



Biofouling and Microbially Influenced Corrosion

Hector A. Videla

Bioelectrochemistry Section, INIFTA, University of La Plata, cc.16.suc.4.1900, La Plata, Argentina

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William G. Characklis

Center for Interfacial Microbial Process Engineering, Montana State University, Bozeman, MT 59717-0007, USA

ABSTRACT

Biofouling and microbially influenced corrosion (MIC) are mediated by micro-organisms attached to the metal surface and/or embedded in a gelatinous organic matrix (the biofilm). Microbial adhesion processes lead to an important modification of the metal/solution interface, inducing changes in the type and concentrations of ions, pH, oxygen levels, flow velocity and buffering capacity of the liquid microenvironment or the interface. This feature drastically changes the classical concept of electrochemical interface used in corrosion studies. Metal dissolution at a biofouled surface will be conditioned by two different processes occurring at the metal/solution interface: passivity, directed from the metal to the solution, and biofouling settlement, orientated towards the metal substratum. Electrochemical concepts, adapted to the characteristics of the biologically conditioned interface to interpret the corrosion process, and process analysis to interpret biofouling, are used in a unified approach for understanding biofilms, MIC and their interactions.

INTRODUCTION

Fouling refers to the undesirable formation of deposits on equipment surfaces, which significantly decrease equipment performance and/or

its useful life. Several types of fouling and their combinations may occur, including biological, corrosion, particulate and precipitation fouling. In most operating plant environments, more than one type of fouling will be occurring simultaneously.

This paper will refer to biofouling and its effects on the corrosion of the metallic substratum. Biofouling and corrosion are mediated by microorganisms attached to the metal surface and/or embedded in a gelatinous organic matrix termed the biofilm.

Biofilms affect the interaction between metal surfaces and the environment, not only in biodeterioration processes like corrosion, but also in several biotechnological processes applied to materials recovery and handling.

The adsorption/adhesion process, mediated by extracellular polymeric substances (EPS) production, is a particular property of natural or industrial microbial contaminants, which can grow with very low levels of nutrients in the medium (Costerton *et al.*, 1978).

Microbial adhesion processes lead to an important modification of the metal/solution interface, now partially or totally covered by biofilms. Due to biofilms presence, a barrier to the exchange of elements between the metal surface and the aqueous environment is formed. In addition, reactions between metabolites, derived from bacteria, and metals take place underneath biofilms. When compared with the surrounding EPS, the small mass of bacteria in the biofilm, as well as the high degree of hydration of the latter (Geesey, 1982), suggests that the whole interfacial system would be governed by the different transport processes taking place within the biofilm. This feature drastically changes the electrochemical concepts of electrical interface used in the study of inorganic corrosion.

Most confirmed cases of microbially influenced corrosion (MIC) are characterized as localized corrosion. Although the electrochemical model(s) of corrosion remain valid for MIC, the participation of microorganisms in the process introduces several unique features. Among the multiple microbial effects on corrosion, it should be emphasized that the main one could be related to the modification of the metal/solution interface structure, owing to biofilm accumulation.

In most, if not all, reported research on biofilms, certain observed or measured quantities are reported: net biofilm accumulation and substrate (or oxygen) removal. A difficulty with these observed quantities is that they reflect the contribution of several processes of more fundamental importance. For example, net biofilm accumulation results from the combination of: (a) transport of cells to the substratum; (b) adsorp-

tion of cells by the substratum; (c) growth and other metabolic processes within the biofilm; and (d) detachment of portions of the biofilm. If all of these processes occur in series, the slowest step of the sequence exerts the greatest influence and limits the overall process rate ('rate-determining step'). If the overall process consists of a number of parallel processes (or processes in series and parallel) the slowest process becomes the rate-determining step. Identifying the rate-determining step is critical to scale-up procedures, and its determination contributes significantly to the insight gained from experimental results. Process analysis permits the determination of the rate-determining step in the overall process at different environmental, operating and physiological conditions (Characklis, 1990).

A sequence of inorganic changes occurs simultaneously with bacterial colonization and biofilm formation. This sequence is related to the process of metal dissolution (corrosion) and corrosion products formation (passivation).

Corrosion products can have marked effects on the corrosion behaviour of metals. For instance, oxide films formed spontaneously over several metal surfaces when exposed to the air can provide good protection against further attack in many environments. The extent to which these films are able to adhere firmly, resist detachment by turbulence, or recolonize when detached, finally determines the capability of the alloy to remain unreactive. The means by which microbial biofilms modify the protective nature of inorganic passive films is not known at present. Corrosion and biofouling on metal surfaces in aqueous media may occur within the same time scale, beginning immediately after the immersion of the specimen in the aqueous environment. A reciprocal conditioning between the passive layer arrangement and biofilm development at the interface can then be expected. The consequent corrosion behaviour of the metal substratum will vary according to the extent of this reciprocal interaction (Videla, 1991).

