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ROLE OF SULFATE-REDUCING BACTERIA IN CORROSION OF MILD STEEL: A REVIEW

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This paper is dedicated to the memory of William G Characklis.

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The influence of sulfate-reducing bacteria on corrosion of mild steel is reviewed, with special emphasis on the effects of biofilm structure and function, medium composition (dissolved oxygen and ferrous ion concentrations) and the physical and chemical properties of iron sulfides. A summary of different corrosion mechanisms is critically discussed, based on electrochemical and rate process analyses. A mechanism is proposed which explains the high corrosion rates observed in the field.

KEYWORDS: sulfate-reducing bacteria, SRB, corrosion, mild steel, biofilm, oxygen, iron sulfides

INTRODUCTION

The mechanisms of chemical and biological processes contributing to the degradation of mild steel immersed in natural waters are adequately described only under simplified laboratory conditions. Sulfate-reducing bacteria (SRB)-related corrosion in industrial water systems, which is of vital importance to many industries, is much less comprehensively understood. The majority of review papers describing the influence of SRB on corrosion are limited to consideration of planktonic organisms (Miller & Tiller, 1970; Miller, 1981; Gragnolino & Tuovinen, 1984; Tiller, 1985; Hamilton, 1985; Ringas & Robinson, 1987; Pankhania, 1988; Edyvean & Videla, 1991) and experiments have been conducted in batch, semi-continuous, and continuous (chemostat) reactors (Booth & Tiller, 1960; 1962a; 1962b; Booth *et al.*, 1964; 1968; Mara & Williams, 1972a; King *et al.*, 1973; Costello, 1974; King *et al.*,1976; Hardy & Bown, 1984; Gaylarde & Videla, 1987; Weimer & Ng, 1988; Weimer *et al.*, 1988; Pedersen & Hermansson, 1991). The influence of sessile SRB on corrosion has only been appreciated recently (Sanders & Hamilton, 1985; Hamilton & Maxwell, 1985; Maxwell & Hamilton, 1985; Maxwell, 1986; Kochelek & Stone, 1989). It has been well documented, for example, that accumulation of mixed population biofilms containing SRB in industrial water systems causes corrosion (Tiller, 1985; Hamilton, 1985; Pankhania, 1988). Field observations are influenced by a variety of environmental factors which obstruct the study of corrosion mechanisms. Consequently, there is a need to bridge the gap between mechanisms derived from studies in the laboratory, and the reality

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of field observations. This can be accomplished by careful examination of factors which are relevant to the over-all corrosion process. Process analysis is therefore indispensable prior to designing laboratory experiments.

SRB-related corrosion occurs through a combination of microbial and chemical factors (McKenzie & Hamilton, 1992; Lee & Characklis, 1993; Lee *et al.*, 1993a; 1993b; Nielsen *et al.*, 1993). The presence of many chemical compounds such as reduced ferrous sulfides, sulfur, pyrite, ferrous/ferric hydrates, and dissolved oxygen in the bulk liquid and in the fouling deposits are known to influence the SRB-related corrosion processes. The combined action of microbial metabolites and chemical compounds dissolved in the bulk liquid and precipitated in the fouling deposits on metal surfaces is complex. Consequently, it is not a single mechanism but a variety of different mechanisms which contribute to the deterioration of mild steel in industrial water systems.

This review focuses on experimental systems simulating environmental conditions associated with SRB-related corrosion of mild steel surfaces. Process analysis involves the following steps: (1) defining the system, (2) identifying the contributing processes, and (3) evaluating the rate-controlling step. The latter is used to integrate the electrochemical, chemical, physical, and microbiological factors contributing to corrosion of mild steel. The objective is to identify the rate-limiting or rate-controlling steps in the overall corrosion process under different environmental conditions. Critical analyses of experimental results described in the literature, and of experiments conducted by the authors of this review, are used to achieve this objective.

The System

SRB-related corrosion is invariably associated with biofilm formation at the metal surface. Local anaerobic conditions favoring the growth of SRB can readily arise under mixed microbial growth in industrial water systems, such as open recirculating cooling water (Thierry, 1987; Tantall, 1981), heat exchangers cooled by river water (Tantall, 1981; Pope *et al.*, 1982), paper mill closed water (Thierry, 1987), or waste water treatment (Thierry, 1987). By far the greatest number of recorded instances of corrosion problems caused by SRB, however, have been in oil field water flood systems (Galbraith *et al.*, 1985; Dewar, 1986; Stott *et al.*, 1988).

To simplify the analysis, the systems undergoing microbial corrosion can be categorized as follows: (1) gas, (2) bulk liquid, (3) fouling deposits, and (4) substratum (Fig. 1). The interactions between these compartments occur via interfacial transport processes. Interfacial transport between gas and bulk liquid, and between bulk liquid and deposit occur primarily by convection and molecular diffusion of dissolved and/or particulate components (Characklis, 1990). Transport between fouling deposits and substratum occurs primarily by molecular diffusion of dissolved components, and by volumetric replacement of particulate components (Characklis, 1990). Interfacial transport processes have significant impact on microbial transformation and electrochemical corrosion processes.

Process Analysis

Microbial corrosion may be considered as the net result of the following processes: (1) Transport and accumulation of materials from the bulk liquid to the metal surface. Materials can be soluble (microbial nutrients and corrosive chemicals) or particulate (viable microorganisms or inorganic particles). (2) Microbial and electrochemical transformation processes within the biofilm and at the metal surface. The extracellular

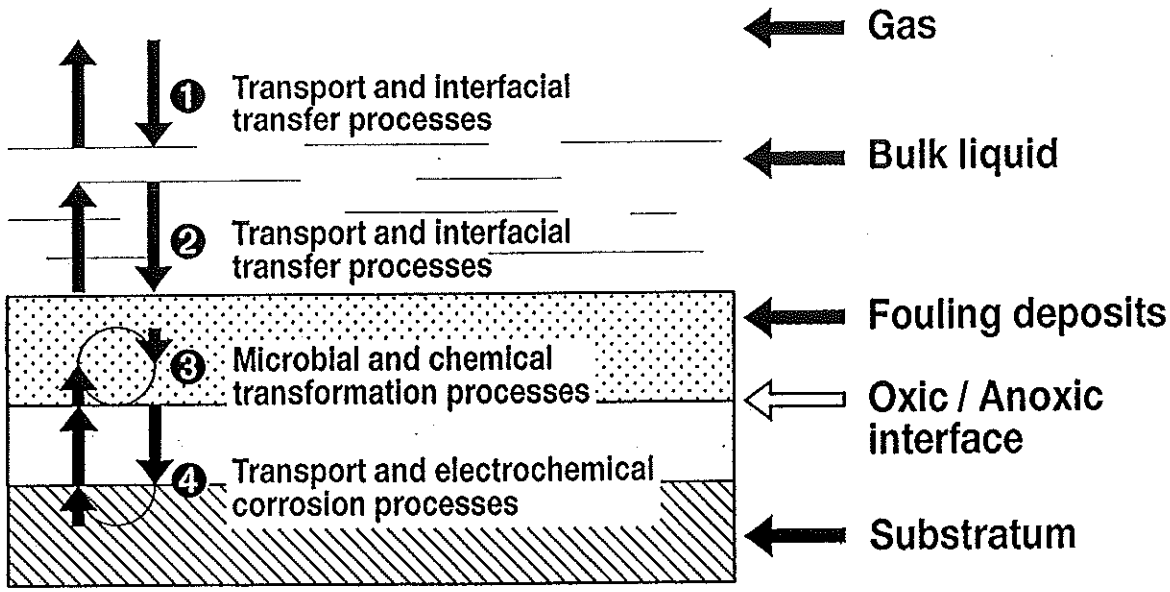

Fig. 1 The microbial corrosion system: interaction between the various compartments.

polymers excreted by the microorganisms contribute to the biofilm deposit and promote adherence of corrosion products. Microbial transformation processes influence the corrosivity of the microenvironment at the biofilm-metal interface. Abiotic corrosion processes influence the rate, extent, and distribution of colonizing microbial species, as well as the chemical composition and physical properties of the resulting biofilm (Characklis, 1990). (3) Erosion and detachment from the surface of the film. These processes limit the overall extent of fouling deposit accumulation.

Depending upon the water chemistry and fluid dynamics of the system under study, different types of biofilms develop and this, in turn, affects the corrosion rate and probably also the corrosion mechanism. The ecological structure of biofilm communities may be extremely heterogeneous and their composition can show substantial variation depending on environmental parameters. The following biofilm systems are considered here: (1) a totally aerobic biofilm, where oxygen is present in the bulk liquid and also penetrates through the entire biofilm; (2) a totally anaerobic biofilm, where oxygen is absent from both bulk liquid and biofilm; (3) an aerobic/anaerobic biofilm, where oxygen is present in the bulk liquid and where anaerobic microniches and/or an anaerobic layer exists in the biofilm.

Processes contributing to corrosion of mild steel in abiotic systems, and corrosion of mild steel in biotic systems will be analyzed and compared.

Aerobic Processes

1. Corrosion of mild steel in an abiotic, oxic bulk liquid

At ambient temperatures in neutral or near-neutral oxic bulk liquid, corrosion of mild steel is driven by dissolved oxygen, DO (Uhlig, 1971). At anodic areas the following reaction takes place:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{1}$$

Corrosion rate is independent of pH within the range of pH 4 to 10. Electrons reduce oxygen at the cathodic regions:

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \quad (2)$$

The presence of strong electrolytes influences positively the corrosion rate. In waters of low conductivity the anodic and cathodic sites are located in close proximity to each other. Consequently, OH^- ions formed at cathodic sites are always in the proximity of Fe^{2+} ions forming at anodic sites. This results in the formation of a compact film of $Fe(OH)_2$ tightly adherent to the steel surface. Such a film provides an effective diffusion barrier to DO penetration. In dilute NaCl solutions of high electrical conductivity, on the other hand, the anodic sites and cathodic sites are further apart. In such cases, OH^- ions do not react immediately with Fe^{2+}. Instead, these ions diffuse into the solution bulk phase and react with Fe^{2+} away from the steel surface forming porous deposits. Such deposits of $Fe(OH)_2$ do not provide a protective barrier to DO penetration. Consequently, the steel corrodes faster in dilute NaCl than in distilled water.

Ferrous ions can then be further oxidized to ferric ions (Uhlig, 1971):

$$Fe(OH)_2 + 1/2H_2O + 1/2O_2 \rightarrow Fe(OH)_3 \quad (3)$$

An intermediate corrosion product includes both Fe^{2+} and Fe^{3+} (Uhlig, 1971).

Ultimately, the rust deposited on steel consist of three layers of iron oxides at different stages of oxidation. The innermost adherent layer is largely greenish ferrous hydroxide ($Fe(OH)_2$). The outer layer consists largely of orange ferric hydroxide ($Fe(OH)_3$). Magnetite (Fe_3O_4) forms a black intermediate layer between the ferrous and ferric hydroxides. Oxygen transport takes place not only in the bulk liquid but also through the porous layers of corrosion products. The corrosion rate is controlled by the rate of DO reduction which is under either diffusional or mixed (reaction + diffusion) control depending on the structure of the corrosion products (Bonnel *et al.*, 1983). Bare mild steel does not passivate except at very high DO concentration (Uhlig, 1971). Initially localized corrosion occurs but eventually general corrosion is established (Szklarska-Smialowska, 1986).

The most dangerous form of localized corrosion of mild steel is tuberculation. According to Herro (1991), tubercle formation originates from a differential oxygen concentration cell. Oxygen reduction occurs around the tubercle base and at the inner magnetite shell, while anodic iron dissolution occurs underneath the tubercle (Fig. 2). Ferrous ions generated in the anodic region migrate through the overlaying material, producing an anion flux opposite to the outward ferrous ion migration. Eventually the pH decreases within the tubercle due to the increased concentration of anions such as chloride. The pitting corrosion rate beneath the tubercle is suggested to be a transport controlled process (Butler & Ison, 1966), *i.e.* the corrosion rate is determined by the ion mobility through the corrosion products.

2. *Corrosion of mild steel beneath a totally aerobic biofilm*

Since the corrosion rate of steel in aerobic bulk liquid is controlled by the transport of DO to the steel surface, a uniform coverage by an aerobic biofilm may substantially decrease the corrosion rate due to the oxygen consumption and increased mass transfer resistance. Smith *et al.* (1973) reported that an agar-coated steel (simulated slime) demonstrated very high polarization resistance and correspondingly low corrosion rates (0.01–0.03 mpy).

The accumulation of a biofilm on a steel surface may result in local oxygen depletion under thick and non-uniform biofilms. In the authors laboratory, tubercle formation at the initial stages of biofilm accumulation has been observed (Fig. 3). The DO concentration

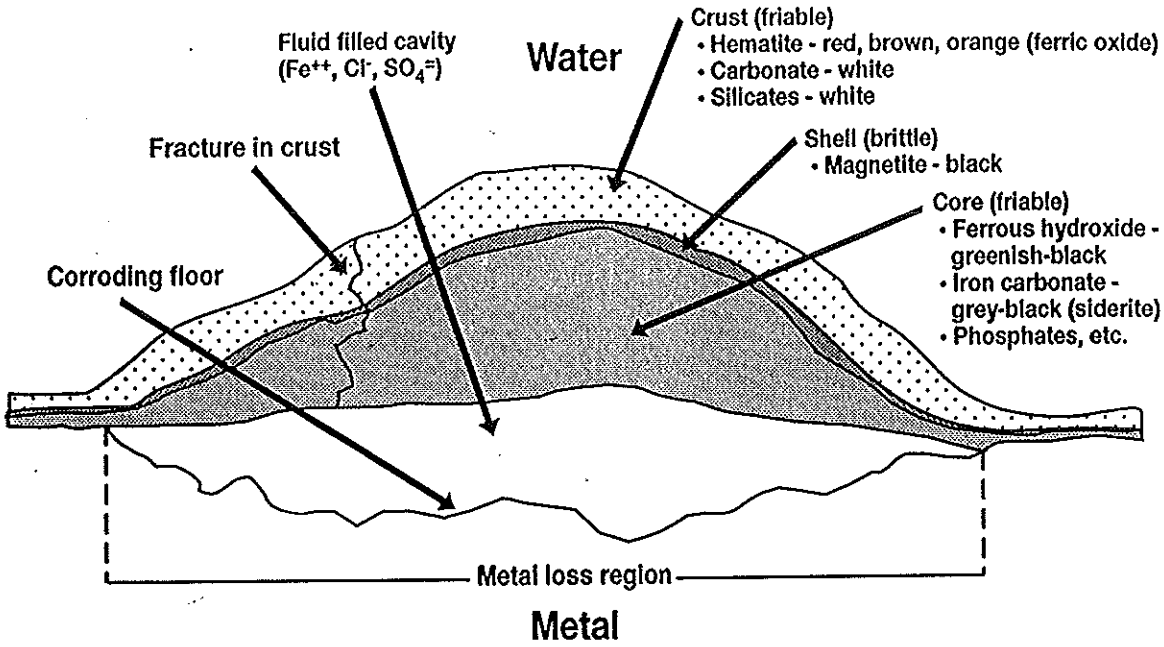

Fig. 2 Structural features of a typical tubercle. (After Herro, 1991.)

was zero within the tubercle but was about 2 $mg \cdot l^{-1}$ near the steel surface next to the tubercle (Lee *et al.*, 1993a, 1993b). Aerobic biofilms can also be associated with the formation of ion concentration cells, biopolymer-metal interactions, and the activity of acid producing bacteria. However, the microbial influences of these effects on the corrosion of mild steel has still to be quantified (Ford & Michell, 1990).

