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BIOFOULING AND EFFECTS OF ORGANIC COMPOUNDS AND MICROORGANISMS
ON CORROSION PROCESSES

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BIOFOULING AND EFFECTS OF ORGANIC COMPOUNDS AND MICROORGANISMS
ON CORROSION PROCESSES

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ABSTRACT

The corrosion rate of metals in natural waters is a function of their metallurgical characteristics and of environmental factors such as temperature, velocity, and chemical makeup of the waters. It was observed that metal surfaces in natural waters became populated with periphytic bacteria in as little as a four-hour exposure time. Subsequent colonization by a variety of microorganisms produced a complex microfouling layer composed of periphytic microorganisms, their extracellular metabolites and cellular breakdown products, and metal corrosion products. The succession of periphytic microorganisms on solid surfaces submerged in natural seawater will be described, and the implication of this primary film in corrosion processes will be discussed.

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INTRODUCTION

Biofouling of surfaces immersed in seawater has long been accepted as a natural phenomenon. The development of a fouling layer on a ship's hull, making it heavier and reducing its speed, has placed a heavy burden on the maritime economy since ancient times. It must be recognized, however, that the appearance of visible organisms such as barnacles, tubeworms, mussels, etc. is a relatively late occurrence in a chemical and biological sequence of events.

Solid substrates in contact with seawater will adsorb organic matter on their surfaces (e.g., Zobell, 1943; Smith, 1961; Chave, 1965; Loeb and Neihof, 1977). Whether the resulting organic film is glycoprotein (Baier, 1973) or "humic" (Loeb and Neihof, 1975) in nature, its presence affects the surface charge (Neihof and Loeb, 1974; Loeb and Neihof, 1977) and surface wettability (Dexter, et al., 1975) of the substrate. These properties no doubt play an important role in the subsequent attachment of bacteria to the "conditioned" surfaces (Marshal, 1973).

Bacteria are the first biofouling organisms to attach to surfaces exposed to seawater (Marshal, et al., 1971; Corpe, 1974). While the primary bacterial film on glass and stainless steel surfaces develops with time into a diverse periphytic community (which includes diatoms, filamentous algae, ciliated protozoa, etc.), bacteria continue to increase in numbers (Gerchakov, et al., 1976). In contrast, the surfaces of copper-based alloys, when exposed under the same conditions (Gerchakov, et al., 1977) develop less diverse periphytic communities, with bacteria being the dominating organisms. The ecology of microbial attachment and growth on solid surfaces is reviewed by Corpe (this volume) and Marshal (1976), and will not be discussed here.

The presence of a primary fouling layer composed of living microorganisms, detrital particles, and organic material may attract cyprids of some common barnacles (Barnes, 1970) as well as larvae of other marine animals (Crisp and Ryland, 1960; Meadow and Williams, 1963).

Fouling is particularly troublesome in the more fertile coastal waters, and although it diminishes with distances from the shoreline, it does not disappear in mid-oceanic regions and in the abyssal depths. The increasing utilization of coastal and estuarine waters for cooling purposes in power plants increases the magnitude of the fouling problems. The presence of a limited number of macrofouling agents such as barnacles, tubeworms, etc. on a ship's hull may be tolerated, but their presence on the inner surfaces of a piping system may impede water flow to an unacceptable degree. The existence of a microfouling layer on a ship's hull is of relatively little concern, while its existence as a 250-micron thick layer may result in a 50% reduction in the heat transfer coefficient of a heat exchanger in an ocean thermal energy conversion (OTEC) power plant (Stupian, 1976). In a recent report, Haderlie (1977) reviewed the subject of microfouling in seawater and its significance for OTEC heat exchange surfaces, calling attention to an additional potential problem associated with microfouling -- microbial corrosion.

In this paper, we will review some of the information available on biological corrosion, and discuss possible mechanisms involved.

MICROBIOLOGICAL CORROSION

The implication of microorganisms in metal corrosion processes was suggested as early as 1891 when Garrett (1891) postulated that the corrosive action of water on lead could be due to ammonia, nitrites, and nitrates produced by bacterial action. Gaines (1910) concluded that underground corrosion of iron and steel structures was partially due to bacterial activity. In fact, the iron bacterium Gallionella ferruginea was isolated from corrosion products on buried steel conduits, and high concentrations of sulfur and organic matter found in the products indicated the presence of sulfur bacteria. Iron in deaerated water does not corrode appreciably, but the corrosion rate in some anaerobic natural environments is abnormally high. Von Wolzogen Kuhr and van der Wlugt (1934) postulated in their classical paper that certain organisms, primarily those of the bacterial genus Desulfovibrio, depolarize the cathode of the corrosion cell by removing hydrogen that accumulates on the surface of iron, and thus promote corrosion under anaerobic conditions. Thomas (1942) noted the growth and accumulation of bacteria in steel water pipes. He proposed that bacteria might be the reason for the degree of corrosiveness of the water, unexplainable by its mineral composition. Drabell (1944), serving as a consulting engineer for the Iowa Electric Power and Light Company, posed in an article the question, "Do bacteria cause condenser tube corrosion?"

