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I. INTRODUCTION

Mild steel is commonly used in industrial water systems such as recirculating cooling water and water injection during oil production. Biofouling and biocorrosion are major concerns in those systems. Considerable attention has been devoted to the microbial corrosion of ferrous metals, and, in particular, the corrosion of mild steel by sulfate-reducing bacteria (SRB) has been the subject of investigation since 1934.[1]

Microbial corrosion usually results from the presence of biofilms at the metal surface. The biofilm system consists of three compartments: (1) the bulk liquid, (2) the biofilm, and (3) the substratum. Biofilms influence the corrosion processes by changing the local chemistry near the metal surface. The interfacial water chemistry between metal surface and biofilm is determined by (1) corrosion processes, (2) microbial activity and metabolic products, (3) mass transport processes within the system compartments, and (4) bulk water chemistry. As corrosion and biofilm accumulation are dynamic processes, the interfacial water chemistry changes with time. Thus, microbial corrosion is the net result of the interaction between various compartments which are in dynamic flux. To study microbial corrosion, both the conceptual models and experimental methodology must reflect and respond to these circumstances.

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Our approach to simulate microbial corrosion was to grow a biofilm containing SRB on a metal substratum either in a totally anaerobic system or in a system containing aerobic bulk liquid. The microbial activities were limited to the sessile biofilm cells by conducting experiments at a high dilution rate to wash out the planktonic cells. *In situ* electrochemical measurements (DC and AC methods), *in situ* microelectrode measurements (dissolved oxygen, pH, and dissolved sulfide), sulfide compounds analysis, and surface analysis were performed periodically on coupons introduced into the systems.

This chapter reviews several mechanisms proposed to account for the SRB-enhanced corrosion of mild steel. The rate-controlling step for SRB-enhanced corrosion is suggested.

II. PROPOSED MECHANISMS FOR SRB-ENHANCED CORROSION

Based on laboratory and field studies, four mechanisms for SRB-enhanced corrosion were suggested to explain the high corrosion rate observed in the field:

1. Hydrogenase mechanism
2. Iron sulfide mechanism
3. Hydrogenase + iron sulfide mechanism
4. Aerobic/anaerobic mechanism

Von Wolzogen Kühr and van der Klugt[1] proposed the cathodic depolarization theory for SRB-enhanced corrosion in a soil environment. They suggested that SRB could remove hydrogen from a cathodic area on the iron surface by the hydrogenase enzyme. This enhances the anodic dissolution of iron.

Miller and Tiller[2] have proposed cathodic depolarization induced by microbially produced FeS to be the major factor affecting corrosion. King et al.[3] and Booth et al.[4] demonstrated that weight losses of steel were proportional to the concentration of ferrous sulfide present and were dependent on the stoichiometry of the particular ferrous sulfides. They concluded that the accelerated corrosion of mild steel in the presence of SRB was due to formation of iron sulfide.

King and Miller[5] supported the hydrogenase theory, but proposed that cathodic depolarization occurred on the iron sulfide instead of the unreacted iron surface. The role of bacteria could be either to remove the accumulated hydrogen or to produce iron sulfide to depolarize the steel.

The importance of oxygen on the SRB-related corrosion of ferrous metal and alloys has been emphasized by several authors. Accelerated corrosion rates have been observed when iron, corroded in the presence of SRB, is exposed to intermittent aerobic/anaerobic conditions.[6] Hardy and Bown[7] showed a similar effect of aeration on mild steel. They observed that sulfide film formed in a batch reactor during growth was not uniform, but consisted of an adherent base layer and loose deposits of precipitated material at a few sites. Pitting corrosion occurred beneath these loose deposits during an aeration period subsequent to growth. However, the role of dissolved oxygen in SRB-related corrosion is not well understood.

III. SRB BIOFILM

Accumulation of biofilm in a totally anaerobic bulk liquid is linked to the activity of a number of facultative anaerobic and obligately anaerobic microorganisms (SRB), which reduce sulfate to sulfide. Usually the growth rates and biofilm accumulation are slower than that for aerobic (or denitrifying) biofilms.[8] However, if high concentrations of an organic electron donor and sulfate as the only electron acceptor are present, a thick (several millimeters) sulfate-reducing biofilm will usually develop within days or weeks if SRB are present in the bulk water. The activity of SRB in the biofilm is frequently expressed as the sulfate reduction rate or sulfide production rate. In systems with low sulfate concentrations, e.g., some freshwater systems, the concentration of sulfate can be limiting for the SRB activity within the biofilm. Nielsen[8] showed an example of sulfate limitation in a totally anaerobic biofilm growing at high lactate concentration in a continuous-flow biofilm reactor. Diffusion of sulfate into the biofilm was limiting for the activity at sulfate concentrations below 0.5 to 1.0 m*M*, depending on the biofilm thickness. Once the biofilm thickness exceeded the depth of sulfate penetration into the biofilm, the sulfate removal rate was unaffected by further biofilm accumulations. The specific biofilm activity (56 to 93 μmol SO_4 cm^{-3} h^{-1}) was very high in this study due to the presence of high concentrations of lactate, which are seldom characteristic of natural or industrial water systems. At lower concentrations of metabolizable electron donors, much lower specific activities are to be expected.

