88-008

Prepared for EPRI Workshop on Microbial Induced Corrosion,
Charlotte, North Carolina, 18-19 Oct 1988

BIOFILMS AND THEIR EFFECT ON LOCAL CHEMISTRY

W.G. CHARACKLIS[1], B.J. LITTLE[2], AND M.S. MCCAUGHEY[3]
INSTITUTE FOR BIOLOGICAL AND CHEMICAL PROCESS ANALYSIS
MONTANA STATE UNIVERSITY
BOZEMAN, MT 59717

ABSTRACT

Fouling and corrosion is frequently mediated by microorganisms attached to the metal surface and/or embedded in a gelatinous organic matrix termed a biofilm. Biofilms substantially change the local chemistry of the adjacent metal and, thereby, influence corrosion processes. The extent of changes in local chemistry is influenced by the microenvironmental conditions at the metal surface including the number and types of microorganisms present, the dissolved oxygen concentration, the flow velocity, the buffering capacity of the bulk water, and many other factors. Since microbial-influenced corrosion is generally localized, the spatial distribution or patchiness of the microbial activity also affects the corrosion processes. A unified approach to understanding and controlling biofilms and the related corrosion will be presented in the context of a case study recently conducted by CCE, Inc. at a nuclear power plant site.

INTRODUCTION

Fouling refers to the undesirable formation of deposits on equipment surfaces which significantly decreases equipment performance and/or the useful life of the equipment. Several

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[1]also President, CCE, Inc., P.O. Box 1409, Bozeman, MT 59771.
[2]Research Chemist, Naval Research and Development Activity, NSTL Station, MS.
[3]Research Engineer, CCE, Inc., P.O. Box 1409, Bozeman, MT 59771.

types of fouling and their combinations may occur: biological, corrosion, particulate, and precipitation fouling. In most operating plant environments, more than one type of fouling will be occurring simultaneously. Microbial films of varied composition and thickness develop in the deposits and metabolic reactions mediated by certain microorganisms residing in biofilms can promote (1,2) or impede the biodeterioration of materials including metals, concrete and plastics.

Most confirmed cases of microbial corrosion (MC) are characterized as localized corrosion. Discrete mounds or columns related to tuberculation can develop on metal surfaces as a result of microbial activities. The morphology and location of deposits are sometimes indicative of the microbial species that caused the deposit. For example, distinctive hemispherical or conical tubercles on the surface of steel and subsurface pitting are characteristics of iron-oxidizing bacteria. Sulfate-reducing bacteria (SRB) produce open pitting or "gouging" on stainless steel. When SRB are active along the edges of gasketed joints, shallow crevice corrosion is often found under adjacent gasket areas. SRB attack on cast iron typically produces graphitization, whereby the corroded areas are filled with a soft skeleton of graphite. On nickel and cupro-nickel alloys, SRB are reported to produce conical pits containing concentric rings (3). These types of observations have been used to document MC problems. Despite the recognition and the documentation, the identification of specific mechanisms for MC has remained elusive because of the complexity of microbiological processes and the lack of analytical techniques to quantify localized corrosion. In this paper, we will review techniques that have been applied to the investigation of MC, the microbial activities known to impact biodeterioration, the impact of corrosion on biofilm formation, control of biofilm formation, and monitoring of biofilm accumulation.

In power plant water systems, microbial biofilms are the cause of substantially costly problems. Biofouling films in condensers reduce heat transfer resulting in excessive energy losses (4). Biofilms can also result in premature failure of condensers as illustrated by McCaughey et al (4). In service water systems, biofouling, combined with sedimentation and inorganic scaling deposits result in performance and safety problems. For example, excessive fouling deposition in a service water system may result in unacceptably high fluid frictional resistance under emergency service conditions. Under-deposit corrosion in service water systems also may result in decreased lifetime of the piping system. An example of such a fouling/corrosion problem has been observed by Northern States Power Company (NSPC), Monticello Nuclear Generating Plant.

> NSPC has experienced a biofouling and corrosion problem in river water supplied piping. Corrosion product accumulation with some pipe wall loss below corrosion tubercles was discovered on stagnant and low flow portions of the service water system. NSPC has chlorinated the intake service water for two hours every day, adjusting the chlorination rate to provide a residual of less that 0.2 ppm in the discharge canal. The chlorination system used gaseous chlorine from plant startup in 1971 until the spring of 1987 when a sodium hypochlorite system was installed.
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> The complex fouling deposits found at NSPC consisted of biofilms in intimate association with inorganic particles, inorganic precipitates, and corrosion products. These complex deposits often form more rapidly and are more tightly bound than biofilm alone.

The goal of this paper is to begin to integrate the influence of bulk water quality on biofilm accumulation and activity and, in turn, determine the influence of biotic activity on corrosion processes. In this way, a rational means to monitor and control biofouling in a cost effective manner can be established. The NSPC case study will be used as an illustration of fundamental concepts whenever possible. The text relevant to this case study will be indented and appears as smaller type.

PROCESS ANALYSIS

In most, if not all, reported results on biofouling, certain observed or measured quantities are reported: heat transfer resistance and/or fluid frictional resistance. A difficulty with these observed quantities is that they reflect the contribution of several processes of more fundamental significance. For example, net biofilm accumulation results from the combination of the following processes (5): a) transport of cells to the substratum, b) adsorption of cells to the substratum, c) growth and other metabolic processes within the biofilm, and d) detachment of portions of the biofilm. If all of the processes occur in series, the slowest step of the sequence exerts the greatest influence and limits the overall process rate. This step is called the "rate-determining step" or "rate-limiting step." If the overall process consists of a number of parallel processes (or processes in series and parallel), the slowest process becomes the "rate-controlling step". Identifying the rate-controlling and/or rate-limiting step is critical to successful scale up procedures and its determination contributes significantly to the insight gained from experimental results. Process analysis permits the determination of the rate-limiting or rate-controlling step in the overall process at different environmental, operating or physiological conditions.

The complex fouling deposits at NSPC consisted of microorganisms in intimate association with inorganic particles, inorganic precipitates, and corrosion products which accumulated from river water flowing in the piping. Corrosion product accumulation with some pipe wall loss below corrosion tubercles was discovered on stagnant and low flow portions of the service water system (Figure 1).

A scenario for accumulation of fouling deposition at NSPC is suggested by the results to date. First, microbial cells adsorb to the metal pipe surface, probably with the help of organic polymers excreted by the cells. The adsorbed cells then begin to grow and reproduce at the expense of nutrients being continuously introduced with the river water.

Thus, more cells accumulate on the surface producing more extracellular polymers which make the surface "stickier". Silt and clay particles, also borne by the water, are now easily trapped in the deposit. The organic matrix may also concentrate cations such as calcium and may result in precipitation of inorganic salts. As the deposit becomes thicker, fluid shear forces at the deposit-water interface increase and more of the "new" deposit detaches. Ultimately, a steady state or "plateau" in deposit accumulation may result when PRODUCTION = DETACHMENT.

The microbial counts in the river water were similar to microbial counts at an unchlorinated power plant site (4) and higher than samples taken at a chlorinated power plant site (6) that CCE had investigated. Also, the microbial counts were higher in the deposit than in the water suggesting that the microorganisms are transported to the pipe walls with the water, adsorb, and continue to grow on the pipe wall with little or no influence from the biocide. Microbial activity directly and indirectly enhances the deposit accumulation in the system. The present fouling control treatment apparently has little effect.

The microbial cell numbers in the inlet water are not atypical for river water. However, a large increase (approximately 4 fold increase) in Pseudomonas species was observed from the distribution inlet to the outlet. Pseudomonas is unique in that it can only use oxygen or nitrate (when anaerobic conditions exist) as an electron acceptor. Since nitrate was not detectable and the distribution system is essentially aerobic, Pseudomonas could have been growing in the water. A more plausible explanation is that Pseudomonas was growing near or on the surface of the pipe deposits and daughter cells were detaching and being reentrained in the water. Relatively large numbers of Pseudomonas were observed in the deposit analyses. Only a small fraction of these biofilm organisms need be multiplying to produce the approximate increase of 350 organisms/ml across the service water system. The service water source quality (Table 1) was certainly sufficient to support heterotrophic growth to this extent since organic carbon was greater than 5 g m^{-3} and nitrogen and phosphorous were sufficient for carbon-limited microbial growth.

The overall result is a sigmoidal progression of events characterized by three identifiable periods (Figure 2): 1) A lag (or induction) phase - no detectable fouling occurs, 2) A rapid increase in accumulation which is characterized by the maximum rate of fouling, and 3) an asymptotic or plateau phase which signifies the extent of fouling.

The case study at NSPC was not initiated until the fouling deposit reached or was approaching plateau or steady state.

MICROORGANISMS AND CORROSION

Electrochemical Nature of Corrosion

Corrosion is a spontaneous reaction characteristic of almost all metals driven by the thermodynamic tendency to revert to a combined form. The corrosion reaction is caused by a flow of electrons from one metal to another or from a metal to another electron sink. The electrochemical reaction at the metal surface requires an electrolyte solution to conduct the electron flow. Thus, inorganic corrosion requires the presence of two elements: the metal and the electrolyte. Metal dissolution or corrosion is an electron-producing reaction in which metal ions flow into solution while electrons flow to another area where they are consumed, thereby closing the electrical circuit. When the corrosion process is conducted in an electrochemical cell, the metal dissolution reaction occurs at the anode and the other electron consuming reaction occurs at the cathode. In most applications the cathodic reaction will be oxygen reduction in aerobic solutions near neutral pH or hydrogen ion reduction and hydrogen production in deaerated solutions at low pH. If both reactions are occurring in an aerated acidic solution, protons are more readily available than oxygen and the second reaction will occur.

The current flow induces a change at the metal-bulk liquid interface called polarization which determines the rate of the overall electrochemical process. The corrosion reaction tends to slow as corrosion products accumulate at the metal-bulk liquid interface and polarization generally refers to this decrease in reaction rate. Conversely, any acceleration of the reaction is termed depolarization. If the rate of metal dissolution is measured, the corrosion current at the anode will be equivalent

to the rate of metal ions leaving the metal and going into solution. Since the electric current must migrate through the solution and return to the metal at the cathode, the cathodic current equals the anodic current.

Corrosion products accumulate at the metal-bulk liquid interface and have a marked effect on the corrosion rate. Oxide films form on metal surfaces exposed to aerobic environments and provide protection against further corrosion. The extent to which these products can adhere firmly, resist removal by turbulent flows, or be restored if damaged determines the ability of an alloy to remain passive and resist corrosion. The manner in which microbial colonization influence the stability of the passive film cannot be predicted and remains the major challenge in microbial corrosion.

Influence of Gradients and Patchiness on Corrosion

Prior to colonization of a surface by microorganisms, 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. The physical adsorption of microbial cells on a metal surface, as well as their metabolic activities, impacts electrochemical processes. The adsorbed cells grow and reproduce, forming colonies that constitute physical anomalies on a metal surface resulting in formation of local cathodes or anodes (Figure 3). Nonuniform 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 (Figure 4). Colony formation gives rise to potential differences and, consequently, to corrosion currents. Under aerobic conditions,

the areas under the respiring colonies become anodic (metal dissolution occurs) and the surrounding areas become cathodic (oxygen is reduced). If microroughness of the substratum is considered (Figure 5), corrosion currents may form between the "peaks" and "valleys" of the roughness elements.

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 metabolism within the film. Microelectrode measurements (unpublished results) in a biofilm which accumulated in a flow containing approximately 50 g carbon m^{-3} and 4 g dissolved oxygen m^{-3} indicate that the dissolved oxygen decreased to 0 approximately 180 μm from the metal surface. The biofilm, in this case, was approximately 400 μm thick and very active. The microbial activity consumed the organic carbon and dissolved oxygen as they diffused through the biofilm. Since the bottom 180 μm of the biofilm is anaerobic, sulfate-reducing bacteria (obligate anaerobes) can proliferate despite a measurable dissolved oxygen concentration in the bulk water (7).

