutrient Agar (Oxoid) or to tubes of MRL-SRB medium for assessment of SRB (NaCl, 5.0 g; MgSO₄·6H₂O, 1.0 g; Na₂SO₄, 1.0 g; K₂CO₃, 0.5 g; K₂HPO₄, 0.5 g; CaCl₂·2H₂O, 0.1 g; (NH₄)₂SO₄·FeSO₄·6H₂O, 0.2 g; sodium lactate (70%), 4.0 g; tryptone (Oxoid), 0.4 g; yeast extract (Oxoid), 0.2 g; ascorbic acid, 0.2 g; agar (Oxoid No 4), 4.0 g; filtered tap water 1.0 l; pH adjusted to 7.0). Plates and tubes were incubated at 30°C ± 1°C. The aerobic plates were counted after 7 days and the SRB tubes assessed after 14 days.

Table 1: Detergents and Nutrients added for Bacterial Growth Analysis

Organic Nutrient	Volume (ml) added per 100 ml of medium
"Comprox F46"	0.1
"Gamosol D5"	0.1
"Cleanphase II"	1.0
"Vecom"	1.0
"Ameroid"	1.0
Glucose 5% solution in water	1.0
Distilled water (blank)	1.0

2.5 Effect of Detergent Concentration

Portions of the basal culture medium 100ml, (as 2.4.1) were autoclaved in 100 ml bottles. After cooling, a detergent and 5 ml of inoculum B were added. "Gamosol", "Cleanphase", "Vecom" and "Ameroid", at concentrations of 0, 0.01%, 0.05%, 0.1%, 0.5% and 1.0%, were used and each treatment was repeated in triplicate. All samples were incubated at $30^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 14 days, analysed for sulfate concentration and the redox potential measured.

3. Results

3.1 Comparison of Different Detergents

Sulfate reductions, in the presence of the test detergents as organic substrates (duplicate series) are presented in Figure 1. Results from bottles in which SRB growth and thus sulfate reduction were inhibited by entry of oxygen, were discarded. Sulfate reduction was used to measure SRB respiration in preference to hydrogen sulfide production because of its greater stability in the presence of oxygen and lower volatility, which reduce the likelihood of error.

The greatest sulfate reduction occurred in the treatments containing lactate, indicating that enzyme saturation was not occurring in the bottles that contained detergents. The detergent formulations all induced some sulfate reduction, with "Comprox" generating the most, then "Gamosol", and then the fast breaking detergents. This trend was observed in both series.

The redox potentials for the blanks were around -100 mV, so anaerobic conditions were maintained throughout the experiment. Samples containing nutrient (glucose) or detergents generally had a redox potential after 14 days incubation of less than -200 mV. The pH of the blanks and samples containing nutrients was between 6 and 7, so the pH did not exceed the limits for SRB growth.

Growth of the aerobic and sulfate-reducing bacteria in media containing detergents and the two controls, are presented in Figures 2 and 3 respectively. Growth of the aerobic bacterial population during the first 24 hours of incubation provides an indication of the relative availability of nutrients in the detergent solutions and controls. All five detergents supported an increase of three orders of magnitude, whereas the non-nutritional control gave less than three and the nutrient control gave more than 4. By 96 hours, aerobe numbers in all but "Ameroid" were static. However, since the non-nutrient controls were required to provide adequate basal conditions for SRB growth they contained some tryptone and yeast extract which would also have supported much of the aerobic bacterial population.

With the exception of "Ameroid", the detergents examined supported a hundred fold increase in SRB numbers at 96 hours. Those gains had occurred between 48 and 96 hours and the steeply rising growth curves suggest that this rate of increase would have continued. The non-nutrient control showed a ten fold increase in SRB at 48 hours, then showed no further increase after that time presumably having exhausted the available electron donor molecules. The relative

increase of SRB in the detergent tests over the non-nutrient control indicated that electron donor molecules were being produced from the detergents by the bacterial consortium.

SRB were not recovered after 24 or 96 hours in the "Ameroid" tests. This effect was not consistently observed. In separate unpublished tests, no inhibition was observed when nutrients were abundant.