The approach for developing a unified theory of MIC must be then interdisciplinary, and include a thorough process analysis combined with well-defined bioelectrochemical and microbiological methodologies. A brief review of some practical cases will illustrate this approach.

BIOFOULING AND PROCESS ANALYSIS

Biofilm accumulation is the net result of the following physical, chemical and biological processes:

1. Organic molecules are transported from the bulk liquid to the substratum where some of them adsorb, resulting in a 'conditioned substratum'.
2. A fraction of the planktonic microbial cells are transported from the bulk water to the conditioned substratum.
3. A fraction of the cells that strike the substratum adsorb to it for some finite time and then desorb. This process is termed reversible adsorption.
4. Desorption may result from fluid shear forces, but other physical, chemical or biological factors may also influence the process.
5. A fraction of the reversibly adsorbed cells remain immobilized beyond a 'critical' residence time and become irreversibly adsorbed.
6. The irreversibly adsorbed cells grow at the expense of substrate and nutrients in the bulk water, increasing biofilm cell numbers. The cells may also form a significant number of products, some of which may be excreted. One class of product is the EPS, which hold the biofilm together. Thus, biofilm accumulation increases through microbial metabolism at the expense of substrate energy in the bulk water.
7. Cells and other particulate matter attach to the biofilm, increasing biofilm accumulation. Attachment is the immobilization of cells and other particulate matter in the biofilm, while adsorption refers to the same processes occurring on the substratum.
8. Portions of the biofilm detach and are re-entrained in the bulk water. Detachment refers to the loss of material from the biofilm, while desorption means the loss of cells and other material from the substratum. Detachment may be termed erosion or sloughing, depending on the nature of the biofilm loss. Cell multiplication can also lead to the release of daughter cells into the bulk water.

A simplified scheme of the general process above described is shown in Fig. 1.

The progression of biofilm accumulation frequently takes the form of a sigmoidal curve, which can arbitrarily be classified in three phases: initial events, exponential or log accumulation, and plateau or steady state. The individual processes can be grouped into transport, interfacial transfer and transformation processes. Interfacial transfer processes transfer energy or material between the environment and the system in question (interphase transport), while transport describes the transport of energy or material from the system boundary through the system (intrapphase transport). Of the fundamental processes listed above, all

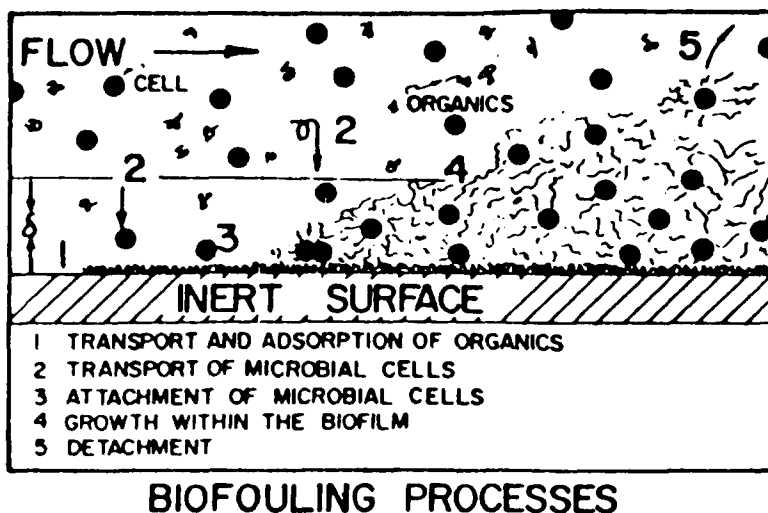


Fig. 1. A schematic summary diagram of processes contributing to biofilm accumulation and detachment. (From Characklis, 1981.)

can be classified as interfacial transfer or transport processes, except for metabolism by the immobilized cells and the production of cells and products, which are transformation processes. These are processes resulting in molecular transformation of matter, i.e. chemical or biochemical reactions. Transformation processes are described by rate equations or, more specifically, constitutive or kinetic expressions of the following form:

$$r = r(C_1 \dots C_n)$$

where r is the reaction or transformation rate, and $C_1 \dots C_n$ are concentrations of the various reacting components. The microbial transformation processes can be classified further: (a) microbial growth and reproduction; (b) product formation (e.g. EPS); (c) maintenance; and (d) decay.