The following microbial types were analyzed from pipe surfaces at the Monticello Nuclear Generating Plant: heterotrophic plate count (HPC), Pseudomonas aeruginosa, sulfate-reducing bacteria (SRB), and the presence or absence of iron bacteria. The HPC was performed to estimate the total number of cells in the deposit which obtain their energy from organic compounds (heterotrophs). Ps. aeruginosa, a specific heterotroph, uses a wide variety of organic compounds as carbon and energy sources and is an obligate aerobe (requires oxygen to grow). SRB are a group of specialized microorganisms that grow in aqueous environments in the absence of oxygen using sulfate as a final electron acceptor (as opposed to oxygen). The main nutrients for SRB are simple organic acids and molecular hydrogen (H_2) from decomposing natural organic matter. The nutrients are oxidized with sulfate being reduced to sulfide. Some SRB can produce short chain organic acids and excrete them. The H_2S and short chain acids which are produced can play an important role in the disastrous effects caused by SRB, namely corrosion of iron and steel in the absence of oxygen (anaerobic corrosion).

Substantial numbers of sulfate reducing bacteria (SRB) are present in the NSPC deposits and their activity corresponds to the pipe surface area covered by large sulfide mineral deposits observed on the pipe sections cleaned of deposit. The SRB may be contributing significantly to corrosion processes in the pipe.

A mature biofilm composed of microorganisms and their extracellular secretions prevents the diffusion of oxygen to cathodic sites and the diffusion of aggressive anions, such as chloride, to anodic sites. Outward diffusion of metabolites and corrosion products is also impeded. For example, an organism which produces a short chain fatty acid (e.g., acetic acid) will accumulate the acid within the biofilm and local pH will decrease dramatically. Little et al. (8) estimate that the pH can be as low as zero within an Acetobacter aceti colony. Lewandowski et al. (9) have used a microelectrode to measure the pH at a cathodically protected stainless steel surface. Their measurements indicate a substantial pH gradient between the bulk medium and the metal surface. The magnitude of the pH gradient is greatly influenced by the buffer capacity of the bulk water. Obviously, the pH gradient influences precipitation of calcium salts at the metal surface. Perhaps more importantly, the pH gradient strongly influences abiotic and biotic corrosion processes at the metal surface.

Metabolic processes within the biofilm significantly impact corrosion. It is traditional to discuss specific mechanisms for MC in terms of aerobic and anaerobic conditions and to further discuss selected mechanisms for specific microorganisms. However, microorganisms form synergistic communities that conduct combined processes that individual species cannot. For example, anaerobic and aerobic microorganisms coexist in naturally occurring biofilms in oxygenated environments (Figure 6). Thus, aerobic bacteria and sulfate-reducing bacteria (obligate anaerobes) can proliferate in the same biofilm along with other anaerobic heterotrophs. Furthermore, a single type of

microorganism can simultaneously impact electrochemical processes via several mechanisms. The relationship between anaerobic heterotrophs, sulfate-reducers, and methanogens in a biofilm has been described by Parkes (10) and is diagrammatically presented in Figure 7. Clearly, the interaction among the species within the biofilm community is an important consideration in a MC analysis.

Sulfate-reducing and iron-oxidizing microorganisms are the most frequently cited causative agents for MC. However, all microorganisms colonizing metal surfaces have the potential for effecting electrochemical processes.

Low Molecular Weight Extracellular Product

Most heterotrophic bacteria secrete organic acids during the fermentation of organic substrates. The types and amounts of acids produced depend on the kinds of organisms, the microenvironment, and the available substrate molecules. Organic acids may result in a physical shift in the tendency for corrosion to occur as measured by the potential shift between anodes and cathodes. The impact of metabolites secreted by microorganisms is intensified as they are trapped at the colony/metal interface. Corrosive metabolic products, such as hydrogen sulfide (H_2S) from Desulfovibrio desulfuricans, acetic acid (CH_3COOOH) from Clostridium aceticum, and sulfuric acid (H_2SO_4) from Thiobacillus thiooxidans, are obvious contributors to corrosion processes. In addition, it has been demonstrated that the organic acids of the Krebs cycle can promote the electrochemical oxidation of a variety of metals by preventing or removing an oxide film (11). Little et al. (8) have demonstrated that isobutyric and isovaleric acids accelerated nickel corrosion in concentrations that are environmentally relevant. Gerchakov

and Udey (12) have suggested that such metabolites as amino and dicarboxylic acids may also be aggressive ions to some metal substrata, such as copper. Little et al. (13) have demonstrated that, under laboratory conditions, an aerobic acetic acid-producing bacteria can accelerate the corrosion of a cathodically protected stainless steel electrode in synthetic salt solution. The acetic acid destabilized or dissolved the calcareous film that formed during cathodic polarization.

Experiments with sulfate-reducing bacteria indicate that SRB can produce significant quantities of acetate. For example, using lactate as a carbon source, the following approximate stoichiometry has been observed for Desulfovibrio desulfuricans at 35° C (unpublished results):

$$CHOHCH_3COOH + 0.7\ H_2SO_4 + 0.2\ NH_3 \text{ -----> } 0.02\ CH_{1.4}O_{0.4}N_{0.2} + 0.7\ H_2S + 0.7\ CH_3COOH + 1.0\ CO_2 + 2.2\ H_2O \quad [1]$$

Thus, approximately 0.7 moles of acetic acid are produced for each mole of lactate consumed. Obviously, the acid can contribute significantly to corrosion processes at the metal surface. However, there may be other organisms present in the biofilm consortium which may utilize the acetate as indicated in Figure 7.

Sulfate-reducing Bacteria (SRB)

Anaerobic bacteria, particularly SRB, have been the focus of most microbiological corrosion investigations. The early work of von Wolzegen Kuhr and van der Vlugt (14) suggested that the overall process was due to depolarization resulting from bacterial hydrogen removal from the surface of iron. The electron removal as a result of hydrogen utilization results in cathodic depolarization and forces more iron to be dissolved at the anode. The direct removal of hydrogen from the surface is equivalent to lowering the activation energy for hydrogen removal by providing a "depolarization" reaction. The enzyme, hydrogenase, synthesized by many species of Desulfovibrio, may be involved in this specific depolarization process. Booth et al. (15), using polarization techniques and weight loss measurements versus hydrogenase activity, have provided additional evidence to substantiate this theory. However, Iverson (16) first presented direct evidence for cathodic depolarization using benzyl viologen as an indicator of reduction. Bacteria, by removing adsorbed hydrogen to produce sulfide and water, increase the rate of dissolution of Fe_2S. Nonhydrogenase-producing strains of Desulfovibrio can also stimulate corrosion.

Miller and Tiller (1) have proposed cathodic "depolarization" induced by microbially-produced FeS. King et al. (17) and Booth et al. (15) demonstrated that weight losses of steel were proportional to the concentrations of ferrous sulfide present and the stoichiometry of the particular ferrous sulfide minerals. They concluded that the accelerated corrosion of mild steel in the presence of sulfate-reducing bacteria was due principally to the formation of iron sulfide. Duquette (18) has reviewed the possible electrochemical consequences of the formation of FeS and concluded that if FeS is the cathodic site for hydrogen reduction, the activation energy for hydrogen evolution may be

reduced. In such an instance, a simple increase in the effective area of a sulfide film would also lead to an increase in the cathodic reaction rate.

Salvarezza and Videla (19), using potentiostatic polarization techniques, evaluated the breakdown of passivity of mild steel in seawater in the presence of sulfate-reducing bacteria. The experiments were performed in a synthetic medium in the presence and absence of Desulfovibrio. Experiments with sterile media indicate that pitting potential is virtually unaffected by aeration or deaeration. Polarization curves obtained in the presence of sulfate-reducing bacteria of different ages and sulfide concentrations showed pitting potentials more active than those corresponding to sterile media. The progression of total sulfides and redox potential was as follows:

time	total sulfides	pH	redox potential
(h)	(M)		(mV)
72	1.4×10^{-4}	7.5	-500
96	1.0×10^{-3}	7.8	-510
240	8.0×10^{-4}	7.2	-510

The addition of sulfate-reducing bacteria and sodium sulfide resulted in pitting potentials that were 100-200 mV more active than in seawater alone, and pits were physically observed on the surfaces. The results indicate that the effect of sulfate-reducing bacteria is to add sulfide to the system and the sulfide species behave similarly to chemically added sulfide. Furthermore, the authors demonstrated that deaerated solutions required lower levels of sulfide or metabolic products to induce pitting.

At NSPC, the fouling deposits were removed from the pipe surface by a reductive electrochemical method (20). The method blasted the oxidized portions of the deposit from the pipe surface but the reduced deposits, such as the sulfide deposits, remain. A significant area of the NSPC pipe samples was covered with a sulfide film (Figure 8) which is apparent after the deposit is removed by the treatment. The pipe samples with the largest areas of sulfide corrosion deposits also contained the most SRB. The pipe surface was covered with pits of a wide diameter and depth distribution (Figure 9).

The impact of oxygen on obligate anaerobic, sulfate-reducing bacteria was examined by Hardy and Bown (21) using a synthetic seawater medium and a Desulfovibrio strain. Corrosion rates were determined by weight loss measurements and by electrical resistance probe measurements. Corrosion rates were low under totally anaerobic conditions, but increased with the addition of oxygen. Successive aeration-deaeration shifts caused variation in the corrosion rate. High rates were observed during periods of aeration. The attack was confined to areas beneath tubercles that consisted of loosely adherent material as opposed to the hard, tightly adherent films on uncorroded metal. The authors concluded that the presence of tubercles fixed the anode and forced the cathodic reaction to occur on the adherent sulfide film. Since significant corrosion rates were only observed when oxygen was present, some of the reported laboratory tests with SRB may have been contaminated with oxygen.

Dissolved oxygen was present throughout the NSPC service water system. As a consequence, any bare surface, perhaps resulting from the sloughing or detachment of deposit, would result in the formation of a cathode where oxygen could be reduced and rapid corrosion would ensue for a period until deposition occurred again. No historical data on the progression of corrosion rates in the service water system were available.

Metal Oxidation by Bacteria

In recent years, the role of metal-oxidizing bacteria in MC has been emphasized. Ghiorse (22) has pointed out that metal oxidation has not been demonstrated in some cases and that

certain microorganisms can catalyze the oxidation of metals. Other microorganisms accumulate abiotically oxidized metal precipitates. The iron-oxidizing genera most often cited are the filamentous forms of Sphaerotilus, Crenothrix, and Leptothrix (which may be different forms of the same organism), and the stalked organism, Gallionella. These organisms oxidize ferrous ions to ferric ions or manganous to manganic ions to obtain energy for growth. There are also reports of microbial oxidations and reductions of chromium. Metal-oxidizing organisms create environments for the accumulation of chloride ions (to maintain charge neutrality) and form acidic ferric chloride and manganic chloride, which are highly corrosive to stainless steel.

> Iron was detected in relatively high amounts in all the deposit samples at NSPC. Chloride concentration in the river water used by NSPC in their service water system is rather low (in some cases, less than 10 g m^{-3}).

Further pit development is enhanced as an oxygen concentration cell develops. Duquette (18) has summarized these developments on a schematic anodic polarization diagram for a passive metal or alloy (Figure 10). In this diagram, curve 1 represents sufficient cathodic reduction of oxygen to passivate the alloy, while curve 2 shows the result of decreasing the oxygen concentration to a level that will not support passivity. A stably passive alloy is indicated by the intersection of the anodic and cathodic curves at point 3. When chlorides are present, pitting occurs. The pitting potential shifted in the active direction by chloride ion as indicated by line 4. The potential may be fixed above the pitting potential by an Fe^{2+}/Fe^{3+} redox couple illustrated by line 5. Curve 3 demonstrates the effect of increasing chloride concentration, which lowers the pitting potential.

