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USS PRINCETON (CG 59): MICROBIOLOGICALLY INFLUENCED CORROSION (MIC) AND MACROFOULING STATUS OF SEAWATER PIPING SYSTEMS

BY DR. JOANNE M. JONES DR. BRENDA LITTLE

RESEARCH AND TECHNOLOGY DEPARTMENT

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NAVAL SURFACE WARFARE CENTER

Dahlgren, Virginia 22448-5000 • Silver Spring, Maryland 20903-5000

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FOREWORD

This report summarizes research/observations on failure/corrosion problems associated with marine macrofouling (marine mussels and hydroids) in seawater piping systems on an AEGIS cruiser (USS PRINCETON CG 59). The presence of sulfate reducing bacteria (SRB) was confirmed in two test areas of the ship's seawater piping system and the potential for failures of the carbon steel (in sea chest) and/or the copper-nickel alloys used in the seawater piping systems is discussed.

Dr. Jones was funded for this investigation by the AEGIS Combat Systems Program Office (Code NO5) at the Naval Surface Warfare Center/Dahlgren, VA and by the Office of Naval Research Funding No. N0001490WX22209 (Program Element 61153N). Dr. Little was funded for this investigation by the Office of Naval Research Program Element 61153N through NOARL Defense Research Science Program. The authors wish to thank John DePalma (2408 Shadyside Lane, Picayune, MS 39466; 601-798-5516), Dr. Marianne Walch (Center of Marine Biotechnology, Baltimore, MD) for information and analyses on marine mussels, and Dr. Ruth Turner (Mollusc Laboratory, Zoology Department, Harvard University, Boston, MA) for helpful discussions on marine mussel habitats and macrofouling problems due to mussels.

The officers and men of the USS PRINCETON (CG 59) were extremely helpful in opening up systems for inspection and for sampling, which was necessary to evaluate the biological problems affecting the seawater piping systems. We appreciated the assistance and helpful discussions provided by LCDR George Croy and LtJG Richardson.

We thank Norm Clayton (NAVSSES, Code 053) and Gemma Meloni (NAVSSES, Code 053B) for their assistance in having shipboard systems opened for microbial sampling and visual observation of MIC and Steve Boyle (NAVSSES, Code 022E) for the fiber optics inspection that clearly showed the extensive macrofouling problems in the sea chest. We thank Bill Burk (NAVSSES, PMS400F43N) for: (1) his trip to the USS ANTIETAM (CG 54) to collect mussels from the #1 main sea water strainer and hydroids from the #2 Spy Radar Skid (70% fouled with hydroids; some barnacles present), (2) diagrams of the seawater systems design that helped to explain the macrofouling problems associated with CG 59 sea

chests, and (3) discussions on how heat (steam) could be applied to sea chests (with flushing to the outside of the ship and rigorous cleaning of the strainers and baskets after heat treatment) to try to decrease the macrofouling (predominately mussels) populations.

Approved by:

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Materials Division

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CHAPTER 1

INTRODUCTION

Preliminary results and observations on the microbiologically influenced corrosion (MIC) and other failures/corrosion problems associated with macrofouling in seawater piping systems on the USS PRINCETON (CG 59) were reported from a shipboard investigation on 23-26 January 1990 in a Naval Ship Systems Engineering Station (NAVSSES) report entitled "Investigation of seawater piping system deterioration on USS PRINCETON (CG 59)".[1]

The NAVSSES report concludes that while there was no single cause for all the reported failures, the majority were due to "damaging flow conditions such as cavitation, turbulence and impingement".[1] This report acknowledges a pervasive problem of crevice corrosion under "soft fouling" and under-deposit corrosion.

This technical report will describe the microfouling and macrofouling within the seawater piping system of the USS PRINCETON (CG 59) and assess their contribution to the corrosion problems observed. We will further demonstrate that biocorrosion can contribute to the corrosion mechanisms cited in the NAVSSES report.

CHAPTER 2

BACKGROUND

HISTORY OF CG 59 SEAWATER PIPING SYSTEM CORROSION PROBLEMS

The following are the NAVSSES failure/corrosion problems with the seawater piping and firemain systems that were reported from the Fall of 1988 through the Fall of 1989:

Strainers. Failed duplex strainer housings and vent lines were related to Fleet problems with poor quality C. M. Bailey strainers. A Monel 400 strainer basket experienced long-term corrosion under heavy macrofouling.

Piping. Corroded piping on HPAC, SPS-49 and CIWS systems (erosion-corrosion problem on every ship of the class); numerous firemain leaks were traced to poorly tightened flange joints and weld cracking during a severe storm.

Valves. SPS-49 inlet regulating valve totally corroded; severe close-in weapon system (CIWS) corrosion including 19 of 20 valves replaced, corroded strainer, corroded low flow alarm plungers, hole in check valve body and piping problems (fleet-wide problems with CIWS components); galvanic corrosion of improperly installed steel plug.

Coolers. Main engine lube oil cooler failures caused by under-deposit pitting in static seawater; CG 59 Prairie, Masker and Hydraulic Oil coolers are at risk due to seawater stagnation and under-deposit corrosion; failed CRP and Masker coolers; SPS-49 cooler failure and plugged tubes; #2 control condenser leaking; condensate drain cooler failures show extensive tube fouling with mussel shells, barnacles and wood chips. There was also extensive inlet tube and tubesheet damage. This problem may be a class problem (CG 59, CG 52 and CG 58).

Zn anodes. Rapid zinc anode deterioration in A/C condenser needing replacement every three weeks.

MICROBIOLOGICALLY INFLUENCED CORROSION

Marine corrosion is a potential hazard for metals, coated metals, alloys and composites that come in contact with the sea. Deposits on metals, whether organic or not, are likely to increase localized corrosion. Under bacteria-rich deposits, corrosion is much worse than what has been observed under "inert" deposits. A large part of marine corrosion may be initiated or

influenced by the attachment and growth of bacteria and other marine organisms.[2] Metal interfaces in aquatic systems are sites of intense microbial activity and after only one week, the metal surfaces can harbor complex communities of bacteria, protozoa and algae.[3]

The significance of microbial attachment to surfaces and the basic sequence of events in marine biofilm formation have been elucidated.[4-12] Both the kinetics and type of corrosion can be affected by the build up of a biofilm. Some of the basic mechanisms by which various microbes initiate or accelerate corrosion are: (1) production of corrosive metabolic products, such as hydrogen sulfide; (2) formation of a discontinuous deposit on the surface, which results in differential aeration and concentration cells; (3) production of organic (acetic, butyric) and mineral (nitrous) acids; (4) iron and manganese oxidation; (5) depolarization of cathodic or anodic reactions; (6) disruption of natural or other protective films and breakdown of corrosion inhibitors and coatings; or (7) hydrogen embrittlement in susceptible metals.

The problem of biocorrosion in natural environments, like seawater, is extremely complex and there may be several mechanisms for localized attack by biocorrosion operating concurrently. In a biofilm, there is the potential for both aerobic corrosion mechanisms involving oxygen concentration cells and anaerobic corrosion from microbes such as sulfate reducers growing in the anodic region.

Sulfate reducing bacteria are a diverse group of anaerobic bacteria. SRB can be isolated in many anaerobic environments but their principal habitat is the marine environment where the concentration of sulfate in seawater is high and fairly constant.[13] The ubiquity of SRB in seawater has led to MIC problems in steel[14-17] and copper-nickel[18,19] seawater piping systems. Aquatic piping systems have relatively high levels of nutrients and a high surface area, which predisposes these systems to biofilm formation.[20] The adherent populations can plug filters and injection faces, generate harmful metabolites (i.e., H_2S) and produce biofouling deposits.[20] Bacterial biofilms on the cooling-water side in heat exchangers can effectively reduce the exchange efficiency.[5,20,21]

OVERVIEW ON MARINE MACROFOULING

Macrofouling organisms are found at all depths and in all seas. At least 4,000 different species of organisms are recorded as marine-fouling nuisances. The accumulation of macrofouling deposits impacts the performance of all materials exposed to marine environments. Macrofouling organisms are most numerous along the margins of continents where they are sometimes organized in communities of up to 500 species. A few of the larger, more prolific taxa dictate the size and shape of fouling communities. The ability to predict fouling conditions is based on knowledge of the habits and range of these dominant taxa and on their rates of colonization in various parts of the world's oceans.

Most marine fouling invertebrates have a larval or pseudolarval form that is released into the water and although they possess some mobility in the water, they are carried by the currents, facilitating their distribution away from their place of origin.[22]

The size of most macrofouling larvae is quite uniform, slightly less than one millimeter in length or diameter, regardless of the size of the adult. The larval forms have to be of a dimension that allows them to occupy a safe position in the laminar sublayer of the boundary layer. This relatively stationary boundary layer provides larvae with protection against the current so that within this environment they have adequate time to attach.

In spite of the fact that the microscopic larval forms do not have enough swimming mobility to counteract strong currents and are therefore carried to their destinations, most do not settle down on the first available substratum but make their selection for settlement very carefully. Selection is absolutely necessary for survival, for these species settle more or less permanently and have little or no mobility in their adult stage. Since they cannot change location, they have to choose a location which will provide them with a continuous and adequate food supply, with mates for sexual reproduction, with protection from predators, and often with adequate supplies or an environment for building protective living quarters. Settlement, therefore, is not a simple attachment to any substratum, but an elaborate search for adequate sites preceding the final attachment. This search requires sensory perception to identify the desired parameters and a temporary attachment mechanism to break loose and move to another site in case the tested site proves to be inadequate. After the satisfactory site has been located, the permanent attachment is made. Most sedentary fouling organisms establish gregarious communities, a process that requires the settling larvae to recognize their own species.

Biological fouling results from the development of a microbial biofilm (microbial fouling), deposition and growth of macroorganisms such as barnacles and mussels (macrobial fouling) and assorted detritus.[5] Microbial biofilms have been discussed previously in the MIC background section of this report. The macrofouling problems on the USS PRINCETON (CG 59) were due to the presence of hydroids and marine mussels.

