Traditional methods for metal protection use organic coatings as a barrier to corrosive agents. One disadvantage of these artificial coatings is that a mechanically induced damage in the protective layer can result in a locally enhanced corrosion rate. A living aerobic film of bacteria consumes the oxygen dissolved in the aqueous medium, therefore it is possible to decrease corrosion by oxygen depletion at the metal surface. Because bacteria can coat metals with a natural, cheap, and regenerative biofilm, they might be used as a barrier to corrosive agents. One disadvantage of these artificial coatings is that a mechanically induced damage in the protective layer exists. Solution of the model equations gives spatial distribution of concentrations, potential, and current in solution, as well as as metal potential and corrosion current at the metal surface. We tested the influence of pH, aeration, salinity, and biofilm characteristics on the rate of metal corrosion. Model results show that a metal surface largely covered with purely aerobic biofilms can be protected against corrosion. The degree of metal coverage with bacteria significantly influences the heterogeneity of the corrosion pattern. In certain regions of the parameter space, formation of differential aeration cells leads to localized enhancement of corrosion under biofilm colonies, although the average corrosion rate decreases by decreasing oxygen concentration.

A three-dimensional mathematical model was developed to investigate interactions between aerobic biofilms and a metal surface, and to clarify conditions under which the onset of localized corrosion caused by aerobic microorganisms is likely to occur. The model includes transport of seven chemical species by diffusion and migration, electrochemical reactions at the metal surface, and homogeneous reactions in solution. The rate equation for iron dissolution reflects an active-passive-transpassive dependence on potential, influenced by pH and chloride ions. The model does not require a priori specification of where the anodic and cathodic regions exist. Solution of the model equations gives spatial distribution of concentrations, potential, and current in solution, as well as as metal potential and corrosion current at the metal surface. We tested the influence of pH, aeration, salinity, and biofilm characteristics on the rate of metal corrosion. Model results show that a metal surface largely covered with purely aerobic biofilms can be protected against corrosion. The degree of metal coverage with bacteria significantly influences the heterogeneity of the corrosion pattern. In certain regions of the parameter space, formation of differential aeration cells leads to localized enhancement of corrosion under biofilm colonies, although the average corrosion rate decreases by decreasing oxygen concentration.

In the present study, we investigate theoretically the possibility of reducing the corrosion rate by covering the metal surface with aerobic heterotrophic biofilms. A system of mass balances including diffusion, migration, and reaction terms for all relevant chemical species are transported to the metal/biofilm/liquid system by physical processes like molecular diffusion, convection, and migration of ions. The heterogeneity is three-dimensional, with strong concentration gradients making the chemical environment at the metal surface much different from the environment in bulk liquid. There are also important differences between places covered with bacterial colonies and the noncolonized areas. All these localized interactions pose an important challenge for experimentalists. Mathematical models therefore prove useful because they allow testing of hypothesis and, in addition, can direct experimental efforts to complex regions of operation that can easily confound the general intuition. Models based on reaction/transport principles can be used not only to test soundness of scientific concepts on biocorrosion mechanisms, but also “to establish rational engineering strategies for corrosion prevention.”

In the present study, we investigate theoretically the possibility of reducing the corrosion rate by covering the metal surface with aerobic heterotrophic biofilms. A system of mass balances including diffusion, migration, and reaction terms for all relevant chemical species and the electroneutrality condition must be solved to find concentration, potential, and current spatial distribution. Influence of dissolved oxygen concentration, salt concentration, and pH are examined in conjunction with the degree of metal surface covered by biofilm to study conditions under which the onset of localized corrosion is likely to occur.

Model Development

Model geometry.—The physical model consists of a planar metal surface (pure iron) on which colonies of microorganisms are distributed in an uneven manner (Fig. 1). The three-dimensional computational domain is rectangular. The top plane is the limit of the concentration boundary layer, assumed parallel with the metal surface. This parallelism is a fair approximation of the boundary layer only at low liquid velocities over the metal-biofilm system, when the metal area covered with biofilm is high, or when the biofilm
height is much smaller than the boundary layer thickness. A similar assumption has been made also in the biofilm model by Picioreanu et al.13

Chemistry and reaction stoichiometry.—Reactions taken into account are those leading to iron corrosion at pH values typically encountered in marine environments, thus in neutral and alkaline media.