The above processes are considered fundamental because accepted mathematical descriptions for each process exist. In addition, further detailed structuring of these processes is difficult if experimental validation of the mathematical expressions is desired. To accomplish an analysis of MIC processes, the biofouling processes must be interpreted through the electrochemical and physical processes occurring at the metal surface. Specific matters which must be addressed include: (1) the influence of chemical gradients and colonization 'patchiness' on

corrosion; (2) the production and accumulation of low molecular weight extracellular products in biofilms and their influence on corrosion; and (3) the role of microbially produced EPS on biofilm accumulation and corrosion. In addition, the impact of corrosion on biofilm formation should not be ignored, since abiotic corrosion processes undoubtedly influence biofilm accumulation.

ELECTROCHEMICAL NATURE OF MIC

Metallic corrosion can be defined as the attack produced on a metal surface by reaction with an aggressive environment, with the consequent deterioration of the substratum properties (Gellings, 1985). To avoid the undesirable effects of corrosion, either the attack on the metal or the damage caused by the attack must be minimized.

Corrosion is an electrochemical process caused by a flow of electricity from one metal either to another metal or to another sort of electron sink. As a result of this reaction, metals move from their elemental state to a combined form. Corrosion is then a natural or spontaneous process and, with the exception of the noble metals, all other metallic substrata display a thermodynamic tendency to revert to the oxides, from whence they came (Bockris & Reddy, 1970).

Corrosion involves oxidation and reduction processes and, because of its electrochemical nature, the corrosion reaction needs a solution to conduct the electron flow (the electrolyte) to proceed. Seawater and many industrial waters, owing to their saline content, are good electrolytes for permitting flow of electrons from a negative area to a positive one. Thus, inorganic corrosion is accomplished in the presence of two elements: the metal and the electrolyte.

By analogy with a reaction taking place in an electrochemical cell, the corrosion reaction is an anodic process (oxidation reaction) and its final result is the dissolution of the metal surface. A cathodic process necessary to return the current to the metal can be provided by the same metal if the electrolyte composition is varied. Thus, the cathodic reaction implies a reduction reaction or an electron-consuming reaction.

The current flow induces a change at the metal/solution interface called polarization, which determines the rate of the overall process occurring in the hypothetical electrochemical cell. Corrosion reactions tend to slow down as the corrosion products form at the metal surface (polarization effect). Conversely, any accelerating effect on the corrosion reaction rate is called depolarization.

If the rate of the metal dissolution reaction is measured, the corrosion

current (anodic current) will be equivalent to the rate of metal ions leaving the metal and entering into the solution. Since the electrons migrate through the electrolyte to return to the metal at the cathode, the cathodic current must be equal to the anodic one. In corrosion studies, it is not sufficient to know whether a certain metal can corrode under given conditions. It is necessary to know the rate at which the corrosion reaction occurs. The corrosion rate of a metal can be expressed as the equivalent anodic current. However, in general, the current density is preferred (i.e. the current per unit area) because it is directly related to the degree of metal attack (Gellings, 1985).

When a single electrode is not in equilibrium, the corresponding potential differs from the spontaneous corrosion potential or open circuit potential in the given solution. This change in potential is termed overvoltage and is directly related to the polarization concept. For a net cathodic reaction a negative overvoltage will occur.

These electrochemical parameters are widely used in corrosion kinetics, as well as for assessing microbial effects on corrosion rate. If two separate reference electrodes are used to measure the variation of the anodic and cathodic processes separately, a potential-current diagram (polarization diagram) for the reaction in the cell can be constructed. Generally, both anodic and cathodic currents and potentials are plotted to the right (Evans diagram), as shown in Fig. 2.

Corrosion products formed at the metal/solution interface can alter the interface structure, leading to a loss of chemical reactivity. The polarizing effect caused by the formation of inorganic layers at the metal surface is usually called passivity. It is generally agreed that passivity is due to the formation of a surface film which acts as a barrier to transport and further corrosion. For example, stainless steel exhibits spontaneous passivity in many aggressive environments due to an adherent and continuous oxide film on the metal surface. The mechanism by which microbial biofouling processes modify the protective effect of inorganic passive films is not completely understood at present. This case of biofouling/MIC interactions deserves special consideration in forthcoming research.