HYDROIDS

Hydrozoans form a very large class with 7 orders, numerous families and genera, and about 250 species on the Atlantic coast.[23] Most typical hydrozoans (hydroids and hydromedusae) are recognizably polypoid or medusoid or have alternating generations of each phase.[23] Hydroids are animals with a stem (pedicel) and a flowerlike hydranth (usually central mouth and ring of tentacles). Most hydroids have a tough, chitinous periderm covering the stem (may extend up around the hydranth). Colonies of hydroids can be small or they can be large, bushy or plant-like colonies several feet tall.[23] Hydroids

can form dense growths (often tangled knots of battered stems) on pilings, buoys, and jetties.[23]

MARINE MUSSELS

The following generalized information related to Mytilus was taken from Marine Mussels: Their Ecology and Physiology.[24] The sexes of Mytilus are separate with no external signs of dimorphism. Development of the resting gonad commences during October and November, gametogenesis occurs over the winter until the gonad is ripe the following spring. This is followed by rapid gametogenesis and by early summer the gonads are once again fully ripe. Sperm are emitted into the water column and sucked into the female where fertilization takes place. Periods of spawning may occur in late summer though records of extended periods of spawning are not uncommon. Larvae have been reported over a considerable period of the year. Of all the factors that may influence reproduction, sea temperature has received the most attention.

The duration of larval life varies with temperature and food supply. Mytilus larvae can also delay settlement until suitable substrata are encountered. Mussel larvae require between 15 and 35 days to grow from fertilization to the stage when settlement and metamorphosis first become possible. Although 3-4 weeks seems to be the normal duration of planktonic existence, up to 10 weeks can elapse between fertilization and settlement. It has been demonstrated that mussels pass successively from the plankton, to sites of temporary attachment on filamentous algae and from these to sites of more permanent attachment.

The mussel Mytilus is sessile, anchoring its body to hard or gravelly substrata by numerous byssal threads. The act of settlement consists of the descent, followed by a pattern of swimming and crawling behavior that ends with the secretion of byssal threads that attach the larvae to the substratum and signals the beginning of benthic existence. Mussels are gregarious, requiring that the settling larvae recognize their own species. Mussels will settle on practically any stable substratum especially when the surface is roughened. However, Mytilus mussels do not settle on copper-containing surfaces. Cupric ions cause respiratory and cardiovascular depression in Mytilus. The LC_{50} for Cu^{2+} is 3.5 X 10^{-4} M.

Mussels feed by forcing water through an inhalant siphon. Food particles are bound onto the mucous strings on the gill lamellae, directed into the mouth and into the stomach. Intracellular and extracellular digestion occurs in the digestive gland, which also stores nutrient reserves and regulates their transfer to other tissues. Mytilus can also absorb organic compounds such as amino acids and sugars from solution. The extraction of oxygen from water occurs at the gill surface. Mussels are capable of regulating oxygen consumption under hypoxic conditions and can tolerate fluctuations in oxygen tension. Intertidal bivalves, such as Mytilus, are facultative anaerobes whose mode of existence results in regular periods of aerobic and anaerobic metabolism.

The size of the whole organism can be related to age. Growth is rapid in spring and summer and slight or absent in the winter. Optimum growth occurs between 10-20°C, with growth declining sharply above 20°C. Data regarding the impact of light levels on growth are contradictory. There is some evidence that light has a detrimental effect on growth, suggesting that light may injure the exposed growing edge of the shell mantle. Moderate light has also been reported as beneficial. Mytilus shells grown in the dark are often thinner and less densely pigmented than those grown in light.

CHAPTER 3

METHODS

VISUAL INSPECTION FOR MIC AND MICROBIAL SAMPLING FOR SULFATE REDUCING BACTERIA

Many shipboard systems were visually examined for the presence of SRB. Habitats where SRB exhibit a high metabolic activity are readily apparent by the smell of hydrogen sulfide and the blackening of water/sediment/systems material due to the formation of iron and/or copper sulfide. Suspected areas of MIC were tested for the presence of SRB using a partially selective medium for SRB that uses lactate as the electron donor and carbon source for growth.[25] The medium was supplemented with 2.5% (wt/vol) NaCl for enrichment of marine (halophilic) bacteria. Samples were obtained by aseptically scraping the test areas. All cultures were grown at room temperature in a candle extinction jar, which yields an incubation environment with 5-10% CO_2. This incubation method has been successfully used to isolate SRB from corroding, in-service combat systems materials.[26,27]

SCANNING ELECTRON MICROSCOPY

Deposits obtained from the fouled waster piece of the #6 sea chest and a section of pipe with flange labeled AFT MASKER Cooler Discharge Piping were examined using a Kevex 7000 energy dispersive X-ray spectrometer (EDAX) coupled to an Amray 1000 scanning electron microscope.

FIBER OPTICS EXAMINATION AND WATER SAMPLING OF THE #6 MAIN SEA CHEST

A fiber optics videotape of piping going in from the side of the #6 main sea chest and of the inside of the sea chest was obtained. Heavy biofouling (shrimp, a crab, sponges, and a matrix of microbial/macrobial growth) and what appears to be a layer of sand/sediment on one area was observed during a shipboard screening of this videotape. Seawater (approximately 400 ml) was removed by suction through tubing placed approximately two feet from the bottom of the seachest. The carbon content of the turbid sea chest water was compared with a water sample taken outside the ship (Long Beach Harbor seawater). The water samples were analyzed for total organic carbon[28] and heavy metal concentration.[29] A dissecting microscope was used to look for mussel larvae in the seawater samples from Long Beach Harbor and from the #6 sea chest.

RETRIEVAL OF MUSSEL SHELLS AND HYDROIDS FROM STRAINERS, BASKETS AND COOLING TUBES

Macrofouling samples were removed from the locations listed in Table 1. The mussel samples were identified to genus and stored in glass vials or plastic bags in an ice chest with liquid ice. Samples of mussel shells and hydroids from fouled systems were examined at the Naval Oceanographic and Atmospheric Research Laboratory (NOARL) and at the Center of Marine Biotechnology (COMB; Baltimore, Maryland). Identification of genus and species for the mussels was obtained along with information on growth patterns, habitats and methods for inhibiting macrofouling (mostly mussels) in seawater inlets/sea chests.

CHAPTER 4

RESULTS/OBSERVATIONS

MICROBIAL SAMPLING FOR SULFATE REDUCING BACTERIA

Table 2 shows that halophilic (salt-requiring), mixed cultures of obligate and facultative anaerobes (sulfate reducers and non-sulfate reducers) were obtained from shipboard seawater piping systems. Some of the test areas had been opened to the air (oxygen) and were dry or only damp when sampled. SRB are stressed (less viable or even killed) when biofilms are exposed to oxygen and are allowed to dry.

Most of the seawater piping systems examined (by visual observation, by checking for the smell of hydrogen sulfide and by microbial sampling) showed no evidence of MIC. However, two test areas in the seawater piping system did have biofilms that contained sulfate reducing (H_2S producing) bacteria. The waster piece from the #6 sea chest (carbon steel) and an area right off the valve used to enter the #6 sea chest had biofilms containing SRB. The EDAX spectrum from deposits taken from the waster piece (see Figure 1) contained sulfur (from the sulfate reducing bacteria), iron and chlorine.

As stated previously in the background section on MIC, SRB are known to cause corrosion in mild steels, stainless steels, iron, aluminum, and copper-nickel. Therefore, over the long-term, one should continue to monitor for SRB and for possible MIC problems in the sea chest and/or the copper-nickel piping systems. In the laboratory, long-term (6 month) incubations of copper-nickel coupons (both 90:10 and 70:30) with the mixed, microbial communities isolated from CG 59 piping (includes SRB) are underway. The MIC results from these studies will be published at the end of the experiments and will yield important information regarding the corrosion caused by the SRB isolated from shipboard piping systems.

WATER ANALYSES

Mussel larvae could not be identified in the water that was removed from the sea chest. This result was expected since the end of January is not a month in which one would predict a large number of mussel larvae to be in seawater (see the background section on mussels in this report; see Figure 2).

The water sample, removed by suction within two feet of the sea chest bottom, was very turbid compared to the water sample from outside the ship (Long Beach Harbor). The total organic carbon in the Long Beach Harbor seawater was 1.73 mg/l compared to 5.08 mg/l in the sea chest. The

concentration of copper was 0.10 mg/l for the Long Beach Harbor seawater and 8.65 mg/l in the sea chest.

SEM AND EDAX ANALYSES OF PIPE SURFACES

The surface of the pipe section removed from the AFT MASKER Cooling Discharge Piping (see Figures 3-6) was characterized with deep pitting 5 cm from the flange (see Figure 4) and with shallow pitting along the entire length (see Figures 5 and 6). The surface film was patchy, ranging in color from light green to dark black. The EDAX spectrum for the base metal is shown in Figure 7. The areas within the pits (see Figure 4) were enriched in iron and chlorine with trace amounts of sulfur (see Figure 8). The blackened areas (see Figure 6) were enriched in iron, nickel, chlorine and calcium relative to the base alloy (see Figure 9). Deposits scraped from the waster piece for the #6 main sea chest contained elevated levels of sulfur, chlorine and iron (see Figure 1).

USS PRINCETON MACROFOULING

Mussel shell fouling (macrofouling) of the forward condensate drain cooler in MER-1 was observed (see Figures 10 and 11) during a NAVSSES shipboard investigation and pitting of tubes and tubesheet was visible after the macrofouling debris was removed (see Figure 12). Table 1 shows the sites from which macrofouling organisms and their fragments were removed. These macrofouling organisms were not directly attached to those substrata. Most of the biofouling was not alive at the time of removal. Instead the dead mussels, shell halves, shell fragments, hydroids and serpulids had been trapped in these locations. The mussels shown in Figure 13 were identified as Mytilus edulis by John DePalma (2408 Shadyside Lane, Picayune, MS 39466) and Dr. Marianne Walch (COMB). The mussel shells could be divided into four size classes indicating four age groups ranging from approximately two weeks old to two months old. Intact mussels were typically 8mm X 11mm, 11mm X 18mm, 15mm X 22mm and 17mm X 30mm. It is impossible to accurately determine the precise age of the mussels without specific information about the growth medium and habitat conditions. Some of the intact mussels were attached to other mussel shells to form long strings. The white spots on the shells indicate the former positions of byssus threads used to attach mussels to surfaces.

Mytilus edulis has previously been cited as causing fouling problems in sea chests and seawater piping systems.[30] Local factors, such as extreme salinity and available substratum, limit the local abundance of mussels such as Mytilus but it is temperature that controls the overall distribution. The most severe mussel fouling conditions occur in the high and middle latitudes where Mytilus mussels are the dominant fouling species (see Figure 14). Their numbers decrease with distance from the shore (see Figure 15). Little and DePalma[18] have suggested that cold water mussel communities, under ideal conditions, could accumulate to a thickness of about 15 centimeters in one year with a weight-in-water of about 20 kg/m^2.