Superficial reactions.—On the metal surface, the electrochemical transformations considered are: (i) iron dissolution (oxidation), as the anodic process which releases ferrous cations into the solution, and (ii) oxygen reduction, as the cathodic process which creates an alkaline medium

\[
\text{Anodic process } \quad \frac{1}{2} \text{Fe} \rightleftharpoons \frac{1}{2} \text{Fe}^{2+} + e^- \ \ i \ E_{e,i}^0 \quad \text{[1]}
\]

\[
\text{Cathodic process } \quad \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} + e^- \rightleftharpoons \text{HO}^- \ \ i \ E_{e,i}^0 \quad \text{[2]}
\]

Acid corrosion due to cathodic reduction of protons was neglected, being a much slower reaction in neutral or basic solutions. It should be mentioned here that the model does not explicitly specify which areas on the metal surface are the cathodes and which are anodes. The two reactions are both possible at the same time in a certain point on the metal-liquid interface. Repartition of anodic and cathodic areas results naturally from the predominance of one these processes, caused by the continuous oxygen and pH gradients of concentration. A similar approach exists in the modeling study of differential aeration corrosion by Alkire and Nicolaides.5

Homogeneous reactions.—We assumed as being essential two irreversible homogeneous reactions that consume the oxygen dissolved in water. First, in the biofilm volume, the process of aerobic heterotrophic microbial growth takes the dissolved oxygen and an organic source of carbon (generically denoted S) to produce new biomass, X, and other metabolic products. The oxygen consumption equation by microorganisms can be written as

\[
s_{\text{SO}}S + \text{O}_2 \rightarrow s_{\text{XO}}X \quad r_1
\]

It is assumed in what follows that the protons and other metabolites that may be either produced or consumed in the process will not considerably affect the pH of the medium. It is also assumed that the organic substrate S is neither kinetically nor stoichiometrically limiting the growth process. Therefore, stoichiometric coefficients \(s_{\text{SO}}\) and \(s_{\text{XO}}\) are of no further relevance. No other microbial activity takes place in the biofilm, like possible anaerobic growth, sulfur compounds reduction, or acid production.

The second irreversible reaction taking place both in the liquid and biofilm volume is the ferrous ion oxidation, a reaction that generates alkalinity, as in the case of electrochemical oxygen reduction

\[
\text{Ferrous ion oxidation } \quad \text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2 \text{HO}^- \quad r_2
\]

The model includes also two essential reversible reactions, considered to be at equilibrium because they occur very fast. Thermodynamic data show that ferric oxide (hematite) or ferric oxyhydroxide (goethite) precipitation is important at pH higher than 7.

![Figure 1. Schematic representation of the physical model.](image)

![Figure 2. Current-potential curves for anodic (\(i_1 - E\)) and cathodic (\(i_2 - E\)) reactions, calculated with the kinetic equations used in the model.](image)
Ferric ions precipitation $\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{FeOOH}^- + 3\text{H}^+ \quad [5]$

This causes a reduction of the alkalinity formed in the previous oxidation steps. Other hydrolysis reactions involving diverse ferrous and ferric ions were neglected, as well as the iron carbonate precipitation. The water dissociation equilibrium has also to be taken into account.

Water dissociation $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HO}^- \quad K_4 \quad [6]$

If a supporting electrolyte (e.g., NaCl) is present, then, besides all chemical species present in the above reactions, specified concentrations of electrolyte constituent ions (e.g., Na$^+$ and Cl$^-$) must also be included in the model formulation. The species included in the model are numbered for convenience as follows: (1) O$_2$, (2) Fe$^{2+}$, (3) Fe$^{3+}$, (4) HO$^-$, (5) H$^+$, (6) Na$^+$, and (7) Cl$^-$. To each solute $i$, a molar concentration $C_i$ was assigned.

**Reaction kinetics and thermodynamics.—Surface reactions.—I.**

The anodic dissolution rate of iron is calculated with an empirical equation based on a combination of Butler-Volmer type of kinetic expressions. Although apparently too complicated, this kinetic equation was designed to include three essential aspects: (i) an active-passive-transpassive dependence of the corrosion current on potential, (ii) dependence on pH, and (iii) influence of chloride ions on the 