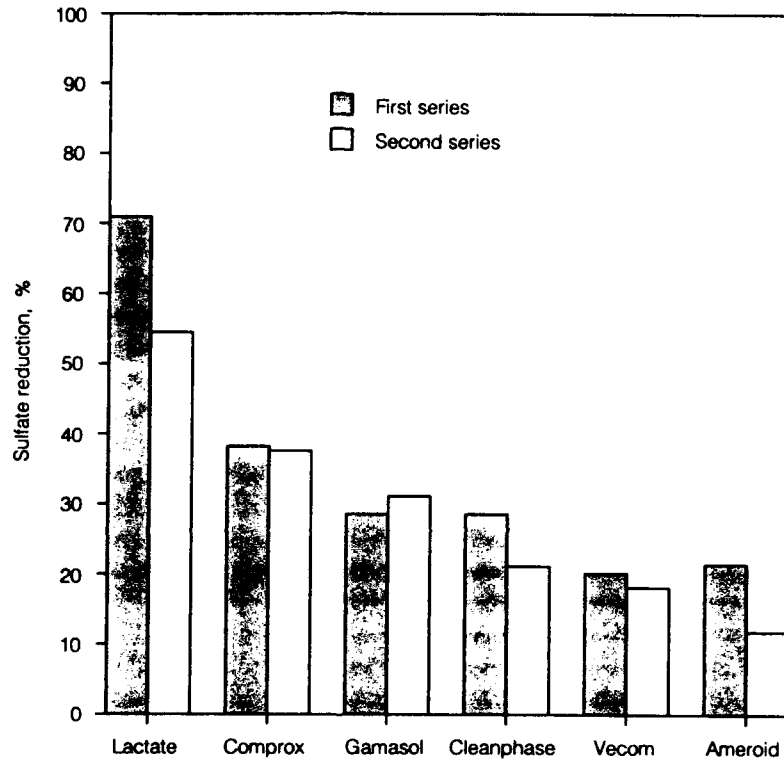


Figure 1: Comparison of sulfate reduction when in the presence of various detergents.