Mussels will settle on practically any stable substratum especially when the surface is roughened.[24] However, Mytilus mussels do not settle on copper-containing surfaces. Cupric ions cause respiratory and cardiovascular depression in Mytilus. The LC_{50} for Cu^{+2} is 3.5×10^{-4} M. Mussels are capable of regulating oxygen consumption under hypoxic conditions and can tolerate fluctuations in oxygen tension. Intertidal bivalves, such as Mytilus, are facultative anaerobes whose mode of existence results in regular periods of aerobic and anaerobic metabolism.[24]

The hydroids that were removed (see Figure 16) had collected large amounts of chlorine, sulfur and copper (see Figure 17). Copper (from the copper-nickel seawater piping) gives the hydroids a green color so that they have the appearance of seaweed. The heavy fouling of some of the seawater piping systems with hydroids and/or mussel shell fragments clearly shows the importance of frequent cleaning of strainers and baskets, as well as, the need for a procedure that could reduce biofouling growth in the sea chests. Fromm and Budaraju[21] have reported on the importance of inhibiting biofouling in heat-transfer applications.

OBSERVATIONS FROM FIBER OPTICS EXAMINATION OF THE #6 MAIN SEA CHEST

The fiber optics examination was limited to the piping used to enter the sea chest and to a section inside the seachest (could be a side or bottom of the chest). Part of the videotaped area was under water. Shrimp (see Figure 18), a crab, sponges (see Figure 19), and a significant amount of fouling deposits (see Figure 20) were observed in the fiber optics examination of the sea chest. Also, in one section of the videotape, there appeared to be a layer of sand/sediment. A more detailed examination of the significant macrofouling populations in the sea chest was not possible due to the movement/vibrations of the fiber optic scope during the videotaping. If a better quality videotape is obtained for future fiber optic examinations of seachests/inlet piping, then a photographic enhancement of the tape will allow a more detailed study of the macrofouling in the seawater piping systems. One can not rule out mussel colonization in the sea chest due to the following: (1) the quality of the videotape was such that the fiber optics scope was not close enough to the surface for direct observation of mussel shells, (2) a photographic enhancement of the videotape was not possible due to vibrations/movements of the scope during the taping and (3) the majority of the sea chest/inlet piping surface was not examined by fiber optics.

CHAPTER 5

ANTIFOULING CONTROL USED ON CG 59 CARBON STEEL WATER BOX

U.S. Navy MIL-P15931 Formula F121/63 containing copper (I) oxide was specified as the antifouling coating to be used on the carbon steel water box on the USS PRINCETON (CG 59). This coating is capable of delivering static (ASTM D3623)[31] barnacle resistance of over 90% for as much as four years, but total fouling resistances of over 90% for as little as ten months. The performance of U.S. Navy Formula 134 polyisobutylene rubber/rosin/copper (I) oxide is somewhat more variable, but is still capable of delivering approximately four years of hard-fouling resistance. The U.S. Navy has found that these paints typically provide from eighteen to a maximum of thirty months of protection against hard fouling in ship service use.[32] However, once antifouling coatings are colonized by biofilms, the release rate of the toxins is controlled by microorganisms.[33] Furthermore, biofilms can insulate hardfouling from the toxins incorporated into the coatings.

CHAPTER 6

OVERVIEW ON FOULING CONTROL

The following sections on injectable biocides, antifouling materials, deaeration, scrubbing, sonics, electric currents and fields, optical methods, thermal control, osmotic control, and velocity control have been described in detail by Fischer.[32]

INJECTABLE BIOCIDES

There are many equipment configurations where antifouling paints can not be used- such as interiors of pipes, heat exchanger systems or other enclosed, flowing seawater systems. Such flow systems provide marine organisms with an optimum environment because the moving seawater replenishes nutrients and oxygen. Also, warmer temperatures are provided within and downstream of an operational heat exchanger, which enhances the growth of many fouling organisms.

For these situations, "injectable" biocides have been developed. The earliest and most widely employed biocide was hypochlorous acid.[34,35] Other biocides include: acrolein, bromine, iodine, bromine chloride, ozone, chlorine dioxide, various trialkyl organometallic tin compounds, peroxides;[36] methylene-bis-thiocyanate;[37] mercuric salts and silver salts;[38] potassium permanganate;[39] chlorinated phenols;[37,39] free and polymerized quaternary ammonium salts.[37,39,40]

INHERENTLY ANTIFOULING STRUCTURAL MATERIALS

Sometimes systems such as the interior of piping systems, screens and strainers requiring antifouling protection can not use toxic coverings, coatings or impregnants. Materials are used in these systems that are considered to be inherently fouling-resistant.

The most widely used antifouling structural materials are copper and some of its alloys. Systematic studies have confirmed that copper surfaces in both surface and deep waters retard macrofouling.[41-43]

Biocontrol using copper and its alloys is possible since they corrode at a slow rate in seawater and release copper ions into the immediate environment. High copper concentrations may contribute to improper shell formation in macrofouling organisms or may interfere with various enzymatic processes.[44,45] However, copper surfaces are rapidly colonized by bacteria

that can control the leach rate from the substratum. Furthermore, copper is susceptible to microbiologically influenced corrosion.[19,46]

DEAERATION

The removal of air from cooling water for heat exchangers has been proposed as an environmentally safe way to control fouling in closed systems. It can be achieved by several physical and chemical methods. Deaeration has several advantages: it is independent of design and it reduces corrosion to some alloys (except, notably, aluminum). Its advantages are offset, however, by the effects of anaerobiosis on materials such as copper-nickel alloys and other alloys sensitive to pitting in the presence of organic substrates.[2]

SCRUBBING

Scrubbing is a broad-spectrum approach to fouling control which uses mechanical energy to remove fouling organisms from the surface. This method removes both non-biological and biological fouling. Scrubbing can be accomplished using rotary-powered brushes or cavitating jets that use high pressure and imploding cavitating bubbles to clean various surfaces.[47]

SONICS

High frequency sound, ultrasound, has been used successfully for cleaning materials, sterilizing milk and controlling algae in reservoirs. High-intensity ultrasound induces three types of responses effective in repelling or disinfecting: cavitation especially at high frequency,[48] heat generation, and pressure wave deflections. Shipboard trials and plate tests of ultrasonic devices operating in the range of 23-27 kHz and 250-1,000 watts were reported to be effective.[49] Berkowitz et al.[50] evaluated ultrasound as an antifouling mechanism (operating a 19 kHz echo-sounding device on a duty cycle of 2% of the time during experimental submergence) and found that ultrasound had an inhibitory effect on Mytilus settlement.

In vitro studies with barnacle and mussel larval forms have been reported for pulsed ultrasonics between 28 kHz and 200 kHz, the higher values being more effective.[51] Fischer[32] evaluated the use of ultrasonics specifically as a control measure of fouling in sea chests and intakes. He found significant antifouling action at swept frequencies of 37.3-62.5 kHz and 100 watts input power. Devices with lower ultrasonic frequency range (unswept at 20-100 kHz) were effective in keeping large insonified areas protected. At lower swept frequencies (12-120 kHz), barnacle fouling was negligible on the transducer face (reduced by an order of magnitude over control surfaces). Lowering the power input produced lower efficacy. Fifty kHz was an especially effective frequency for preventing fouling by a variety of forms. Devices operating at approximately 60 Hz were ineffective.

ELECTRIC CURRENTS AND FIELDS

Electric currents and fields (from DC to microwave) have been shown to have biocidal activity,[52-55] although to a very variable extent[54] and have been considered for use in the marine environment.

Seawater, because of its high ionic strength and accompanying conductivity, limits the usefulness of most of these methods.[54] Neverthcless, direct currents have been shown to provide macrofouling control[56] for short periods (forty days) when the current density approaches 1 amp/ft^2. Mild increases in the polarization voltages (100-200 mv) have been shown to retard the rate of fouling, though the effects depend on the composition of the substratum.[57] Alternating currents have provided similar results,[58] although they are somewhat more difficult to reproduce. The electrical current may not, in fact, be the actual agent of control but may provide an electrochemically produced chemical which inhibits biological growth.[44] Both hydrogen peroxide[59] and chlorine[60] can be produced at similar voltages.

OPTICAL METHODS

The use of optical sources to control fouling also has been investigated. Mercury vapor and incandescent lights were ineffective in the control of macrofouling,[61] but ultraviolet light at 253.7 nm showed complete effectiveness in repelling all forms of macrofouling. Several reviews are available on this subject.[44,62,63] Other optical sources, such as lasers, may also be of value as a fouling removal tool. Recently, the U.S. Navy[32] has investigated the feasibility of using high-energy light to clean biofouled (barnacles) surfaces. The initial work demonstrated the removal of algae but not barnacle shells.

THERMAL CONTROL METHODS

Biological systems respond very strongly to temperature. Marine organisms, possibly as a result of the relative stability of their natural environment, are extremely sensitive to temperature fluctuations. Relatively small increases in temperature cause significant mortality in Mytilus.[64-68]

Efforts to use thermal control to inhibit Mytilus have been successful.[34,64,65] The following temperature-time requirements have been established for total kill of Mytilus: 106°F for 1 hour; 95°F for 7 hours; 82°F for 4 days and 77°F was completely ineffective for all durations evaluated. Tests also demonstrated the synergistic effect of chlorine in this process.[65]

OSMOTIC CONTROL METHODS

Most marine macrofouling organisms are not tolerant of very low salinities [<3 ppt].[69,70] Distinct changes in salinity kill most macrofouling organisms, but hard-shelled varieties have their calcareous shells left intact. Nevertheless, salinity variation can be used[34,71] as an antifouling technique and has been evaluated.[44] As commonly used, this approach employs introducing lower salinity fresh waters rather than higher salinity waters.

VELOCITY CONTROL TECHNIQUES

The relative motion between seawater and substratum determines the type and amount of fouling. Therefore, it can be used to prevent and, in some cases, remove fouling organisms. Organisms can, in general, withstand significantly higher relative velocities for short acute periods than they can for longer chronic periods. In the case of protected, hard-shelled organisms, such as Mytilus and Balanus, that require low relative velocities for their initial attachment, stop-and-go operation can lead to higher fouling rates than continuous operation.

The first systematic studies of the effects of velocity and turbulence on the attachment and growth of common fouling organisms were conducted in the 1940s. Under all conditions investigated, attachment of Mytilus was inhibited completely by linear velocities in excess of 1.3 knots, but their growth was stimulated at very low (<1 knot) velocities.[72] Furthermore, once the organisms were attached, increased velocity (<3 knots) had no short-term effect and only retarded growth in the long-term.[72] By injecting air from small holes in the surface being protected, these principles were extended to cover the situation where the relative velocity was in the form of microturbulence.