Anaerobic Processes

1. Corrosion of mild steel in an abiotic, anoxic bulk liquid

Corrosion by dissolved H_2S. The anodic behavior of iron or steel in neutral or alkaline sulfide solution was investigated by Shoesmith *et al.* (1980). The anodic reaction occurs by sequential chemisorption and anodic discharge reactions.

$$Fe + H_2S \rightarrow FeSH^-_{ads} + H^+ \tag{4}$$

$$FeSH^-_{ads} \rightarrow FeSH^+_{ads} + 2e^- \tag{5}$$

Subsequent to reaction (5), $FeSH^+_{ads}$ + may be incorporated directly into a growing layer of mackinawite.

$$FeSH^+_{ads} \rightarrow FeS_{1-x} + xHS^- + (1-x)H^+ \tag{6}$$

Reaction (5) is the rate-limiting step exercising control over the anodic processes, *i.e.* charge transfer control. The cathodic reaction is governed by hydrogen sulfide reduction (Bolmer, 1965; Costello, 1974).

$$2H_2S + 2e^- \rightarrow H_2 + 2HS^- \tag{7}$$

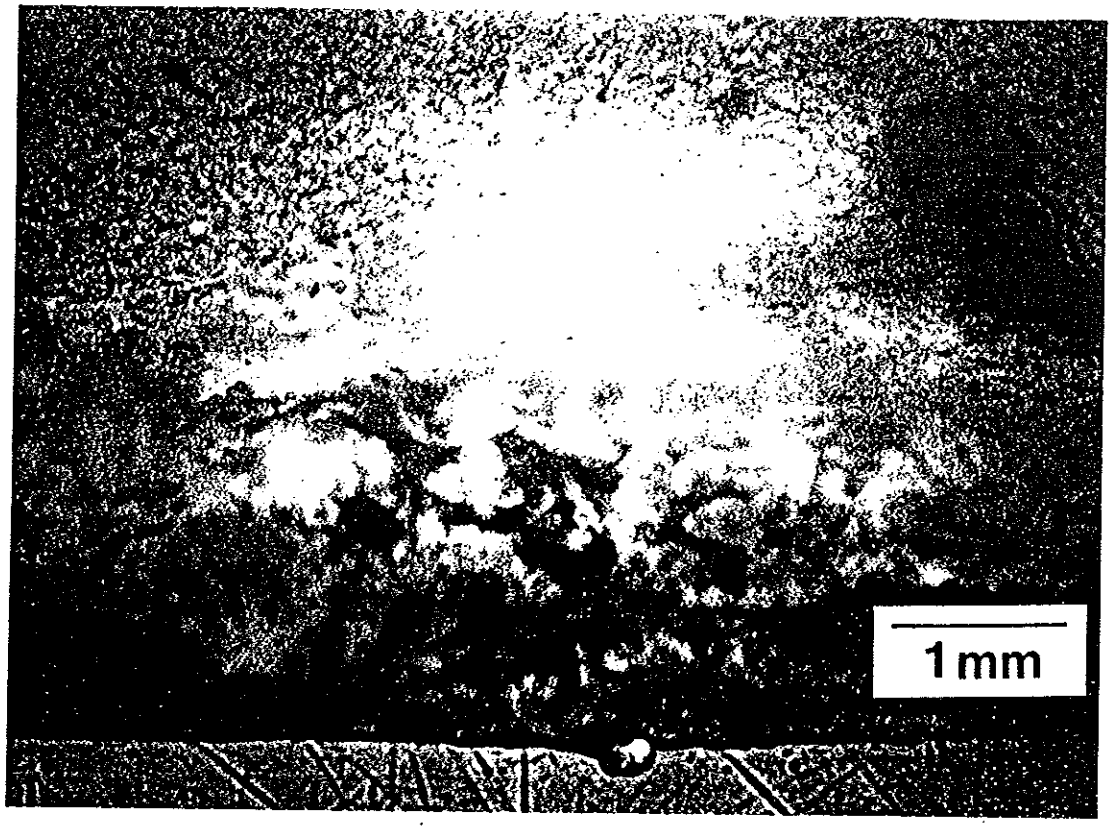

Fig. 3 Optical micrograph of a fouled steel coupon after 2 weeks experimental exposure. Pitting is observed directly beneath a tubercle. (After Lee *et al.*, 1993b.) (see colour section)

This reaction is considered to be limited by both H_2S diffusion and hydrogen overvoltage.

Mild steel normally corrodes quite uniformly in saturated H_2S bulk liquid (3.55 $g \cdot l^{-1}$) in the pH range 6 to 13 (Dvoracek, 1976). Pitting of passivated steel (mill scale) in saturated H_2S bulk liquid occurs only in the presence of chlorides (Dvoracek, 1976). The passivated oxide-covered steel serves as the cathodic site for proton reduction while the anodic site is the bare steel surface. Pitting of bare steel occurs only in neutral or alkaline solutions where formation of a passive iron sulfide film is possible (Salvarezza *et al.*, 1982; 1983; Vera *et al.*, 1986). At lower H_2S concentrations (150 to 300 $mg \cdot l^{-1}$) at pH 6 through 14, a passive iron sulfide film forms on the steel surface, and pitting corrosion is significant even in the absence of chlorides (Salvarezza *et al.*, 1983; Vera *et al.*, 1986). At very low H_2S concentrations (0.0032–3.2 $mg \cdot l^{-1}$) at pH 8, the pitting tendency is found to increase with increasing H_2S concentrations (Salvarezza *et al.*, 1983).

Several investigators have related corrosion behavior of mild steel in H_2S bearing fluid to the chemical nature and physical character of the iron sulfide surface film (Ewing, 1955; Meyer *et al.*, 1958; Sardisco *et al.*, 1963; Sardisco & Pitts, 1965; Greco & Sardisco, 1969; Hausler *et al.*, 1972; Taylor, 1978; Tewari & Campbell, 1979; Tewari *et al.*, 1979; Tapping *et al.*, 1983; Craig, 1984; Das & Venkateswaren, 1987; Ramanarayanan & Smith, 1990; Wikjord *et al.*, 1980). In oxygen-free solutions, Wikjord *et al.* (1980) demonstrated that the evolution of corrosion products on the steel progressed from iron-rich to sulfur-rich phases according to the sequence, mackinawite (tetragonal FeS_{1-x}) → ferrous sulfide (cubic FeS) → troilite (hexagonal FeS) → pyrrhotite (hexagonal $Fe_{1-x}S$) → pyrite (cubic FeS2), with the last product being thermodynamically favored. The film becomes increasingly protective as it evolves from mackinawite to

pyrite. The formation of a highly protective pyrite film depends on local ferrous ion concentration, fluid dynamics, and temperature. High temperature accelerates the sequential transformations, while high shear stress retards it. At low shear stress the boundary layer thickness increases resulting in the high local Fe^{2+} concentration required for sequential development of a pyrite film.

The corrosion rate of mild steel in neutral H_2S bulk liquid depends also on the presence of strong electrolytes, especially NaCl. Meyer *et al.* (1958), using saturated H_2S solutions, observed that NaCl influenced both the corrosion rate and the corrosion products. When H_2S was used in triple-distilled water, the initially formed mackinawite tarnish was first converted to a thicker mackinawite scale, and finally covered by protective pyrrhotite and pyrite scales. In the presence of NaCl, however, mackinawite tarnish formation was followed by a mackinawite scale. No protective pyrrhotite-pyrite scale was detected under these conditions.

Sardisco and colleagues (Sardisco *et al.*, 1963; Sardisco & Pitts, 1965; Greco & Sardisco, 1969) concluded that the corrosion rate for iron in an H_2S–CO_2 atmosphere is controlled partially by interface reactions and partially by diffusion of ions and electrons across the film. The iron sulfide film formed at low H_2S concentrations, mainly composed of pyrite and troilite, was relatively protective. However, the iron sulfide film formed at high H_2S concentration, mainly composed of mackinawite, was not protective. Thus, at low H_2S concentration the nature of the protective film is a dominant factor in the mechanism of the over-all reaction. Consequently, they concluded that the corrosion reaction is diffusion controlled. At high H_2S concentrations the surface film become less protective, and the corrosion becomes reaction controlled. The authors also demonstrated that the composition and protectiveness of iron sulfide film depends upon the pH of the system. The least protective (mackinawite)is formed when the pH of the medium is between 6.5 and 8.8. Outside this range, protective films of pyrrhotite and/or pyrite are formed. Taylor (1978), in a Girdler-Sulfide heavy water system, has shown similar results. The carbon steel corroded very rapidly (1000 mpy) on initial contact with H_2S and water, but subsequently the iron sulfide corrosion products formed a protective film on the steel which reduced the corrosion rate to less than 1 mpy. The corrosion resistance imparted by certain sulfide films, pyrite and pyrrhotite in particular, on carbon steel surfaces is clearly of major significance.

Corrosion by iron sulfides. The corrosion attack in anoxic hydrogen sulfide bulk liquid has been found to be not only by dissolved sulfides, DS, but also by precipitated iron sulfides. The nature of the various iron sulfides and their influence on the corrosion of steel has been reviewed by Smith and Miller (1975). The corrosiveness of the iron sulfides is based on their good electron conductivity, low overvoltage for hydrogen evolution, noble electrode potential, and defect structure. These properties cause iron sulfides to be excellent cathodes in galvanic corrosion cells with unreacted iron. For adherent surface sulfides, corrosivity shows a minimum for pyrite and troilite (Sardisco *et al.*, 1963; Greco & Sardisco, 1969; Taylor, 1978). For loosely accumulated iron sulfides, polarization studies (Mara & Williams, 1972b) have shown that all sulfide-based minerals added to steel coupons in H_2S-free bulk liquid caused both anodic and cathodic depolarization. Pyrrhotite, mackinawite, and greigite caused similar degrees of depolarization of iron. Pyrite was the least active depolarizer. These observations were contradicted, however, by King and Wakerly (1973) who showed that the corrosivity of iron sulfides increased with increasing sulfur to iron ratio. The authors explained this apparent inconsistency by a hydrogen absorption theory; pyrrhotite, though potentially corrosive as shown by the polarization results, becomes rapidly polarized by hydrogen

absorption, whereas pyrite only absorbs hydrogen slowly and thus causes more corrosion. Although this mechanism remains speculative, the evidence of corrosion acceleration by the various insoluble metal sulfides is clear.

2. *Corrosion of mild steel beneath a totally anaerobic biofilm*

Biofilm SRB activities. The activity of SRB in an anaerobic biofilm is limited by mass transfer resistance into the biofilm and/or diffusional resistance within the biofilm (Nielsen, 1987; Nielsen & Hvited-Jacobsen, 1988). Activity is normally expressed as the sulfate reduction rate or sulfide production rate.

Accelerating corrosion of steel by SRB activities can be attributed either directly to removal of hydrogen or indirectly to the production of H_2S. Moosavi *et al.* (1990) found only an indirect correlation between biofilm SRB activity and corrosion rate. The mechanisms of corrosion appeared to depend on the chemical and physical nature of the corrosion products rather than on SRB activity. Lee and Characklis (1993) have demonstrated a similar lack of correlation between biofilm SRB activity and corrosion rate in an iron-free medium. In this instance, the biofilm SRB activity was controlled by the substrate loading rate, which equaled the product of the dilution rate and consumed substrate concentration divided by the surface area:

$$\text{SRB activity} = D(S_i - S)V/A \tag{8}$$

where D = dilution rate (t^{-1}); S_i = influent sulfate concentration ($mol \cdot l^{-1}$); S = effluent sulfate concentration ($mol \cdot l^{-1}$); V = working volume in the reactor (l^{-1}); A = working area in the reactor (m^2).

There was no detectable difference in either weight loss or electrochemical measurements as SRB activity was increased from 2 to 32 $mgS \cdot m^{-2} \cdot h^{-1}$. Scratch lines on the steel surface were observed to have been unaffected, even at high SRB activity within the biofilm (Fig. 4).

Suspended iron sulfides. Rickard and colleagues (Rickard, 1969; Morse *et al.*, 1987) examined the iron sulfides formed in the presence of iron and *Desulfovibrio desulfuricans* in a batch culture. Mackinawite, greigite, pyrrhotite, marcasite, and pyrite were all formed. The biogenic iron sulfides were identical with those produced by purely inorganic processes under the same conditions. These authors concluded that the biogenic and abiogenic iron sulfides could not be distinguished.