Ehrenberg (23) first described the twisted, iron-encrusted stalk structures of Gallionella in ochre deposits and suggested they

were fossil "infusoria." The true nature of the structures called Gallionella was not discovered until Cholodny (24) showed that bean-shaped bacteria were delicately attached to the ends of the twisted stalks. Based on careful microscopic observations, Cholodny proposed that the bacteria secreted the twisted stalk as they grow.

> No stalked forms of iron bacteria were detected in the deposit samples. However, there are still many problems with analyses because forms of the sheathed iron bacteria are able to change morphology under different growth conditions (25).

It is possible that these fastidious Fe- and Mn-depositing bacteria require other organisms to create conditions conducive for their growth. The possibility of synergistic associations of Gallionella with other bacteria has been suggested (26). Furthermore, it can be argued that gradient-loving bacteria such as Gallionella are likely to depend on sulfate-reducing and other anaerobic bacteria to maintain microaerophilic conditions in their environments.

Metal-oxidizing organisms efficiently scavenge oxygen and, therefore, provide conditions for the growth of obligate, anaerobic bacteria. Numerous reports document the presence of sulfate-reducing bacteria in the tubercles formed by metal-oxidizing species (27, 28, 1).

Cell Death

Cell death, or lysis, within a well-developed biofilm does not necessarily mean a cessation of the influence on electrochemical processes. Miller and Tiller (1) have confirmed that iron-oxidizing microorganisms such as Gallionella oxidize ferrous ions to ferric ion to obtain energy for growth reactions. This oxidation results in thick deposits of ferric hydroxide. Pitting

corrosion can proceed under these deposits independent of the biochemical activity of the bacteria. Similarly, Booth and Tiller (29) found that microbiologically generated FeS was corrosive in the absence of viable cells. Thus, the deposits containing extracellular products create differential aeration that may persist after cell death, a most important conclusion relevant to measures for MC prevention and/or control. Control of MC may require the complete removal of the biofilm, rather than killing or inactivating the cells within the biofilm.

Inactivation of Corrosion Inhibitors

Organic compounds such as aliphatic amines are used as corrosion inhibitors. These compounds are degraded by microorganisms, decreasing the effectiveness of the compounds and increasing the microbial populations. Some bacteria reduce NO^{3-} or NO^{2-} to N_2 gas that escapes the system. Characklis (unpublished results) analyzed a closed recirculating cooling system in a nuclear power plant which was requiring unusually high amounts of nitrite (NO_2^{-}) corrosion inhibitor. The system was maintained anaerobic and pH was continually increasing despite attempts to control it. The cause was microbial denitrification. Denitrification may be described conceptually by the following stoichiometric equation using methanol as an illustrative electron donor:

$$2\ NO_2^- + CH_3OH \text{ -----> } N_2 \uparrow + 2\ OH^- + CO_2 + H_2O \qquad [2]$$

The methanol is the electron donor (energy source) while nitrite is the electron acceptor. Nitrite corrosion inhibitor is degraded at the expense of organics. The Biochemical Oxygen Demand (BOD), an assay for biodegradable carbon in the water, was almost 30 g m^{-3} in the cooling system. Note that "denitrification" results in an increase in pH.

IMPACT OF CORROSION ON BIOFILM FORMATION

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 microfouling films in seawater (30, 31). Nonuniform corrosion (localized anodes and cathodes) promotes patchy adsorption of microorganisms. The pH and electrolyte concentration increase at the interface of corroding surfaces at cathodic sites and decrease at anodic sites, thus influencing bacterial adsorption (32). Similarly, different inorganic ions produced at the two electrodic areas may affect adsorption (33, 34). The depletion or reduction of oxygen at cathodic sites will also influence settlement. The presence of hydrated oxide or hydroxide passivating films on metal surfaces (Figure 11) provides bacteria with sites for film attachment (35). 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. The microbial cell immobilization process for a number of metal hydroxides presumably involves replacement of hydroxyl groups on the metal hydroxide surface by suitable ligands from the cell, resulting in the formation of partial covalent bonds. Kennedy et al. (35) have demonstrated that cells become firmly adsorbed to the metal hydroxide and are not just loosely trapped in the gelatinous oxide matrix.

Spalling or sloughing of corrosion products results in the detachment of biofilm patches associated with the corrosion products (36). Copper-based alloys have long been considered as toxic or inhibitory surfaces, since biofilm accumulation on copper alloys is usually less than on titanium or stainless steel

alloys. An alternate explanation for reduced biofilm accumulation on copper alloys is that copper-based alloys corrode faster and, thus, carry away biofilm with the spalled corrosion products.

CONTROL OF MICROBIAL ACTIVITY

There are physical and chemical methods available for preventing/controlling fouling deposition. However, none of these methods is universally cost effective or biofouling would no longer be a problem. The decision regarding a method for controlling fouling biofilm in a specific operating environment must consider the following system factors:

1) Environmental control
2) Water quality
3) Influence of treatment on corrosion losses (cost)
4) Cost of treatment program or process

The extent to which these factors influence fouling control varies with season, process operation, and other variables. Hence, the cost effectiveness of a fouling control program will generally be site-specific.

Chlorination

Some chemical treatments are quite effective but are undesirable due to their impact on environmental quality. Chlorine has been used for years because it is a reasonably effective method for controlling biofouling. But concern over toxicity of chlorine and its reaction products has spurred the search for alternatives. However, thoughtful engineering approaches permit use of

compounds such as chlorine while maintaining the environmental concentrations within satisfactory limits.

Intermittent chlorination has been the most widely used biofouling control process for power station condensers in the United States. A small number of utilities employ continuous low level chlorination to control macrofouling and microfouling when other control options are not feasible. However, the use of chlorine has been restricted by the effluent limitations imposed because of potential adverse environmental impact to aquatic organisms. Total chlorine residual in the discharge of power plants is restricted to 0.2 g m^{-3} for two hours per day because of its environmental/health effects in the receiving waters. The effluent limitations on chlorine can be met either by reducing dosage or by dechlorination. Minimizing chlorine dosage to ensure that effluent limitations are not exceeded may not allow flexibility to increase the chlorine dosage as required to control biofouling at every plant site.

NSPC has chlorinated the intake service water for two hours every day, adjusting the chlorination rate to provide a residual of less that 0.2 ppm in the discharge canal. The chlorination system used gaseous chlorine from plant startup in 1971 until the spring of 1987 when a sodium hypochlorite system was installed.

Water Quality

Frequently, other reacting components interfere with the intended control procedure. Chlorine is a useful biofouling control compound but, in heavily contaminated waters, chlorine is rapidly consumed in side reactions (chlorine demand reactions) and is rendered ineffective. Even copper-nickel alloys possess a significant chlorine demand (36). Therefore, water quality and pipe wall composition are at least two factors which influence the effectiveness of a treatment program to minimize fouling.

The chlorine demand of the intake for the service water at another nuclear power plant was evaluated by CCE, Inc. at various time intervals. From these data, the free chlorine residual profile along the length of the emergency service water system supply line was determined under the following conditions (Figure 12): a) chlorine was injected 600 to 800 ft. upstream of the heat exchanger where fouling problems were occurring, c) flow rate in the 14 in. pipeline was approximately 0.7 fps (volumetric flow rate was approximately 350 gpm), and d) alloys in contact with water were titanium and admiralty brass. The calculations clearly indicate that no free chlorine was reaching the heat exchanger. Thus, the effectiveness of any chemical oxidant dissipates rapidly with time and travel distance so chemical injection appreciably upstream of the system where fouling is occurring is not satisfactory unless massive, generally environmentally unacceptable, doses were applied.

Frequently, the criterion for dosage is the maintenance of a residual at the outlet which presumably nullifies the chlorine demand in the water. Recent results, however, indicate that mass transfer resistance in the bulk water and the chlorine demand of the pipe may reduce the effectiveness of chlorine.

Water quality parameters related to microbial activity and/or biocide effectiveness are frequently not measured in power plant surveys. Biodegradable or assimilable organic carbon are rarely, if ever, reported. Surrogate parameters, such as total organic carbon or Biochemical Oxygen Demand (BOD), are generally not conducted. Although numerous inorganic anions and cations are frequently reported, those of biological interest (e.g., NH_3-N, PO_4^{3-}) are not.

No historical data on NH_3 or PO_4^{3-} were available at NSPC. CCE, Inc. conducted one set of water quality analyses reported in Table 1.

Influence of Treatment on Corrosion Losses

Some equipment materials are vulnerable to corrosion induced by high chlorine concentrations. For example, chlorine increases corrosion rate of copper alloys and, in some cases, mild steel (36).

Process Considerations in Fouling Control

Chlorine controls biofouling by inhibiting microbial metabolism and/or growth. Chlorine is added periodically to inactivate (i.e., "kill") the biofilm cells. Since microbial growth rate is proportional to viable cell numbers, the biocide reduces the rate of growth leading to biofilm accumulation.

Both mechanical and chemical methods are used to disrupt the bonds between biofilm cells and the pipe wall or to destroy cohesiveness of biofilm cells within the deposit resulting in detachment of cellular material. Chlorine, added periodically, causes detachment of accumulated fouling biofilms in addition to "killing" cells. Chlorine is applied in "shock" doses to strip microbial slimes from the fouled surfaces.

MONITORING OF MICROBIAL FOULING AND CORROSION

Presume you are asked to control pH in a recirculating cooling tower system in which pH varies considerably with the seasons and even climatic conditions. You are given a storage tank of acid and a storage tank of base with the ancillary pumps, flow meters, valves, etc. Before any effective pH control is possible, however, you will need a pH electrode. The electrode reading will provide feedback (manual or automatic) so that you can assess the necessary flow rate or amount of acid or base addition. In a similar manner, presume you are asked to determine the necessary amount of treatment chemical (e.g., chlorine) needed to control biofouling and still operate within the environmental regulations.

> There is no means for monitoring fouling or corrosion rates in the NSPC service water system.

Numerous factors influence (1) the rate and extent of biofouling and (2) the chemical demand of the cooling water and fouling biofilm. Both variables significantly affect the efficient operation of the operating equipment. Therefore, determining an effective chemical dosage (e.g., chlorine minimization) can be a complex task. The problem is further complicated by seasonal (and other uncontrollable variations) changes in the effective chemical dosage. A fouling monitor (analogous to the pH electrode above) will permit the frequent evaluation of a dosing frequency, duration, and concentration. The costs for fouling monitors vary considerably depending on their level of sophistication and the accessories provided. However, the cost of the most expensive fouling monitor pales in relation to energy losses, downtime, and even chemical costs related to fouling processes.

Sidestream or *in situ* measurements?

Sidestream monitors are attractive for optimization studies, where flexibility in experimental design and accuracy are required, while risk to the operating unit is eliminated. In addition, using multiple sidestream test units provides a means for evaluating various control treatments simultaneously. Parallel testing of different treatments is important since the fouling characteristics of the source water may be constantly changing. Using the operating unit to develop treatment strategies only provides information on a single treatment during one period of time. Although simulating operating equipment in every detail with a sidestream test apparatus is virtually impossible, important parameters, i.e., water flow velocity, tube material, heat flux, can be matched to assure that a realistic *effective* treatment regime can be developed.

In situ monitoring of fouling and corrosion and evaluating failures caused by these processes in industrial water systems is difficult. Several factors contribute to this situation. First, collecting representative samples of water, deposits, and system materials is expensive and very time consuming. Typically, samples are rendered useless after lengthy delays or through decontamination actions. Second, portions of the systems suitable for visual inspection are quite limited. And third, post failure evaluations are often limited by the lack of trended fouling and/or corrosion data. In other words, without an indication of fouling or corrosion rates, tendencies, or potentials, it is difficult to determine whether a failure was caused primarily by recent operating conditions or pre-operational/outage conditions which existed years ago. Without the necessary information, monitoring results may, thus, be more theoretical than empirical and remedial action recommendations more reactive instead of proactive.