CHAPTER 7

CONCLUSIONS/DISCUSSION

MICROBIOLOGICALLY INFLUENCED CORROSION (MIC)

Most of the seawater piping systems examined (by visual observation, by checking for the smell of H_2S and by microbial sampling) showed no evidence of MIC. However, sulfate reducing bacteria (SRB; marine isolates = halophilic) were isolated from the following two test areas of the USS PRINCETON (CG 59) seawater piping system: the waster piece from the #6 main sea chest and an area right off the valve used to enter the #6 sea chest. The EDAX spectrum showed sulfur, chlorine and iron in the deposits taken from these test sites. As pointed out previously in this report (background and results/observation sections), biofilms containing SRB are known to cause corrosion problems in a wide variety of materials including copper-nickel, carbon steel, stainless steel, iron, aluminum and epoxy-coated steel. Therefore, over the long-term, one should continue to monitor for SRB and for possible MIC problems from SRB in the sea chest and/or copper-nickel seawater piping systems. In the laboratory, long-term (6 month) incubations of copper-containing alloys with mixed, microbial communities (including sulfate reducing bacteria) isolated from CG 59 seawater piping are currently underway. The MIC results from these studies will yield important information regarding the corrosion of copper-containing alloys used in shipboard piping systems by SRB.

Copper alloys prevent or retard the settlement of macrofouling species, such as barnacles and mussels.[73-75] However, bacteria, microalgae, protozoa and their cellular exudates form a slime layer on copper-containing surfaces. Marszalek et al.[76] documented that copper fouled at a slower rate than stainless steel and glass surfaces and that the microflora on copper surfaces was less diverse than that found on steel and glass exposed under identical conditions to Gulf Stream water in Key Biscayune, Florida. They reported that fungi were conspicuously absent on the copper surfaces and diatoms appeared only after copper surfaces were covered with an extracellular polymer.

Corrosion can range from highly uniform to highly localized. In uniform corrosion, the anodic and cathodic sites are physically inseparable while in localized corrosion, the anodic and cathodic sites are separated. Crevice corrosion, filiform corrosion, pitting, selective leaching and erosion-corrosion are typical forms of localized corrosion. No general theories apply to all forms of localized corrosion, nevertheless, the following factors are frequently important: cathode/anode surface area ratio, differential aeration, and pH changes at anodic and cathodic sites. Most confirmed cases of MIC are characterized as localized corrosion.[77-80] Discrete mounds or columns related to tuberculation develop on metal surfaces as a result of microbial activities

and result in a localized of anodic and cathodic reactions.

Pitting in predominantly copper alloys has been attributed to under-deposit attack. Under-deposit corrosion is extremely important for these alloys because it initiates a series of events that are individually or collectively extremely corrosive.[81] Dead barnacles, mussels, filaments of algae, dirt, debris or microbiological colonies accumulating on the surface result in the formation of a deposit. In an oxygenated environment, like unpolluted natural seawater, the area immediately under the deposit is deprived of oxygen. That area becomes a relatively small anode compared to the large surrounding oxygenated cathode. Cathodic reduction of oxygen may result in an increase of pH of the solution in the vicinity of the metal. At the anodic site the metal will form metal cations and if it is assumed that the metal hydroxide is the thermodynamically stable phase in the solution, the metal ions will be hydrolyzed by water with the formation of H^+ ions. If the cathodic and anodic sites are separated from one another, the pH at the anode will decrease and that at the cathode will increase. Cl^- from the electrolyte will migrate to the anode to neutralize any buildup of charge.[82]

Cu_2Cl_2 forming within the pits prevents dissolved oxygen from gaining access to the bottom of the pit and the formation of a protective film of Cu_2O.[83] The low solubility of Cu_2Cl_2 maintains the activity of copper ions at a low value and thus facilitates anodic dissolution of the copper. In summary, under-deposit pitting due to the presence of microbial colonies on copper surfaces involves the conventional features of differential aeration, a large cathode:anode surface area and the development of acidity within the pit by the hydrolysis of Cu_2Cl_2 that prevents a protective film from forming. These same mechanisms are observed under soft fouling deposits.

Geesey et al.[84] have demonstrated that the exopolymers which anchor bacterial cells to surfaces exhibit saturation binding of copper ions in aqueous suspensions. The exopolymer also promoted deterioration of a copper surface. Microcolonies within a biofilm have the capacity to form copper concentration cells with adjacent areas in a biofilm that contain less reactive polymer. These concentration cells are maintained by the acid-producing activities of the biofilm microflora.

In oxygenated seawater, once a biofilm reaches a thickness of 200 microns the metal/biofilm interface is anaerobic and provides a niche for acid production by various anaerobic microorganisms and for sulfide production by anaerobic SRB.[85] The impact of sulfides on the corrosion of copper alloys has received a considerable amount of attention. Little[18,19,45] has published several reports documenting localized corrosion of copper alloys by SRB. Failure of copper alloys has been reported in polluted seawater containing waterborne sulfides that stimulate pitting and stress corrosion cracking.[86] CDA 706 suffers accelerated corrosion attack in seawater containing 0.01 ppm sulfide after 1 day exposure.[87] A porous layer of cuprous sulfide with the general stoichiometry $Cu_{2-x}S$, $0<x<1$ forms in the presence of sulfide ions.[88] Cu^{2+} ions migrate through the layer, react with more sulfide and produce a thick, black scale. Under these conditions, corrosion is under cathodic

control limited by the diffusion of H^+ ions to the cathodic sites.

It has been argued that if the copper sulfide layer were djurelite ($Cu_{1.96}S$) the sulfide layer would be protective.[89] Even is such a sulfide film were technically passivating, the film's mechanical stability is so poor that sulfide films are useless for corrosion protection. In the presence of turbulence the loosely adherent sulfide film is removed, exposing a fresh copper surface to react with the sulfide ions. For these reasons turbulence-induced corrosion and sulfide attack of copper alloys can not easily be decoupled. In the presence of oxygen, the cathodic reaction increases and the corrosion rate increases as Cu^+ ions diffuse through the porous sulfide scale to combine with oxygen to produce Cu_2O. The sulfide film is converted to the oxide with the concomitant production of SO_2 ions or elemental sulfur. A reduction in the sulfur content of the oxide-type scale will also occur. The transformation of sulfide to oxide results in a change in volume that weakens the bonds between the thick, black sulfide scale and the oxide subscale and leads to spalling. Bared areas repassivate forming cuprous oxide.

MACROFOULING PROBLEMS

The macrofouling problems of the USS PRINCETON (CG 59) were due to the mussel, Mytilus edulis, and hydroids. Serpulids were also observed but to a lesser degree than mussels and hydroids. The total organic carbon was 3-fold higher inside the CG 59 sea chest as compared to the Long Beach harbor seawater. The water from the sea chest was very turbid and it is obvious that there was a high concentration of organic matter (nutrients) within the sea chest/inlet piping that could support the macrobial fouling observed in the sea chest. The environment in the sea chests and the operating procedures of the ship ensure an adequate supply of nutrients and oxygen and a minimum number of predators for ideal growth and propagation of the species.

Table 1 shows the seawater piping sites where macrofouling organisms (marine mussels and hydroids) were removed. Mussel shells were identified as Mytilus edulis and the shells represented four size classes, indicating four age groups from two weeks old to two months old. Some of the intact mussels were attached to other mussel shells to form long strings. The white spots on the shells indicate the former positions of byssus threads used to attach the mussels to surfaces.

Mytilus edulis has previously been shown to cause fouling problems in sea chests and seawater piping systems.[30] During the fiber optics examination of the #6 main seachest, the biofouling observed included crab, shrimp, sponges, and a matrix layer(s) macrobial growth. In addition to the biofouling, there appeared to be a layer of sand in one section of the system examined. Also, there was a hard material buildup that was scraped off the piping wall used to enter the sea chest for the fiber optics examination and from the waster piece of the #6 sea chest. This material contained SRB and the EDAX analysis showed S, Cl and Fe in this material buildup. A photographic enhancement of the videotape from the fiber optics examination of the USS PRINCETON (CG 59) #6

main sea chest was not possible due to constant vibrations/movements of the scope during the videotaping. One can not rule out mussel colonization in the sea chest due to the following: (1) the quality of the videotape was such that the fiber optics scope was not close enough to the surface for direct observation of mussel shells, (2) a photographic enhancement of the videotape was not possible due to vibrations/movements of the scope during the taping and (3) the majority of the sea chest/inlet piping surface was not examined by fiber optics. For future fiber optics examinations of seawater piping systems, the scope should be closer to the fouled surfaces and less vibrations or movements in each area taped will allow a more detailed study of the the macrobial fouling.

Mussels will settle on practically any stable substratum especially if the surface is roughened.[24] However, Mytilus mussels do not settle on copper-containing surfaces until the surface has been covered by an insulating biofilm. Cupric ions cause respiratory and cardiovascular depression in Mytilus. The LC_{50} for Cu^{+2} is 3.5×10^{-4} M. However, copper surfaces are rapidly colonized by bacteria that can control the leach substratum. Biofilms can insulate hardfouling from the toxins incorporated into the coatings. The #6 main sea chest (carbon steel with antifouling coatings) had a thick material buildup (obligate and facultative anaerobes in the microbial biofilm along with S, Fe and Cl in the deposits) which allowed macrobial fouling. There was an 86-fold increase in the copper ion concentration inside the sea chest as compared to the Long Beach harbor seawater, but this concentration of copper ions was not sufficient to prevent the macrofouling in the sea chest.

Due to the recurring nature and the extent of the macrofouling in the seawater piping systems, it appears likely that these macroorganisms have colonized the antifoulant coated, carbon steel sea chests (probably the water intakes as well) of the USS PRINCETON (CG 59). The larvae of the mussels were probably taken into these systems during the spring or summer along the Pacific coastline. Gregarious, multilayer communities on the walls of these systems could explain the four (at least) spawning times to produce the four age classes, as well as, the mussel shell problem that has existed over time for this ship's seawater piping systems. When water was pumped from the sea chests, intact mussels and hydroids and fragments of serpulids were removed. These fouling organisms were then located in the downstream strainers. None of the identified macrofouling organisms were attached to the copper-containing piping system, strainers or heat exchangers.