The effect of ferrous sulfide concentration in a suspended culture has been investigated by several authors (Booth *et al.*, 1964; 1968; Mara & Williams, 1972a; King *et al.*, 1973). Booth and his coworkers (Booth *et al.*, 1964; 1968), based on a semi-continuous culture experiment, reported that the presence of a sufficient concentration of 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 (1972a) established in a chemostat study that an adherent film of sulfide on the steel surface was observed in a low iron medium. After this film ruptured, the rate of corrosion was high and was independent of microbial growth. Film breakdown was attributed to compressive stress established at the film/metal interface subsequent to the sulfidation of the primary corrosion product mackinawite, to greigite. There was no evidence of protective film formation and a high rate of corrosion was observed. In a similar study, King *et al.* (1973) found in a semi-continuous culture that increasing the ferrous ion concentration caused a breakdown of the protective mackinawite film. The rate of corrosion after film breakdown increased

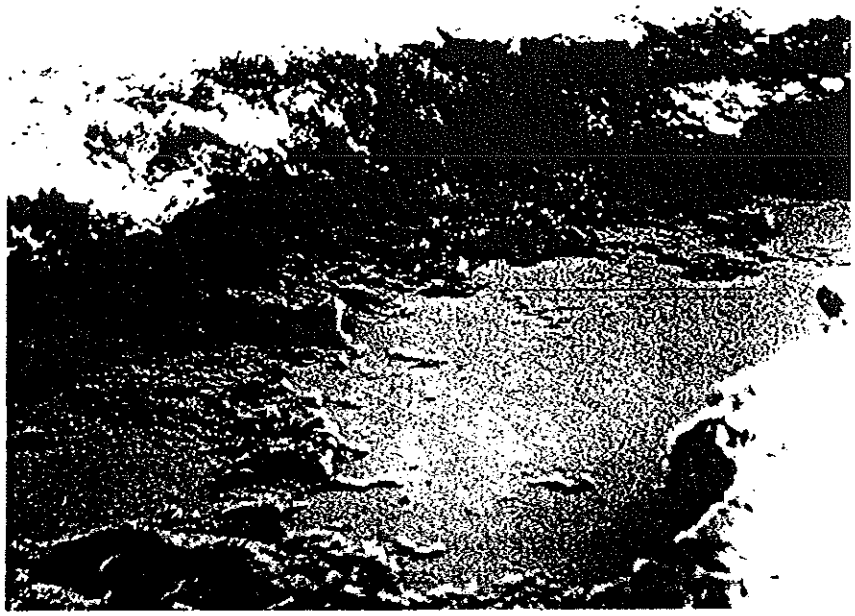

Fig. 4 Scanning electron micrograph of a mild steel surface covered with a thick anaerobic biofilm containing SRB. The scratch lines on the bare steel surface are visualized. (After Lee & Characklis, 1993.) × 50.

proportionally to the ferrous ion concentration (Fig. 5). Film breakdown in this instance was attributed to the transformation of mackinawite to non-protective smythite and pyrrhotite, rather than to greigite.

In a recent series of experiments, the effects of suspended ferrous sulfide on the corrosion of mild steel were studied in an anaerobic biofilm reactor by Lee and Characklis (1993). The biofilm was developed on steel coupons in iron-free medium, followed by step increases in ferrous ion to 1, 10, and 60 $mg \cdot l^{-1}$ in the influent. Precipitation of ferrous sulfide ($Fe^{2+} + HS^- \rightarrow FeS + H^+$) took place mainly in the liquid phase. DS concentration in the effluent decreased from 50 to 40 $mg \cdot l^{-1}$ as ferrous ion concentration in the influence increased from 1 to 10 $mg \cdot l^{-1}$. Very little corrosion occurred under these conditions although iron sulfide particles accumulated in the biofilm. However, addition of an iron-rich medium (60 $mg \cdot l^{-1}$) resulted in the precipitation of all the biogenic sulfide with none escaping in the effluent. Once the iron sulfide in the biofilm contacted the steel surface the corrosion rate increased substantially. There was no continuous or uniform protective coating of iron sulfide film formed beneath the biofilm and intergranular attack was observed over the entire steel surface. Apparently, therefore precipitated iron sulfide is more corrosive to steel than DS, but direct contact with the steel is necessary for the enhanced corrosion to be evident. This study does not, however, give any further information on the relative corrosivity of the different iron sulfides.

Adherent sulfide film. As discussed above, an adherent sulfide film is formed in the presence of SRB when the system contains low concentrations of dissolved iron. Videla (1985) demonstrated that the passive film formed under active SRB biofilm may lead to a pitting attack of steel. Lee and Characklis (1993) showed that when the steel surface was precoated chemically with a layer of iron sulfide, followed by biofilm accumulation in an iron-free medium, some localized corrosion occured. Aggregates of bacteria and iron

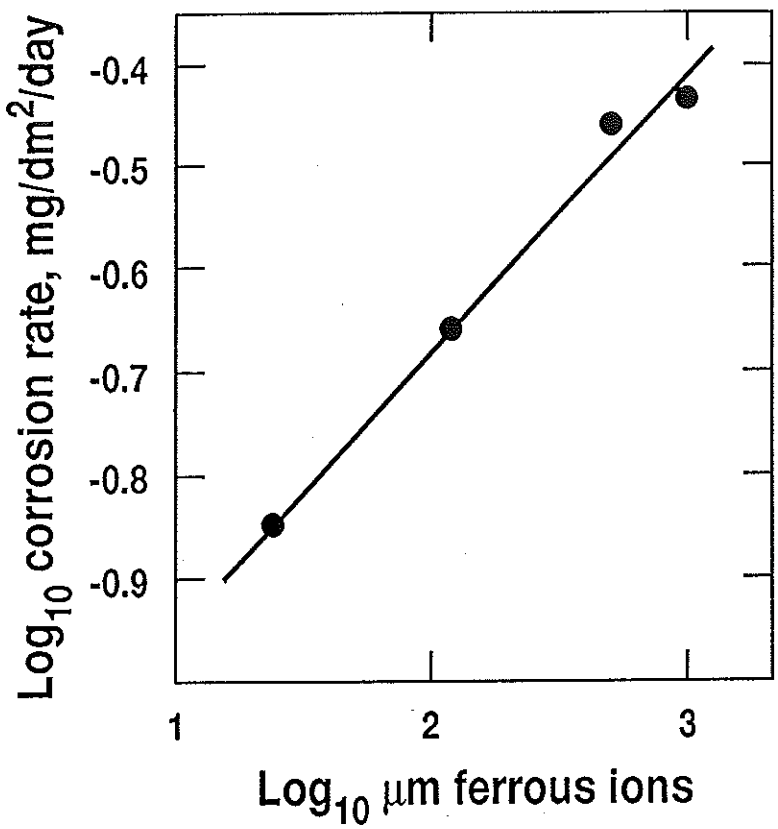

Fig. 5 Effect of ferrous ion concentration on the corrosion rate of pure iron specimens exposed to a growing culture of SRB. (After King *et al.*, 1973.)

sulfide crystal associated with inclusions were found in the localized corrosion areas beneath the sulfide film and biofilm. Although biofilm accumulation reduced the spalling of the iron sulfide layer, as compared with abiotic conditions (Lee & Characklis, 1991), the risk of localized corrosion is significant.

Further evidence of the importance of the morphology of the iron sulfide scale in a biofilm system is provided by the work of Moosavi *et al.* (1990). They observed a clearly defined layering of corrosion products on mild steel coupons recovered from the seabed close to an offshore platform after 1–2 years exposure. Next to the steel surface there was a thin black adherent layer; and superimposed on this was a looser bulky black deposit. Enhanced corrosion was associated with places where the adherent film lost integrity.

Aerobic/Anaerobic Processes

1. Corrosion of mild steel in an abiotic, H_2S–O_2, bulk liquid

The corrosion rate of steel in H_2S–O_2 bulk liquid is higher than that in the presence of O_2 or H_2S alone, and the prevalent corrosion product appears to be ferrous sulfide (Bond & Marsh, 1950; Sheppard, 1950; Craig, 1979; Martin & Annand, 1981). There is no general agreement about the corrosion mechanism in H_2S–O_2 mixture, however. Sheppard (1950) showed that elemental sulfur and greigite are highly corrosive to pipe lines in a sour gas environment, which may explain the observed high corrosion rate in H_2S–O_2 mixture. Craig (1979) demonstrated that mackinawite was the sole initial corrosion product in various H_2S–O_2 mixtures, and that corrosion rate increased with increasing percentage of

oxygen concentration. He suggested that the DO acts directly as a cathodic depolarizer. Martin and Annand (1981) reported an increase in corrosion rates of steel from 155 to 410 mpy when a ferrous ion-containing solution previously sparged with H_2S was subsequently sparged with air. They attributed the role of DO in the system being to modify the nature of the suspended iron sulfide, *e.g.* formation of pyrite, which accelerates the cathodic reduction of hydrogen ions.

The kinetics of sulfide oxidation by DO have been extensively studied (Cline & Richards, 1969; Snavely & Blount, 1969; Chen & Morris, 1971;1972; Almgren & Hagstrom, 1974; O'Brien & Birkener, 1977; Lefers *et al.*, 1978; Kuhn *et al.*, 1983; Jolley & Forster, 1985; Wilmot *et al.*,1988) and they have been shown to be affected by a number of factors such as temperature, pH, total sulfide ion concentration, DO concentration, neutral salts, and transition metal ions (Kuhn *et al.*, 1983). The order of reaction with respect to sulfide was reported to be one, and that with respect to oxygen to be less than one (Chen & Morris, 1972; Wilmot *et al.*, 1988). The variation of rate constant, k, with pH indicates a complex mechanism. In acid solutions, pH < 6, where H_2S is the predominating sulfide species, the rate of oxidation is very slow. The specific rate constant increases greatly as pH increases through 7 to a maximum at pH 8, then decreases to a minimum near pH 9 (Chen, & Morris, 1972) (Fig. 6). Ferrous ions were found to catalyze the oxidation strongly in moderate alkaline solution, pH 7.5 to 9.5 (Chen & Morris, 1971).

The products of the reaction of H_2S and O_2 depend on the system variables such as pH and [S]/[O] ratio (O'Brien & Birkener, 1977). The effects on product formation are summarized as follows: (1) a high [S]/[O] ratio, along with a total reduced sulfur concentration greater than 10^{-3} M, leads to the formation of elemental sulfur; (2) a low ratio favors the production of sulfite, thiosulfate, and sulfate; (3) at low pH (less than 6)

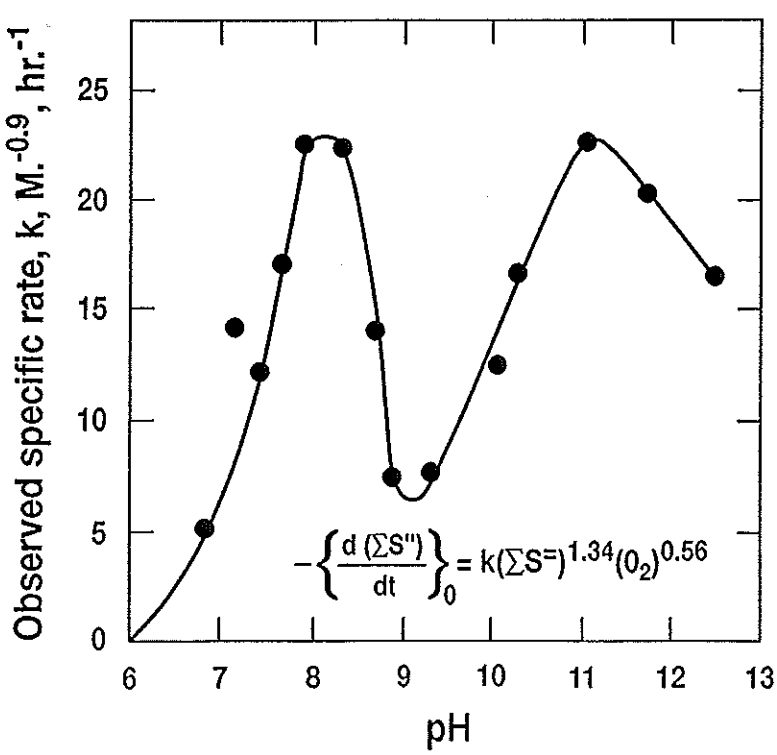

Fig. 6 pH dependence of observed specific rate of H_2S oxidation. (After Chen & Morris, 1972.)

in dilute bulk liquid, the favored reaction product is principally sulfate; and (4) at high pH and with total sulfide concentrations below 10^{-3} M, sulfite, thiosulfate, and sulfate are the predominant products.

Chen and Morris (1972) indicated that polysulfide ions, S_x^{2-}, may be formed through the interaction of elemental sulfur and DS. The polysulfide is highly reactive and can combine with oxygen to produce several products (Fig. 7). The sulfur compounds thus produced are metastable and probably form a complex mixture of elemental sulfur, polysulfides, thiosulfate, and sulfite. Introduction of oxygen into sulfide-bearing bulk liquid can also promote the formation of pyrite (Berner, 1970; Luther, 1991; Schoonen & Barnes, 1991a; 1991b). Luther (1991) demonstrated that pyrite can be formed very fast in the presence of polysulfide ions, ferrous iron and DS at room temperature.

$$Fe^{2+} + S_4S^{2-} + HS^- \rightarrow FeS_2 + S_3S^{2-} + H^+ \quad (9)$$

It should be emphasized that sulfide-covered surfaces can catalyze chemical transformations of sulfur compounds (Gragnolino & Tuovinen, 1984). For example, the reaction between ferrous sulfide and DO produces mainly elemental sulfur at neutral pH.

$$4FeS + 3O_2 \rightarrow 4S^\circ + 4FeO(OH) + 2H_2O \quad (10)$$

DS can also react with oxidized iron and form ferrous sulfide and elemental sulfur (Schmitt, 1991).

$$3H_2S + 2FeO(OH) \rightarrow 2FeS + S^\circ + 4H_2O \quad (11)$$

The corrosion systems described by Craig (1979) and by Martin and Annand (1981) were always operated in an excess of H_2S. Consequently, the enhanced corrosion rate in H_2S–O_2 bulk liquid may be attributed to the presence of the elemental sulfur and/or polysulfides, and pyrite. The corrosive interaction of wet elemental sulfur with steel has been reviewed by Schmitt (1991). He demonstrated that elemental sulfur is more corrosive than polysulfides and can lead to considerable weight loss and shallow pitting of carbon steel. The corrosion rate caused by the elemental sulfur can be as high as several hundred mpy. A diagram of the proposed sulfur corrosion mechanism was presented by Schmitt (1991) (Fig. 8). Five reaction steps were recognized: (1) sulfur disproportionation in water (Eqn 12); (2) formation of iron sulfide film on steel (Eqn 13)

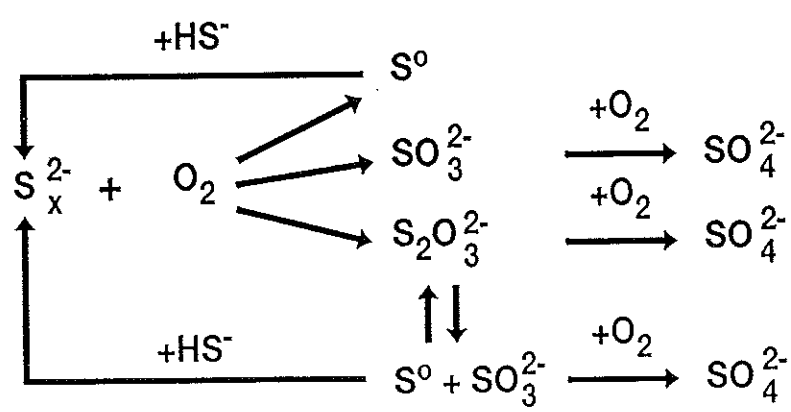

Fig. 7 Reaction pathway of oxygenation of sulfide. (After Chen & Morris, 1972.)

