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INTERACTIONS BETWEEN PROCESS WATERS, MICROBIAL BIOFILMS, AND METAL SUBSTRATA

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Abstract - Transport processes control the rate of virtually all corrosion processes including corrosion mediated by microorganisms. In addition, resolving microbial corrosion questions will require observations at different scales (micro-, meso-, and macroscale). Thus, relating observations at different scales (i.e., for purposes of scale up) requires delineation of the transport processes in the system.

INTRODUCTION

Microbial corrosion research has been increasing in intensity for some years. Most experimental observations have been concerned with microscopic phenomena at the cellular or molecular level. Microscale observations are necessary to formulate solutions to industrial or macroscale problems but do not necessarily lead to solutions at the macroscale. Are there important considerations in the progression from laboratory to industrial scale which are being ignored? Two issues are addressed in this paper: 1) the role of transport processes in microbial corrosion and 2) the need for observations at different scales for resolving microbial corrosion questions.

The biofilm system of concern consists of three compartments (Figure 1): 1) metal substratum, 2) biofilm, and 3) bulk water. Several phases can be present in each compartment. For example, biofilm consists largely (as much as 99%) of water (liquid phase) but contains microorganisms and other particulates ("solid" phases).

Certain "general" observations are reported in most biofilm systems as illustrated by biofilm accumulation. These observed quantities, however, reflect the contribution of several processes of more fundamental significance. For example, net accumulation of biofilm on a metal substratum (Characklis, 1990) results from the combination of the following processes: 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 is the "rate-limiting step." In the case 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 and its determination contributes significantly to 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 (Characklis, 1990).

Burrill (1981) has conducted an analogous process analysis describing abiotic metallic corrosion in an aqueous environment. For both biofilm and abiotic corrosion processes, one point is clear: *transport and/or interfacial transfer processes limit the rate of the observed process.*

SCALES OF OBSERVATION: A recirculating cooling tower system

A useful approach for conducting research which can contribute to solutions to industrial problems at the plant scale focuses on at least three scales of observation: 1) the microscale ($\leq 10^{-3}$ m) where cellular or molecular processes are generally examined by biologists and chemists, 2) the mesoscale (10^{-3} - 10 m) where fluid dynamics and geometry significantly influence the processes, and 3) the macroscale (> 10 m) where industrial system configuration (e.g., a recirculating cooling tower system) defines the system variables and parameters (Figure 2). Using a recirculating cooling tower as an example, which variables must be considered at these different scales of observation and how do they influence the corrosion process and the role of microorganisms in the process? These questions will be addressed but, obviously, unequivocal statements await more conclusive data.

Macroscale

The recirculating cooling tower system (RCTS) can be considered a continuous flow stirred tank reactor (CFSTR) at the macroscale (Figure 3). Consider a CFSTR with a volumetric flow rate Q containing all of the essential nutrients for microbial growth. The liquid volume of the reactor is V so the mean residence time in the reactor is θ (= V/Q). Initially, the reactor contains both biofilm cells and suspended cells ($\theta >> t_g$). The cells have a generation time of t_g. If θ = 10 h and t_g = 1 h, both biofilm and suspended cells will proliferate in the reactor with suspended daughter cells and cells detached from the biofilm being washed from the reactor by dilution. However if Q is increased to yield a θ = 10 minutes, the suspended cells will be completely washed out of the system before they can reproduce ($\theta << t_g$). The biofilm cells will proliferate because they no longer must share the nutrients with suspended cells and the nutrients are now entering the reactor at an increased rate.

Lee and Characklis (1990) has observed this phenomena experimentally with a sulfate-reducing bacterial population. At relatively high residence time, a very thin biofilm accumulated while at low residence time a thick biofilm accumulated:

residence time	max. generation time	biofilm thickness
25.0 h	1.7 h	5 μm
1.3 h	1.7 h	1000 μm

Thus, θ in the RCTS may significantly influence biofilm accumulation because of its influence on dilution and nutrient flux into the system. *Advective transport processes at the macroscale determine the bulk water quality in the RCTS.* Another important macroscale variable in the RCTS is cycles of concentration (CC = Q_M/Q_B) which is the ratio of make-up (Q_M) to blowdown (Q_B) flow rate. CC is the major determinant of recirculating water quality in the RCTS.

Mesoscale

At the mesoscale, the influence of fluid dynamics and geometry are evident in biofilm and corrosion processes. For example, a heat exchanger tube in the RCTS represents a cylindrical geometry and contains a turbulent flow.

Metal. At the mesoscale, the alloy is characterized by its average composition. Geometry at the mesoscale can significantly influence abiotic corrosion rate (e.g., erosion corrosion). Fluid dynamics in a specific geometry controls transport of oxygen to the metal surface and the rate of passivation during system start up. For example, corrosion of stainless steel in an aqueous environment is controlled by the rate of dissolved oxygen transfer to the passive layer-electrolyte interface.