A number of reports have implicated a variety of different environments which apparently support microbial corrosion. For example, Thiobacillus concretivorus was isolated in large numbers from corroded concrete obtained from widely separate localities (Parker, 1945a). However, it was found that in an

atmosphere similar to sewer conditions, rapid corrosion occurred only after the environment became favorable to Th. concretivorus growth and the proliferation of the organisms (Parker, 1945b).

Kalinenko (1959) found bacterial colonies on aluminum, brass and bronze plates immersed in natural seawater, and suggested that the bacterial colonies accelerate the electrochemical processes of metal corrosion. Rozenberg and Ulanovskii (1960) stated that bacteria may enhance corrosion of stainless steel in seawater through decreasing the protective effects of cathode polarization, or bacteria may retard corrosion by sedimentation of CaCO_3 and Mg(OH)_2 from seawater on the steel surface.

Wacks, et al. (1964) found Desulfovibrio desulfuricans to be responsible for the corrosiveness occurring in aviation gasoline stored in tanks containing small amounts of water. In fact, gasoline stored on culture media inoculated with this organism became corrosive after one week of incubation. Hendey (1964), investigating Cladosporium resinae as a fuel contaminant in kerosene fuel storage tanks and fuel tanks of aircraft, suggested that fungal metabolites are capable of attacking aluminum.

Comparisons were made in the relative corrosiveness of bacteria and fungi for metals in containers being used in space voyages. Tennyson and Brown (1976) compared Rhizopus sp. and Scopulariopsis sp. with pure strains of unidentified species of bacteria isolated from human sources. Visual inspection was made of Aluminum 1100 specimens which were subjected to cultures of these organisms. Fungi were noted to promote corrosion to a considerably greater extent than did bacteria, when Tang instant breakfast drink was used as a substrate. Brown and Pabst (1976) confirmed this observation in their study which included 25 bacterial

and fungal isolates acting on aluminum 1100, aluminum alloys 6061-T6 and 2014-T6, and stainless steel 321, in the presence of Tang or Armour Starr bouillon.

A variety of additional metal substrates have been studied for biological corrosion. Copper was investigated by Thiam (1968) who demonstrated an increased dissolution of this metal in the presence of Aspergillus sp. utilizing soil extract as a medium. Tawadsi and Kemchadse (1972) reported that chrome-manganese steel corroded more rapidly in a variety of pure cultures of heterotrophic marine bacteria including Bacillus tumescens compared with sterile controls. Smith, et al. (1973), however, failed to see any difference between the corrosion rate of 1016 carbon steel in raw and sterile aerated seawater.

Additional literature reports of the biological corrosion of metals may be found in reviews by Rogers (1948), Costello (1969) and Iverson (1972).

CORROSION MECHANISM

General:

Zajic (1969) briefly described corrosion as follows:

"In its broadest concept, corrosion is an electrochemical reaction. It is caused by any kind of heterogeneity at different points on a metal surface. Once a surface makes contact with an electrolyte, however weak, different heterogenous points show a variance in potential. They develop an electromotive force (emf) and form small local piles or corrosion cells. The more reactive metal acts as the anode, and its atoms pass into the ionic state; at the same time, hydrogen ions are driven back to the less reactive metal which acts as the cathode. When hydrogen forms at the cathode, the corrosion cell becomes polarized. The surface seeks an equipotential state and, as this state is reached, metallic dissolution on the anode follows and continues until the emf decreases and corrosion

stops. Outside forces, of course, can intervene and it is these intervening forces which sustain or increase corrosion."

This description, although cursory in nature, directs attention to outside factors which contribute to corrosion processes. An in-depth discussion of corrosion and its mechanisms can be found elsewhere (e.g., Fontana and Green, 1967; Uhlig, 1971; Shreir, 1976), and will not be presented here.

Biological Involvement.

Although the mechanism of biological corrosion is not clear, and the literature on this subject -- specifically as it concerns the seawater environment -- is scant, it can be related to three different considerations:

- (a) Primary effect of microorganisms through the formation of differential concentration cells on the metal surfaces (for example, a respiring periphytic colony of organisms causing a difference in oxygen concentration between its microenvironment and the surrounding area). This will give rise to potential differences, with subsequent corrosion currents between the bacterial colony sites and the surrounding metal surface.
- (b) Direct removal of corrosion products (e.g., a periphytic community removes the oxidized metal (at anodic sites) or utilizes the formed hydrogen (at cathodic sites) will cause the electrochemical corrosion reactions to be biased towards metal dissolution. These respectively may be considered as anodic or cathodic depolarization which will sustain corrosion currents.