From personal communications with Dr. Ruth Turner (Hollusc Laboratory, Zoology Dept., Harvard Univ., Boston, MA), Dr. Marianne Walch (CCMB) and John DePalma (2408 Shadyside Lane, Picayune, MS 39466), the source of the recurring mussel macrofouling of the sea chest and the seawater piping systems would not be coming from the pier/pilings as suggested in the NAVSSES report.[1] Also, if CG 59 was at or near the mooring depth specified for this cruiser (navigational draft of 31 feet), then the large quantities of mussel shells that repeatedly foul the seawater piping systems would not be coming from mussels on the sea bottom (not known at this time if there even are mussel beds below the ship) as suggested in the NAVSSES report.[1]

However, fathometer readings from CG 59 from December 1986 through December 1989 showed many readings (6, 9, 11, 13 14, and 17 feet) that were significantly below the recommended navigational draft of 31 feet. If these fathometer readings were correct, and if there are mussels beds on the sea bottom below the ship's anchorage, and if the pumps or pumps and propellors are on, then it may be possible for marine mussels to be pulled into the seawater piping systems as suggested in the NAVSSES report.[1] However, the macrofouling problem (not just mussels but also hydroids) is of a recurring nature, therefore, large quantities of macroorganisms would have to be repeatedly pulled into the seawater piping system to yield the shell problems in the strainers and baskets along with the blockage of heat exchanger tubes by mussel shells and hydroids which leads to some of the failures/corrosion problems in the CG 59 seawater piping systems. The marine mussel macrofouling could be a combination of mussels attached in the sea water inlets/sea chests, as well as, mussel shells pulled into the seawater system when the ship is moored at lower depths. Further investigations should include future macrofouling problems that occur on CG 59 (along with fathometer readings, anchorage sites, and dates of moorage) and fiber optics examination of other sea chests on CG 59, as well as, some sea chests on other AEGIS cruisers with sea chest/seawater piping systems like CG 59.

The heavy macrofouling (from marine mussel shells/shell fragments and hydroids) and associated failures/corrosion problems in some of CG 59's seawater piping systems clearly show the importance of frequent cleaning of strainers and baskets, as well as, the need for a procedure that could reduce (control) the macrofouling in the sea chests/inlet piping. Biological systems respond very strongly to temperature. Marine organisms, possibly as a result of the relative stability of their natural environment, are extremely sensitive to temperature fluctuations. Relatively small increases in temperature cause significant mortality in Mytilus.[64-68] Efforts to use thermal control to inhibit Mytilus have been successful.[34,64,65] The following temperature-time requirements have been established for total kill of Mytilus: 106°F for 1 hour; 95°F for 7 hours; 82°F for 4 days and 77°F was completely ineffective for all durations evaluated. These early tests also demonstrated the synergistic effect of chlorine in this process.[65]

Several procedures for control of fouling (injectable biocides, deaeration, scrubbing, sonics, electric currents and fields, optical, thermal, osmotic, and velocity control methods) have been discussed in this report. An environmentally safe (also easily managed without equipment modifications) way to control the macrobial fouling (predominantly mussels) is a heat (steam) treatment regime that includes flushing to the outside of the ship rather than through the seawater piping systems. The temperature regime should take into account military specifications on temperature constraints for electronic equipment (i.e., 105°F for indefinite periods of time; MIL-STD-1399 NAVY Section 101; 14 January 1972) using seawater cooling systems and for the lubricating oil and hydraulic oil coolers (i.e., 90°F for large surface ships using inlet seawater cooling; MIL-C-15730K ships; 12 November 1973).

If flushing to the outside of the ship after thermal treatment is not possible, then a dilution of the organic nutrients in the sea chest is necessary to prevent downstream macrofouling and MIC problems. It is essential that all systems be up and running since stop-and-go operations could lead to higher fouling and MIC in the piping systems from the organic matter (nutrients) released from the sea chests and left stagnant in the piping systems. Also, more frequent checking and cleaning of the strainers and baskets would be needed after any control treatment for biofouling in the sea chests.

We would predict that without a control procedure for the biofouling described in this report, other failures/corrosion problems are likely in ships: (1) with seawater piping systems like CG 59 that are moored in regions (high and middle latitudes) where Mytilus mussels are the dominant fouling species, (2) that are anchored at times of the year for Mytilus spawning and (3) that are at mooring depths below the recommended navigational draft.

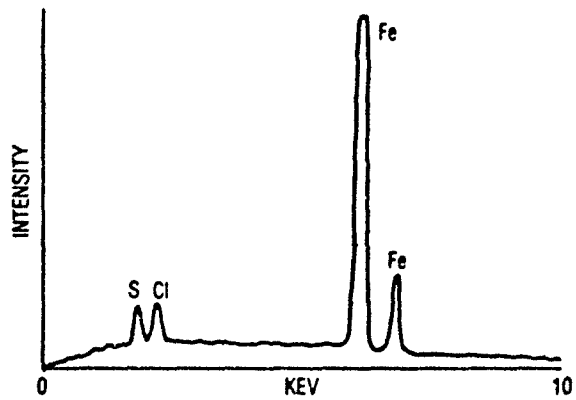

FIGURE 1. EDAX SPECTRUM OF THE BLACK DEPOSIT REMOVED FROM THE WASTER PIECE OF THE #6 MAIN SEA CHEST (SRB WERE ISOLATED FROM THIS DEPOSIT)

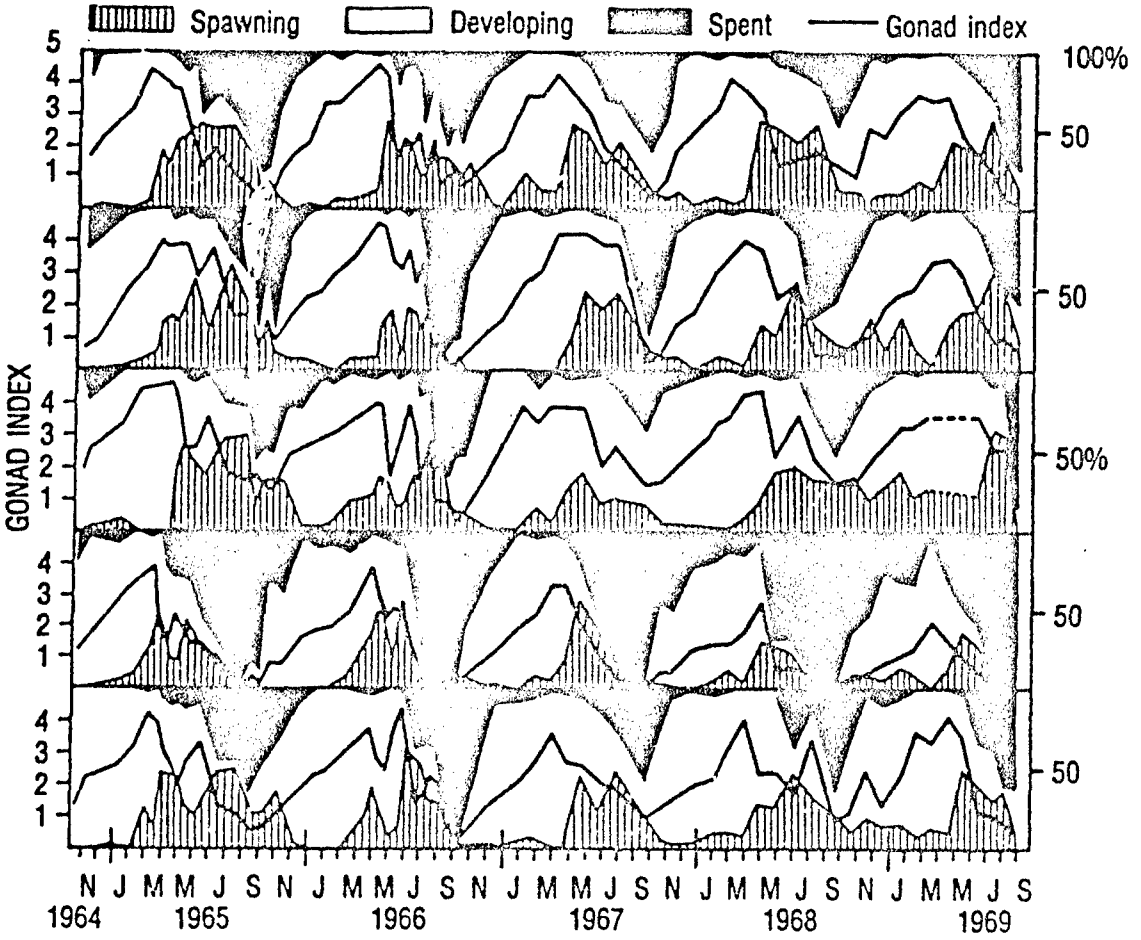

FIGURE 2. GONAD INDEX AND PERCENTAGE DISTRIBUTION OF SPAWNING, DEVELOPING AND SPENT MARINE MUSSELS (MYTILUS EDULIS) IN FIVE POPULATIONS OVER A FIVE YEAR TIME PERIOD (FROM SEED, 1975)[91]

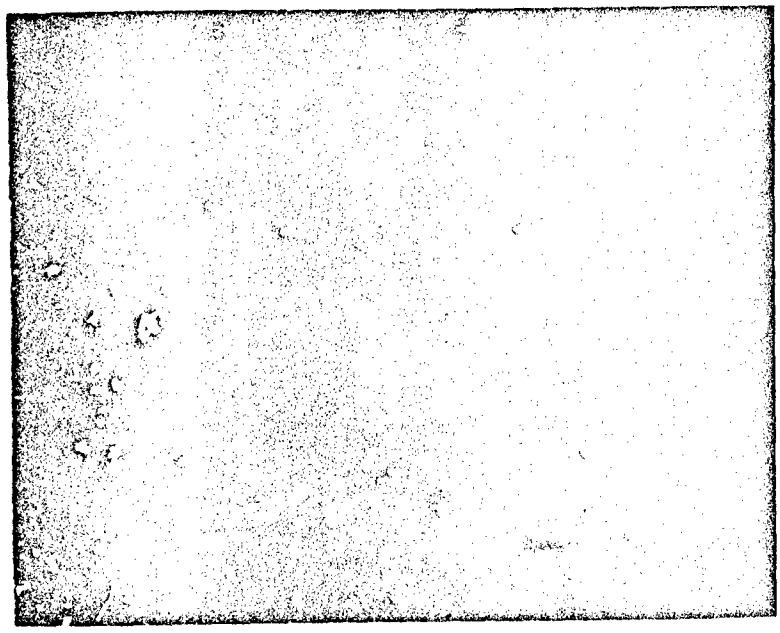

FIGURE 3. SECTION OF 90:10 COPPER-NICKEL PIPE FROM THE AFT MASKER COOLING DISCHARGE WITH DEEP PITTING CLOSE TO THE FLANGE