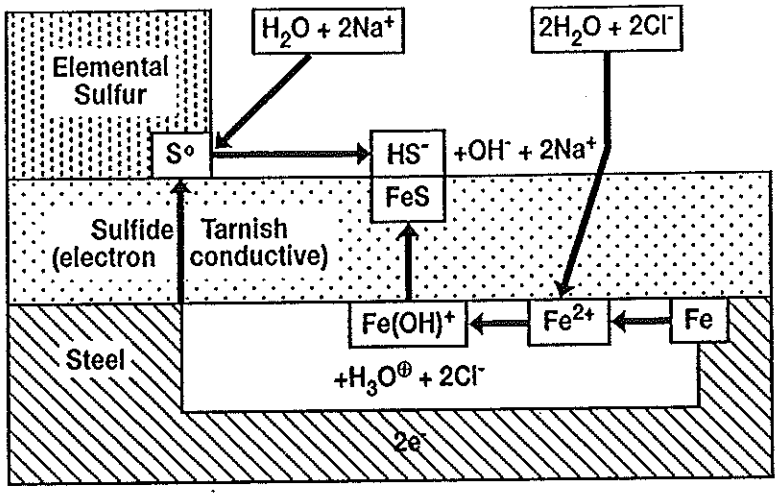

Fig. 8 Scheme for the sulfur corrosion mechanism in the presence of salt. (After Schmitt, 1991.)

(3) sulfide-catalysis cathodic reduction (Eqn 14); (4) anodic metal dissolution (Eqn 15); (5) chemical formation of iron sulfides (Eqn 16)

$$4S^\circ + 4H_2O \rightarrow 3H_2S + H_2SO_4 \tag{12}$$

$$Fe + H_2S \rightarrow FeS + H_2 \tag{13}$$

$$S^\circ + H_2O + 2e^- \rightarrow HS^- + OH^- \tag{14}$$

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{15}$$

$$Fe^{2+} + HS^- + OH^- \rightarrow FeS + H_2O \tag{16}$$

There is an induction time for the initiation of the reaction sequence in Equation 12 through 16. MacDonald *et al.* (1978) suggested that the induction period may be due to the formation of a protective mackinawite film on the steel surface, and that the corrosion rate may be subject to anodic control (*e.g.* by ionic diffusion through the sulfide film). This film then breaks down to form a non-protective mackinawite. At this point the corrosion rate is controlled by the reduction of sulfur to conductive iron sulfide. The autocatalytic effect of iron sulfides was attributed to their high electronic conductivity, which due to their defective structure, can catalyze the cathodic reaction (Macdonald *et al.*, 1978).

The accelerated corrosion of steel by DO in aqueous H_2S solution occurs either indirectly through corrosive product formation, or directly by oxygen acting as a cathodic depolarizer. In an H_2S–O_2 bulk liquid, oxygen can remove the cathodically formed hydrogen and reduce cathodic polarization. Martin (1974) and Berkovitz and Horowitz (1982) observed that hydrogen permeation began dropping or stopped immediately after air entered an anaerobic system containing H_2S. From these data, it is difficult to indicate the actual corrosion mechanism, but the accelerated corrosion rate always appears to result from facilitating the cathodic reaction.

2. *Corrosion of mild steel beneath an aerobic/anaerobic biofilm*

The importance of DO on the SRB-related corrosion of ferrous metal and alloys has been emphasized by several authors (Starkey, 1985; Moosavi *et al.*, 1990; Pedersen &

Hermansson, 1991; McKenzie & Hamilton, 1992; Lee *et al.*, 1993a; 1993b; Nielsen *et al.*, 1993). Accelerated corrosion rates have been observed when iron, corroded by SRB, is exposed to intermittent aerobic-anaerobic environments (Starkey, 1985). Hardy and Bown (1984) showed that corrosion rates of mild steel increased substantially when after several days' incubation anaerobic cultures were sparged with air. Pitting corrosion was the characteristic type of attack. McKenzie and Hamilton (1992) suggested that environmental factors, most notably oxygenation, are central to determining the rate and extent of SRB-related corrosion. They established that higher 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. The corrosion products in the aerobic zone contained a higher percentage of non-acid-volatile sulfides (NAVS) than in the anaerobic zone where acid-volatile-sulfides (AVS) dominate the corrosion products. The principal forms of NAVS are considered to by pyrite and elemental sulfur, and of AVS to be mackinawite and greigite. The effect of DO on corrosion rates of mild steel caused by SRB in a number of experimental and environmental systems is summarized in Table 1 (Hardy & Bown 1984; Moosavi *et al.*, 1990; McKenzie & Hamilton, 1992).

There are two fundamental questions to be addressed in order to define the role of DO on SRB-related corrosion. Firstly, are corrosion products the major contributing factor to the increased corrosion rate? Secondly, why is pitting corrosion the characteristic mode of attack in aerobic/anaerobic environments?

With respect to the first question, it is known from studies in the abiotic system that DO reacts with DS to produce elemental sulfur and other oxidized sulfur compounds such as polysulfide, thiosulfate, sulfite and sulfate (Fig. 7, Eqs 10–11). In addition to these products, pyrite may be formed through the reaction of elemental sulfur and polysulfide (Eq. 9). Although the corrosivity of each sulfur compound toward mild steel is not known, the authors own experimental results have shown that the combined effect of elemental sulfur and sulfides is more corrosive than that of the individual compounds (Fig. 9). Consequently, the accelerated corrosion rate with DO in the presence of SRB can be attributed to the combined effect of AVS and NAVS. Quantitative studies of the effects of AVS, NAVS, and dissolved sulfides (H_2S, polysulfide, thiosulfate, sulfite, and sulfate) on the corrosion rate of mild steel in a biofilm system are therefore needed to provide an unambiguous answer to this question.

To answer the second question, the effect of the DO concentration in the bulk liquid on corrosion of mild steel should be considered. The initial corrosion behavior of mild steel under an aerobic/anaerobic biofilm has been systematically studied by changing the bulk DO concentrations at constant substrate loading rate (Lee *et al.*, 1993a; 1993b). The

Table 1 Corrosion rates of mild steel caused by SRB activities in the absence and presence of oxygen

Environment		Corrosion Rate (mpy)
Seabed	(An O_2)	0.7
Platform/Seabed	(O_2)	3.6–11.3
Column	(An O_2)	0.7
Column	(O_2)	10–17
Flask	(An O_2)	1.2
Flask	(O_2)	25.6
Geothermal	(An O_2)	5.9
Geothermal	(O_2)	13.8–53.1

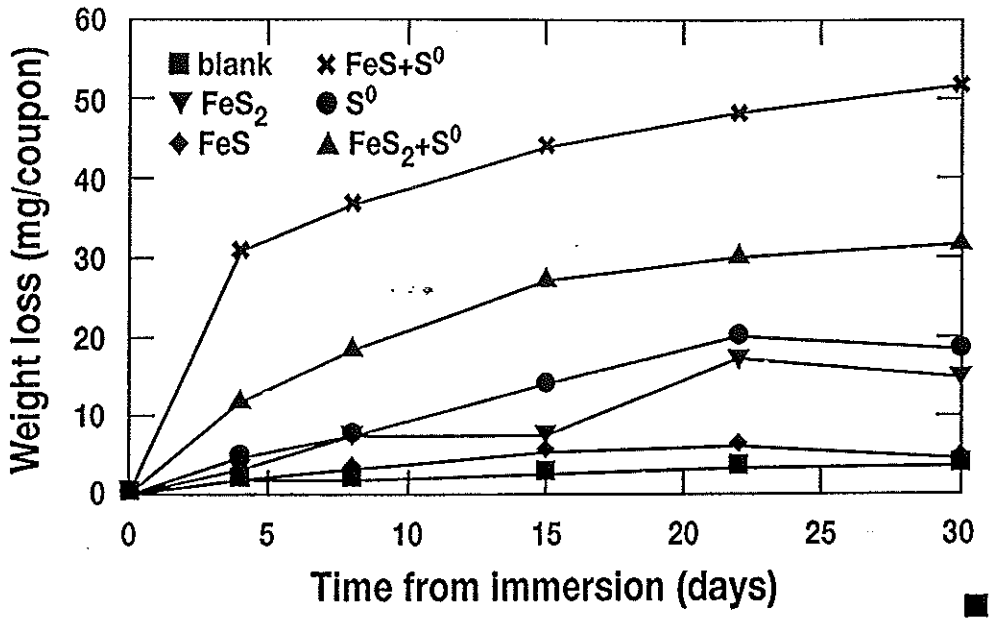

Fig. 9 Weight loss vs time curves for mild steel in the presence of various sulfides. The total sulfide concentration for each run is 20 mM as S.

mixed population biofilms were heterogeneous (or "patchy") with respect to the spatial distribution of microbial species. SRB were found to proliferate in anaerobic microniches even when DO penetrates the entire biofilm at other locations. In summary, these findings show that during the initial stage of biofilm accumulation aerobic corrosion was evident and the corrosion rate decreased with time. During the later stages of biofilm accumulation, however, SRB-enhanced corrosion began as a localized attack which was eventually propagated over the entire steel surface. This corrosion was significant only when there was sufficient conductive iron sulfide deposit to establish a galvanic cell (Fig. 10). The influence of bulk DO concentration on the second-stage SRB-related corrosion is significant. At low bulk DO concentration, several sulfide-attacked areas were observed in the form of small, shallow pits. At high bulk DO concentration, initial sulfide attack was concentrated at one spot. Consequently, large, deep pits were observed within the sulfide-attacked areas. These results suggest that it is likely to be the patchiness of the SRB biofilm which is responsible for the observed localized attack, rather than any special features of either the anodic or cathodic reactions within the electrochemical corrosion cell.

INTERPRETATION OF CORROSION MECHANISMS

Stimulation of the Cathodic Reaction by SRB Directly by Removal of Hydrogen

The role of hydrogenase activity in SRB-related corrosion of mild steel is unclear. Hydrogenase-positive SRB can oxidize the molecular hydrogen generated at the cathodic sites to facilitate cathodic depolarization (Von Wolzogen & Ven der Vulgt 1934; Booth & Tiller, 1960; 1962a; 1962b; Cord-Ruwisch & Widdel, 1986; Daumas *et al.*, 1988; Bryant *et al.*, 1991). In this mechanism, where the combination of adsorbed H atoms to produce H_2 gas is considered to be the rate-controlling step, bacteria effectively increase the hydrogen evolution rate and increase the corrosion rate accordingly. The correlation

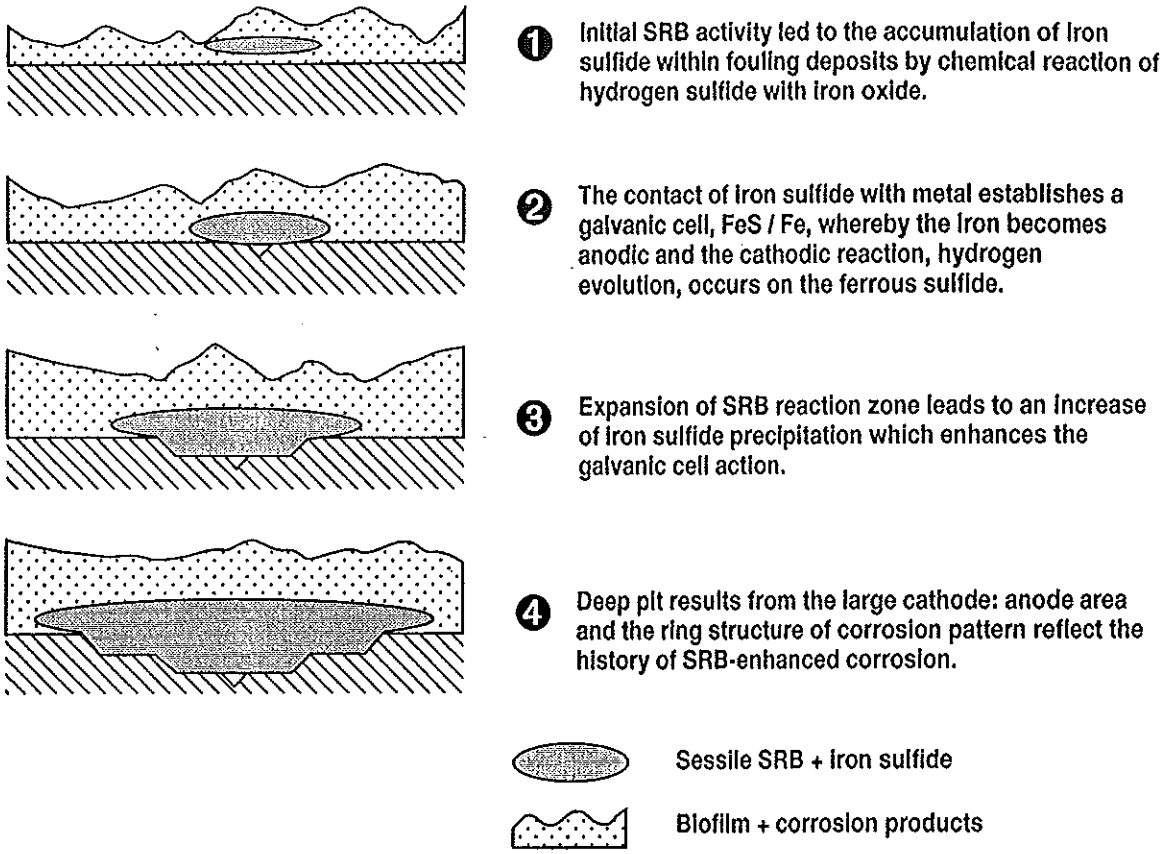

Fig. 10 Sequence of SRB-enhanced corrosion of mild steel in oxic bulk liquid. (After Lee *et al.*, 1993b.)

between hydrogenase activity and corrosion rate has been confirmed in a batch culture but shown to be very weak in semi-continuous and continuous culture (Booth *et al.*, 1964; 1968; Mara & Williams, 1972a; King *et al.*, 1973).

The following mechanism for the hydrogen electrode reaction in the absence of H_2S is generally accepted (Carta *et al.*, 1988). A primary step (Eqn 18) is coupled with the molecular recombination desorption step (Eqn 19) or with the electrochemical desorption step (Eqn 20):

$$M + H^+ + e^- \rightarrow M\text{–}H_{ads} \tag{18}$$

$$M\text{–}H_{ads} + M\text{–}H_{ads} \rightarrow H_2 + 2M \tag{19}$$

$$M\text{–}H_{ads} + H^+ + e^- \rightarrow H_2 + M \tag{20}$$

When H_2S is present, there is an increase in proton discharge rate but the hydrogen evolution rate is suppressed (Berkowitz & Horowitz, 1982).