Even though the electrochemical nature of corrosion remains valid for MIC, microbial participation in the corrosion reaction introduces several distinctive features:

- (i) As a consequence of their reproduction, micro-organisms form aggregates of cells, EPS and metabolic products that significantly alter the formerly 'clean' metal surface. The microbial metabolic activities (e.g. respiration) and/or products may change the local

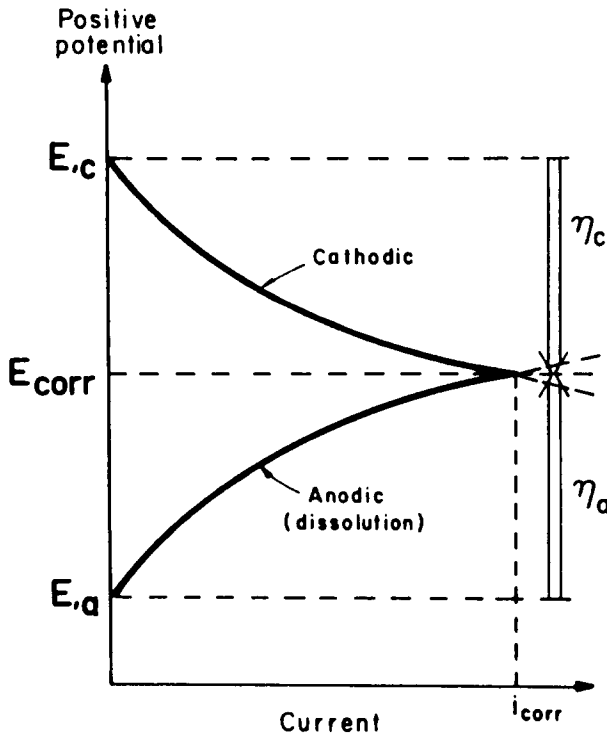


Fig. 2. Anodic and cathodic polarization curves for a corroding metal (Evans diagram).

chemistry of the environment at the metal/biofilm interface. Thus, the passive behavior of the substratum can be rapidly changed so that of active dissolution, or pitting attack occurs in restricted areas underneath biofouling deposits.

- (ii) Modification of the metal/solution interface may be related to high turnover rates for many of the metabolic reactions influencing corrosion rate. The microbial activity can affect both anodic and cathodic processes, determining the final passive or active behavior of the metallic substratum.

BIOFOULING EFFECTS ON MIC

Influence of gradients and patchiness on MIC

Prior to colonization of a surface by micro-organisms, a 'conditioning' film of macromolecules is adsorbed. This spontaneous adsorption of organic material from the aqueous phase alters the interfacial free energy

of the solid as well as the corrosion potential of metal surfaces (Dexter, 1976).

The physical adsorption of microbial cells on a metal surface, as well as their metabolic activities, impact electrochemical processes. The adsorbed cells grow and reproduce, forming colonies that constitute physical heterogeneities on the metal surface resulting in the formation of local cathodes or anodes (Fig. 3). Non-uniform or 'patchy' colonization by bacteria results in the formation of differential aeration cells, where areas under respiring colonies are depleted of oxygen relative to surrounding non-colonized areas (Fig. 4). Colony formation gives rise to potential differences and, consequently, to corrosion currents. Under aerobic conditions, the areas under the respiring colonies become anodic and there, metal dissolution occurs. Conversely, surrounding areas become cathodic, and the counter reaction of oxygen reduction occurs.

The biofilm accumulates and forms a significant diffusion barrier for certain chemical species. For example, diffusion of oxygen in aerobic waters is impeded by the diffusion and reaction resulting from aerobic metabolites within the biofilm. Microelectrode measurements (Lewandowski *et al.*, 1988) in a biofilm which accumulated in a flow, containing *c.* 50 g m^{-3} of carbon and 4 g m^{-3} of dissolved oxygen, indicate that the dissolved oxygen decreased to 0 *c.* $180 \mu\text{m}$ from the metal surface. The biofilm, in this case, was *c.* $400 \mu\text{m}$ thick and very active. The microbial