A means of monitoring the extent and progression of fouling within the NSPC service water system was recommended by CCE, Inc. as a necessary first step for controlling microbial corrosion. The following monitoring methods could be used: 1) on-line fouling monitors in the water system, 2) a small side-stream facility utilizing a fouling monitor.

The monitoring system ideally should accomplish the following: 1) monitor water quality in the water system and establish the basis for flushing frequencies and wet lay-up treatments, 2) provide a facility for testing the impact of proposed water treatment programs on various system components and water system materials, 3) determine biofouling/biocorrosion rates in the water system under stagnant, low, and high flow conditions, 4) monitor both short and long-term rates for general and localized pitting corrosion, 5) monitor corrosion in various valves and localized galvanic corrosion at welds, 6) provide for visual inspection and removal of samples for destructive analysis, 7) provide for expansion of sidestream facility to include additional fouling/corrosion testing equipment.

A sidestream facility dedicated to continual monitoring of fouling and corrosion tendencies is a necessity for mitigating the costly effects of fouling and corrosion. The investment in such a facility should be proportional to the value of the water system and will be remunerated many times over in production savings and extended system lifetime.

SUMMARY AND CONCLUSIONS

Microbial corrosion is the result of microbial activity occurring in the immediate vicinity of the metal surface. The fouling biofilm alters the microenvironment and, in so doing, influences corrosion rates in a variety of ways. Methods to analyze and evaluate the extent of corrosion attributable to the microorganisms are imperfect but are improving as the potential importance of microbial corrosion is substantiated.

Microbial corrosion can be controlled or minimized by controlling microbial activity at the metal surface. The choice of a method

for controlling fouling biofilm in a specific operating environment is based on overall cost which includes costs related to environmental control, corrosion losses, necessary plant modification, and even safety. The extent to which these factors influence fouling control varies with season, process operation, and other variables. Thus, process considerations are important which result in the appropriate choice of chemical concentration, duration of treatment, and frequency of treatment. Chlorine is the most commonly used chemical for controlling biofouling. However, other chemical treatments (e.g., bromine compounds) and mechanical treatments are beginning to prove very cost effective. The effectiveness of biocides depends on their ability to inactivate biofilm organisms and/or detach significant portions of the biofilm matter.

Effectiveness of biofouling control procedures vary with environmental and operating variables. Consequently, monitors are needed to provide feedback so that process adjustments can be made. More sensitive monitors are needed in some instances as well as instruments or analytical methods which assess deposit composition. In addition, a major need is a mathematical model for simulating the action of a biocide (or mechanical treatment) on a biofilm. The model will serve to distill the convoluted methods presently being used to assess "kill" efficiency into rational process parameters which can be easily interpreted in the context of the operating equipment. The model will also enable fouling monitors to provide feedback response to the treatment process. Models are needed urgently.

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

ACKNOWLEDGMENTS

The authors acknowledge the assistance of the following Nothern States Power Company personnel: Keith Peterson and Mike Kartz. In addition, the senior author gratefully acknowledges the support of the IPA Industrial Associates, the National Science Foundation (CBT-8714639 and INT 8701986), and Office of Naval Research (N00014-84-0309). The senior author gratefully acknowledges Dr. H.A. Videla for many helpful discussions on topics of microbial corrosion. The water quality analyses and the microbial enumerations were conducted at the Institute for Biological and Chemical Process Analysis, Montana State University under the direction of Paul Stoodley. Whonchee Lee electrochemically cleaned the pipe samples.

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Table 1. NSPC service water analyses. Samples were taken as the water enters the service water piping system (Influent) and as the water exits the piping system (Effluent). Results of chemical analysis are in units of g m^{-3} and results of microbiaological enumerations are in units of ml^{-1} unless otherwise noted.

	INFLUENT	EFFLUENT
Total Organic Carbon	6.52	6.58
Dissolved Organic Carbon	5.84	5.85
Particulate Organic Carbon	0.68	0.73
Total Kjeldahl Nitrogen	<1.00	<1.00
Nitrate+Nitrite N	ND	ND
Total Phosphorous	0.40	0.07
General Anaerobic Bacteria[1]	≥240.00	≥240.00
Sulfate-reducing Bacteria[1]	0.30	0.40
Pseudomonas aeruginosa[1]	93.00	460.00
Heterotrophic Plate Count	3.15×10^4	3.10×10^4
Total bacterial numbers[2]	1.03×10^6	1.16×10^6

[1]MPN technique
[2]epiflourescence method

LIST OF FIGURES

sulfate-reducing bacteria in a biofilm accumulated on a metal substratum (Hamilton, 1985).

Figure 7. Schematic diagram of the hypothetical interrelationship between heterotrophic anaerobes, sulfate-reducing bacteria, and methanogens in a biofilm (Parkes, 1987).

Figure 8. Photograph of two pipe sections from the same location in the NSPC service water system. One section has been cleaned by the electrochemical technique of Dahlberg and Zipp (1985). The black colored areas on the clean pipe surface indicate sulfide deposits. The area of sulfide deposition was proportional to the number of sulfate-reducing bacteria found in the deposits. The pipe is 3 in. ID and was in service 5 years.

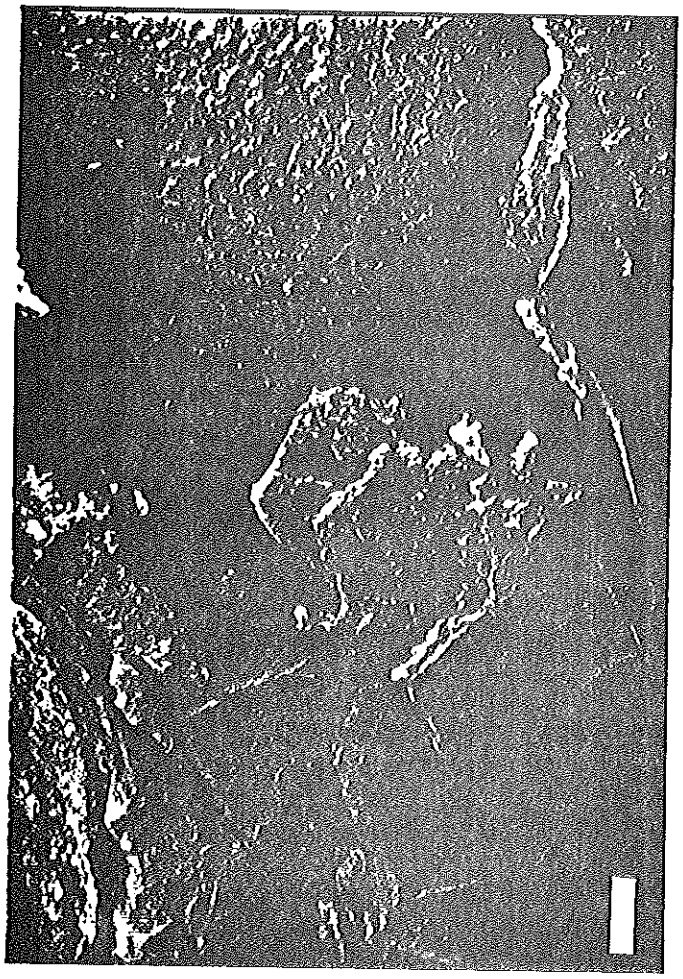
Figure 9. A microphotograph of an NSPC service water pipe surface after electrochemical cleaning indicates substantial pitting of the metal (bar = 10 mm).

Figure 10 Schematic diagram of anodic polarization of a passive alloy under varying conditions (Duquette, 1985).

Figure 11. The presence of hydrated oxide or hydroxide passivating films on metal surfaces provides bacteria with sites for film attachment (Kennedy et al., 1976).

Figure 12. Calculated free chlorine residual profile in a 14" ID pipeline in an emergency service water system within a nuclear power plant. The exponential decay of chlorine was determined from chlorine demand tests on intake water. The intial free chlorine concentration was 3.54 g m^{-3}. HR refers to heat exchange units.

1a



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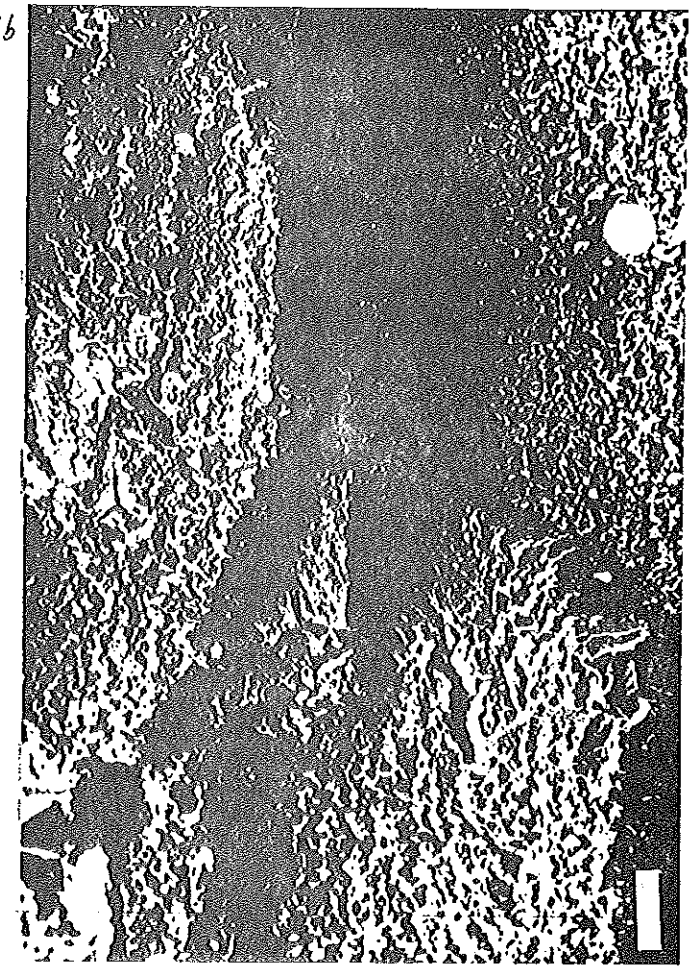

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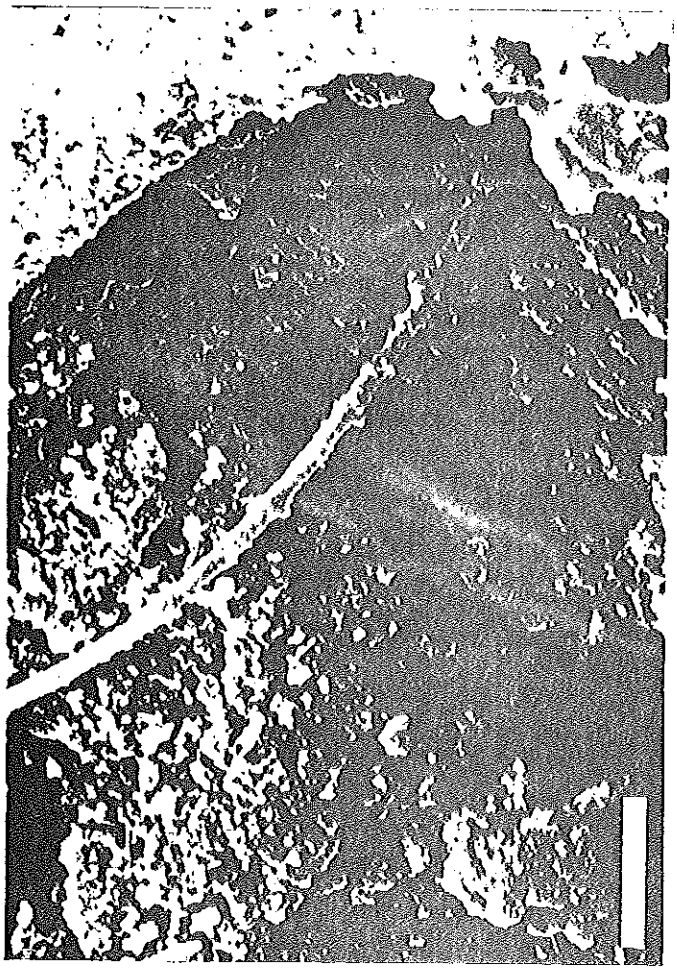