The accumulation of SRB on steel surfaces minimizes the diffusional distance between the cathodic hydrogen and the bacteria within the biofilm system. Thus, such a mechanism should be more pronounced in a biofilm reactor than in a batch or a chemostat reactor. The lack of a direct correlation between biofilm activity and corrosion rate under high organic loading rate does not support this mechanism. Furthermore, the hydrogen evolution rate is suppressed in the presence of H_2S. It is doubtful that the bacteria uptake of H_2, as related to the hydrogenase activity, is the rate-controlling step for SRB-enhanced corrosion.

Stimulation of the Cathodic and Anodic Reactions by Dissolved Hydrogen Sulfide

Under abiotic conditions, hydrogen sulfide is known to be corrosive with regard to ferrous materials. H_2S can accelerate both anodic and cathodic reactions (Bolmer, 1965; Iofa, 1970; Morris *et al.*, 1980; Shoesmith *et al.*, 1980; Gupta, 1981; Pound *et al.*, 1989). Stimulation of the cathodic reaction by bacterially produced hydrogen sulfide has been suggested by Costello (1974), as in abiotic conditions. The rate of cathodic reduction of hydrogen sulfide is limited by diffusion of H_2S to the cathodic sites, and by hydrogen overvoltage (Bolmer, 1965). The concentration of H_2S in one experimental study was 320 $mg \cdot l^{-1}$ (Costello, 1974). In this region, the corrosion rate of mild steel is low (about 4 mpy), and independent of H_2S concentration, but depends on the iron sulfide film formed on the steel surface. The corrosion rate is subject to anodic control (Sardisco & Pitts,1965).

Stimulation of the anodic reaction by bacterially produced sulfide has been suggested by Wanklyn and Spruit (1952), Salvarezza and Videla (1980), Salvarezza *et al.* (1983), and Crolet (1992). Crolet proposed that an anode is first created by local H^+ production at a focus of SRB activity, with ensuing steel dissolution. This initial phase of corrosive activity may be generalized across the exposed steel surface with random nucleation being by statistical fluctuation in the anodic reaction. If kinetic conditions become favorable, however, a chain reaction can be established leading to both a stable galvanic current associated with a particular anode, and the initiation of pit growth at that site. A key element in generating the necessary kinetic conditions is the increased localized acidification at the anode resulting from the formation of iron sulfide corrosion products. Crolet *et al.* (1993) and Daumas *et al.* (1993) demonstrated that SRB are capable of regulating their immediate environmental pH to that value at which H^+/HS^- is zero. The growth of SRB is required in order to establish the galvanic current.

Anodic depolarization offers a mechanism to explain the characteristic attack of mild steel caused by SRB activity, *viz.* localized pitting. However, the environmental conditions which cause the continuing local introduction of acidity have not been verified experimentally.

Stimulation of the Cathodic Reaction by SRB Indirectly by Formation of Iron Sulfides

For corrosion to occur by this mechanism, iron sulfides must have access to the bare steel surface. Once a galvanic cell is established, mild steel behaves as an anode and proton discharge and electron transfer occur on and through the iron sulfide. Iron sulfides increase the rates of corrosion by decreasing hydrogen overvoltage and/or adsorbing the cathodically produced hydrogen (King *et al.*, 1973). The effect of the physical and chemical properties of iron sulfides on the corrosion rate of mild steel in H_2S-containing bulk liquid can be explained through the electrochemical theory.

In the abiotic system, for the adherent surface sulfides, the corrosivity seems to show a minimum for pyrite (Sardisco *et al.*, 1963; Sardisco & Pitts, 1965; Greco & Sardisco, 1969; Taylor, 1978). Because of the more perfect crystal lattice of pyrite, the ability of the cations and electrons to diffuse through the film during corrosion is kept at a minimum (Sardisco & Pitts, 1965). This is further evidenced by polarization measurements. Ramanarayanan and Smith (1990) demonstrated that both anodic and cathodic reactions were polarized when a corrosion scale was deposited, composed of either mackinawite, pyrrhotite, or pyrite. Despite the imperfect nature of the mackinawite crystal structure, the adherent mackinawite film still offers some degrees of protection against corrosion. Shoesmith *et al.* (1980) demonstrated that anodic and cathodic reactions are both polarized in the presence of the mackinawite base layer. In biotic systems, Booth

et al. (1967) also reported that, in minimal iron medium, cathodic depolarization was stifled by the ferrous sulfide film formed on the steel electrode. Results obtained from abiotic and biotic experiments reinforce the mechanism suggested by Greco and Sardisco (1969) and indicate that the adherent sulfide film plays a protective role in determining the rates of corrosion in H_2S environments.

In abiotic systems, all suspended iron sulfides are excellent anodic and cathodic depolarizing agents (King & Wakerley, 1973). Despite this, the types of iron sulfides which are corrosive remains a matter of debate. Accelerated corrosion of steel by suspended iron sulfides in H_2S-bearing liquid was shown to be by cathodic depolarization (Sheppard, 1950). In biotic systems, the initial corrosion rate accelerated by iron sulfide in a biofilm system was attributed to both anodic and cathodic depolarization (Lee *et al.*, 1993a; 1993b) (Fig. 11). The initial anodic depolarization is due to a change of mechanism related to the sulfide-free system. Continuing polarization studies of the subsequent corrosion showed only increased cathodic current, with little change in anodic behavior (Lee & Characklis, 1991) (Fig. 12). The cathodic-only acceleration associated with the loosely accumulated iron sulfide suggests that the cathodic surface area increases, and that the hydrogen evolution reaction occurs at the iron sulfide/biofilm interface. Loose accumulation of sulfide particles at the steel surface does not constitute any barrier to the transport of ferrous ions and so results in little or no change in anodic polarization curves.

Stimulation of the Cathodic Reaction by Dissolved Oxygen

As discussed above with references to the abiotic system, the accelerated corrosion of steel by DO in aqueous H_2S solution is either indirectly through the formation of corrosion products or directly with DO acting as a cathodic depolarizer. The direct

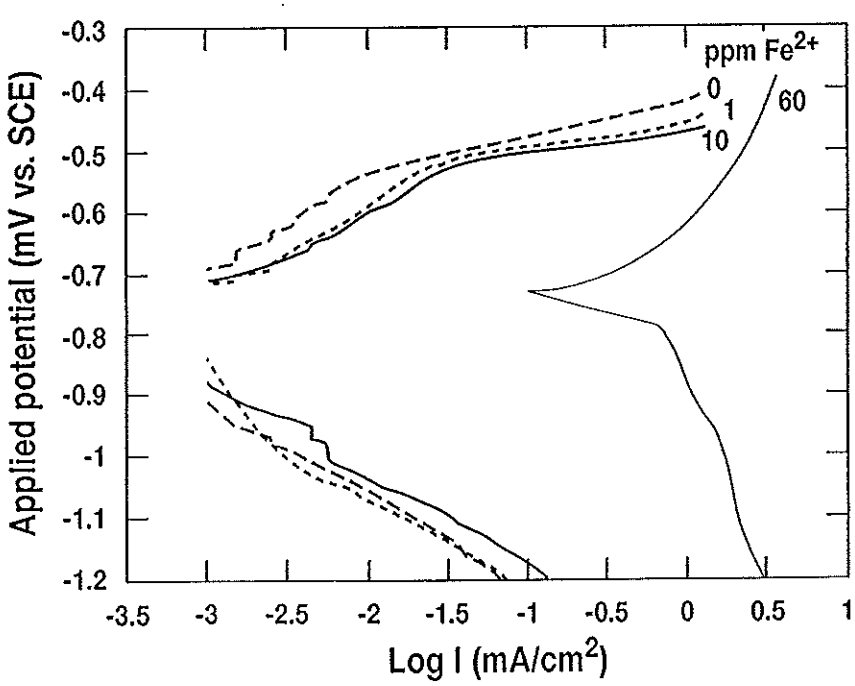

Fig. 11 Cathodic and anodic polarization curves of mild steel precoated with a biofilm in an iron-free medium followed by step increases in ferrous ion concentration in the influent. (After Lee & Characklis, 1993.)

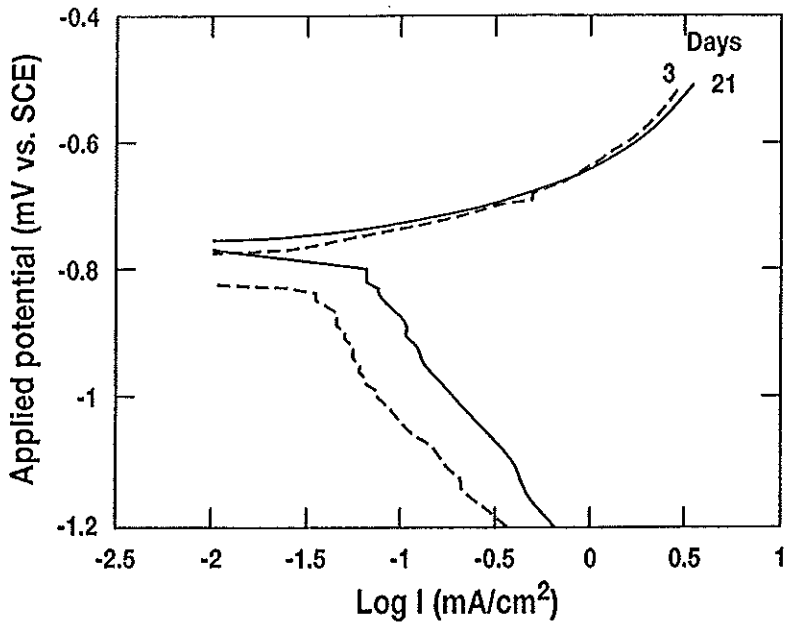

Fig. 12 Cathodic and anodic polarization curves of mild steel with suspended ferrous sulfide at different exposure times. (After Lee & Characklis, 1991.)

reduction of DO by a steel surface is unlikely in an aerobic/anaerobic biofilm system as microelectrode measurements have shown that the surface DO concentration was zero, the surface DS concentration was about 10 $mg \cdot l^{-1}$, and that SRB-enhanced corrosion was evident (Lee *et al.*, 1993b) (Fig. 13). Although the direct reduction of DO at ferrous

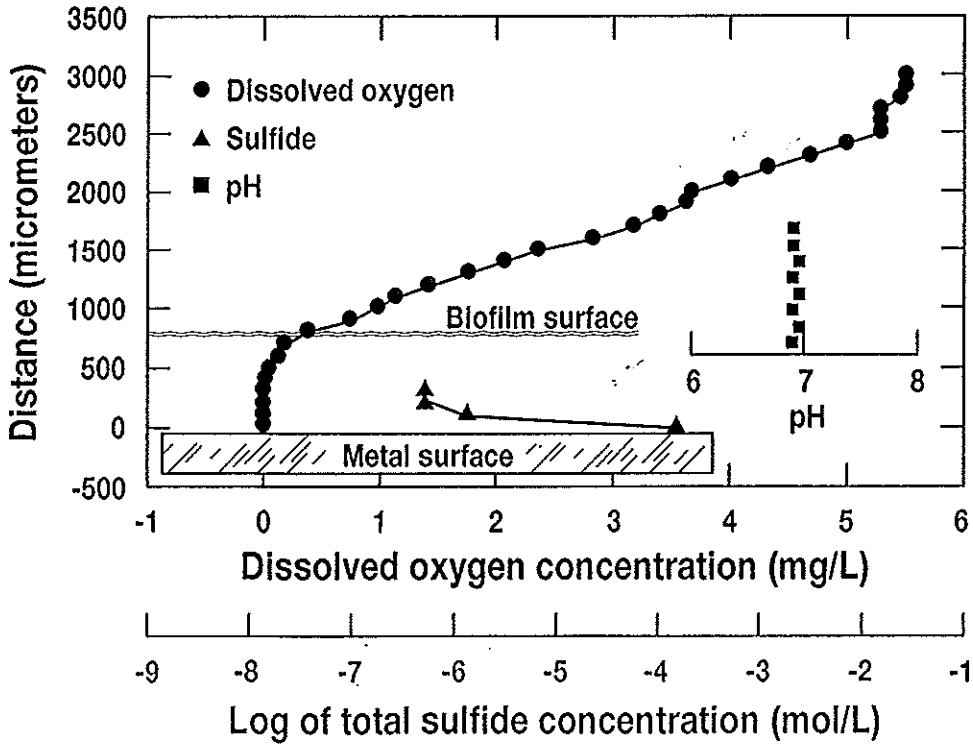

Fig. 13 pH, dissolved oxygen, and dissolved sulfide profiles through a biofilm to the steel surface after biofilm accumulation for 8 weeks. (After Lee *et al.*, 1993b.)

sulfides could consume hydrogen and cause cathodic depolarization, there is no experimental evidence to support this mechanism. On the other hand, the correlation between the corrosion rate and the amount of NAVS (McKenzie & Hamilton, 1992) indicates that the role of DO on SRB-related corrosion is most likely through the nature of the corrosion products formed. This point of view is further confirmed by results from electrochemical measurements.