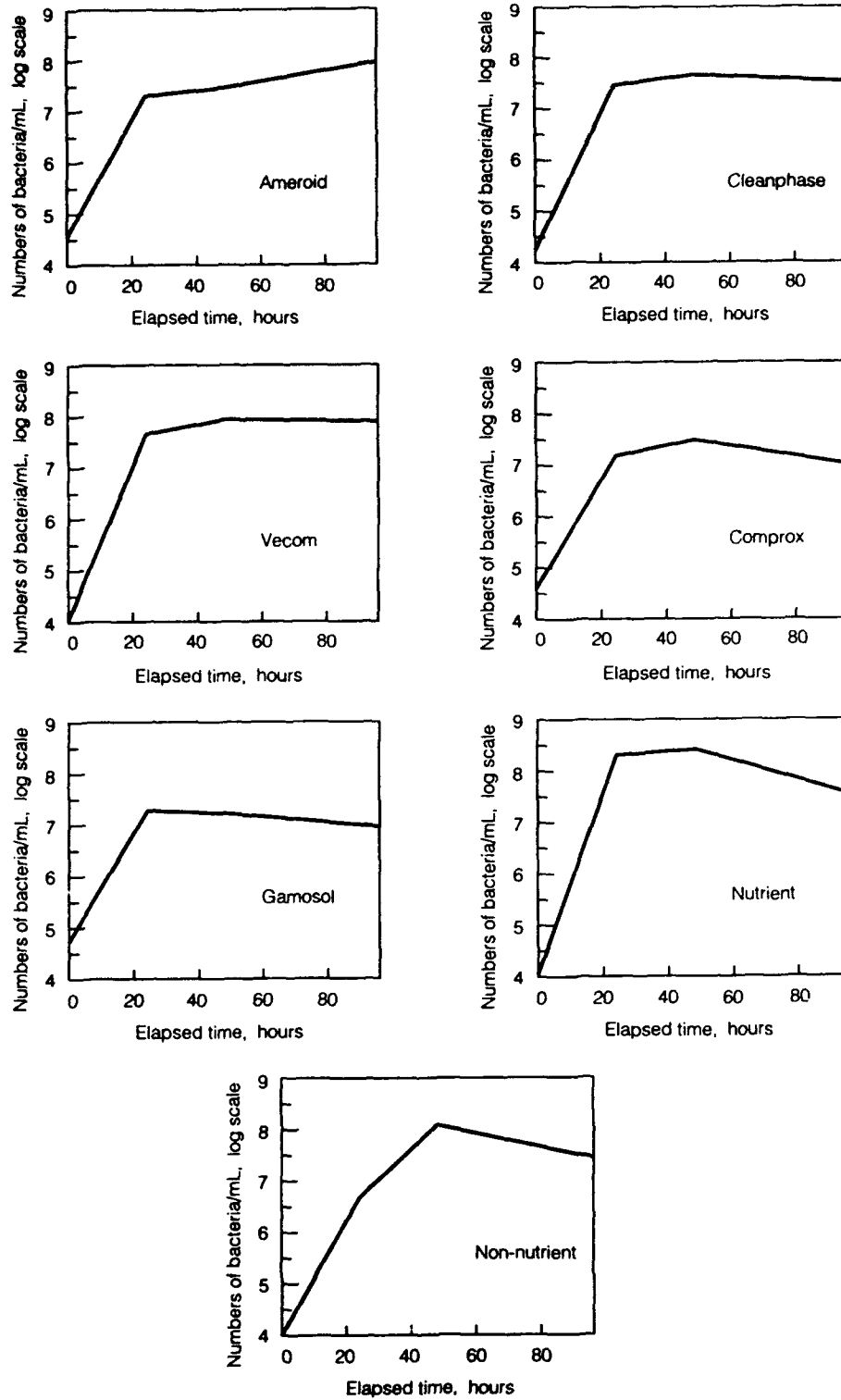


Figure 2: Change in number of aerobic bacteria when grown with different organic sources.