FIGURE 4. SECTION OF 90:10 COPPER-NICKEL PIPING FROM THE AFT MASKER COOLING DISCHARGE WITH DEEP PITTING CLOSE TO THE FLANGE

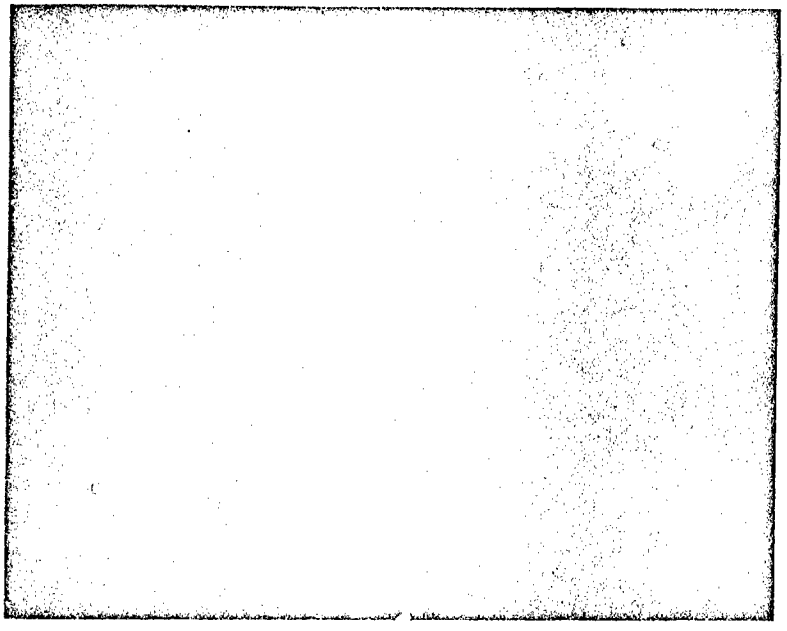

FIGURE 5. SECTION OF 90:10 COPPER-NICKEL PIPE FROM THE AFT MASKER COOLING DISCHARGE WITH SHALLOW PITTING ALONG THE ENTIRE LENGTH

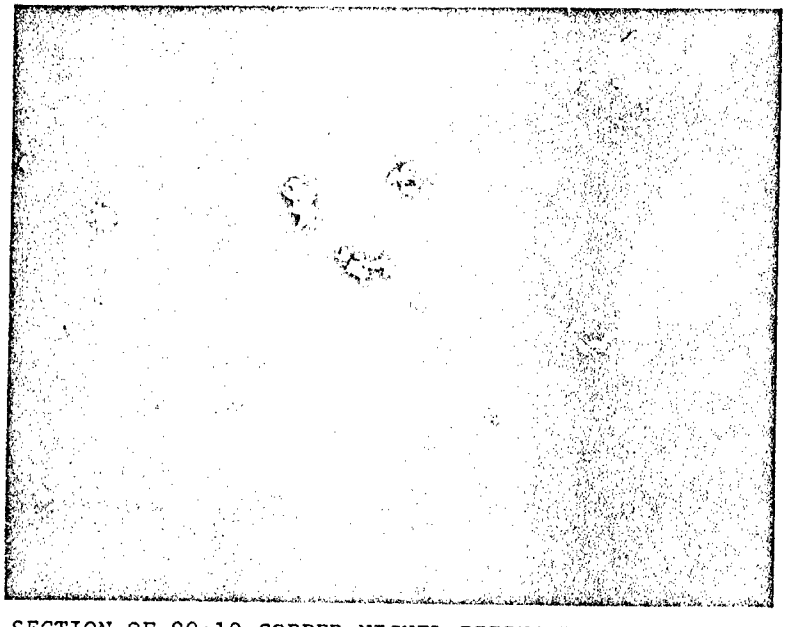

FIGURE 6. SECTION OF 90:10 COPPER-NICKEL PIPING FROM THE AFT MASKER COOLING DISCHARGE WITH SHALLOW PITTING ALONG THE ENTIRE LENGTH

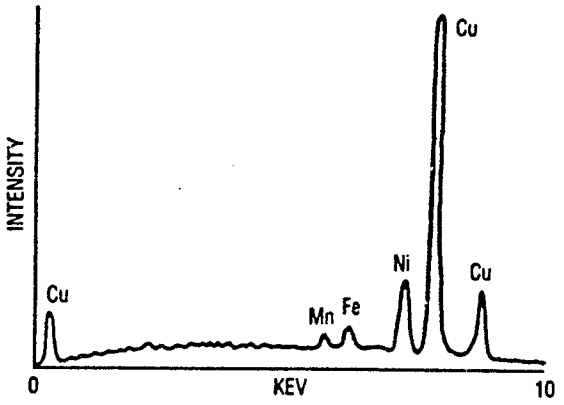

FIGURE 7. EDAX SPECTRUM FOR THE BASE METAL (90:10 COPPER-NICKEL) OF THE AFT MASKER COOLING DISCHARGE PIPING REMOVED FROM CG 59

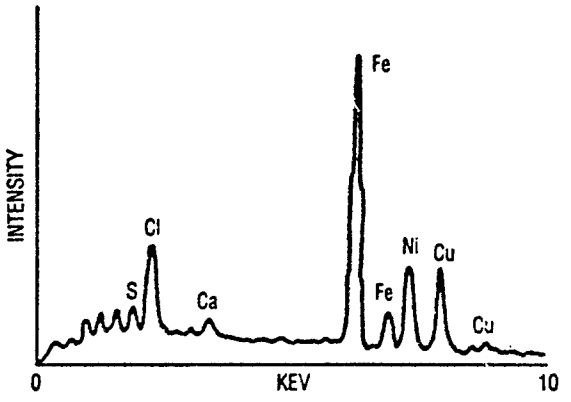

FIGURE 8. EDAX SPECTRUM WITHIN A PIT IN THE AFT MASKER COOLING DISCHARGE PIPING (90:10 COPPER-NICKEL) REMOVED FROM CG 59 SHOWED AN ENRICHMENT FOR IRON AND CHLORINE COMPARED TO THE BASE METAL

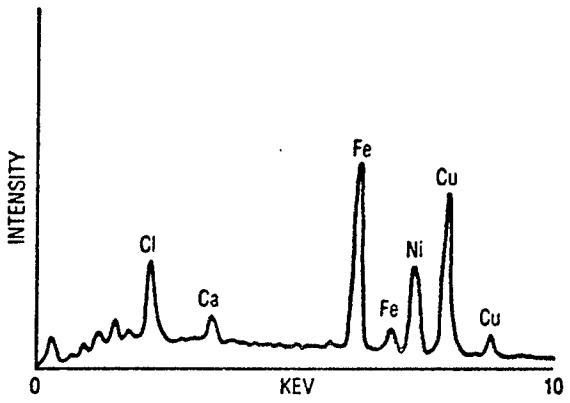

FIGURE 9. EDAX SPECTRUM FOR A BLACKENED AREA ON THE AFT MASKER COOLING DISCHARGE PIPING SHOWED HIGHER LEVELS OF IRON, NICKEL, CHLORINE AND CALCIUM COMPARED TO THE EDAX SPECTRUM FOR THE BASE ALLOY

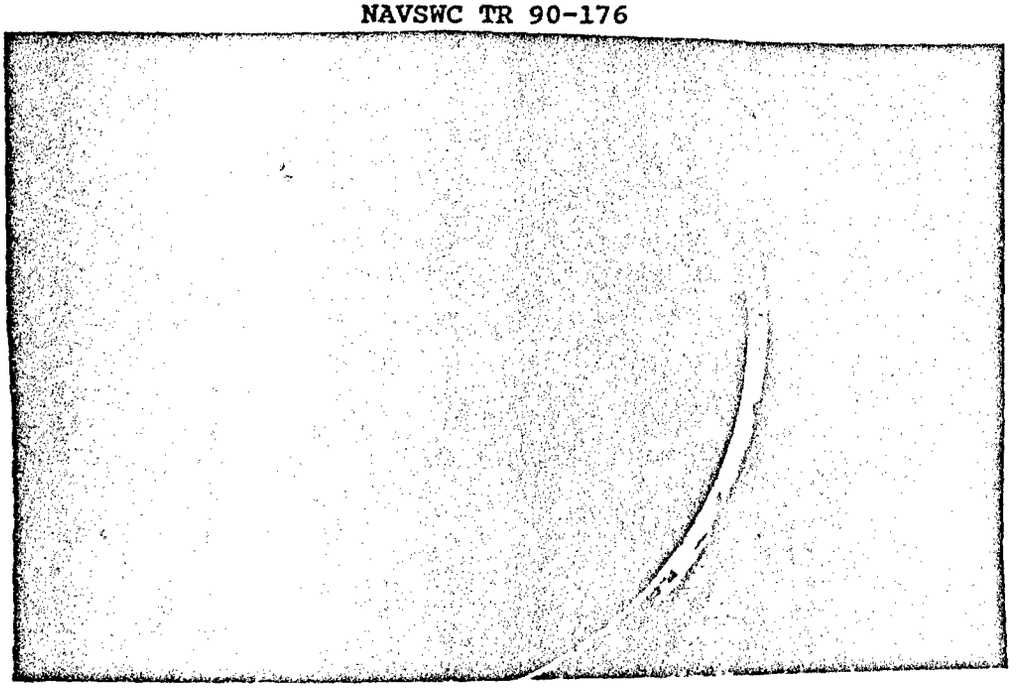

FIGURE 10. MACROFOULING DEBRIS OBSERVED IN THE INLET END BELL OF THE FORWARD CONDENSATE DRAIN COOLER IN MER-1 (FROM NAVSSES PUBLICATION 10310-1, MARCH 1990)[1]