In an abiotic system, Onuchukwu (1982) demonstrated that the sulfur derivatives of different types of iron rust (α-Fe_2O_3, α-FeO(OH), and Fe_3O_4) showed higher performance in the hydrogen evolution reaction than the sulfide prepared from fresh steel electrodes (Fig. 14). Even though the apparent correlation between the amounts of NAVS and corrosion rates in the biotic system is only indirect, polarization results obtained from abiotic system strongly indicate that NAVS are more corrosive toward mild steel than AVS. Polarization results conducted in a biofilm reactor further illustrate the high aggressiveness of AVS and NAVS in steel corrosion. Under conditions of continuous oxic bulk liquid, the aerobic process dominated corrosion during the early stage of biofilm accumulation and iron hydrates were the major corrosion products. Iron hydroxides are readily converted into iron sulfides and are consequently more cathodically active in stimulating corrosion than unreacted steel. During the later stage of biofilm accumulation, both AVS and NAVS were detected within fouling deposit and their areal concentrations increased with time (Lee *et al.*, 1993b) (Fig. 15). The initial

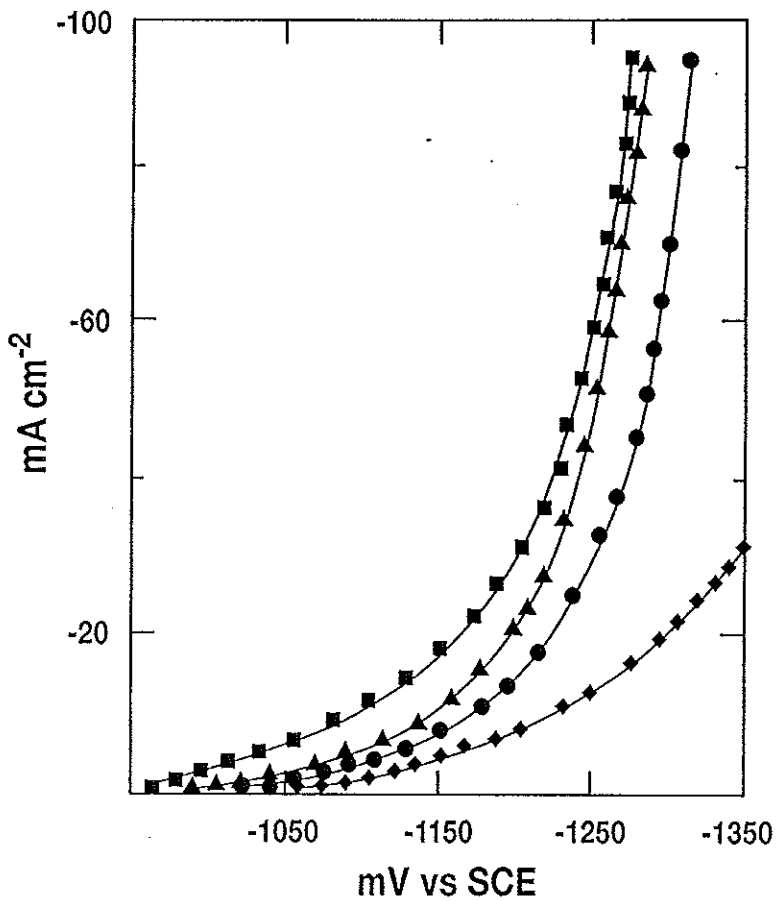

Fig. 14 H_2 evolution from various forms of iron sulfides. ♦ = sulfide of anodized steel; ● = sulfide from air-decomposed ferric nitrate; ▲ sulfide from Fe(II)–Fe(III) chlorides; ■ sulfide from rust (electrolyte 3.5% NaCl solution at 25°C, ir corrected). (After Onuchukwu, 1982.)

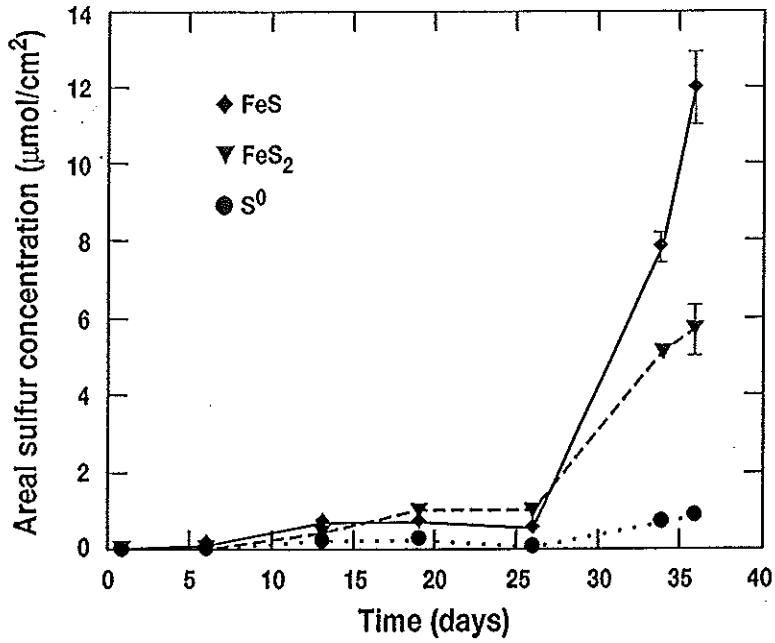

Fig. 17 Accumulation of acid-volatile sulfide (FeS) and non-acid-volatile sulfides (FeS_2 and S°) on a steel surface in alternating oxic and anoxic bulk liquid after different exposure times. (After Nielsen *et al.*, 1993.)

(160 mpy) were then observed and the mechanism was by cathodic-only depolarization (Nielsen *et al.*, 1993) (Fig. 18).

DISCUSSION

Rate-Controlling Step for SRB-Enhanced Corrosion

1. The totally anaerobic system

Processes contributing to corrosion of mild steel in a totally anaerobic biofilm are summarized in Figure 19 and are as follows: (1) transport of nutrients to the biofilm, (2) general anaerobic metabolic processes, (3) sulfate reducing process, (4) ferrous sulfide precipitation, and (5) electrochemical corrosion process. It has been demonstrated that mass transfer to the biofilm and diffusional resistances within the biofilm are major factors controlling biofilm SRB activity (Nielsen, 1987; Nielsen & Hvited-Jacobsen, 1988). Once SRB activity is established within the biofilm, iron sulfide nuclei quickly form and cover the steel surface as a result of the availability of sufficient ferrous and sulfide ions. At low ferrous ion concentrations, where an excess of sulfide ions results from bacterial growth, adherent and temporarily protective films of iron sulfides are formed on the steel surface with a consequent reduction in the observed corrosion. High rates of corrosion by SRB are maintained only in media containing high concentrations of ferrous ion. Consequently, the corrosion rate of mild steel is not controlled directly by SRB activity, but indirectly through the nature of reduced iron sulfides formed as corrosion products. The accelerated process is controlled by the cathodic reaction.

Based on the facts that the rates of corrosion are proportional to the rates of ferrous sulfide accumulation, and that activation energy for hydrogen evolution is lower at an iron sulfide surface than at a bare steel surface, it is reasonable to propose that the rate-

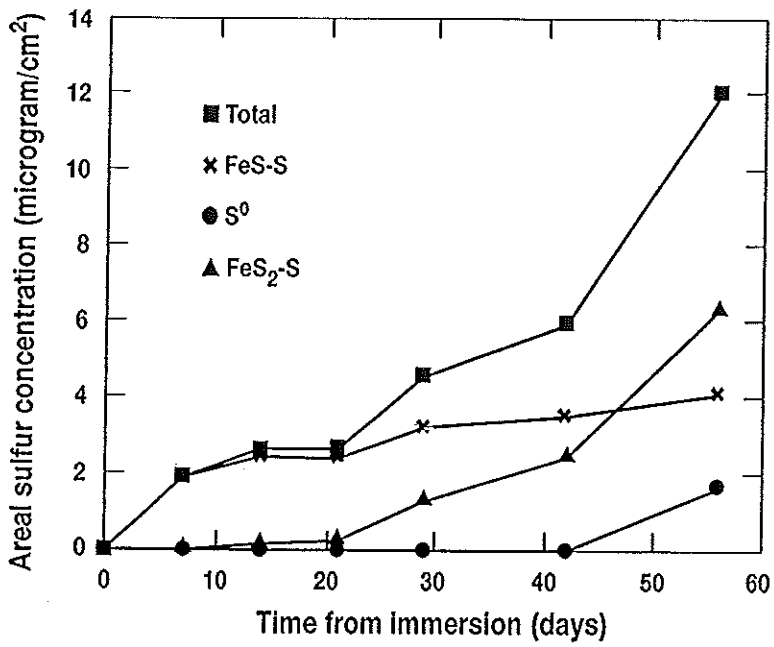

Fig. 15 Accumulation of acid-volatile sulfide (FeS) and non-acid-volatile sulfides (FeS_2 and S°) on a steel surface in continuous oxic bulk liquid after different exposure times. (After Lee *et al.*, 1993b.)

corrosion rate due to SRB activity in this system was attributed to both anodic and cathodic depolarization (Lee *et al.*, 1993a; 1993b) (Fig. 16) When, however, biofilms were developed over a prolonged timescale in alternating oxic and anoxic conditions (12 h oxic–12 h anoxic), this had the effect of maximizing the production of AVS and NAVS within fouling deposits (Nielsen *et al.*, 1993) (Fig. 17). Very high corrosion rates

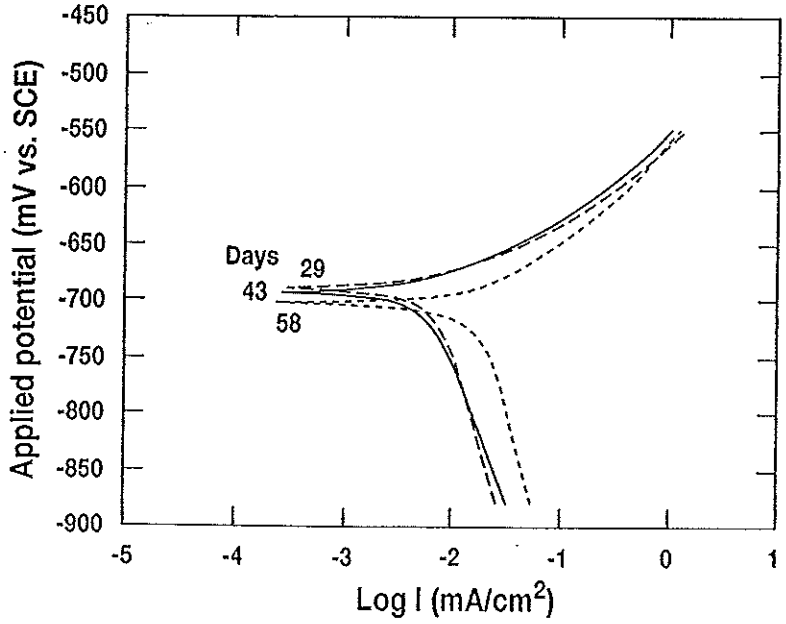

Fig. 16. Anodic and cathodic polarization curves of mild steel in continuous oxic bulk liquid after different exposure times. (After Lee *et al.*, 1993a.)

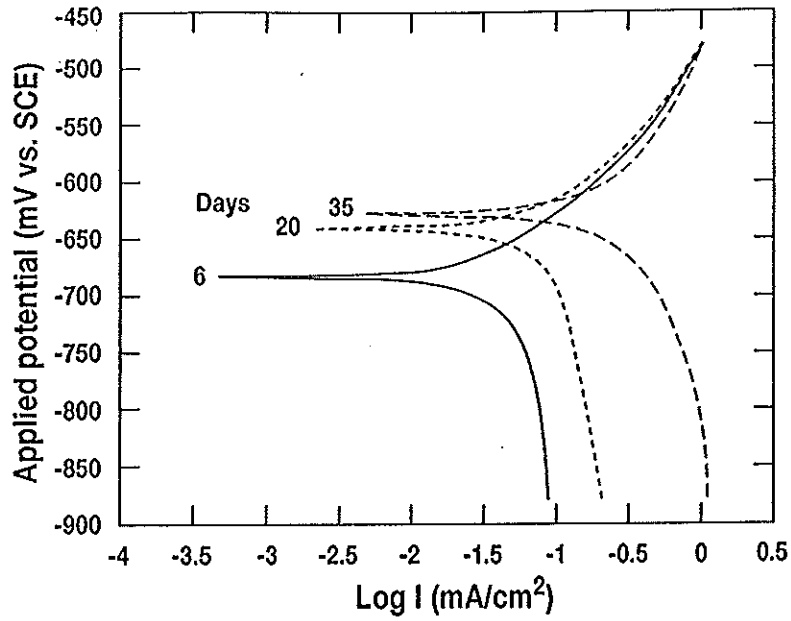

Fig. 18 Anodic and cathodic polarization curves of mild steel in alternating oxic and anoxic bulk liquid after different exposure times. (After Nielsen *et al.*, 1993)

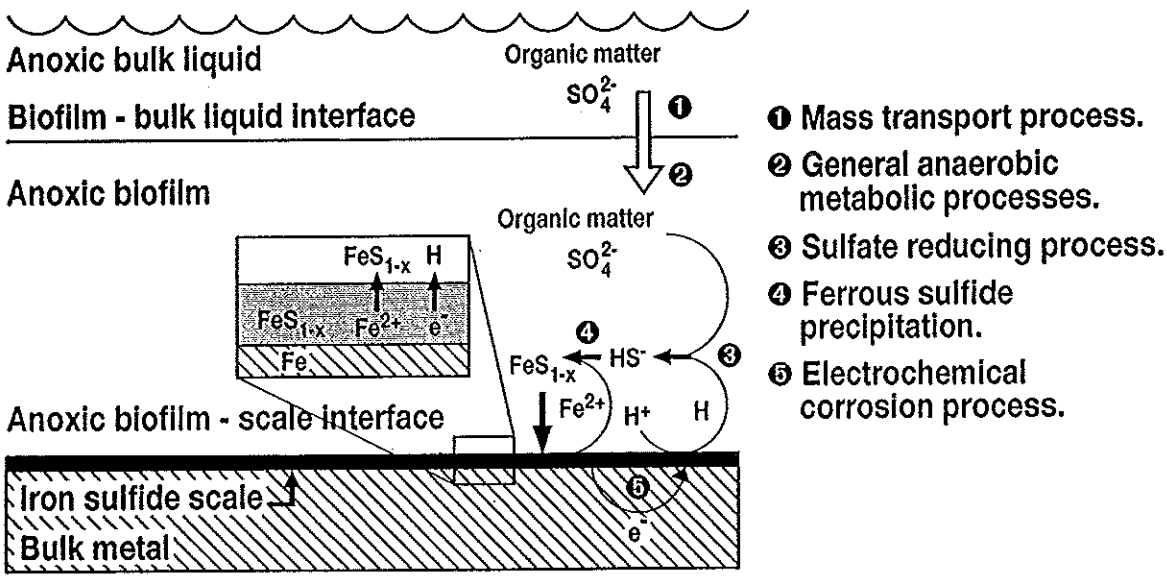

Fig. 19 Schematic diagram of transport and transformation processes contributing to corrosion of mild steel in a totally anaerobic biofilm.

controlling mechanism is associated with the iron sulfide film. An important question would then ask how the sulfides act to accelerate the cathodic reaction in this system. The total exchange current for hydrogen reduction is the product of the exchange current density and the effective cathodic area. If it is assumed that hydrogen ion discharge and electron transfer are occurring on and through the accumulated sulfides, it would be expected that an increase in the effective surface area of sulfide would lead to an increase in the cathodic reaction rate. The observed cathodic-only acceleration due to an increase of areal concentration of ferrous sulfide supports this mechanism. The role of SRB in the

corrosion process in oxygen-free environments is principally dependent on their ability to produce ferrous sulfides, as suggested by King *et al.* (1973).

2. *The aerobic/anaerobic system*

Processes contributing to the corrosion of mild steel in adjacent oxic and anoxic biofilms are summarized in Figure 20. There are more processes involved in the aerobic/anaerobic system than in a totally anaerobic system. In addition to the ferrous sulfide production, the oxygen uptake in the aerobic system needs to be addressed in order to explain the pronounced effect of DO on SRB-enhanced corrosion. The oxygen consumption in the aerobic system can be attributed to the following processes: (1) aerobic respiration processes; (2) microbial and chemical reoxidation of sulfides and ferro compounds (*e.g.* Fe^{2+}, FeS, FeS_2 and S°); and (3) cathodic depolarization process.