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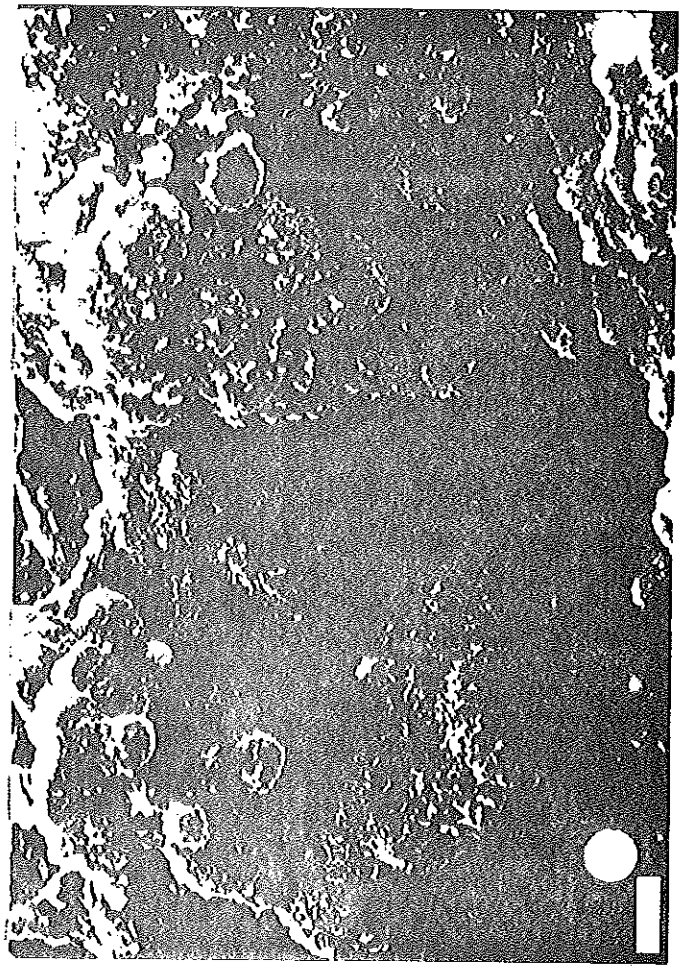
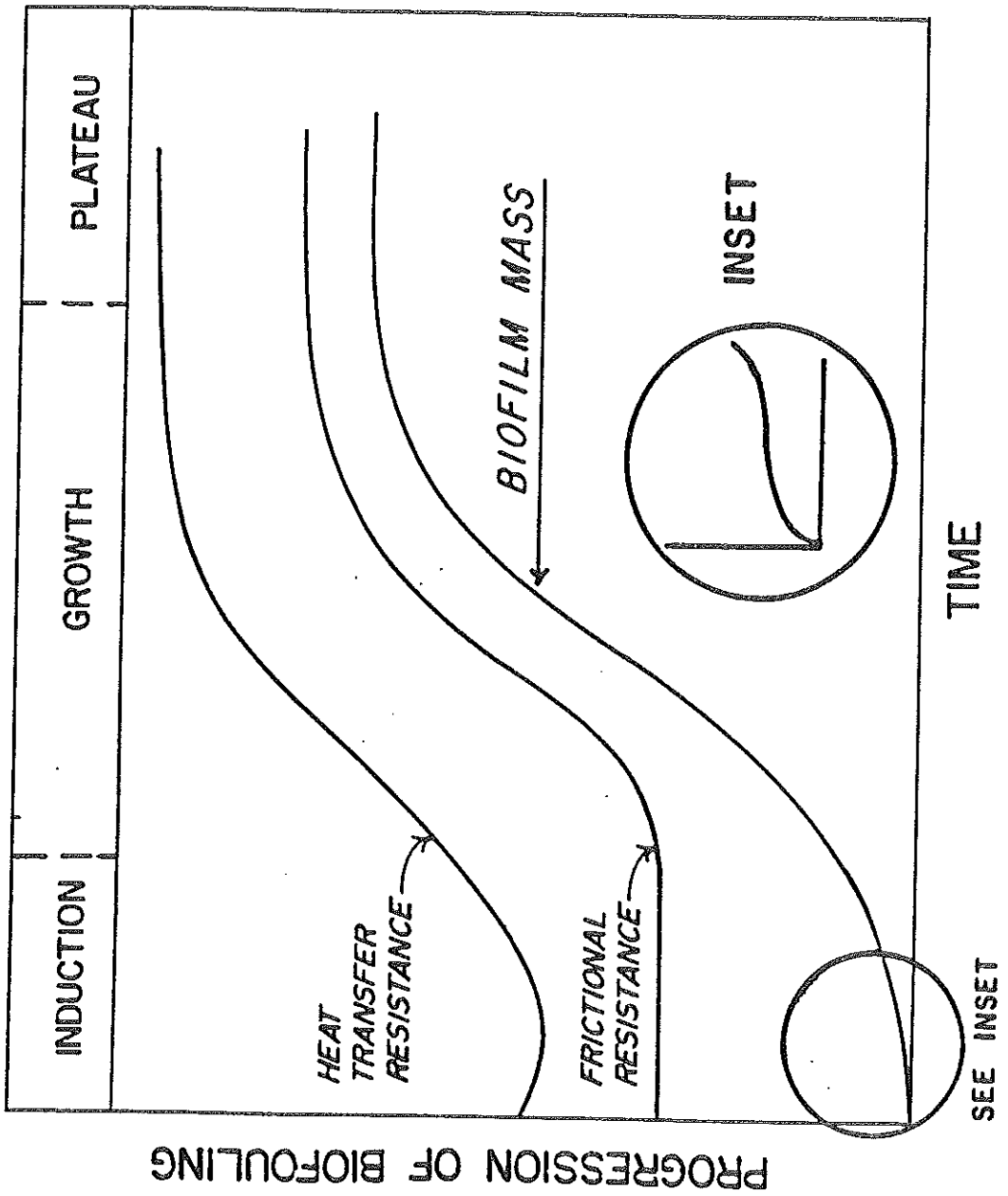
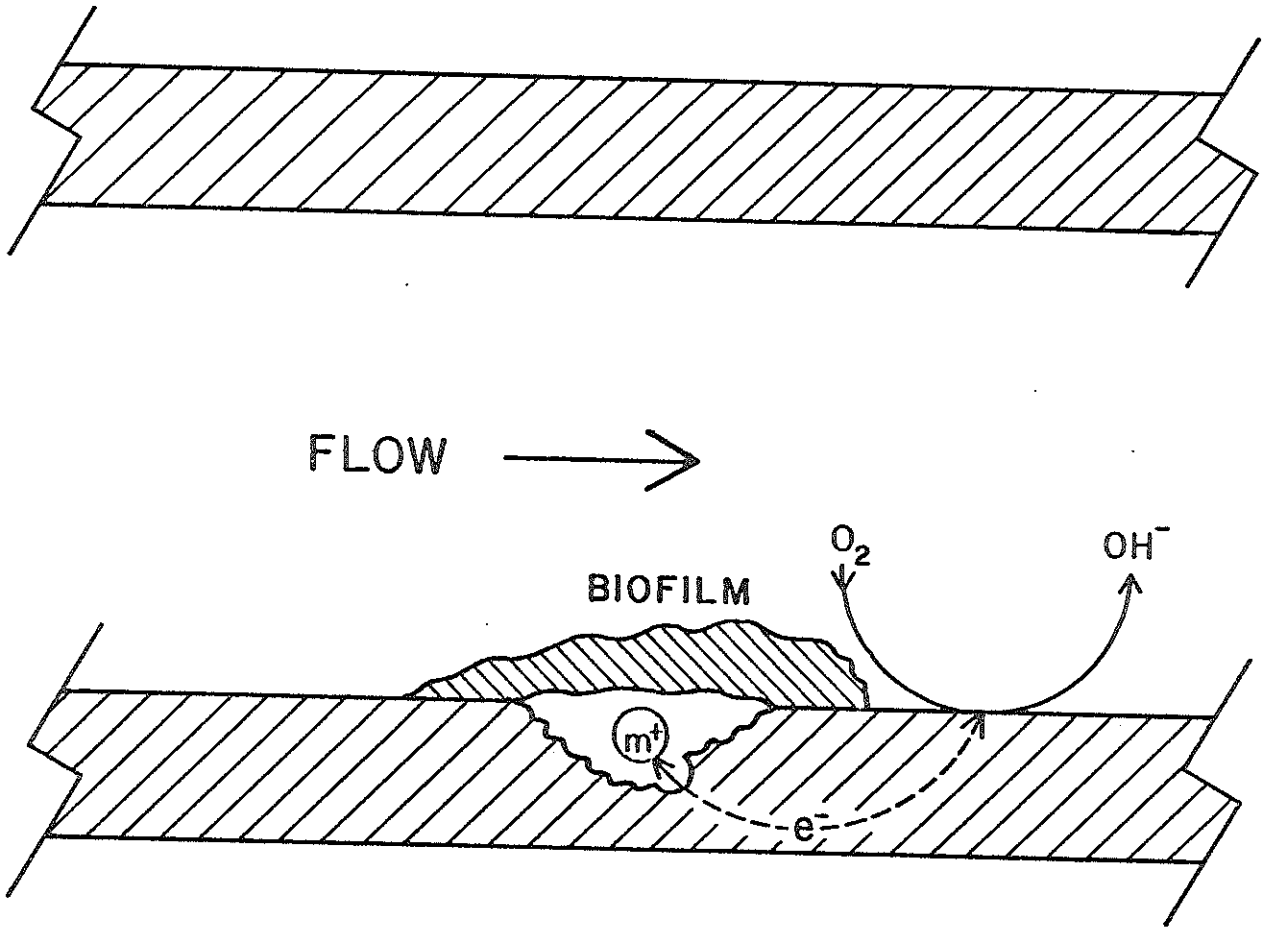
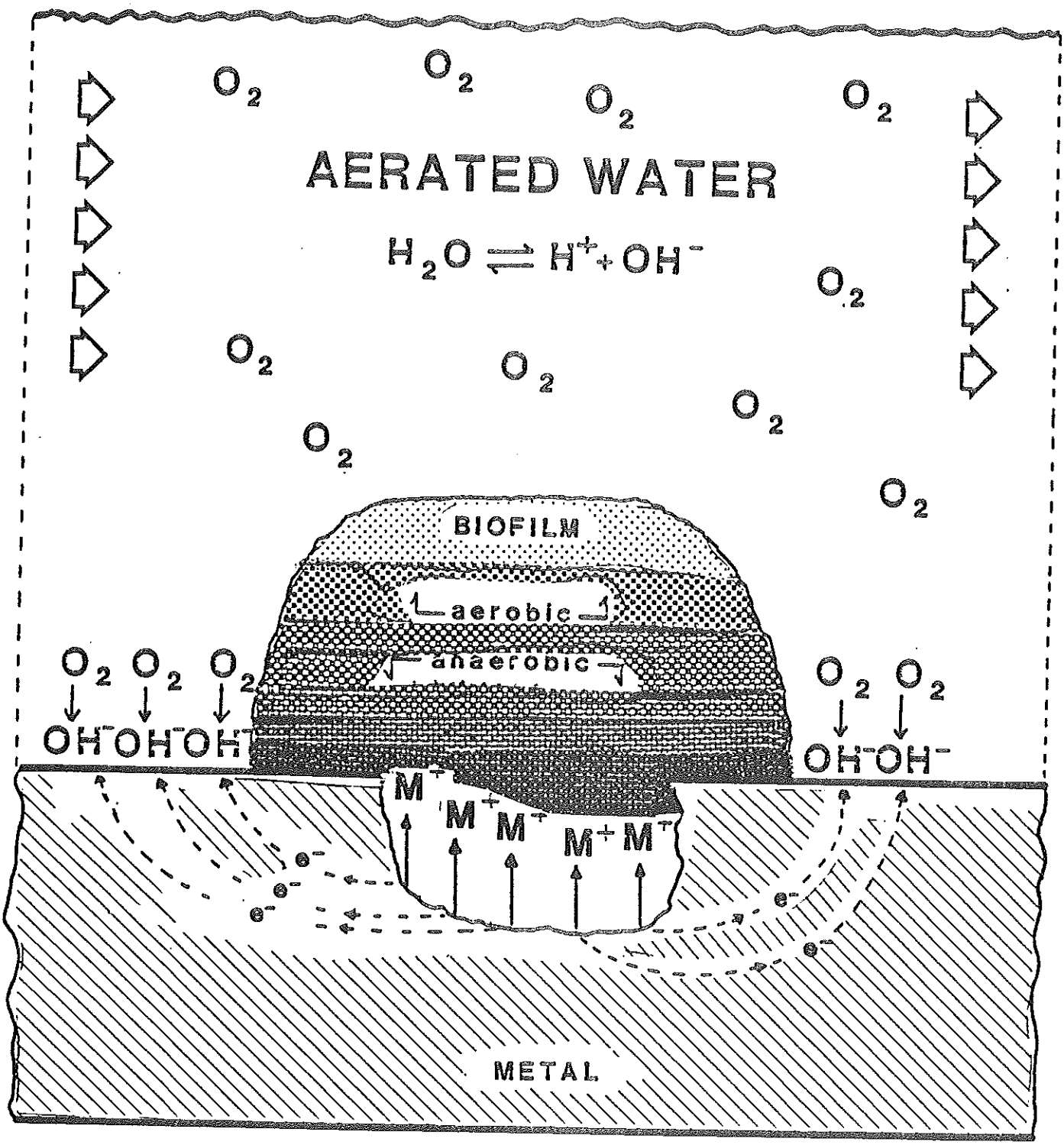
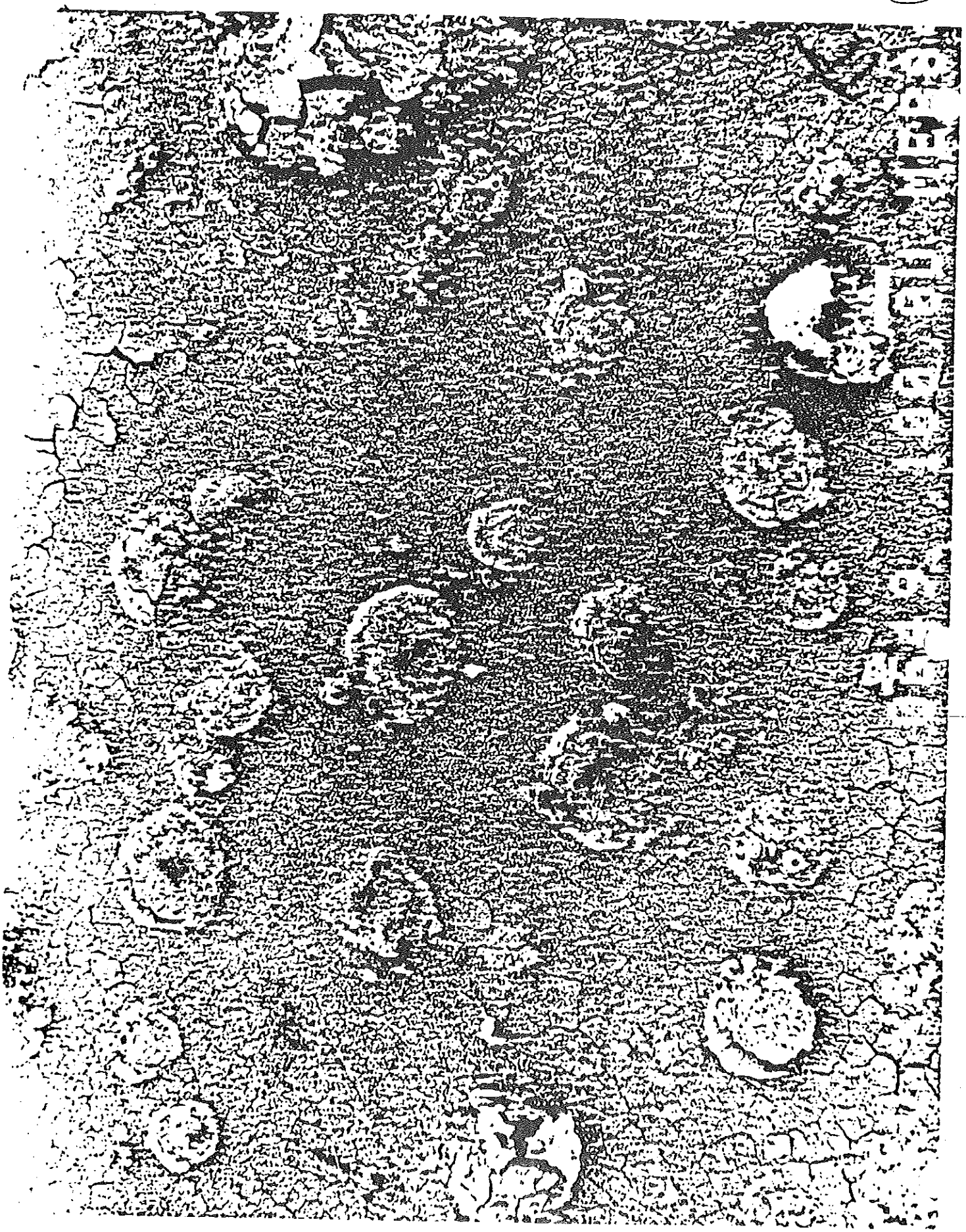