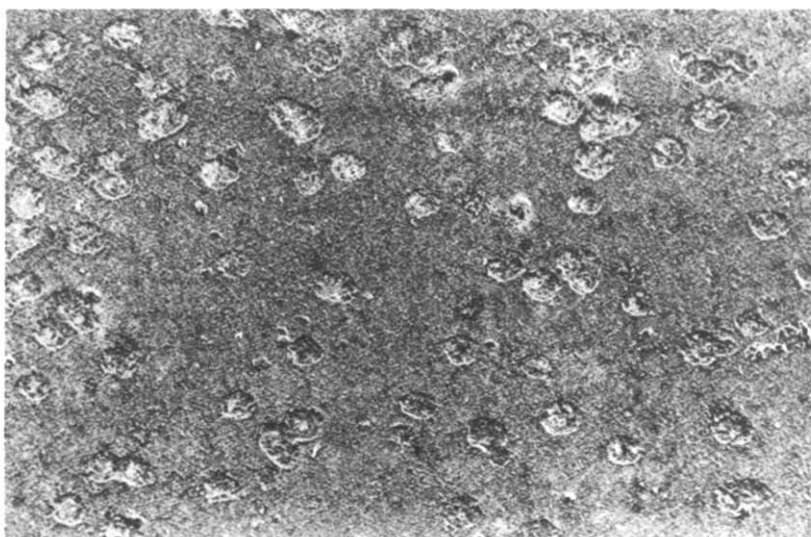


Fig. 3. Scanning electron micrograph of bacterial colonies (*Vibrio alginolyticus*) on a mild steel surface immersed in chloride containing medium. (Magnification $\times 390$.)

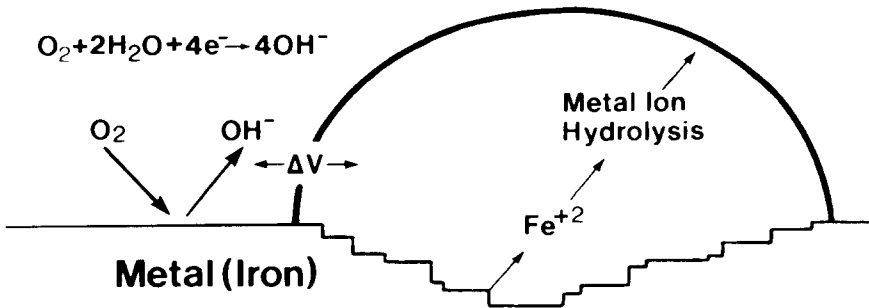


Fig. 4. Schematic representation of differential aeration effects underneath a microbial colony over an iron surface.

activity consumed the organic carbon and dissolved oxygen as they diffused through the biofilm. Since the bottom $180 \mu\text{m}$ of the biofilm is anaerobic, sulfate-reducing bacteria (SRB) can proliferate, despite a measurable dissolved oxygen concentration in the bulk water, in agreement with results reported by other authors (Cypionka *et al.*, 1985).

A mature biofilm, composed of microbial cells and their EPS, prevents the diffusion of oxygen to cathodic areas and the diffusion of aggressive anions, such as chloride, to anodic sites. Outward diffusion of metabolites and corrosion products is also impeded. For instance, an organism which produces a short chain fatty acid (e.g. acetic acid) may accumulate the acid within the biofilm, and local pH will decrease (Little *et al.*, 1986) as indicated by microelectrode measurements (Lewandowski *et al.*, 1988). The magnitude of the pH gradient is greatly influenced by the buffer capacity of the bulk water and possibly other variables. Moreover, the pH gradient influences precipitation of calcium salts at the metal surface and strongly influences abiotic and biotic corrosion processes at the metal/solution interface.

A series of papers has been recently published (Blunn, 1986; Gomez de Saravia *et al.*, 1989; Videla *et al.*, 1989) which illustrate the influence of biofilm patchiness on MIC of copper-nickel alloys in seawater.

Copper-nickel alloy surfaces can be colonized by bacteria and other organisms after long periods of exposure despite their perceived anti-fouling properties. Biofilm formation is markedly conditioned by the chemical nature and distribution of the inorganic passive layers and by the elemental composition of the substratum (Chamberlain & Garner, 1988). Blunn (1986) reports that after exposure periods of several months, bacteria can be found entrapped between corrosion product layers containing EPS. The passive layer structure is altered by EPS, leading to a layered structure (Fig. 5). Under these circumstances, biofilm detach-