Among these processes, only (2) and (3) contribute to the increases in corrosion rate and in cathodic current density. Oxidation of sulfides and ferro compounds produces more corrosive sulfides facilitating the cathodic reaction. The corrosion rate increases as the reduced and oxidized iron sulfides areal concentration increases (Lee *et al.*, 1993a; 1993b; Nielsen *et al.*, 1993). This reinforces the galvanic cell mechanism as described for a totally anaerobic system, and indicates the importance of precipitation of corrosion products in controlling the rate of corrosion. The possible cathodic depolarization process can also be attributed to DO reacting with hydrogen atoms adsorbed on the ferrous sulfide lattice. Atomic hydrogen produced from the cathodic reaction can be adsorbed onto the bare steel surface or dissolved within the ferrous sulfide lattice. Theoretically, it is easier to depolarize ferrous sulfide than it is to depolarize steel, since atomic hydrogen is usually quite strongly adsorbed onto steel surfaces (Stott *et al.*, 1988). The rates of transport of hydrogen through different sulfides and their effects on corrosion rate require further study.

SUMMARY

It has been demonstrated that the interrelationship between biofilm SRB activities and corrosion rate is indirect. Corrosion products accumulating at the steel-biofilm interface

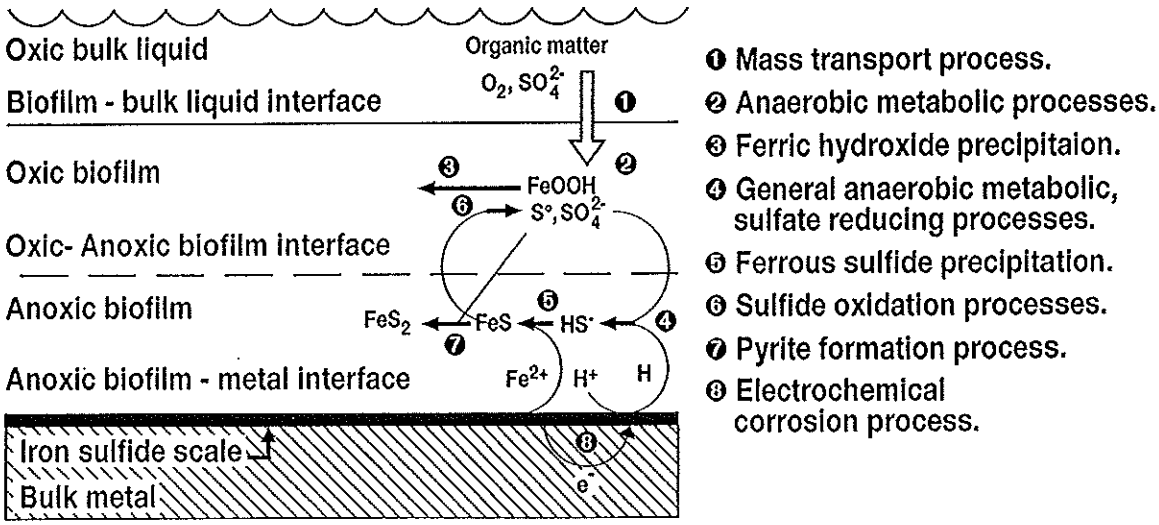

Fig. 20 Schematic diagram of transport and transformation processes contributing to corrosion of mild steel in an aerobic/anaerobic biofilm.

have a marked effect on the corrosion rate. A moderately protective layer of iron sulfide may form on the steel surfaces when steel is exposed to a totally anaerobic environment containing SRB. If dissolved ferrous ions are available, the passivating properties of this layer are destroyed. The resulting porous ferrous sulfide accumulation can enhance the initial corrosion rate through both anodic and the cathodic depolarization, but cathodic-only depolarization controls the later stages of the corrosion process due to continuing ferrous sulfide accumulation and the increase in the cathodic areal density.

Oxide films form on steel surfaces exposed to aerobic environments and provide protection against further corrosion. Development of SRB in this system reduces the stability of the protective film and enhances corrosion processes. The enhanced corrosion rate used by the SRB activity in aerobic systems also occurs through the anodic and the cathodic depolarization initially by the transformation of iron oxide to iron sulfides, but eventually cathodic-only depolarization again controls the corrosion process.

The mechanistic differences between SRB-enhanced corrosion of mild steel in a totally anaerobic system and in an aerobic system lie in the nature of the corrosion products. Only the reduced iron sulfides (such as mackinawite and greigite) are detected in a totally anaerobic system (Mcneil & Little, 1990; Craig, 1991), and they are not permanently cathodic toward mild steel (Tiller, 1985). The activity of SRB is required in this system in order to maintain the electrochemical activity of ferrous sulfide. However, the more oxidized iron sulfides (such as pyrite) and elemental sulfur are detected in addition to the reduced iron sulfides in an aerobic system. The corrosivity of pyrite toward mild steel as compared to the more reduced iron sulfides is not well understood, but the corrosivity of elemental sulfur toward mild steel is clearly illustrated. Once the environmental conditions for the elemental sulfur corrosion mechanism are established the corrosion process is autocatalytic. Consequently, continuing SRB activity may not be required to maintain the corrosion process.

Several areas for research are suggested by the present work, in part because the results to date only permit selection of competing processes but do not enable prediction of the corrosion rates under specified conditions. Sulfide scale growth is involved as an important process under both biotic and abiotic conditions. The approach to developing a unified theory of SRB-related corrosion must therefore be interdisciplinary and include a thorough process analysis combined with well-defined electrochemistry, surface chemistry, and microbiology. Specific matters which must be addressed quantitatively include: (1) the relationship between the rate of sulfide accumulation, the rate of biofilm accumulation, and the rate of dissolution of steel; (2) detailed analytical studies of the composition and the structure of iron sulfide scale, with particular attention to the presence of elemental sulfur, and their influence on corrosion rate; and (3) the chemical and biological conditions which lead to the autocatalytic corrosion process in the aerobic/anaerobic biofilm system.

A further key issue arises from the fact that most confirmed cases of SRB-related corrosion are characterized as localized pitting corrosion. Recently, it has been shown that some SRB are able to respire with Fe^{3+} or even oxygen instead of sulfate at low DO concentrations using hydrogen as electron donor (Dilling & Cypionka, 1990; Roden & Lovely, 1993). Measurements in microbial mats also indicate that sulfate reduction can take place directly in oxic environments (Frund & Cohen, 1992). The assumption hitherto that oxygen prevents all SRB activity may thus be in need of revision. Factors influencing localized corrosion are depicted schematically in Figure 21, in which both metallurgical heterogeneities and patchy biofilms are considered. The relative influences of chemical gradients and of colonization patchiness on localized corrosion should be pursued, with particular attention to the mechanism of tubercle formation. The system of iron bacteria

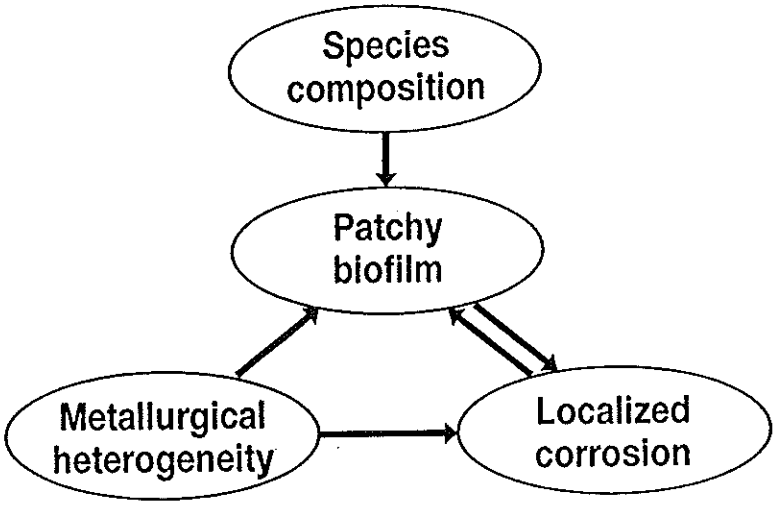

Fig. 21 Factors influencing localized corrosion of mild steel.

in association with SRB under aerobic conditions, and their effect on pitting rate being most urgently in need of further information and clarification. Finally, computer models of biofilm accumulation and corrosion kinetics should help to identify the rate-controlling step in the microbial corrosion processes, and provide perspectives on extending the insights to other metals and/or alloys. Given such efforts, one can anticipate eventual achievement of effective monitoring and control procedures aimed at minimizing SRB-related corrosion in environmental and industrial systems.

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References

Almgren T, Hagstrom I (1974) The oxidation rate of sulfide in seawater, *Water Res* **8:** 395–400

Berkowitz B J, Horowitz H H (1982) The role of H_2S in the corrosion and hydrogen embrittlement of steel. *J Electrochem Soc* **129:** 468–474

Berner R A (1970) Sedimentary pyrite formation. *Am J Sci* **268:** 1–23

Bolmer P W (1965) Polarization of iron in H_2S-NaHS buffers. *Corrosion* **21:** 69–75

Bond D C, Marsh G A (1950) Corrosion of wet steel by hydrogen sulfide-air mixtures. *Corrosion* **6:** 22–26

Bonnel A, Dabosi F, Deslouis C, Duprat M, Keddam M, Tribollet B (1983) Corrosion study of a carbon steel in neutral chloride solutions by impedance techniques. *J Electrochem Soc* **130:** 753–761

Booth G H, Tiller A K (1960) Polarization studies of mild steel in cultures of sulfate-reducing bacteria. *Trans Faraday Soc* **56:** 1689–1696

Booth G H, Tiller A K (1962a) Polarization studies of mild steel in cultures of sulfate-reducing bacteria. Part 2, thermophilic organisms. *Trans Faraday Soc* **58:** 110–115

Booth G H, Tiller A K (1962b) Polarization studies of mild steel in cultures of sulfate-reducing bacteria. Part 3, Halophilic organisms. *Trans Faraday Soc* **58:** 2510–2516

Booth G H, Shinn P M, Wakerley D S (1964) The influence of various strains of actively growing sulfate-reducing bacteria on the anaerobic corrosion of mild steel. In: *Congr Int Cor Marine Salissures Cannes*, Paris, CREO, pp 363–371

Booth G H, Robb J A, Wakerley D S (1967) The influence of ferrous ions on the anaerobic corrosion of mild steel by actively growing cultures of sulfate-reducing bacteria. In: *Third Int Cong Metallic Corrosion*, Moscow, Vol. 2, Section 5, pp 542–544

Booth G H, Elford L, Wakerley D S (1968) Corrosion of mild steel by sulfate-reducing bacteria: an alternative mechanism. *Br Corrs J* **3**: 242–245

Bryant R D, Jansen W, Boivin J, Laishley E J, Costerton J W (1991) Effect of hydrogenase and mixed sulfate-reducing bacterial populations on the corrosion of steel. *Appl Environ Microbiol* **57**: 2804–2809

Butler G, Ison H C K (1966) *Corrosion and its Prevention in Waters*. Reinhold, New York, pp 45

Carta R, Dernini S, Polcaro A M, Ricci P F, Tola G (1988) The influence of sulfide environment on hydrogen evolution at stainless steel cathode in alkaline solution. *J Electroanal Chem* **257**: 257–268

Characklis W G, Marshall K C (1990) *Biofilms*. John Wiley & Sons, New York, NY, pp 233

Chen K Y, Morris J C (1971) Oxidation of aqueous sulfide by O_2: 1. General characteristics and catalytic influence. In: *Advances on Water Pollution Research*. Pergamon press, Oxford, 2, III-32, pp 1–17

Chen K Y, Morris J C (1972) Kinetics of oxidation of aqueous sulfide by O_2. *Environ Sci Technol* **6**: 529–537

Cline J D, Richards F A (1969) Oxidation of hydrogen sulfide in seawater at constant salinity, temperature, and pH. *Environ Sci Technol* **3**: 838–843

Cord-Ruwisch R, Widdel F (1986) Corroding iron as a hydrogen source for sulfate reduction in growing cultures of sulfate-reducing bacteria. *Appl Microbiol Biotechnol* **25**: 169–174

Costello J A (1974) Cathodic depolarization by sulfate-reducing bacteria. *South Af J Sci* **70**: 202–204

Craig B C (1979) The nature of iron sulfides formed on steel in an H_2S-O_2 environment. *Corrosion* **35**: 136–138

Craig B D (1984) Effect of copper on the protectiveness of iron sulfide films. *Corrosion* **40**: 471–474

Craig B D (1991) Discussion of "Mackinawite formation during microbiol corrosion". *Corrosion* **47**: 329–329

Crolet J L (1992) From biology and corrosion to biocorrosion. *Oceanol Acta* **15**: 87–94

Crolet J L, Daumas S, Magot M (1993) pH regulation by sulfate-reducing bacteria. *Corrosion '93* NACE, Houston, Texas, paper No. 303

Das C, Venkateswaren G (1987) On the formation of protective sulfide coatings on carbon steel surfaces. *Corros Sci* **27**: 1287–1299

Daumas S, Magot M, Crolet J L (1993) Measurement of the net production of acidity by a sulfate-reducing bacterium: experimental checking of theoretical models of microbially influenced corrosion. *Res Microbiol* **144**: 327–332

Daumas S, Massiani Y, Crousier J (1988) Microbiogical battery induced by sulfate-reducing bacteria. *Corros Sci* **28**: 1041–1050

Dewar E J (1986) Control of microbiologically induced corrosion and accumulation of solids in a seawater flood system. *Mater Perf* **25**: 39–47

Dilling W, Cypionka H (1990) Aerobic respiration in sulfate-reducing bacteria. *FEMS Microbiol Lett* **71**: 123–128

Dvoracek L M (1976) Pitting corrosion of steel in H_2S solutions. *Corrosion* **32**: 64–68

Edyvean R G J, Videla H A (1991) Biological corrosion. *Interdis Sci Rev* **16**: 267–282

Ewing S P (1955) Electrochemical studies of the hydrogen sulfide corrosion mechanism. *Corrosion* **11**: 497t–501t

Ford T, Michell R (1990) The ecology of microbial corrosion. *Adv Microb Ecol* **11**: 231–262

Frund C, Cohen Y (1992) Diurnal cycles of sulfate reduction under oxic conditions in cyanobactriamats. *Appl Environ Microbiol* **58**: 70–77

Galbraith J M, Mabile N J, Vanbuskirk K A (1985) Monitoring sulfate-reducing microbes at Prudhoe bay, Alaska with corrosion coupons. *Corrosion '85*, NACE, paper No. 292