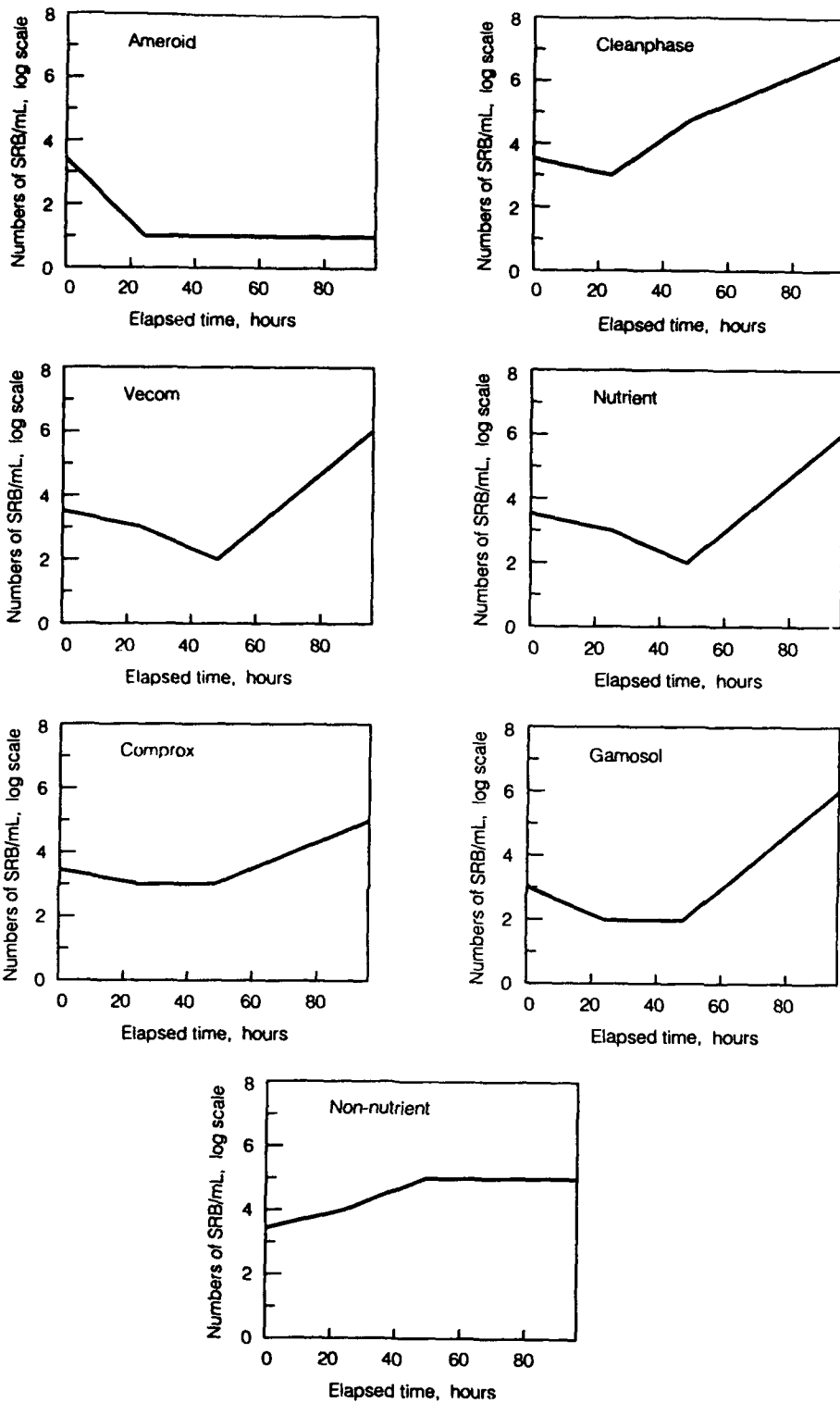


Figure 3: Change in numbers of sulfate-reducing bacteria when grown with different organic substances. Estimated by decimal dilution/estimation.

3.2 Effect of Detergent Concentrations

The effects of detergent concentration on the percentage of sulfate reduced after 14 days of incubation are shown in Figure 4. Increased sulfate reduction was observed with increasing detergent concentrations for "Gamosol", "Cleanphase" and "Vecom". On the other hand, "Ameroid" produced little sulfate reduction throughout the concentration range. This result is not consistent with earlier tests (Fig. 1) however, different inocula were used.

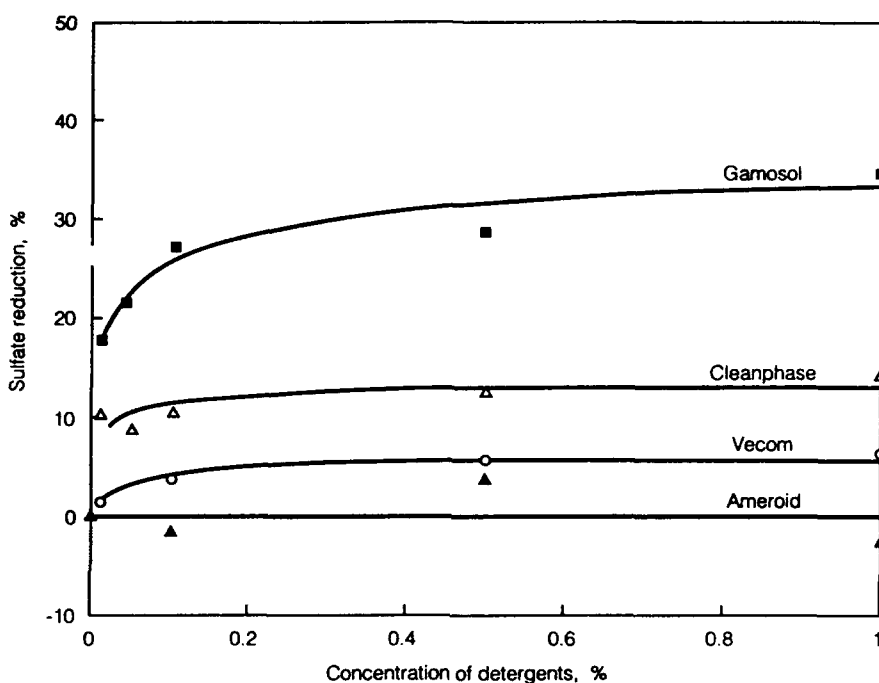


Figure 4: Sulfate reduction as a function of detergent concentration.

The lines of best fit for "Gamosol" and "Cleanphase" rise more rapidly through the lower detergent concentrations (<0.1%); with small increases in detergent concentration resulting in large increases in sulfate reduction. For example, at 0.01% Gamosol, 17% sulfate reduction was observed and at 0.01% Cleanphase, 11% sulfate reduction was observed. At higher concentrations (>0.1%), further increases in sulfate reduction slow, until final levels, dependent on the detergent used, are reached. For example "Gamosol" and "Cleanphase" level off at approximately 40% and 15% sulfate reduction respectively.