PROGRESSION OF BIOFOULING
INDUCTION
GROWTH
PLATEAU
HEAT TRANSFER RESISTANCE
FRICTIONAL RESISTANCE
BIOFILM MASS
INSET
TIME
SEE INSET

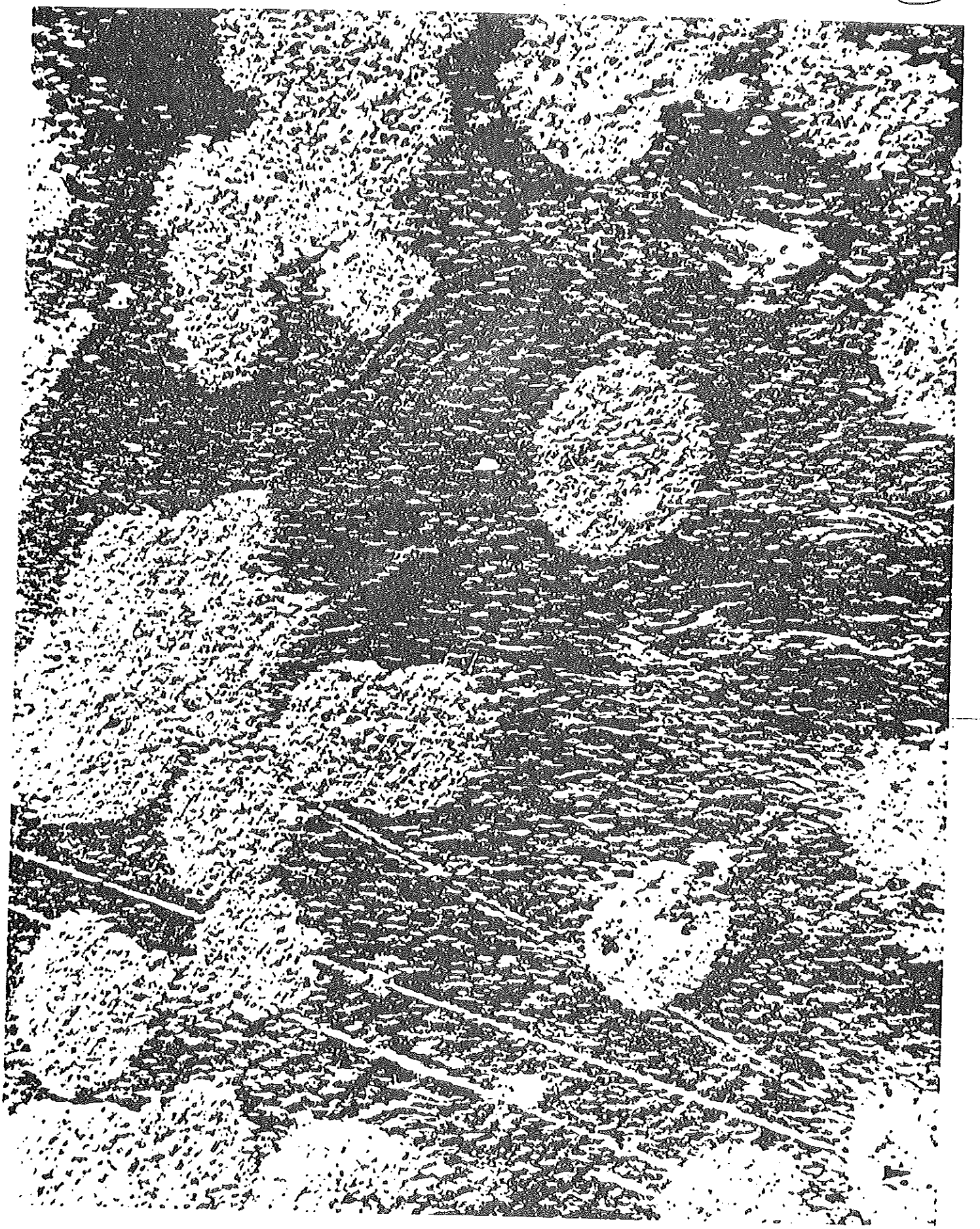
BIOFILM PATCHINESS




O2
O2
O2
O2
AERATED WATER
H2O ⇌ H+ + OH-
O2
O2
O2
O2
O2
O2
BIOFILM
aerobic
anaerobic
O2 O2 O2
OH- OH- OH-
O2 O2
OH- OH-
M+
M+
M+
M+
M+
e-
e-
e-
e-
e-
METAL



(4c)



MICROSCOPIC SYSTEM DESCRIPTION

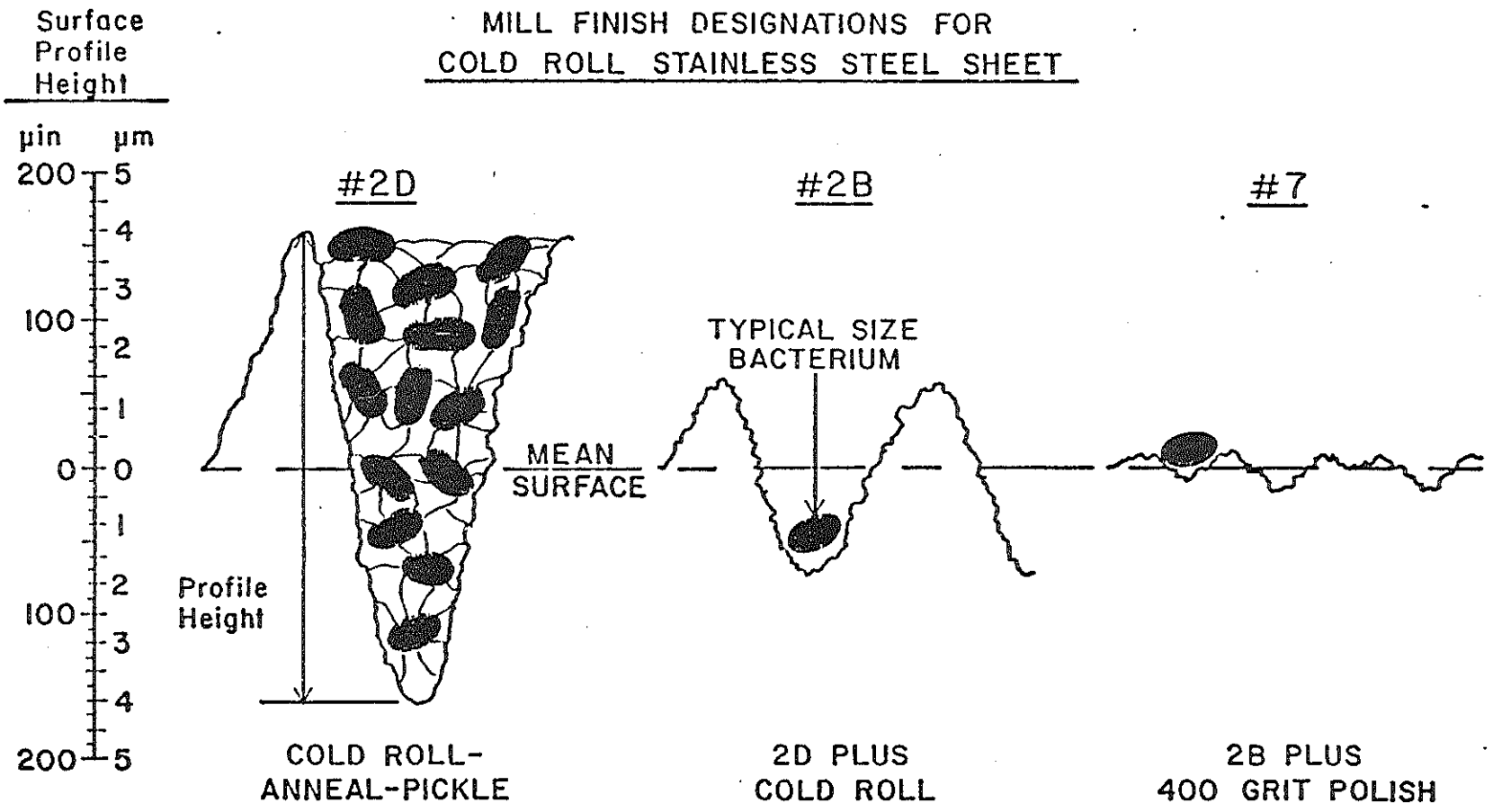
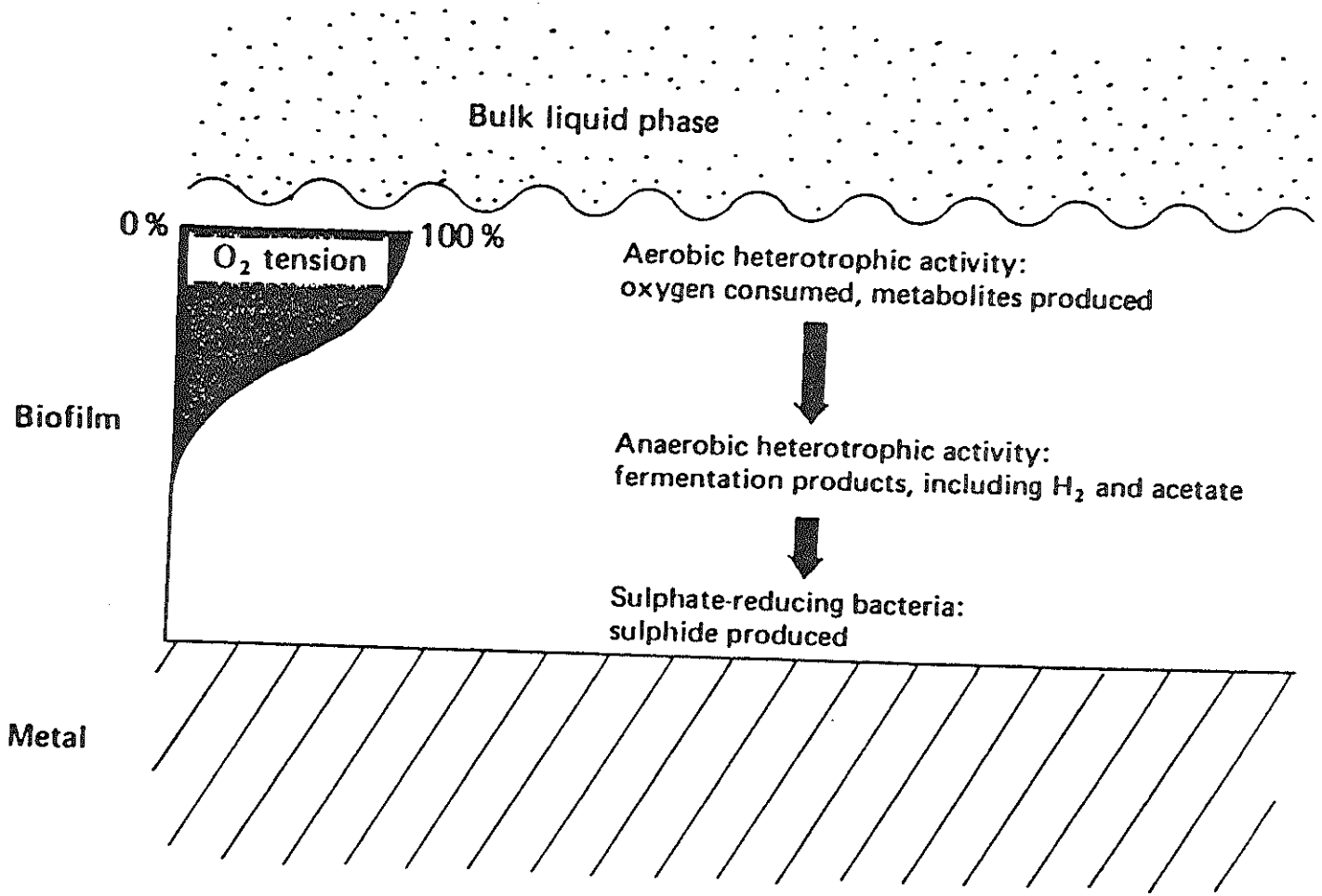
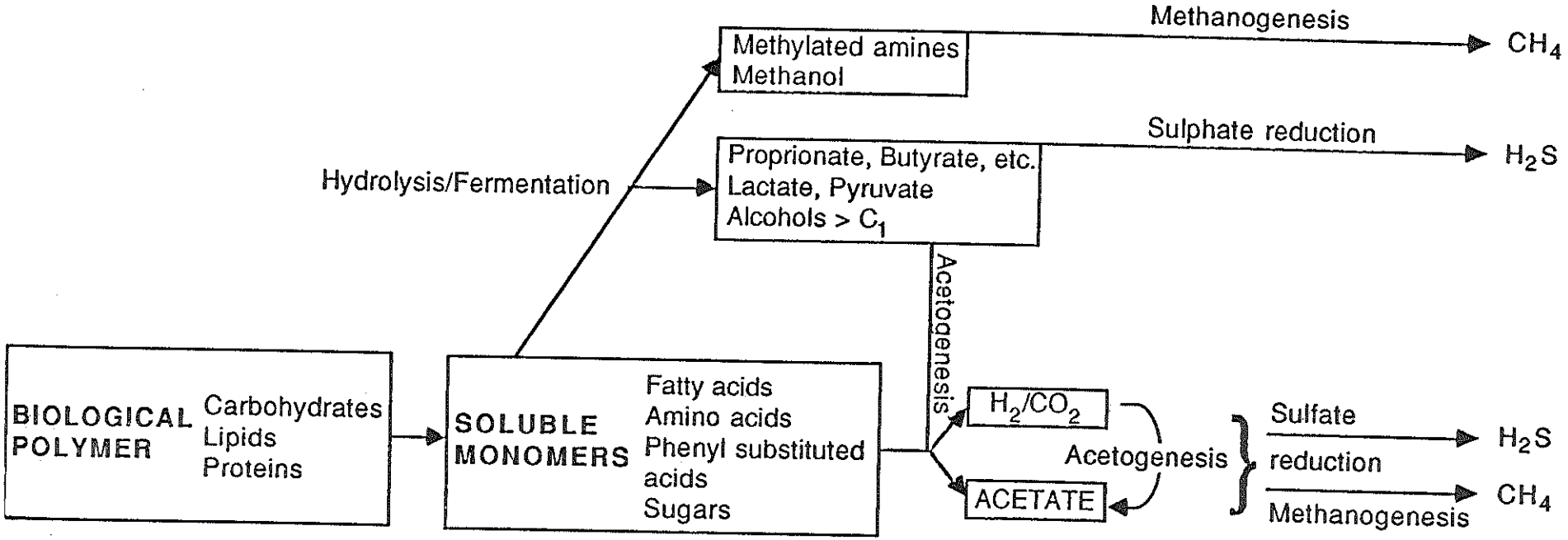
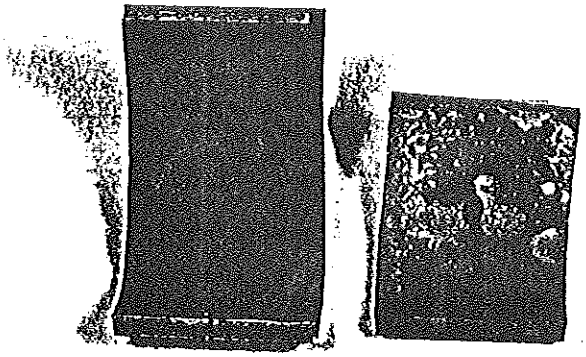


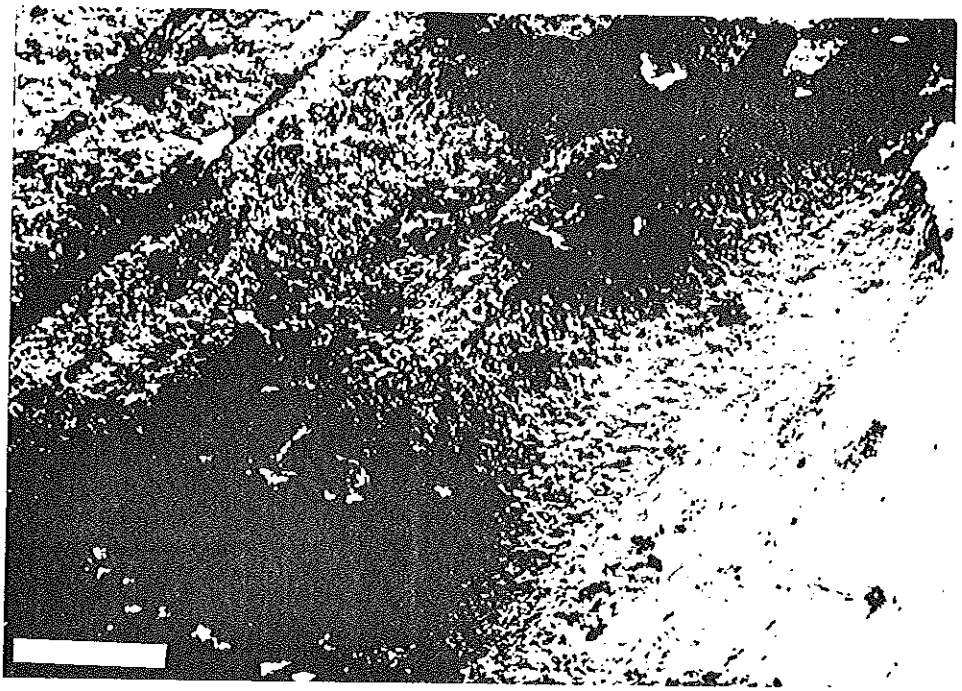
Figure 2. Relationship of bacteria surface roughness at the microscopic level.