Gaylarde C C, Videla H A (1987) Localized corrosion induced by marine vibrio. *Int Biodeterior* **23**: 91–104

Gragnolino G, Tuovinen O H (1984) The role of sulfate-reducing and sulfide-oxidizing bacteria in the localized corrosion of iron-base alloy — a review. *Int Biodeterior* **20**: 9–26

Greco E C, Sardisco J B (1966) Reaction mechanisms of iron and steel in hydrogen sulfide. In: *Proc Third Int Cong Metallic Corrosion*, Moscow, pp 130–138

Gupta D V S (1981) Corrosion behavior of carbon steel I. Effect of pH and sulfide concentrations in aqueous neutral and alkaline solutions at room temperature. *Corrosion* **37**: 611-616

Hamilton W A, Maxwell S (1985) Biological and corrosion activities of sulfate-reducing bacteria within natural biofilms. In: Dexter S C (ed) *Biologically Induced Corrosion*, NACE-8, Houston, TX, pp 131–136

Hamilton W A (1985) Sulfate-reducing bacteria and anaerobic corrosion. *Ann Rev Microbiol* **39**: 195–217

Hardy J A, Bown J L (1984) The corrosion of mild steel by biogenic sulfide films exposed to air. *Corrosion* **40**: 650–654

Herro H M (1991) Tubercle formation and growth on ferrous alloys, *Corrosion '91*, NACE, Paper No. 84

Iofa Z A (1970) Effect of hydrogen sulfide on iron corrosion and on inhibitor adsorption in acidic solutions. *Prot Metals* **6**: 445–450

Jolley R A, Forster C F (1985) The kinetics of sulfide oxidation. *Environm Technol Lett* **6**: 1–11

King R A, Wakerley D S (1973) Corrosion of mild steel by ferrous sulfide. *Br Corros J* **8**: 41–45

King R A, Miller J D A, Smith J S (1973) Corrosion of mild steel by iron sulfides. *Br Corros J* **8**: 137–141

King R A, Miller J D A, Wakerley D S (1973) Corrosion of mild steel in cultures of sulfate-reducing bacteria: effect of changing the soluble iron concentration during growth. *Br Corros J* **8:** 89–93

King R A, Dittmer C K, Miller J D A (1976) Effect of ferrous iron concentration on the corrosion of iron in semicontinuous cultures of sulfate-reducing bacteria. *Br Corros J* **8:** 105–107

Kochelek J T, Stone P J (1989) Monitoring sessile bacteria contamination and the associated corrosion in a west texas water injection system. *SPE Int Symp Oilfield Chemistry*, Houston, TX, paper No. 18491

Kuhn A T, Kelsall G H, Chana M S (1983) A review of the air oxidation of aqueous sulfide solutions. *J Chem Tech Biotechnol* **33A:** 406–414

Lee W, Characklis W G (1991) Anaerobic corrosion processes of mild steel in the presence and absence of anaerobic biofilm. In: Rossmoore H W (ed) *Eighth Int Symp Biodeterioration and Biodegradation*, Windsor, Canada, pp 89–111

Lee W, Characklis W G (1993) Corrosion of mild steel under anaerobic biofilm. *Corrosion* **49:** 186–198

Lee W, Lewandowski Z, Okabe S, Characklis W G, Avci R (1993a) Corrosion of mild steel underneath aerobic biofilms containing sulfate-reducing bacteria PartI: at low dissolved oxygen concentration. *Biofouling* **7:** 197–216

Lee W, Lewandowski Z, Nielsen P H, Morrison M, Characklis W G, Avci R (1993b) Corrosion of mild steel underneath aerobic biofilms containing sulfate-reducing bateria PartII: at high dissolved oxygen concentration. *Biofouling* **7:** 217–239

Lefers J A, Koetsier W T, Van Swaaij W P M (1978) The oxidation of sulfides in aqueous solutions. *Chem Eng J* **15:** 111–120

Luther III G W (1991) Pyrite synthesis via polysulfide compounds. *Geochim Cosmochim Acta* **55:** 2839–2849

MacDonald D D, Roberts B, Hyne J B (1978) The corrosion of carbon steel by wet elemental sulfur. *Corros Sci* **18:** 411–425

Mara D D, Williams D J A (1972a) The mechanism of sulfide corrosion by sulfate-reducing bacteria. *Biodeterior Mater* **2:** 103–113

Mara D D, Williams D J A (1972b) Polarization of pure iron in the presence of iron sulfide minerals. *Br Corros J* **7:** 94–95

Martin R L (1974) Hydrogen penetration and damage to oil field steel. *Mater Perf* **13:** 19–23

Martin R L, Annand R R (1981) Accelerated corrosion of steel by suspended iron sulfides in brine. *Corrosion* **36:** 297–301

Maxwell S, Hamilton W A (1985) The activity of sulfate-reducing bacteria on metal surfaces in an oil field situation. In: Dexter S C (ed) *Biologically Induced Corrosion*, NACE-8, Houston, TX, pp 284

Maxwell S (1986) Effect of cathodic protection on the activity of microbial biofilms. *Mater Perf* **25:** 53–56

McKenzie J, Hamilton W A (1992) The assay of *in situ* activities of sulfate-reducing bacteria in a laboratory marine corrosion model. *Int Biodeterior* **29:** 285–297

Mcneil M B, Little B J (1990) Mackinawite formation during microbial corrosion. *Corrosion* **46:** 599–600

Meyer F H, Riggs O L, McGlasson R L, Sudbury J D (1958) Corrosion products of mild steel in hydrogen sulfide environments. *Corrosion* **14:** 109t–115t

Miller J D A, Tiller A K (1970) Microbial corrosion of buried and immersed metal. In: Miller J D A (ed) *Microbial Aspect of Metallurgy*. Elservier, New York, pp 61–105

Miller J D A (1981) Microbial biodeterioration. In: Rose A D (ed) *Metals*. Academic press, New York, pp 149–202

Moosavi A N, Pirrie R S, Hamilton W A (1990) Effect of sulfate reducing bacteria activity on performance of scarified anodes. In: Dowling N, Mittelman M M, Danko J C (eds) *Proc Int Symp Microbiolly Influenced Corrosion*, Knoxville, TN, pp 3-13 — 3-28

Morris D R, Sampalean L P, Veysey D N (1980) The corrosion of steel by aqueous solutions of hydrogen sulfide. *J Electrochem Soc* **128:** 1228–1235

Morse J W, Millero J M, Cornwell J C, Rickard D T (1987) The chemistry of the hydrogen sulfide and iron sulfide systems in nature waters. *Earth Sci Rev* **24:** 1–42

Nielsen P H (1987) Biofilm dynamics and kinetics during high rate sulfate-reduction under anaerobic conditions. *Appl Environ Microbiol* **53:** 27–32

Nielsen P H, Hvited-Jacobsen T (1988) Effect of sulfate and organic matter on the hydrogen sulfide formation in biofilms of filled sanitary sewers. *J Wat Poll Control* **60:** 627–634

Nielsen P H, Lee W, Lewandowwski Z, Morrison M, Characklis W G (1993) Corrosion of mild steel in an alternating oxic and anoxic biofilm system. *Biofouling* **7:** 267–284

O'Brien D J, Birkener F B (1977) Kinetics of oxygenation of reduced sulfur species in aqueous solution. *Environm Sci Technol* **11:** 1114–1120

Onuchukwu A I (1982) Hydrogen evolution on iron pyrite (FeS_Y) in sodium chloride solution. *Electrochim Acta* **27:** 529–533

Pankhania I P (1988) Hydrogen metabolism in sulfate-reducing bacteria and its role in anaerobic corrosion. *Biofouling* **1:** 27–47

Pedersen A, Hermansson M (1991) Bacterial corrosion of iron in seawater *in situ*, and in aerobic and anaerobic model systems. *FEMS Microbiol Ecol* **86:** 139–147

Pope D H, Soracco R J, Wilde E W (1982) Studies on biologically induced corrosion in heat exchanger systems at the Savannah river plant, Aiken, SC. *Mater Perf* **21:** 43–50

Pound B G, Wright G A, Sharp R M (1989) The anodic behavior of iron in hydrogen sulfide solutions. *Corrosion* **45:** 386–392

Ramanarayanan T A, Smith S N (1990) Corrosion of iron in gaseous environments and in gas-saturated aqueous environments. *Corrosion* **46:** 66–74

Rickard D T (1969) The chemistry of iron sulfide formation at low temperature. *Stockh Contr Geol* **20:** 67–95

Ringas C, Robinson F P A (1987) Microbial corrosion of iron-based alloy. *J S Afr Inst Min Metall* **87:** 425–437

Roden E E, Lovley D R (1993) Dissimilatory Fe(III) reduction by the marine microorganism *Desulfuromonas acetooxidants. Appl Environm Microbiol* **59:** 734–742

Salvarezza R C, Videla H A (1980) Passivity breakdown of mild steel in seawater in the presence of sulfate-reducing bacteria. *Corrosion* **36:** 550–554

Salvarezza R C, Videla H A, Arvia A J (1982) The electrodissolution and passivation of mild steel in alkaline sulfide solutions. *Corros Sci* **22:** 815–829

Salvarezza R C, Videla H A, Arvia A J (1983) The electrochemical behavior of mild steel in phosphate-borate-sulfide solutions. *Corros Sci* **23:** 717–732

Sanders P F, Hamilton W A (1985) Biological and corrosion activities of sulfate-reducing bacteria in industrial process plant. In: Dexter S C (ed) *Biologically Induced Corrosion*. NACE-8, Houston, TX, pp 47–68

Sardisco J B, Wright W B, Creco E C (1963) Corrosion of iron in H_2S–CO_2–H_2O system: corrosion film properties on pure iron. *Corrosion* **19:** 354t–359t

Sardisco J B, Pitts R E (1965) Corrosion of iron in H_2S–CO_2–H_2O system: mechanism of sulfide film formation and kinetics of sulfide film formation. *Corrosion* **21:** 245–253

Schmitt G (1991) Effect of elemental sulfur on corrosion in sour gas systems. *Corrosion* **47:** 285–308

Schoonen M A A, Barnes H L (1991a) Reactions forming pyrite and marcasite from solution: I. nucleation of FeS_2 below 100°C. *Geochim Cosmochim Acta* **55:** 1495–1504

Schoonen M A A, Barnes H L (1991b) Reactions forming pyrite and marcasite from solution: II. via FeS precursors below 100°C. *Geochim Cosmochim Acta* **55:** 1505–1514

Sheppard L R (1950) Corrosion of wet steel by hydrogen sulfide-air mixtures. *Corrosion* **6:** 26–28

Shoesmith D W, Taylor P, Bailey M G, Owen D G (1980) The formation of ferrous monosulfide polymorphs during the corrosion of iron by aqueous hydrogen sulfide at 21°C. *J Eletrochem Soc* **127:** 1007–1015

Smith C A, Compton K G, Coley F H (1973) Aerobic marine bacteria and the corrosion of carbon steel in seawater. *Corros Sci* **13:** 677–685

Smith J S, Miller J D A (1975) Nature of sulfides and their corrosive effect on ferrous metals: a review. *Br Corros J* **10:** 136–143

Snavely E S, Blount F E (1969) Rates of reaction of dissolved oxygen with scavengers in sweet and sour brines. *Corrosion* **25:** 397–404

Starkey R L (1985) Anaerobic corrosion — perspective about causes. In: Dexter S C (ed) *Biologically Induced Corrosion*, NACE-8, Houston, TX, 1965, pp 3–7

Stott J F D, Skerry B S, King R A (1988) Laboratory evaluation of materials for resistance to anaerobic corrosion by sulfate-reducing bacteria: philosophy and practical design. In: Francis P E, Lee T S (eds) *ASTM STP 970*, pp 98–111

Szklarska-Smialowska Z (1986) *Pitting Corrosion of Metals*. NACE, Houston, TX, pp 4

Tantall R E (1981) Case histories: bacteria induced corrosion. *Mater Perf* **20:** 41–47

Tapping R L, Lavoie P A, Davidson R D (1983) Effect of neutralization on protectiveness of sulfide films on carbon steel. *Mater Perf* **22:** 43–47

Taylor G F (1978) The corrosion of steel in heavy water production-operating experience and laboratory development. In: *Proc Seventh Int Congr Metallic Corrosion* pp 1536–1545

Tewari P H, Campbell A B (1979) Dissolution of iron during the initial corrosion of carbon steel in aqueous H_2S solutions. *Can J Chem* **57:** 188–196

Tewari P H, Bailey M G, Campbell A B (1979) The erosion-corrosion of carbon steel in aqueous H_2S solution up to 120°C and 1.6 Mpa pressure. *Corros Sci* **19:** 573–585

Thierry D (1987) Field observations of microbiologically induced corrosion in cooling water systems. *Corrosion '87*, NACE, paper No 364

Tiller A K (1985) A review of European research effort on microbial corrosion. In: Dexter S C (ed) *Biologically Induced Corrosion*. NACE-8, Houston, TX, pp 8–30

Uhlig H (1971) *Corrosion and Corrosion Control*. Johns Wiley & Sons, New York, NY, pp 92

Vera J, Kapusta S, Hackerman N (1984) Localized corrosion of iron in alkaline sulfide solutions. *J. Electrochem Soc* **133:** 461–467

Videla H A (1985) Corrosion of mild steel induced by sulfate-reducing bacteria–a study of passivity breakdown by biogenic sulfides. In: Dexter S C (ed) *Biologically Induced Corrosion*, NACE-8, Houston, TX, pp 162–171

Von Wolzogen Kuhr C A H, Ven der Vulgt L S (1934) Graphication of cast iron as an electrochemical process in anaerobics soil. *Water* **18:** 147–165

Wanklyn J N, Spruit C J P (1952) Influences of sulfate-reducing bacteria on the corrosion potential of iron. *Nature* **169:** 928–929

Weimer P J, Ng T K (1988) Use of continuous culture to assess biocorrosion by sulfate-reducing bacteria. *Corrosion '88*, St. Louis, Missouri, NACE, paper No. 90

Weimer P J, Van Kavelaar M J, Michel C B, Ng T K (1988) Effect of phosphate on the corrosion of carbon steel and on the composition of corrosion products in two-stage continuous cultures of *Desulfovibrio desulfuricans. Appl Environm Microbiol* **54:** 386–396

Wikjord A G, Rummery T E, Doern F E, Owen D G (1980) Corrosion and deposition during the exposure of carbon steel to hydrogen sulfide-water solutions. *Corros Sci* **20:** 651–671

Wilmot P D, Cadee, K, Katinic J J, Kavanagh B V (1988) Kinetics of sulfide oxidation by oxygen. *J WPCF* **60:** 1264–1267