4. Discussion

4.1 Biodegradation of Detergents

Linear alkylbenzene sulfonates, which are present in "Comprox", have been widely used for some decades, so the microflora in OWW and waste-receiving waters, would have been acclimated (Swisher, 1987). In contrast, "Ameroid" and other products containing ethoxylates have been in use for a shorter time and acclimation is not expected to be so widely established.

The major surfactant in "Comprox" is a linear alkylbenzene sulfonate. This can be degraded by oxidation of either the alkyl chain or the benzene ring. Both reactions initially require oxygen (Swisher, 1987; Heyman & Molof, 1968) so under strictly anaerobic conditions, biodegradation of this surfactant is expected to be limited. However, "Comprox" also contains some alkylethoxylates and coconut diethanolamide (Appendix 1) which could be broken down to yield nutrients for SRB.

"Gamosol" and "Cleanphase" both contain alkylethoxylate surfactants in petroleum distillate (Appendix 1). The alkylethoxylate surfactant in "Gamosol" contains up to 15 ethoxylate groups (Appendix 1) and hydrolytic breakdown of the ethoxylate chain yields products suitable for use by SRB. In contrast, the alkylethoxylate in "Cleanphase", has only ~3 ethoxylate groups (Appendix 1) which would provide proportionally less energy and organic nutrient for SRB growth.

The surfactant in "Vecom" has an ester-linked alkyl chain on both ends of the ethoxylate chain (Appendix 1) and is present at a concentration of 2.5%. Before enzymic hydrolysis of the ethoxylate chain can occur, central fission is required in order to expose the ethoxylate groups. Thus, any hindrance to central fission would retard the biodegradation of this surfactant under anaerobic conditions.

In "Ameroid", the surfactant is an m-alkylphenol ethoxylate. Biodegradation of this type of molecule has been shown to be much slower than for alkyl ethoxylates of similar size (Lashen *et al.*, 1967; Patterson, Scott & Tucker, 1970; Mann & Reid, 1971; Swisher, 1987). The central fission pathway has not been reported to occur with this molecular configuration and the oxidation of the alkyl chains has been found to be inconsistent (Swisher, 1987). Under anaerobic conditions, the E-Chain pathway has been observed but as the ethoxylate chain in this surfactant has only ~2 groups (Appendix 1) the amount of breakdown products (acetic acid, ethylene glycol and glycolic acid) will be small. After E-Chain metabolism is complete, an alkylphenol residue accumulates which has been observed to inhibit further growth of bacteria (Wagner & Schink, 1987). Slow and low-yielding breakdown of the "Ameroid" detergent and possible inhibitory effects of metabolites fit with our observations here.

The major products of microbial breakdown of the fast breaking detergents therefore include acetic acid, ethylene glycol, glycolic acid, hydrogen, carbon dioxide and a number of intermediates. The acetic acid and ethylene glycol are utilised by some species of SRB as electron sources and nutrients (Postgate, 1984a; Postgate, 1984b; Pfennig, 1984; Balba & Nedwell, 1982; Dicker & Smith, 1985; Laanbroek & Pfennig, 1981; Skyring, 1988; Thauer, 1982; Schink & Stieb, 1983; Dwyer & Tiedje, 1986). Hydrogen and carbon dioxide are also co-metabolites that augment SRB metabolism of acetic acid (Postgate, 1984a). Therefore, growth of

SRB is feasible in the presence of fast breaking detergents, providing that appropriate strains of SRB and other surfactant-degrading bacteria are present together with other nutrients and favourable physical conditions.

4.2 Biodegradation of Ethoxylate Detergents in OWW

Earlier experiments indicated that "Comprox" and "Gamosol" were associated with greater sulfate reduction than the fast breaking detergents, but less than lactate which is a common electron donor for SRB. This was substantiated in trials to determine the effect of detergent concentration, and can be partially explained by the concentration of the surfactant in the detergent formulations and the different chemical structures of the surfactants. However, if these were the only variables affecting the ability of SRB to reduce sulfate, then eventually at higher concentrations, "Cleanphase" and "Vecom" would reach the same level of sulfate reduction as "Gamosol". Therefore, other processes must also be occurring.