SRB can be active within anaerobic microniches or in an anaerobic bottom layer when the bulk water contains oxygen. Formation and maintenance of such microniches are explained by two factors: (1) the respiration of aerobic bacteria scavenges oxygen and favors growth conditions for SRB, and (2) H_2S produced by SRB is a reductant that reacts with oxygen. Thus, if once established, colonies of SRB can protect

themselves against oxygen. Depending on the physical conditions prevailing and the primary nutrients available, microbial consortia or biofilm may contain a wide range of aerobic, facultative, and anaerobic organisms, which together are capable of hydrolytic and fermentative metabolism of primary nutrient sources such as carbohydrate, protein, and other organic hydrocarbons. The initial activities of the aerobic and facultative species will tend to utilize the available oxygen at a rate faster than the diffusional rate from the bulk liquid into the biofilm with the result that the innermost parts of the consortium will become anaerobic. The sulfate-reducing activity in the anaerobic microenvironment is usually limited by availability of electron donors, but the actual activity is difficult to measure. Use of radiotracer added directly to an aerobic incubation may give some indication about the actual SRB activity,[9] but due to an internal reoxidation of the produced sulfide an underestimation can be expected.

IV. CORROSION OF MILD STEEL UNDER A TOTALLY ANAEROBIC BIOFILM

Effects of SRB on the corrosion of iron or steel have been extensively studied for at least 50 years. Most experiments were conducted in batch, semicontinuous, and continuous (chemostat) reactors containing planktonic populations. SRB biofilm development on steel surfaces and their subsequent influence on corrosion in totally anaerobic systems have only been reported recently.[10,11] The difference between a biofilm reactor and chemostat or batch reactor is that sessile SRB dominate the overall SRB activities in a biofilm reactor while planktonic SRB dominate the overall SRB activities in a chemostat or batch reactor. This section will focus on the influence of system variables — which include (1) effect of SRB activities within biofilms and (2) effect of suspended ferrous sulfide — on corrosion of mild steel in a totally anaerobic biofilm system.

A. Effect of SRB Activities within the Biofilms on Corrosion

Accelerating corrosion of steel by SRB can be attributed either directly to removal of hydrogen or indirectly to the formation of iron sulfides and dissolved sulfides. If the hydrogenase mechanism is the rate-controlling step in the overall corrosion processes, then the sessile (or biofilm) SRB should play a more significant role in determining corrosion rate than the planktonic SRB due to a decrease in diffusional distance from the metal surface. Moosavi et al.[12] have found that, based on field studies, only an indirect correlation exists between SRB activity and corrosion rate, and that the mechanisms of corrosion relate more closely

to the chemical and physical nature of the corrosion products in the seabed close to an offshore platform. A radiorespirometric assay has been used to determine *in situ* SRB activity within the biofilm in those studies which only give qualitative information about SRB activities due to the limitation in simulating the real environmental conditions. McKenzie and Hamilton[13] further identified that sulfate limitation and the production of both acid-volatile and non-acid-volatile sulfides as key factors which must be incorporated into the [^{35}S]-sulfate reduction assay. Lee and Characklis[14] have demonstrated in a laboratory study that there is no correlation between biofilm (or sessile) SRB activity and corrosion rate in an iron-free medium. The biofilm SRB activity, e.g., sulfate removal rate, was controlled by the lactate loading rate. They also demonstrated that the growth rate of SRB within a biofilm was limited by nutrient transport and that the active SRB were located in the uppermost part of the biofilm. There was no detectable difference in either weight loss or electrochemical measurements of corrosion as total SRB activity increased from 21.6 to 338 mg/h during a 3-week experiment. The nature and extent of corrosion were closely related to the physical forms of iron sulfide but not to SRB activity.

B. Effect of Suspended Ferrous Sulfide

The effect of ferrous sulfide concentration on corrosion of mild steel in a suspended culture has been reported by several authors. Based on a semicontinuous culture experiment, Booth et al.[15] reported that the presence of sufficient ferrous ions in the medium to precipitate the biogenic sulfide and inhibit protective film formation led to a great increase in corrosion rate. Mara and Williams,[16] using a chemostat, established that an adherent film of sulfide on the steel surface was observed when the low corrosion rate was proportional to the bacterial growth rate in a low iron medium. After the film ruptured, the rate of corrosion was very high and independent of bacterial growth rate. Film breakdown was attributed to compressive stress established at the film-metal interface subsequent to the sulfidation of the primary corrosion product mackinawite, FeS_{1-x}, to greigite, Fe_3S_4. There was no evidence of protective film formation, and a high rate of corrosion was observed in high iron medium.