- (c) Changes in the chemical environment at the metal/solution interface due to metabolic activity (e.g., changes in pH, or introduction of metabolites) will affect corrosion processes.

Olsen and Szybalski (1950) suggested that aerobic bacteria, such as Gallionella ferruginea, infecting metal surfaces will form microdifferential aeration cells due to a change in concentration of oxygen in the infected areas. As the bacterial colonies grow they form tubercles which further enhance the potential of the differential aeration cells due to poor mixing of water. In fact, Kutznetsov and Verzhbitskaya (1961) observed tuberculation in which species of Leptothrix, Crenothrix, and Spirophyllum ferrugineum participated. Kalinenko (1959) also observed tubercles of bacterial colonies growing on iron, aluminum, copper and bronze plates in seawater.

Anaerobic bacteria are probably the most studied microorganisms in biological corrosion investigations. The enhancing effect of sulfate reducers of the genus Desulfovibrio on corrosion processes was attributed to their ability to remove hydrogen from cathodic sites of corrosion cells. Iverson (1966) presented direct evidence for this cathodic depolarization. Booth and Tiller (1968) demonstrated that Dv. desulfuricans, which possessed hydrogenase activity, stimulated the cathodic reaction, while Desulfotomaculum orientis (hydrogenase-negative) did not. However, Willingham (1966) found that hydrogenase activity of cell-free extracts did not correlate with its corrosiveness to mild steel in seawater.

Similar observations were made in the case of nitrate-reducing bacteria. Mara and Williams (1971) reported that Escherichia coli (hydrogenase-positive) enhanced the corrosion of mild steel, while the effect of Pseudomonas stutzeri

(hydrogenase-negative) was negligible. Ashton, et al. (1973a) investigating the hydrogenase-positive E. coli did not find any relation between nitrate utilization and corrosion of carbon-steel; they concluded that mechanisms other than cathodic depolarization may be operating.

Nelson (1962) challenged the quantitative importance placed on cathodic depolarization as an accelerating factor in anaerobic microbial corrosion. Tiller and Booth (1968), investigating the effect of sulfate-reducing bacteria on aluminum corrosion, concluded that although hydrogenase activity plays a role in the process, the presence of iron sulfide also accelerates corrosion. King and Miller (1971) suggested that the presence of iron sulfide in sulfate-reducing situations is probably more important quantitatively than hydrogenase activity. King, et al. (1973) stated that acceleration of corrosion of mild steel in the presence of sulfur-reducing bacteria is principally due to the formation of iron sulfide, and that hydrogenase activity plays an insignificant role.

Corrosion products such as H_2S from Desulfovibrio desulfuricans, CH_3COOH from Clostridium aceticum, and H_2SO_4 from Thiobacillus thiooxidans metabolism, are obvious contributors to corrosion processes. What may not be so obvious is that metabolic products such as mannitol produced in seawater by the action of bacteria on seaweeds appear to accelerate corrosion of brass (Rogers, 1948), and that high molecular weight biomolecules, such as those isolated from cultures of Pseudomonas aeruginosa (Blanchard and Goucher, 1967), are corrosive substances. Staffeldt and Calderon (1967) found that organic acids of the Krebs cycle promoted the corrosion of copper, while many enzymes were found to be considerably less active. Burns, et al. (1967) reported that solutions of various organic acids (citric, fumaric, ketoglutaric, glutaric, maleic, malic, itaconic,

pyruvic, and succinic acid) formed metallic salts of copper, tin, and zinc in sterile solutions. These investigators found that the presence of oxygen was necessary for the formation of these salts. Thus we may infer that the metals were oxidized electrochemically and that the acids removed the oxide film formed. Ashton, et al. (1973b) found acetic, ketoglutaric, succinic, and lactic acids in an anaerobic culture of E. coli where carbon-steel corrosion was enhanced. They suggested that the acid metabolites were responsible for accelerating the corrosion by dissolution of the iron oxide formed on the metal surface. Webb (1975) demonstrated that amino acids accelerate the corrosion rate of copper. Kramer (1976) confirmed this effect of amino acids and found that dicarboxylic acids also enhanced the corrosion of copper.

It is apparent that, although the precise mechanism of microbiological corrosion is ill-understood, microorganisms and their extracellular metabolites exert a significant influence on the otherwise strict electrochemical process of metal oxidation in the environment.