<table>
<thead>
<tr>
<th>Table I. Model parameters.</th>
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<tbody>
<tr>
<td>Model parameter</td>
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<tr>
<td>Geometry</td>
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<tr>
<td>Kinetics and Thermodynamics</td>
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<td>Exchange current density for iron</td>
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<td>dissolution</td>
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<tr>
<td>Current density for iron</td>
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<td>dissolution in passive regime</td>
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<tr>
<td>Tafel slope for iron oxidation</td>
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<td>Standard reduction potential</td>
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<tr>
<td>for oxygen reduction</td>
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<td>for oxygen reduction</td>
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<td>for oxygen reduction</td>
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<tr>
<td>Standard reduction potential</td>
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<tr>
<td>Maximum specific rate of microbial</td>
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<td>oxygen consumption</td>
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<td>Rate constant for ferrous ion</td>
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<tr>
<td>oxidation</td>
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<tr>
<td>oxidation</td>
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<tr>
<td>FeOOH and Fe$_2$O$_3$</td>
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<tr>
<td>Physical properties</td>
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<tr>
<td>Diffusion coefficients in water</td>
</tr>
<tr>
<td>O$_2$</td>
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<tr>
<td>Fe$^{2+}$</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
</tr>
<tr>
<td>HO$^-$</td>
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<tr>
<td>H$^+$</td>
</tr>
<tr>
<td>Na$^+$</td>
</tr>
<tr>
<td>Cl$^-$</td>
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<tr>
<td>Concentrations in bulk liquid</td>
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<tr>
<td>O$_2$</td>
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<tr>
<td>Fe$^{2+}$</td>
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<tr>
<td>Fe$^{3+}$</td>
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<tr>
<td>HO$^-$</td>
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<tr>
<td>H$^+$</td>
</tr>
<tr>
<td>Na$^+$</td>
</tr>
<tr>
<td>Cl$^-$</td>
</tr>
</tbody>
</table>
Pitting of metal. Our system is characterized by an active-passive metal possibly undergoing differential aeration corrosion. That is, a typical iron dissolution kinetics shows an active range at very negative potentials, followed by a transition range (with decreasing density of current), then a passive range with constant and low current, and finally a pitting region with current increasing again due to the breakdown of the passive layer. The function used to model the density of anodic current, \( i_1 \), is

\[
i_1 = [(1 - \sigma)i_{1,a} + \sigma i_{1,p}](1 - \sigma_p) + [(1 - \sigma_{pd})i_{1,apit} + \sigma_{pd}i_{1,p}] \exp \left(-\frac{\alpha_1F}{RT}(\Phi_M - \Phi - E_{pc})\right)
\]

where \( i_{1,p} \) is the anodic current in the passive state. The density of current for iron dissolution in the active region (below the passivation potential) is represented by a Butler-Volmer kinetic equation

\[
i_{1,a} = i_{1,0} \exp \left(\frac{\alpha_1F}{RT}(\Phi_M - \Phi - E_{ct})\right) - \exp \left(-\frac{\alpha_1F}{RT}(\Phi_M - \Phi - E_{ct})\right)
\]

where \( i_{1,0} \) is the exchange density of current (\( \text{A m}^{-2} \)), \( 2.303RT/\alpha_1F = \beta_1 \) is the well-known Tafel slope (V per dec), \( \Phi_M \) is the electrostatic potential of the metal (V, SHE), and \( \Phi \) the potential of the solution just outside the double layer (V, SHE). The equilibrium potential at the local conditions is calculated from the standard electrode potential of the \( \text{Fe}^{2+}/\text{Fe} \) couple (V, SHE)

\[
E_{ct} = E_{ct}^0 + \frac{0.059}{2} \log(C_2)
\]

The shift from the active to passive region is made by a sigmoidal function, \( \sigma \), as suggested by Hines:

\[
\sigma = \frac{\exp \left[2\frac{\alpha_1F}{RT}(\Phi_M - \Phi - E_p)\right]}{1 + \exp \left[-2\frac{\alpha_1F}{RT}(\Phi_M - \Phi - E_p)\right]}
\]

The passivation potential, \( E_p \), corresponds to the maximum current density, above which passivation begins. \( E_p \), called also the Flade potential, is found to be for iron a linear function of pH:

\[
E_p = E_p^0 - 0.059\text{pH}
\]

with \( E_p^0 \) being the Flade potential at pH 0. The values of exchange density of current in the active regime \( i_{1,0} \), the Tafel slope \( \beta_1 = 2.303RT/\alpha_1F \), the passivation potential \( E_p^0 \) and the anodic current in the passive state \( i_{1,p} \) have been estimated by fitting the experimentally found stationary anodic polarization curves of iron in neutral and alkaline solutions (see Fig. 2a).

The pitting branch of the polarization curve of iron is incorporated in the kinetic expression with the use of other two empirical sigmoidal switch functions.

---

Table II. Structural characteristics of test case biofilms.