The effects of suspended ferrous sulfide on the corrosion of steel in an anaerobic biofilm reactor were studied by Lee and Characklis.[14] The biofilm was developed on steel coupons in iron-free medium, followed by weekly step increases in ferrous ion to 1, 10, and 60 mg/l in the influent. Precipitation of ferrous sulfide ($Fe^{2+} + HS^- \rightarrow FeS + H^+$) took place mainly in the liquid phase. The total dissolved sulfide concentration decreased from 50 to 40 mg/l as ferrous ion concentration in

the influent increased from 1 to 10 mg/l. Very little corrosion occurred at this time, but accumulation of iron sulfide particles increased in the biofilm. However, iron-rich medium (60 mg/l) resulted in the precipitation of all the biogenic sulfide. The iron sulfide in the biofilm contacted the steel surface and the corrosion rate increased dramatically. There was no continuous and uniform protective coating of iron sulfide film formed under the biofilm, and intergranular attack was observed over the entire metal surface.

Further evidence regarding the influence of the morphology of the iron sulfide scale in a biofilm system is provided by the work of Moosavi et al.[12] They observed a clearly defined layering of corrosion products on mild steel coupons recovered from the seabed close to an offshore platform after 1 to 2 years of exposure. Next to the steel surface there was a thin black adherent layer; superimposed on this was a looser bulky black deposit, surmounted by a brown oxide layer. There was evidence of enhanced corrosion associated with break-up of this adherent film.

From the above discussion, it can be concluded that (1) the formation of adherent iron sulfide film is ferrous ion-concentration dependent and (2) the rate of corrosion is determined by the physical nature of sulfides.

V. CORROSION OF MILD STEEL UNDER AEROBIC/ ANAEROBIC BIOFILM

McKenzie and Hamilton[13] have proposed that environmental factors, most notably oxygenation, are central to determining the rate and extent of SRB-related corrosion. They established that high rates of corrosion associated with deep pitting were observed in the aerobic zone as compared to that in the anaerobic zone of a column reactor, and that corrosion products in the aerobic zone contained a higher percentage of non-acid-volatile sulfides (elemental sulfur and/or pyrite) than that in the anaerobic zone.

The initial corrosion processes of mild steel under an aerobic/anaerobic biofilm have been studied by Lee et al.[15] They demonstrated that SRB can proliferate in a biofilm even when oxygen penetrated the entire biofilm at some locations. Sulfate was not the limiting factor for SRB growth within the biofilms. The role oxygen plays in SRB-related corrosion is through the formation of different iron sulfide compounds which are corrosive toward mild steel.[10,11] In general, abiotic oxidative processes are much more rapid than biotic respiration during the early stage of biofilm accumulation. Aerobic-dominated corrosion and the corrosion rate decreased with time. SRB-enhanced corrosion occurred after the SRB had further developed and a significant amount of iron sulfide

had contacted the metal. In addition to the acid-volatile sulfides (mackinawite or greigite), elemental sulfur and pyrite were also detected within the corrosion deposits. Deep pits were observed within a crevice corrosion area caused by sulfide attack. Deep pitting was attributed to a large cathode-anode ratio. The corrosion rate increased from 8 to 160 mpy as the pool of Fe–S compounds (mackinawite, pyrite, elemental sulfur) increased from 12 to 600 μg S cm^{-2}.[10,11]

VI. SUMMARY

From the various mechanisms dealing with SRB-related corrosion, it appears that corrosion caused by SRB activity is highly dependent on the structures and compositions of the corrosion deposits. Key elements in this mechanism appear to be the elemental sulfur and sulfide compounds and their location within corrosion deposits. This reinforces the importance of galvanic theory to SRB-related corrosion. Under totally anaerobic conditions, the corrosion rate of mild steel is not controlled directly by the SRB activities, but indirectly through iron sulfide formation. The corrosion rate followed first-order kinetics with respect to suspended ferrous sulfide concentration.[3,17] McNeil and Little[18] showed that mackinawite is the major corrosion product when iron alloys are corroded by SRB under totally anaerobic conditions. However, elemental sulfur and pyrite were detected in addition to mackinawite in oxic/anoxic conditions.[10,11] The effect of dissolved oxygen on SRB-related corrosion can be attributed to the formation of corrosive sulfides and/or elemental sulfur. It is difficult to determine which iron sulfide is more corrosive to mild steel, but a relationship between corrosion rate and areal sulfide concentration clearly exists.

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