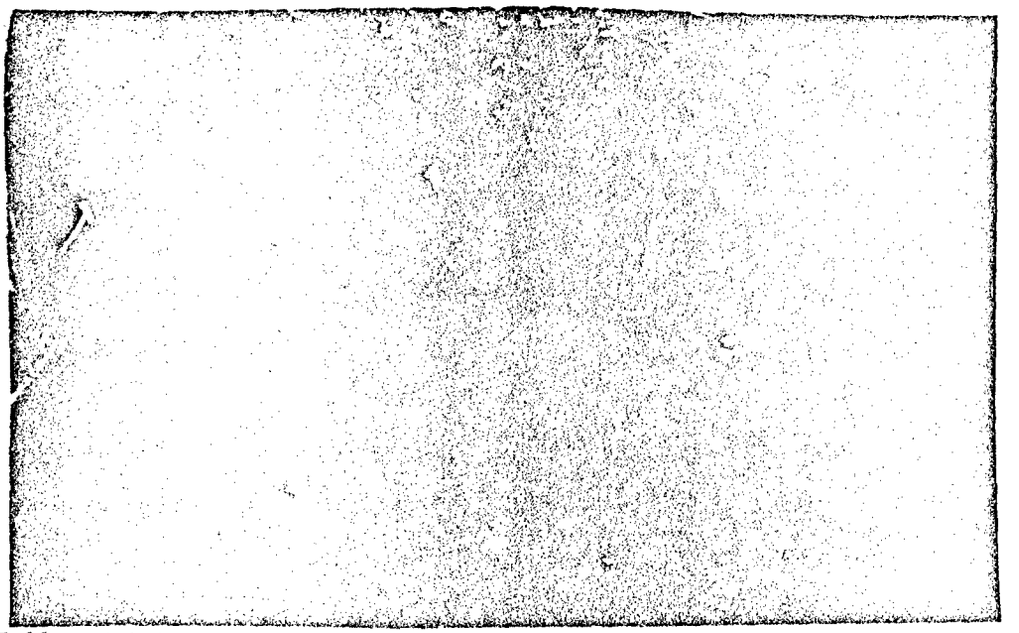

FIGURE 11. MACROFOULING DEBRIS PRESENT IN THE BOTTOM, INLET TUBESHEET OF THE CONDENSATE DRAIN COOLER IN MER-1 (FROM NAVSSES PUBLICATION 10310-1, MARCH 1990)[1]

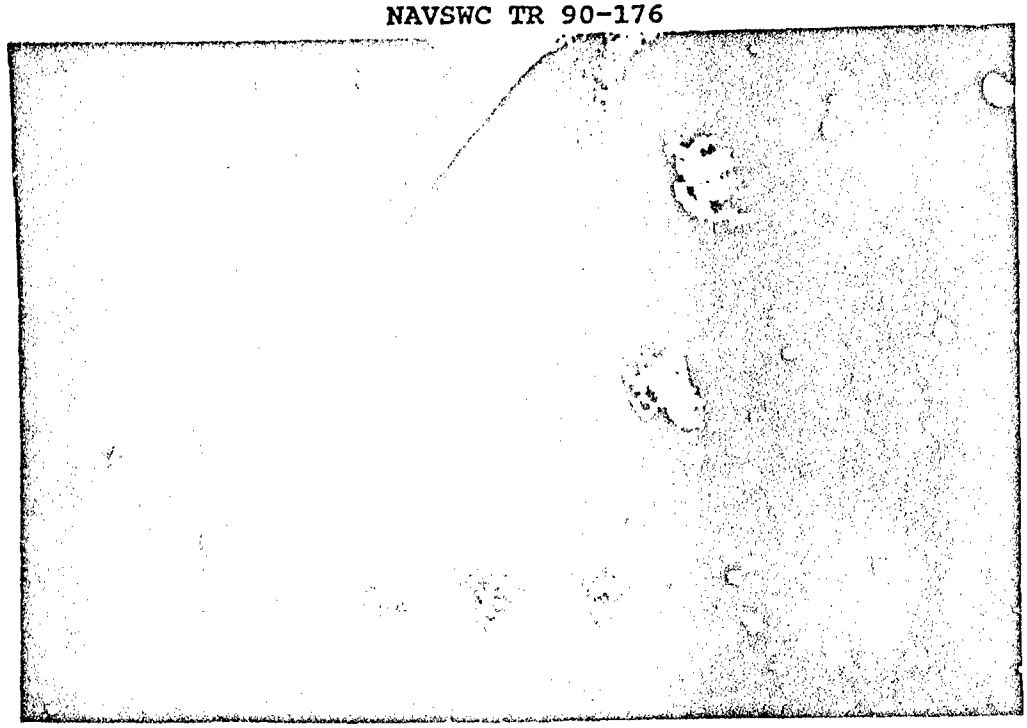

FIGURE 12. PITTING OF BOTH TUBES AND TUBESHEETS WAS VISIBLE AFTER CLEANING OUT THE MACROBIAL FOULING FROM THE INLET TUBESHEET OF THE CONDENSATE DRAIN COOLER IN MER-1 (FROM NAVSSES PUBLICATION 10310-1, MARCH 1990)[1]

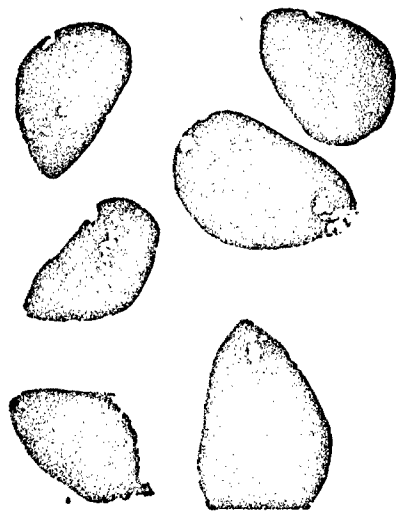

FIGURE 13. INTACT MARINE MUSSEL SHELLS, MYTILUS EDULIS, REMOVED FROM CG 59 SEAWATER PIPING SYSTEMS RANGED IN SIZE FROM APPROXIMATELY 8MM X 11MM (TWO WEEKS OLD) UP TO 17MM X 30MM (TWO MONTHS OLD)

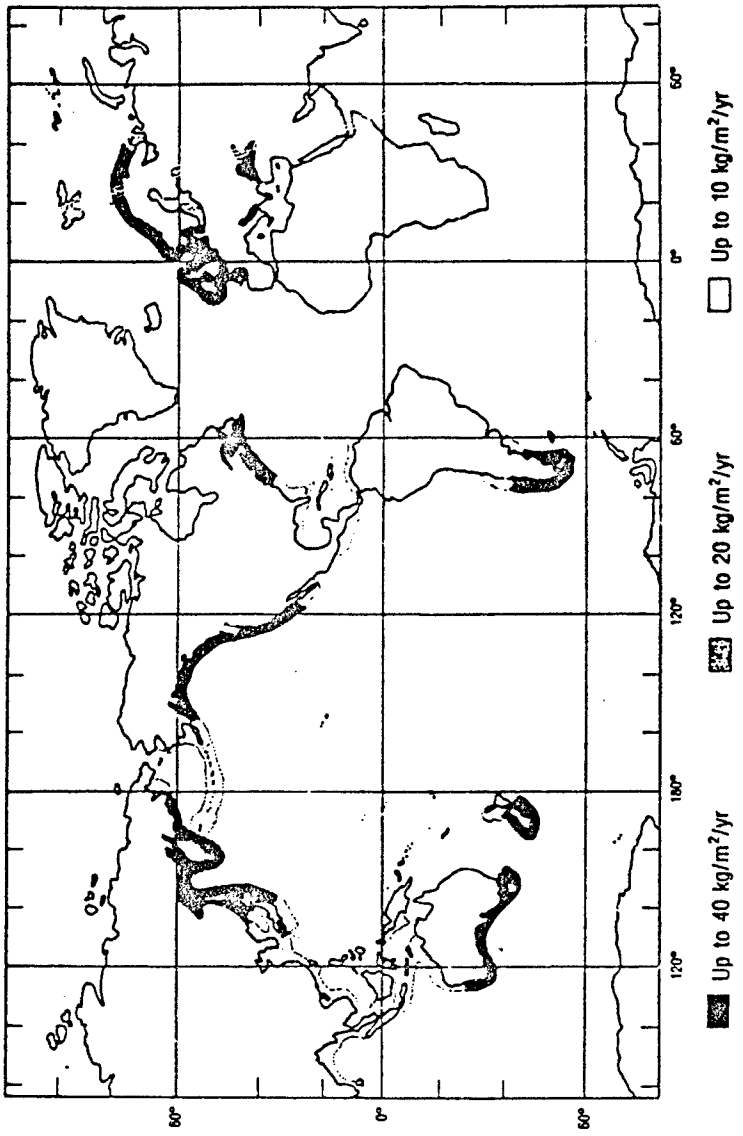

FIGURE 14. DISTRIBUTION OF MYTILUS MUSSEL BEDS SHOWN HERE INDICATES THAT MUSSEL FOULING CONDITIONS ARE MORE SEVERE IN HIGH AND MIDDLE LATITUDES WHERE THESE MUSSELS ARE THE DOMINANT FOULING SPECIES (FROM LITTLE AND DEPALMA, 1998)[18]

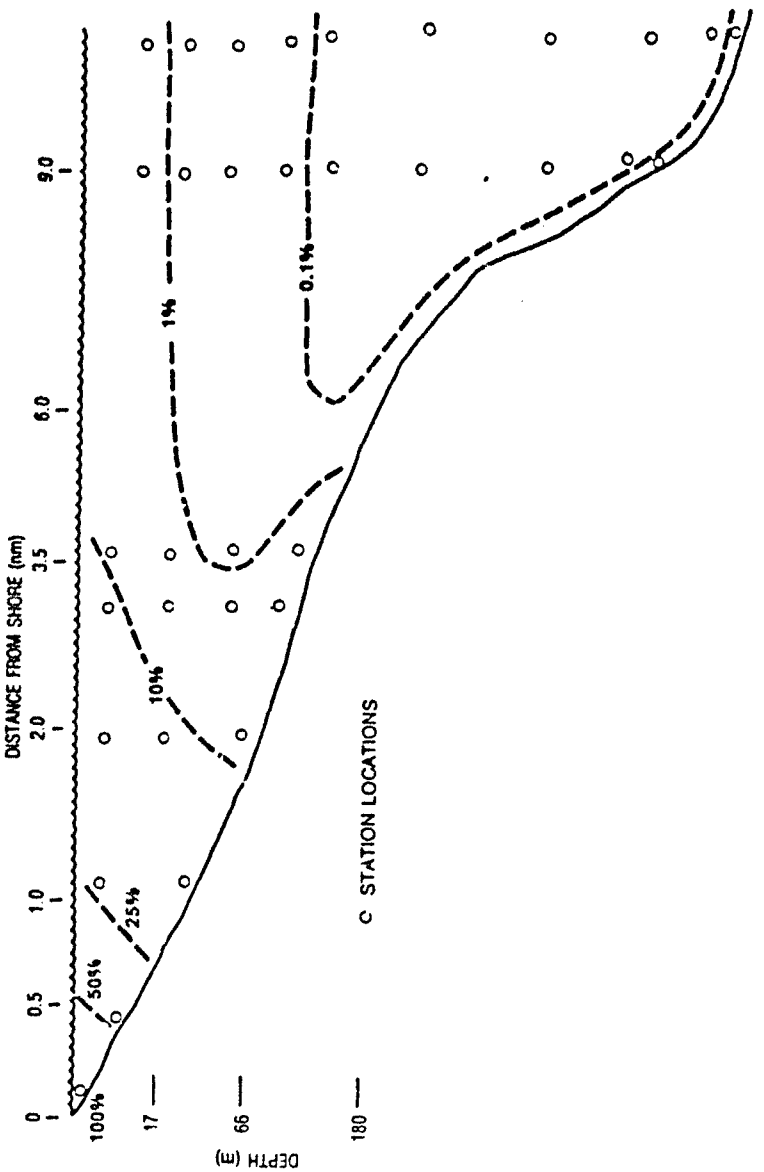

FIGURE 15. NUMBER OF MYTILUS MUSSELS THAT COULD CAUSE FOULING PROBLEMS DECREASES WITH THE DISTANCE FROM THE SHORE (FROM LITTLE AND DEPALMA, 1988)[18]