Detergents in oily-water waste contribute to hydrogen sulfide generation by providing energy, carbon, and hydrogen to the SRB (which then produce hydrogen sulfide) with the amount of energy and nutrients available influencing the numbers of SRB present and their metabolic activity. The rate and efficiency of this process depend also on the pH, redox potential, species of bacteria present, chemical and biochemical reactions and inhibitory substances, either originally present or produced during the biodegradation process.

The experimental conditions were designed to be favourable to SRB; the pH was maintained between 6-7 and the redox potential was below -200 mV. Potentially inhibitory substances initially present in the detergents or produced during surfactant biodegradation may have influenced the results.

Organic compounds must be physically accessible to bacterial cell enzymes, to be utilised by the SRB. Since most enzymes are attached to the cell wall, and these bacteria live in aqueous environments, the nutrient must be soluble in water or in intimate contact with water. At very low concentrations, surfactants are entirely soluble in water but at around 100 ppm, surfactant molecules tend to aggregate to form micelles or to align themselves at surfaces and boundaries (Swisher 1987). The presence of micelles means that the hydrophobic (alkyl) chain is unavailable to bacterial enzymes because this section of the surfactant is aligned inwards, away from the aqueous phase and is surrounded by the hydrophilic chain (e.g. the ethoxylate chain of nonionic surfactants). The initial attack will therefore be mainly by hydrolysis of the ethoxylate chain, making the molecule progressively more hydrophobic and less soluble and resulting in loss of surfactancy.

The length of the ethoxylate chain contributes significantly to hydrogen sulfide production in two ways: firstly, by increasing the amount of carbon and hydrogen available, and secondly, by making the surfactant more hydrophilic and hence more available to bacterial enzymes. The ethoxylate chain is long in "Gamosol" which supported the most sulfate reduction and shorter in the fast breaking detergents which supported less sulfate reduction.

The fast breaking detergents, "Ameroid", "Cleanphase" and "Vecom", have been designed so that the hydrocarbon fraction would separate promptly from the aqueous layer, forming a layered system. The surfactant molecules would then align themselves at the interface. Again, hydrolysis of the ethoxylate group would be the main pathway for biodegradation. Also of significance here is the surface area of this boundary, which would act to limit the availability of the surfactant

molecule. Therefore, the disproportionate sulfate reduction with increasing detergent concentrations and different detergents could be due to a number of factors including: the concentration of surfactant in the detergent formulations; the production of inhibitory substances; the limitation of availability of the surfactant molecule; and enzyme saturation. However, since the absolute composition of the surfactants was not disclosed, it is not possible to propose explanations for the differences in detergent performance in these trials, except in the most general terms.

The fast breaking detergents consistently produced less sulfate reduction than "Gamosol" or "Comprox". The fast breaking detergents have smaller ethoxylate chains, which reduce the amount of nutrients made available by hydrolysis of the ethoxylate groups and reduce the partitioning of the surfactant into the aqueous layer. These detergents also contain a lower concentration of surfactant, which is usually the main source of organic nutrient (as it is readily biodegradable). The capacity of these detergents to separate into two distinct layers, will also reduce the likelihood of surfactants being present in the water layer, further reducing the amount of nutrient available to the bacteria. These factors all could contribute to lowering the percentage of sulfate reduced in the presence of fast breaking detergents.

From Figure 4, it is observed that the amount of sulfate reduced with "Vecom" was lower than "Cleanphase". The surfactant in Vecom has two terminal hydrophobic groups and the partitioning of this surfactant into the water layer could be hindered by the absence of a terminal hydrophilic group. The absence of a terminal ethoxylate group could also retard biodegradation through ethoxylate chain hydrolysis as this is dependent on the occurrence of prior central fission.

"Ameroid" produced inconsistent results. In the first experiment with a different inoculum (Figure 1) it supported >10% sulfate reduction, but in Figure 4 is seen to have caused no significant reduction. As this work was restricted to using the complete detergent formulations, the cause of this inconsistency could not be positively identified but possibilities include:

1. that the surfactant in Ameroid could contribute only very small amounts of energy and organic nutrients for sulfate reduction;
2. the possible existence of substances inhibitory to SRB in the detergent formulation (e.g. dichlorotoluene);
3. the formation of compounds inhibitory to SRB during the initial biodegradation of the surfactant (alkylphenols).