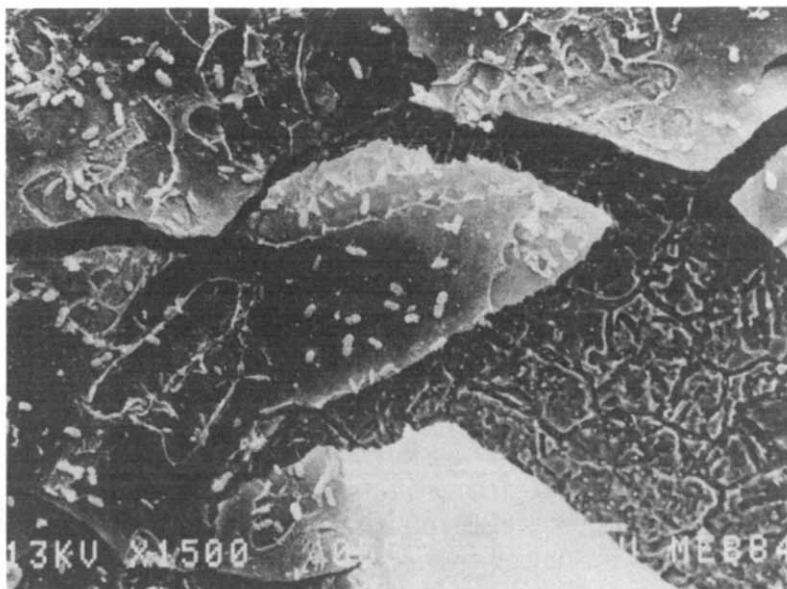


Fig. 5. Scanning electron micrograph of biofilms, passive layers and bacteria on a 70:30 copper–nickel alloy surface after 3 weeks of exposure to flowing seawater. (Magnification $\times 1500$.)

ment could influence the removal of inorganic passive layers, resulting in a ‘patchy’ distribution of the biofilm and possibly accounting for an increase of the corrosion rate by differential aeration. Stalked ciliates, observed as predominant biofouling species (Brankevich *et al.*, 1990), can facilitate passive layer detachment through adhesion effects developed at the fixation points of pseudopodia and assisted by water flow velocity. Videla *et al.*, (1989) have observed the detachment of complex biofouling deposits by sloughing due to water flow velocity. The sloughing revealed a microstructural pattern with clearly defined grain boundaries and precipitated copper oxide crystals (Fig. 5).

Metabolic processes within the biofilm

Metabolic processes within the biofilm significantly impact MIC. It is traditional to discuss specific mechanisms for MIC in terms of aerobic and anaerobic conditions and further to discuss selected mechanisms for specific micro-organisms. However, micro-organisms form synergistic communities that conduct combined processes which individual species cannot. For example, anaerobic and aerobic micro-organisms coexist in naturally occurring biofilms in oxygenated environments. Thus, aerobic

bacteria and SRB (obligate anaerobes) can proliferate in the same biofilm along with other anaerobic heterotrophs (Hamilton, 1985). Furthermore, a single type of micro-organism can simultaneously impact electrochemical processes through several mechanisms. The relationship between anaerobic heterotrophs, SRB and facultative aerobic bacteria like *Pseudomonas* sp., is very common in natural or industrial systems (Ortiz *et al.*, 1990). The interaction among the species within the biofilm community is an important consideration in MIC analysis.

From an electrochemical point of view, microbial activity can affect both the anodic and the cathodic reactions (Videla, 1986a). Some of the anodic effects, derived from microbial activity are as follows: (i) production of corrosive metabolites (e.g. organic acids); (ii) production of metabolites enhancing corrosion indirectly, through a synergistic action with other chemical species already present in the medium (sulfides plus chlorides); and (iii) uptake or degradation of corrosion inhibitors (e.g. nitrate consumption by fungi). On the other hand, microbial activity influences the cathodic process through the following processes: (i) metabolic production of cathodic reactants (e.g. hydrogen ions); (ii) uptake of cathodic reactants (e.g. oxygen by microbial respiration); and (iii) indirect acceleration of the cathodic reaction by means of metabolic products showing cathodic catalytic activity (e.g. iron sulfide).

For example, a metabolic activity within the biofilm that may markedly affect MIC is the reducing capacity of Fe^{3+} to Fe^{2+} inherent with certain bacteria (Ghiorse, 1988). In laboratory biofilms, localized attack of mild steel samples was preferentially found beneath microbial colonies (Gaylarde & Videla, 1987). The attack was explained as follows: (i) differential aeration between covered and uncovered areas; and (ii) depassivation of the metal surface due to the microbial reduction of Fe^{3+} deposits into soluble Fe^{2+} compounds. The effect can be enhanced by microbial consortia within the biofilm which accounts for an increase in concentration and variety of aggressive species.

Crystalline and amorphous accumulations of corrosion products, usually present in mild steel surfaces immersed in aggressive media, also condition the distribution of bacterial cells at the metal/solution interface (Videla, 1989).