DISCUSSION

Microfouling and corrosion processes commence immediately upon exposure of a metallic substrate to a natural aquatic environment. In contrast to what is actually occurring in the environment, these two processes have been traditionally treated separately. Furthermore, in spite of the overwhelming evidence for biological involvement in metal corrosion processes, conventional corrosion studies have been conducted with a chronic absence of biological considerations. This apprehension was expressed by Compton (1970) who pointed

out the naiveté of some scientists who consider seawater a simple solution of sodium chloride contaminated with a few additional salts. He also called attention to the so-called "biological factors" which are so often mentioned with regard to the unique corrosive properties of seawater.

For the sake of discussion we may conveniently classify the elements involved in the microfouling/corrosion process into those which are living and those which are not. The non-living ones can be separated into a solid phase and a liquid phase. These three elements (biota, metal, solution) interact with each other, and the product of the three-way interaction gives rise to the microfouling/corrosion phenomenon.

To illustrate this interaction we will refer to Figure 1, where the three elements, the active zones between any two elements, and the zone of interaction among all three elements, are easily identified.

Consider the biota/solution interaction, and ignore the metal/element for the moment. This interaction is governed by the intrinsic properties of the individual elements and, in turn, may alter their own properties. Now consider the solution interacting with the metal, and ignore the biota element for the moment. This interaction is governed by the prevailing conditions at the solid/liquid interface. These conditions are affected by the nature of the interacting elements, and by the interactive process itself.

Introduction of the biota element into this network of interactions and feedbacks system does not simplify matters but brings us closer to the realization of what is happening in the natural environment. If organisms become periphytic (this will be determined by the nature of the organisms and by the prevailing conditions at the solid/liquid interface), their metabolic activities

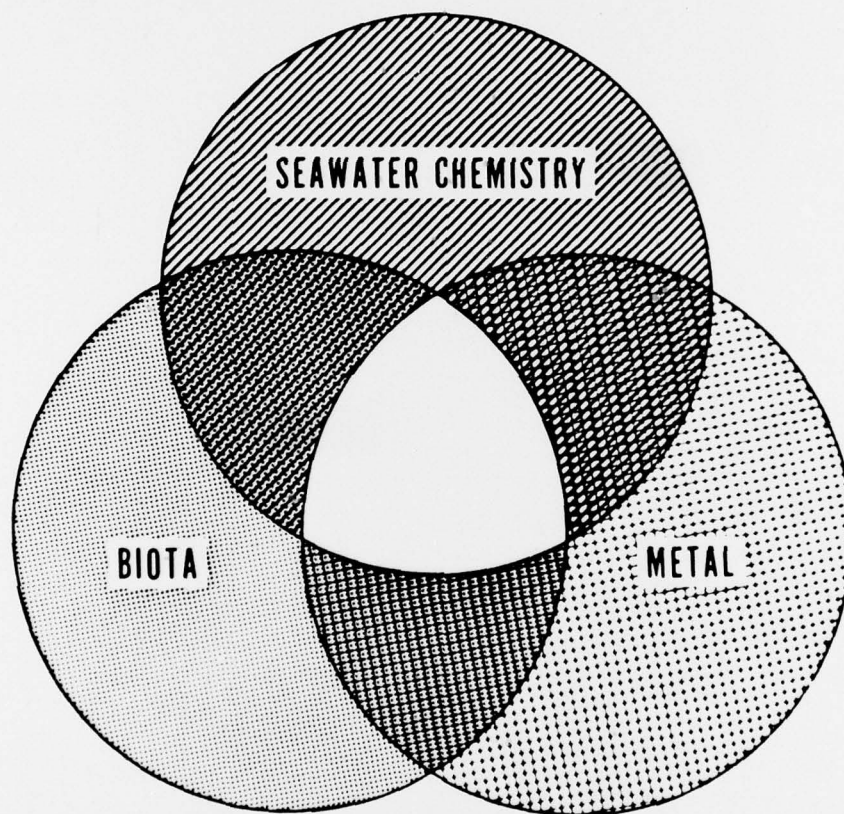


Figure 1: Interaction of the three elements which control the microfouling/corrosion phenomenon in seawater.

may be enhanced (Hendricks, 1974), and they become an additional factor in the system.

From these considerations it is evident that the detailed mechanisms of the fouling/corrosion phenomenon is highly complex and that the much needed understanding of the system will involve the application of a conjoint effort by many branches of science.

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microfouling layer composed of periphytic microorganisms, their extracellular metabolites and cellular breakdown products, and metal corrosion products. This paper reviews some of the information available on biological corrosion, and discusses possible mechanisms involved.

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