Since the "Ameroid" results in these trials were inconsistent, any variations can not be quantified. At best, sulfide production was less than for the other detergents and at worst it provided none. Evidence here indicates that of the detergents examined, "Ameroid" is least likely to fuel the hydrogen sulfide generation process.

5. Conclusions

The fast breaking detergents examined here can support SRB growth and produce hydrogen sulfide but to a lesser degree than the emulsifying detergents. This is probably due to the interaction of several factors including: the concentration of the potentially biodegradable surfactant, accessibility of the surfactant to SRB enzymes, surface active characteristics of the surfactant and the toxicity of the detergent or a breakdown product.

"Ameroid" was found to generate less hydrogen sulfide than the other detergents and appeared under some conditions to actually inhibit the SRB. However, this detergent contains a small quantity of dichlorotoluene, which if it were to remain after exposure to bacteria, could increase the cost of the disposal of oily wastes. "Vecom" which contains no chlorinated hydrocarbon and appeared to generate only marginally more hydrogen sulfide could be as effective.

It is recommended that all organic substances that might eventually end up in OWW collection areas should be used sparingly in order to minimise potential fuelling of the sulfate reduction process. In any OWW, the oil and water layers should be separated promptly and the use of fast breaking detergents will enable the separation process to be completed more efficiently.

6. Acknowledgements

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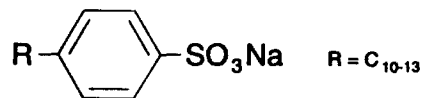
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Appendix 1

Description and Composition of the Detergents

Comprox F46 is an emulsifying general purpose cleaner that contains:

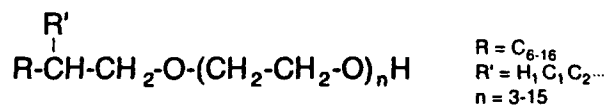
33% linear alkyl-benzene sulfonate;



coconut diethanolamide;
ethoxylated synthetic fatty alcohols;
and water (Premoselli, 1988).

Gamosol D5 is an emulsifying detergent that contains:

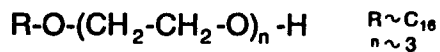
a non-ionic polyether material;



720 g/l aromatic and aliphatic petroleum distillates (Gamlen, 1991).

Cleanphase II is a fast breaking detergent that contains:

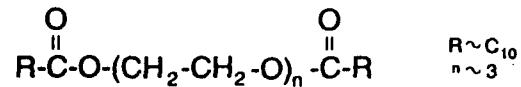
a non-ionic surfactant that has been determined by IR to be an
alkylethoxylate;



760 g/l petroleum distillates (Gamlen, 1987).

Vecom is a fast breaking detergent that contains:

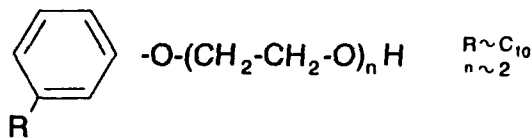
2.5% non-ionic surfactant, that was determined by IR to be a di-fatty acid terminated polyethylene glycol ester;



petroleum distillate (Vecom, 1991).

Ameroid DWS is a fast breaking detergent that contains:

a non-ionic surfactant that has been determined by IR to be an m-alkylphenol ethoxylate;



aromatic and aliphatic petroleum distillates;
dichlorotoluene (Drew Ameroid, 1985).

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ABSTRACT

Fast breaking detergents (FBD) have recently been commissioned for use in naval ships to facilitate separation of oily-water wastes (OWW). They replaced the earlier emulsifying detergents which were known to contribute to the bacterial generation of hydrogen sulfide in OWW. The present investigation was undertaken to determine whether FBD would also contribute to hydrogen sulfide generation. The formulations of the FBD indicated that they would be biodegraded by bacteria and thus power the production of hydrogen sulfide. This was demonstrated for two of the products; the third supported a large bacterial population but did not consistently cause significant hydrogen sulfide production. The potential for hydrogen sulfide production with the FBD examined was found to be less than with the earlier emulsifying detergents.

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Lyn E. Fletcher and F. John Upsher

(MRL-TR-93-11)

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