Biofilm metabolic products which enhance MIC

Organic acids

Many heterotrophic bacteria and fungi produce organic acids during the fermentation of organic substrata. The types and amounts of acid

produced depend on the organism, the micro-environment and the available substrate. Organic acids may result in a physical shift in the tendency for corrosion to occur, as measured by electrochemical parameters like different potentials or currents. The impact of metabolites excreted by micro-organisms on corrosion is intensified when they accumulate at the colony/metal interface. For example, organic acids result in the corrosion of aluminum and aluminum alloys by fungal contamination in kerosene fuels. Microbial growth takes place preferentially at the outer zones of small droplets of water that remain in contact with the metal surface (Videla *et al.*, 1988). The fungal mycelium adheres firmly in those areas where three phases are generally present: water/fuel/alloy (Salvarezza & Videla, 1986). When the mycelium mat is removed by physical methods, the metal attack is evident, reproducing the hyphae contours and showing a preferential dissolution in the attachment areas (Fig. 6). Pitting attack develops preferentially in the adhesion zones where hyphae are active, inducing dramatic changes in pH, ion concentration and redox conditions.

Sulfides and other sulfur compounds

Anaerobic bacteria, particularly SRB, have been the focus of most MIC research. Starting with the cathodic depolarization theory (von Wolzogen

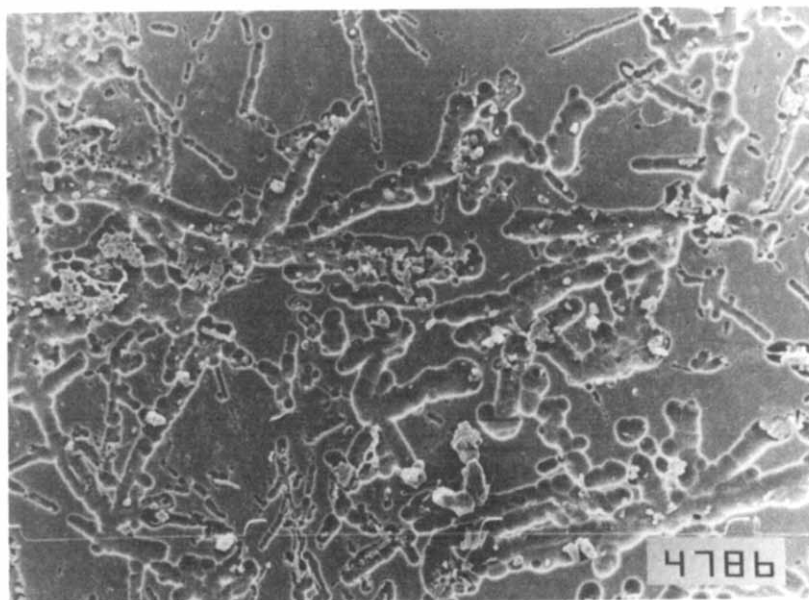


Fig. 6. Scanning electron micrograph of a 2024 aluminum alloy surface after being exposed to a *Hormoconis resiniae* culture for 90 days. Metal attack reproduces fungal hyphae profile in dissolved areas. (Magnification $\times 350$)

Kuhr & van der Vlugt, 1934), a copious list of papers on the anaerobic corrosion of iron has been published. An updated overview of the most relevant effects of SRB metabolites on corrosion (Videla, 1988) would include: (i) SRB provide several sulfur compounds containing corrosive anions for iron and steel; (ii) SRB aggressive metabolites can be produced as final metabolic products (sulfides, bisulfides, hydrogen sulfide) or intermediate metabolic compounds (thiosulfates, polythionates); (iii) SRB metabolites are corrosive to iron and steel mainly through their transformation to sulfide anions through biological and inorganic transformation paths; (iv) the characteristics and intensity of sulfide action is closely related to the nature of the passive film already present on the metal (Videla, 1986b). Cathodic depolarization, attributed to SRB or to iron sulfide in MIC literature, is developed later than passivity breakdown or only on clean metal surfaces seldom encountered in practice; (v) the participation of sulfides in the corrosion process is usually enhanced by other ions (i.e. chlorides) already present in the medium; (vi) physico-chemical characteristics of the environment (pH, ionic composition, oxygen level) modify SRB effects, which could be changed from corrosive to passivating. Finally, SRB effects can be markedly enhanced by the activity of other bacteria forming microbial consortia at the metal/solution interface, within the biofilm structure (Costerton & Geesey, 1986). Bacterial biofilms may develop anaerobic regions, even in aerobic bulk water environments (Hamilton, 1985), thus permitting SRB a very favourable environment for growth. The final result of these processes within biofilms is to produce a wide variety of sites on the metal surface that are markedly different from neighboring sites from a physico-chemical standpoint, thus facilitating the initiation of localized corrosion processes.