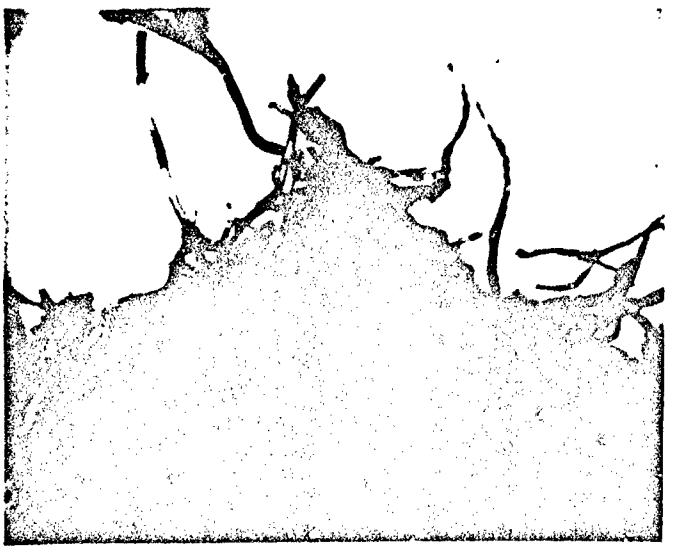

FIGURE 16. DENSE COLONIES OF HYDROIDS (ANIMALS) REMOVED FROM CG 59 SEAWATER PIPING SYSTEMS HAD THE APPEARANCE OF SEAWEED; COPPER (FROM THE COPPFR-NICKEL SEAWATER PIPING) GIVES THE HYDROIDS A GREEN COLOR

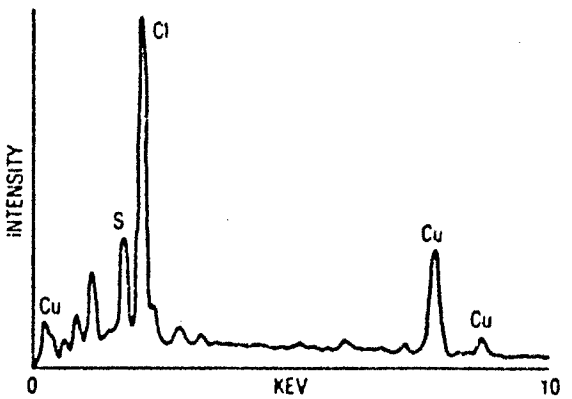

FIGURE 17. EDAX SPECTRUM OF THE HYDROIDS REMOVED FROM CG 59 SEAWATER PIPING SYSTEMS SHOWED LARGE AMOUNTS OF CHLORINE, COPPER AND SULFUR

FIGURE 18. ONE OF MANY SHRIMP OBSERVED FEEDING ON THE MACROBIAL FOULING DURING A FIBER OPTICS EXAMINATION IN THE #6 MAIN SEA CHEST

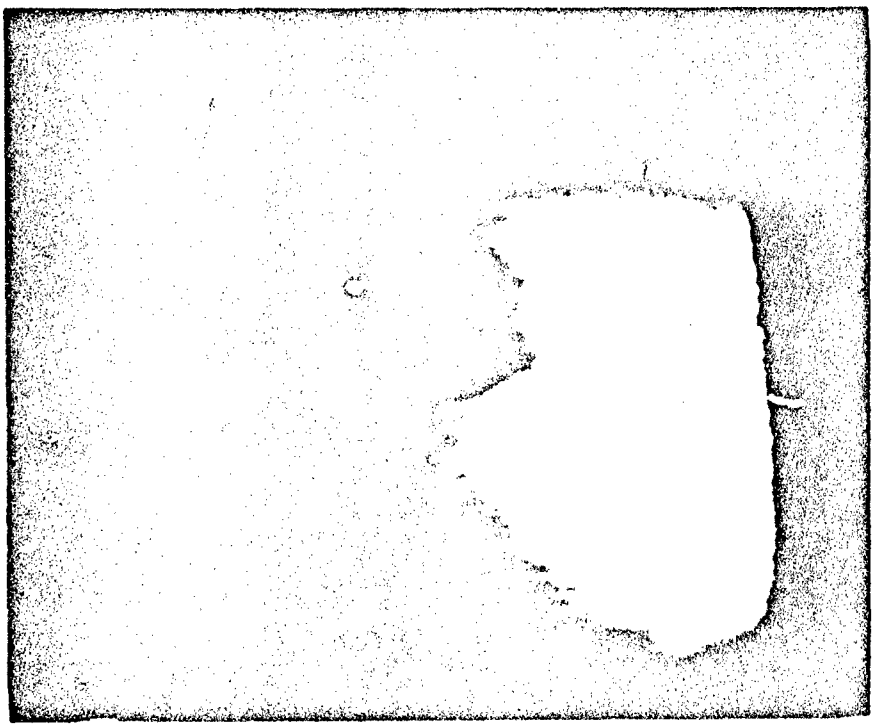

FIGURE 19. MACROBIAL FOULING IN THE #6 MAIN SEA CHEST CONTAINED SPONGES (ORANGE-RED COLOR IN PHOTOGRAPH), INORGANIC MATERIAL DEPOSITS AND DETRITUS

FIGURE 20. MACROBIAL FOULING DEPOSITS IN THE #6 MAIN SEA CHEST OBSERVED DURING A FIBER OPTICS EXAMINATION

TABLE 1. SHIPBOARD SYSTEMS WHERE MUSSEL SHELLS* AND/OR HYDROIDS WERE REMOVED

USS PRINCETON (CG 59)	
FWD Cond. Drain Cooler (inlet tubes)	Small shells, coarse shell fragments
Y-strainer #3 A/C Chilled Water	Very small shells to medium sized shells
FWD MGR LO Strainer	Small to medium sized shells; hydroids
8" Strainer Engine Rm #1	Hydroids; medium sized shells
AFT Prairie Head	Lots of hydroids; fine shell fragments
AFT CRP Head	Lots of hydroids; fine shell fragments
USS ANTIETAM (CG 54)	
#2 Spy Radar Skid	70% fouled with hydroids; some barnacles
#1 Main Sea Water Strainer	Small, medium and large shells (ship reports no massive shell incursion)

* The shells were identified as Mytilus edulis (blue mussel) by John DePalma (2408 Shadyside Lane, Picayune, MS 39466) and by Dr. Marianne Walch at the Center of Marine Biotechnology (COMB; Baltimore, MD). A detailed discussion on Mytilus edulis (including habitats/ecology, growth conditions, reproduction, and biocides) can be found in the macrofouling background section of this report.

TABLE 2. CG 59 SEAWATER PIPING SYSTEMS SAMPLED FOR SRB

System Sampled	Sulfate Reducers[a]
Waster piece #6 sea chest (carbon steel)	Yes
Near the valve used to enter #6 sea chest	Yes
CIWS strainer (top of plug)	No[b]
CIWS strainer (bottom of plug)	No[b]
CIWS strainer (under gasket)	No[c]
CIWS (port) heat exchanger condenser cooler	No[b]
SPS-49 valve (reducing station)	No
Firemain (SPS-49)	No
Forward spy skid (upstream of inlet orifice)	No[c]
Forward spy skid (firemain backup strainer)	No
#1 LPAC duplex strainer (FWD engine room MER-1; H_2S smell)	No[c]
3 GTG start air SW strainer plug	No
FWD Spy Duplex strainer	No
FWD Spy cooler tube (some shell fragments present)	No
Aft masker (downstream Monel orifice plate; repaired area shows flow corrosion)	No[b]
4 ml of seawater from #6 sea chest (very turbid)	No[d]

[a] As expected, all samples showed microbial growth (halophilic, facultative and strict anaerobes). Of interest for MIC is the growth of SRB.

[b] These samples were already dry and had been exposed to oxygen (air), which decreases the viability of SRBs if present.

[c] These samples had been exposed to oxygen (air) but were still damp. If SRBs were present, this could decrease viability.

[d] The number of SRB in seawater ranges from 0 to 100/ml[90]; several weeks incubation may be needed for detection of iron sulfide precipitation. After a two week incubation, this bulk seawater sample shows no sulfate reduction. Most of the SRB are in the biofilm population and not the bulk seawater.

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13. ABSTRACT (*Maximum 200 words*)

This report summarizes the microfouling and macrofouling within the seawater piping system of the USS PRINCETON (CG 59) and assesses their contribution to the failures/corrosion problems observed. Sulfate reducing bacteria (SRB) were isolated from two test areas of the seawater piping system. Biofilms containing SRB are known to cause corrosion problems in a wide variety of materials. Therefore, long-term monitoring for SRB and microbiologically influenced corrosion (MIC) problems from SRB in the sea chest and/or copper-nickel seawater piping systems was recommended. The macrofouling problems were due to the marine mussel, *Mytilus edulis*, and hydroids. Hydroids (animals) formed dense, plant-like colonies. Copper (from the copper-nickel seawater piping) gives the hydroids a green color so that they have the appearance of seaweed. Shrimp, crab, sponges, other unidentified crustaceans and fouling deposits were observed by a fiber optics examination in the main sea chest. Due to the observed failures/corrosion problems and the extent of the macrofouling in the seawater piping system, an environmentally safe, thermal (steam) control method for the macrofouling was recommended. Without a biofouling control procedure, failures/corrosion problems as observed in CG 59 seawater piping systems are likely to occur.

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Macrofouling	Marine Mussel (*Mytilus*)		

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL