

BIOFILMS AND THEIR EFFECT ON LOCAL CHEMISTRY

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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 microbially-induced corrosion is generally localized, the spatial distribution or patchiness of the microbial activity also affects the corrosion processes. The motivation and basis for monitoring and control of microbial corrosion will be discussed.

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 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 (Miller and Tiller, 1970; Obuekwe *et al.*, 1981) 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 (Kobrin, 1976). 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 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.

Microbial biofilms are the cause of substantially costly problems. Biofouling films in heat exchangers and condensers reduce heat transfer resulting in excessive energy losses (McCaughey *et al.*, 1987). Microbial corrosion associated with biofilms can also result in premature failure of condensers as illustrated by McCaughey *et al.* (1987). In service water systems, biofouling, combined with sedimentation and inorganic scaling deposits result in performance and safety problems. 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.

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 (Characklis, 1981): 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 overall result is a sigmoidal progression of events characterized by three identifiable periods (Figure 1): 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.

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 2). 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 3). 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 4), 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 (Cypionka et al., 1985).

Thus, 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. (1986) estimate that the pH can be as low as zero within an Acetobacter acetii colony. Lewandowski et al. (1988) 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.

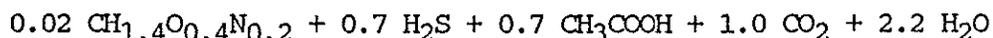
Metabolic processes within the biofilm significantly impact corrosion. It is traditional to discuss specific mechanisms for MC in terms of aerobic and anaerobic conditions and to further discuss selected mechanisms for specific microorganisms. However, microorganisms form synergistic communities that conduct combined processes that individual species cannot. For example, anaerobic and aerobic microorganisms coexist in naturally occurring biofilms in oxygenated environments (Figure 5). 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 (1987) and is diagrammatically presented in Figure 6. 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 (H₂S) from Desulfovibrio desulfuricans, acetic acid (CH₃COOH) from Clostridium acetium, and sulfuric acid (H₂SO₄) 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 (Burnes *et al.* (1967). Little *et al.* (1986) have demonstrated that isobutyric and isovaleric acids accelerated nickel corrosion in concentrations that are environmentally relevant. Gerchakov and Udey (1984) 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.* (1987) 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):



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 6.

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 (1934) 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.* (1968), using polarization techniques and weight loss measurements versus hydrogenase activity, have provided additional evidence to substantiate this theory. However, Iverson (1966) 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 (1970) have proposed cathodic "depolarization" induced by microbially-produced FeS . King *et al.* (1973) and Booth *et al.* (1968) 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 (1985) 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 (1980), 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:

| <u>time</u> (h) | <u>total sulfides</u> (M) | <u>pH</u> | <u>redox potential</u> (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.

The impact of oxygen on obligate anaerobic, sulfate-reducing bacteria was examined by Hardy and Bown (1984) 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 reeported laboratory tests with SRB may have been contaminated with oxygen.

Metal Oxidation by Bacteria

In recent years, the role of metal-oxidizing bacteria in MC has been emphasized. Ghiorse (1984) 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.

Further pit development is enhanced as an oxygen concentration cell develops. Duquette (1985) has summarized these developments on a schematic anodic polarization diagram for a passive metal or alloy (Figure 7). 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 $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple illustrated by line 5. Curve 3 demonstrates the effect of increasing chloride concentration, which lowers the pitting potential.

Ehrenberg (1836) 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 (1926) 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.

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 (Nunley and Kreig, 1968). 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.

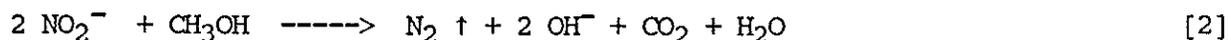
Metal-oxidizing organisms efficiently scavenge oxygen and, therefore, provide conditions for the growth of obligate, anaerobic bacteria. Numerous reports document the presence of sulfate-reducing bacteria in the tubercles formed by metal-oxidizing species (Tatnall, 1981; Postgate, 1979; Miller and Tiller, 1970).

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 (1970) 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 (1962) 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:



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 water. Note that the biodegradation 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 (Marszalek *et al.*, 1979; Zachary *et al.*, 1976). 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 (Daniels, 1980). Similarly, different inorganic ions produced at the two electrodic areas may affect adsorption (Corpe, 1970; Kaneko and Colwell, 1975). 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 8) provides bacteria with sites for film 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. 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.*, (1976) 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 (Characklis *et al.*, 1983). 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.

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 (Characklis *et al*, 1983). Therefore, water quality and pipe wall composition are at least two factors which influence the effectiveness of a treatment program to minimize fouling.

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 chlorine demand of the pipe may reduce the effectiveness of chlorine. 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 (Characklis *et al*, 1983).

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) analyses are generally not conducted. Although numerous inorganic anions and cations are frequently reported, those of biological interest (e.g., $\text{NH}_3\text{-N}$, PO_4^{3-}) are not.

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.

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 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.

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LIST OF FIGURES

- Figure 1. A typical progression for fouling deposition in a pipe. The inset describes initial events of adsorption. Three phases are distinguished for purposes of analyzing fouling progressions at power plant sites: the lag phase, the maximum or logarithmic accumulation phase, and the plateau or "steady state" phase.
- Figure 2. The physical presence 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. (a) 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 noncolonized areas. (b) Scanning electron micrograph show "patchy" colonization of mild steel by *Vibrio alginolyticus* in a simulated marine environment (Gaylarde and Videla, 1987). (c) When the metal is cleaned, intense pitting is noted where the bacterial colonies had accumulated (Gaylarde and Videla, 1987).
- Figure 4. When microroughness of the substratum is considered, corrosion currents may exist between the "peaks" and "valleys" of the roughness elements.
- Figure 5. A schematic diagram of the spatial relationship between aerobes, heterotrophic anaerobes and sulfate-reducing bacteria in a biofilm accumulated on a metal substratum (Hamilton, 1985).
- Figure 6. Schematic diagram of the hypothetical interrelationship between heterotrophic anaerobes, sulfate-reducing bacteria, and methanogens in a biofilm (Parkes, 1987).
- Figure 7. Schematic diagram of anodic polarization of a passive alloy under varying conditions (Duquette, 1985).
- Figure 8. The presence of hydrated oxide or hydroxide passivating films on metal surfaces provides bacteria with sites for film attachment (Kennedy et al., 1976).