Metal oxidation products

Olsen & Szybalski (1949) reported that iron and manganese oxidizing bacteria were able to accelerate the corrosion and tuberculation of cast iron. Generally, MIC problems appear in typically low-flow or stagnant sections of water distribution systems where tubercle-forming bacteria play a role in the corrosion of iron, although not through direct action. It has been pointed out by Ghiorse (1984) that metal oxidation was not demonstrated in some cases and that certain micro-organisms can catalyze the oxidation of metals. On the other hand, some micro-organisms accumulated abiotically oxidized metal precipitates. The iron-oxidizing genera most often cited are the filamentous bacteria of the genera *Sphaerotilus*, *Crenothrix* and *Leptothrix*, which may be different forms of the same organism, and the stalked micro-organism *Gallionella*.

These organisms oxidize ferrous ions to ferric ions or manganous to manganic ions to obtain energy for growth.

Metal-oxidizing micro-organisms create environments for the accumulation of chloride ions and form acidic ferric chloride and manganic chloride, which are corrosive to stainless steel. However, the main mechanism used by this kind of tubercle-forming bacteria is the production of differential aeration cells. A typical differential aeration cell is formed at the tubercle structure: an oxygenated area (cathode) is present at the outer area of the tubercle, due to the continuous oxygen supply from the water. Conversely, an anaerobic area (anode) is found at the bottom of the formation, where access of oxygen is limited.

In all cases, corrosion enhancement is largely due to the presence of SRB in the inner area of the tubercle. It is possible that the fastidious iron and manganese depositing bacteria require other organisms to create conditions conducive for their growth. Furthermore, it can be argued that gradient-loving bacteria, such as *Gallionella*, are likely to depend on SRB and other anaerobic bacteria to maintain microaerophilic conditions in their environments. As a general rule, metal-oxidizing organisms efficiently scavenge oxygen and, therefore, provide conditions for the growth of obligate anaerobic bacteria.

BIOFILM-PASSIVE LAYER INTERACTION

Abiotic corrosion processes probably influence the rate, extent and distribution of colonizing microbial species, as well as the chemical composition and physical properties (e.g. cohesive strength) of the resulting biofilm. It has been demonstrated that the composition of a metal substratum influences the rate and cell distribution of microbial fouling films in seawater (Videla *et al.*, 1989). Nonuniform corrosion (localized anodes and cathodes) promotes patchy adsorption of micro-organisms. Conversely, a patchy biofilm distribution induces differential aeration effects like those observed on biofouled stainless steel and copper-nickel samples exposed to seawater (Brankevich *et al.*, 1990). At cathodic sites of corroding surfaces, there is an increased pH and electrolyte concentration. A decreased pH and electrolyte concentration is produced at anodic sites and this influences bacterial adsorption. Similarly, different inorganic ions produced at the two electrodic areas may affect adsorption. The depletion or reduction of oxygen at cathodic sites will also influence settlement. The presence of hydrated oxides or hydroxide passivating films on metal surfaces provides bacteria with sites for biofilm attachment (Kennedy *et al.*, 1976). Titanium hydroxides,

for example, are insoluble over the normal physiological pH range and have been used for cell immobilization matrices with no inhibitory effect on biologically active molecules.

Spalling or sloughing of corrosion products results in the detachment of biofilm patches associated with the corrosion products (Videla *et al.*, 1989). Copper-based alloys are good examples of these effects.

In a recent report on MIC and biofilm/passive layer interactions, three different metal surfaces were assayed (Videla, 1989). Stainless steel, a noncorrosive surface, is easily colonized by micro-organisms, and biofilm formation facilitates the initiation of pitting attack mainly by differential aeration effects and by altering oxygen concentration gradients through microbial respiration. Electrochemical reactions are influenced by biofilm formation, and by the chemical microenvironment created at the metal/biofilm interface (Little *et al.*, 1990).

Carbon steel, a corrosive surface, exhibits a complex biofilm/passive layer interaction. Microbial dissolution of inorganic passive layers exposes metal surfaces to the direct action of aggressive species present in the medium (e.g. chlorides), enhancing localized attack. The importance of microbial consortia cannot be disregarded.

Copper-nickel alloys, in spite of their anti-fouling properties, are microbially colonized after long periods of exposure. Once a biofilm is established, its interaction with the inorganic passive layers affects the corrosion behavior, mainly through the removal of corrosion products layers as biofilm detachment occurs. Differential aeration cells are formed as a result of the patchy distribution of the biofilm. The effect of biogenic sulfides on the oxide passive layer of copper-nickel alloys in chloride media may also be attributed to MIC. For all three surfaces considered, the interaction between corrosion products and biofilms influences the passive behavior of the metallic substratum.

The motivation for developing a rational approach to biofilm accumulation and its influence on MIC, is the expectation that this approach will lead to more satisfactory methods for preventing and/or controlling biofouling and its undesirable effects.

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