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Microscale

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Biofilm. While bulk water quality is determined by the macroscale system dynamics, the concentration of various dissolved components at the bulk water-biofilm interface is determined by transport in the bulk liquid compartment which is determined by the turbulent intensity. At high transport rates, the concentration at the biofilm-bulk water interface is high and DO penetrates deep into the biofilm (Figure 4). At low transport rates, only a small fraction of the biofilm thickness is aerobic.

Microscale

Metal. At the microscale, the alloy structure includes inclusions or heterogeneities. Lee and Characklis (1990) report that localized corrosion processes on mild steel in sulfide-containing waters is initiated at inclusions in the alloy. Thus, heterogeneities in the metal may contribute significantly to observations of microbial corrosion. Mueller (1990) indicates that roughness of a polished copper surface increases from 0.015 μm to 0.15 μm as corrosion proceeds for 24 h in an aerobic aqueous environment. Thus, increase in roughness creates crevices and protected niches for microbial colonization. The roughness of new heat exchange tubes is on the order of 1-5 μm.

Biofilm. Microbial reactions within the biofilm are believed by many to be largely responsible for effect of microorganisms on corrosion and rightly so. For example, the stoichiometry for sulfate-reducing bacteria growing on lactate at 35 C has recently been determined by Okabe (1988) as follows:

$$
\begin{aligned}
&CH_3CHOHCOOH + 0.48\ H_2SO_4 + 0.02\ NH_3 \dashrightarrow \\
&0.09\ CH_{1.4}O_{0.4}N_{0.2} + 1.00\ CH_3COOH + 0.47\ H_2S + 1.09\ CO_2 + 0.80\ H_2O \qquad [1]
\end{aligned}
$$

Both carbon dioxide and hydrogen sulfide increase acidity in the biofilm (acetate production is counterbalanced by lactate consumption). However, the rate and extent of pH decline is related to substrate concentration and buffering capacity in the bulk water. Consider a uniform SRB biofilm, 30 μm thick, in a completely anaerobic water in which the stoichiometry is described by Eq. [1]. The pH at the metal-biofilm interface varies according to the bulk water lactate concentration and bulk water alkalinity (in this case, represented by bicarbonate alkalinity) as follows:

Lactate	HCO_3^-	pH
300 mg/L	100 mg/L	6.4
300 mg/L	10 mg/L	5.7
100 mg/L	15 mg/L	6.3
30 mg/L	100 mg/L	7.3
30 mg/L	10 mg/L	6.6

The simulation results indicate that acid production in the biofilm does not decrease the pH sufficiently to increase corrosion rate dramatically. Lee and Characklis (1990) have experimentally observed this system (at 100 mg/L and 15 mg/L alkalinity) and observed no significant corrosion over a three to four week period under the SRB biofilm. Lewandowski *et al.* (1989) have reported microsensor techniques to measure these gradients and have reported results from biofilms on metal surfaces.

In the case of a "patchy" biofilm, transport processes may be more important to microbial corrosion. Lewandowski *et al.* (this conference) indicate that a discrete colony causes an anode to be formed on the metal surface which initiates the corrosion processes by forming an oxygen concentration cell. Metal dissolves at the anodic site resulting in metal hydroxides and hydrogen ion.

Thus, the biofilm pH drops as a result of metal hydrolysis. The type of metal being hydrolyzed will influence the extent of pH decrease.

MODELLING

Simulation modelling is necessary for scaling up results from the micro- to macroscale. Modelling is necessary because of the complexity of the microbial corrosion system. Modelling has provided new insights of localized corrosion as recently illustrated by Watson and Postlethwaite (1990) and contributes profoundly to effective experimental design in the field and laboratory. A graduate classroom exercise (Drury *et al.*, 1990) used a biofilm simulation program to estimate the effect of SRB activity on corrosion failures in an operating oil field produced water pipeline. Using laboratory generated stoichiometric/kinetic coefficients and oil field data, the simulation presented a persuasive argument for microbial mediation in the corrosion failures (Figure 5). The results also revealed the location for an additional sampling point needed in the pipeline to conclusively attribute the failures to microorganisms.

SUMMARY

The increase or decrease in corrosion rate following microbial colonization is dependent on interactions between the metal, the biofilm, and the bulk water as observed at the macroscale, mesoscale, and microscale. One cell adsorbed to a metal substratum will influence the corrosion rate of the metal. Needless to say, the effect may not be measurable but surface properties have changed. In most cases, corrosion rate of the metal will be controlled by a transport process. The species of microorganism present may not necessarily be an important factor. Experimental design must carefully consider transport processes if extrapolation to the real system is to be successful.

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