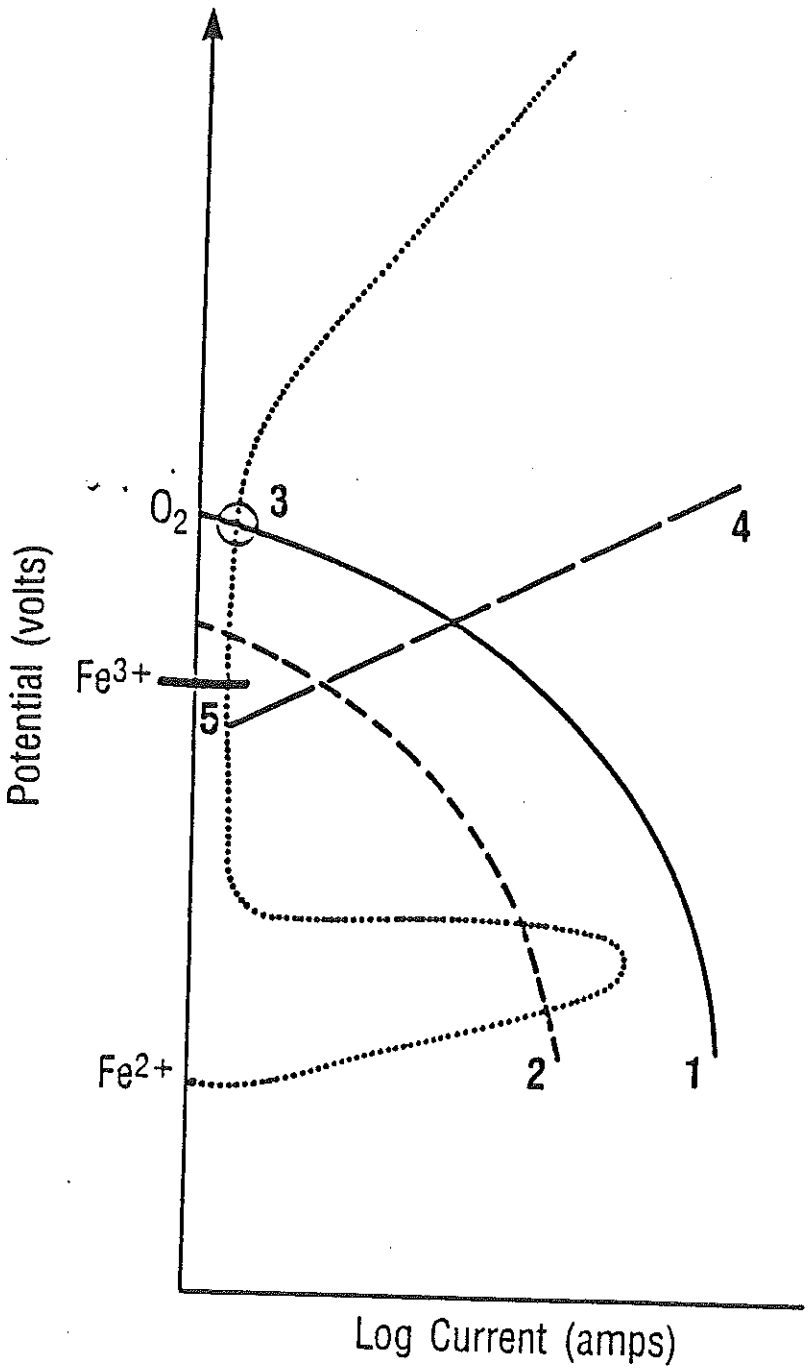

Bulk liquid phase
0%
100%
O_2 tension
Biofilm
Aerobic heterotrophic activity:
oxygen consumed, metabolites produced
Anaerobic heterotrophic activity:
fermentation products, including H_2 and acetate
Sulphate-reducing bacteria:
sulphide produced
Metal

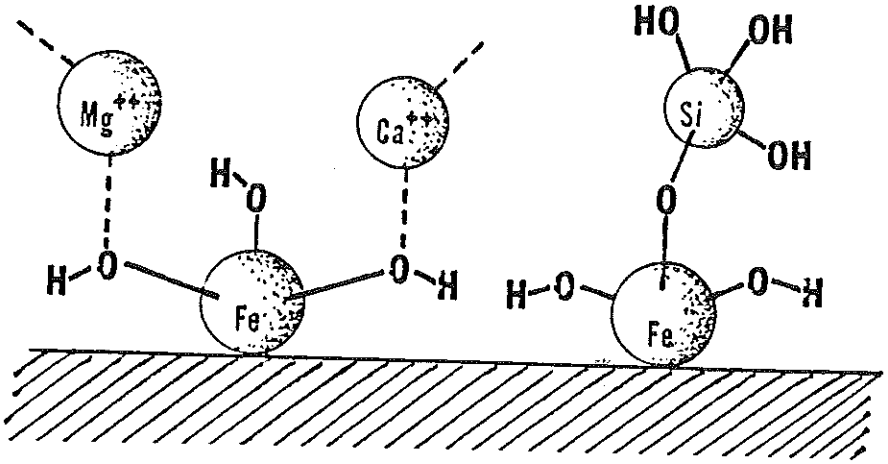

BIOLOGICAL POLYMER
Carbohydrates
Lipids
Proteins
SOLUBLE MONOMERS
Fatty acids
Amino acids
Phenyl substituted acids
Sugars
Hydrolysis/Fermentation
Methylated amines
Methanol
Proprionate, Butyrate, etc.
Lactate, Pyruvate
Alcohols > C_1
Acetogenesis
H_2/CO_2
ACETATE
Acetogenesis
Methanogenesis
CH_4
Sulphate reduction
H_2S
Sulfate reduction
H_2S
Methanogenesis
CH_4

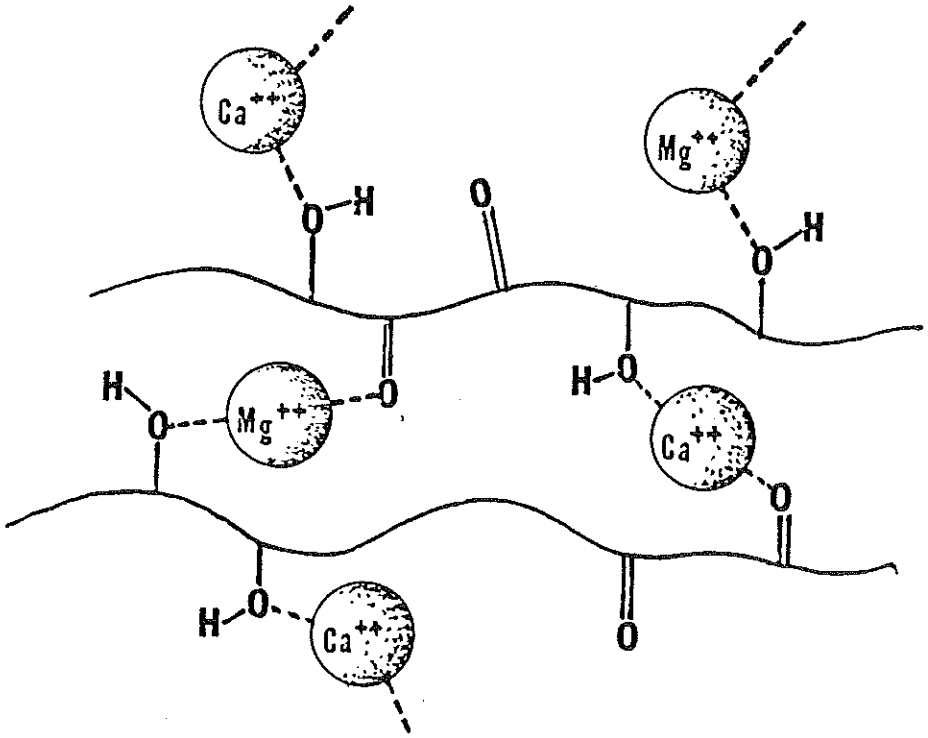


3A




Potential (volts)
O_2
3
4
Fe^{3+}
5
Fe^{2+}
2
1
Log Current (amps)


Mg++
Ca++
HO
OH
Si
OH
H
O
Fe
O
H
H
O
Fe
O
H


Ca++
O
H
O
Mg++
O
H
H
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Mg++
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Ca++
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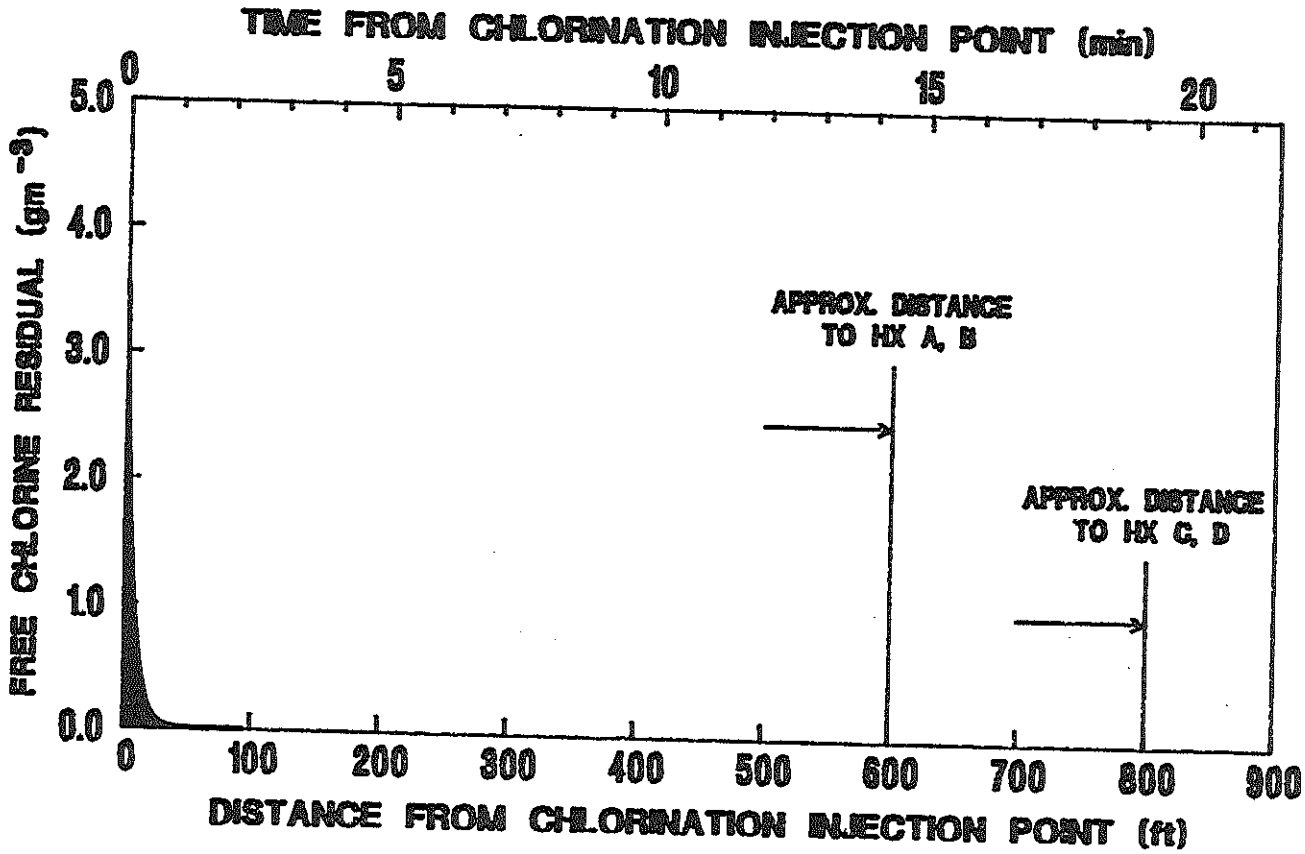
Ca++
O
O

PLANT A, Case History

FREE CHLORINE RESIDUAL PROFILE



CCE, INC.