<table>
<thead>
<tr>
<th>Biofilm</th>
<th>Superficial biomass density ((\text{g m}^{-2}))</th>
<th>Biofilm surface area enlargement (\text{(m}^2\text{ biofilm-liquid interface m}^{-3}\text{ metal}))</th>
<th>Biofilm maximum thickness (\mu\text{m})</th>
<th>Roughness coefficient of biofilm</th>
<th>Biofilm compactness (\text{(m}^3\text{ biofilm m}^{-3}\text{ total space}))</th>
<th>Metal surface coverage (\text{(m}^2\text{ biofilm m}^{-2}\text{ metal}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.28</td>
<td>0.425</td>
<td>120</td>
<td>0.375</td>
<td>0.110</td>
<td>0.162</td>
</tr>
<tr>
<td>2</td>
<td>0.58</td>
<td>1.115</td>
<td>120</td>
<td>0.363</td>
<td>0.201</td>
<td>0.380</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>1.336</td>
<td>120</td>
<td>0.354</td>
<td>0.290</td>
<td>0.469</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>1.791</td>
<td>120</td>
<td>0.319</td>
<td>0.314</td>
<td>0.742</td>
</tr>
<tr>
<td>5</td>
<td>1.20</td>
<td>1.986</td>
<td>120</td>
<td>0.311</td>
<td>0.455</td>
<td>0.861</td>
</tr>
<tr>
<td>6</td>
<td>1.40</td>
<td>2.004</td>
<td>120</td>
<td>0.278</td>
<td>0.542</td>
<td>0.954</td>
</tr>
<tr>
<td>7</td>
<td>2.90</td>
<td>1.000</td>
<td>120</td>
<td>0</td>
<td>1.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Figure 3. Three-dimensional visualization of biofilm structures no. 1-6 [(a)-(f), respectively]. Structural characteristics are in Table II. Note that because of the boundary conditions imposed, these geometries repeat themselves periodically in \( y \) and \( z \) directions.
The behavior of current-potential function $i_1$, at variable pH or variable chloride concentration is presented in Fig. 2b. The cathodic rate of oxygen reduction is represented also with Butler-Volmer kinetic expressions

$$i_2 = i_{2,0} \left\{ \exp \left[ \frac{\alpha_2 F (\Phi_M - \Phi - E_{e,2})}{RT} \right] - \exp \left[ -\frac{-\alpha_2 F (\Phi_M - \Phi - E_{e,2})}{RT} \right] \right\}$$  \hspace{1cm} [16]$$

with the equilibrium potential for the O$_2$/HO$^-$ half reaction at 298 K being

$$E_{e,2} = E_{e,2}^0 + \frac{0.059}{4} \log \left( \frac{C_1}{C_1^0} \right) - 0.059 \log(C_4)$$  \hspace{1cm} [17]$$

and the Tafel slope $\beta_2 = 2.303RT/\alpha_2 F = 0.059/\alpha_2$. The exchange current $i_{2,0}$ depends on molar concentrations of participant solutes (oxygen and hydroxyl ion)$^{20,21}$

$$i_{2,0}(C_1,C_4) = i_{2,0}^\infty(C_1)^{\gamma_1}(C_4)^{\gamma_4}$$  \hspace{1cm} [18]$$

Homogeneous reactions.—1. The oxygen consumption rate by microorganisms, $r_1$, follows a Monod equation with oxygen limitation

$$r_1 = q_{om} C_X \frac{C_1}{K_1 + C_1}$$  \hspace{1cm} [19]$$

where $q_{om}$ is the maximum specific rate of microbial oxygen consumption (s$^{-1}$), $K_1$ is a saturation (Monod type) constant for oxygen (kg m$^{-3}$), and $C_X$ is the local concentration of active biomass (kg m$^{-3}$). Typical values of the parameters for aerobic heterotrophic microorganisms were assumed.$^{22}$ Ferrous ion oxidation rate depends on concentrations of Fe$^{2+}$, dissolved oxygen, and pH$^{23,24}$

$$r_2 = C_2 \left( k_2 + C_1^2 C_4^2 \frac{C_1}{C_1^0} \right)$$  \hspace{1cm} [20]$$
where \( k_2 \) and \( K_2 \) are rate constants, and \( C_1^* \) is the oxygen solubility in water at 1 atm.

3. Ferric ion precipitation is a very fast homogeneous reaction taking place in the solution; therefore, the equilibrium equation, with the equilibrium constant \( K_3 \), is assumed true at each point in the solution

\[
K_3 = \frac{C_i^3}{C_3} \quad [21]
\]

4. Finally, the ionic product of water (water dissociation equilibrium) is represented by

\[
K_4 = C_4C_5 \quad [22]
\]

Values of all kinetic parameters used are in Table I.

**Figures 5.** Spatial distribution of potential in solution \( \Phi \) (V, SHE) for the biofilm structure no. 3 with 0.75 g biomass/m². Bulk concentrations are \( [O_2] = 0.5 \text{ g/m}^3 \), \( [Cl^-] = 10^{-7} \text{ M} \), and pH 7. Top contour maps are vertical sections in the plane \( z = 280 \mu \text{m} \). Bottom contour maps are at \( x = 0 \) (metal surface). Isopotential lines are equally spaced at 1 mV. The biofilm position is shown by a gray shade on the potential distribution map.

**Figure 6.** Spatial distribution of ionic currents for the biofilm structure no. 3 with 0.75 g biomass/m². Bulk concentrations are \( [O_2] = 0.5 \text{ g/m}^3 \), \( [Cl^-] = 0.1 \text{ M} \), and pH 7. Top \( x-y \) vector map is a vertical slice at \( z = 280 \mu \text{m} \). Bottom \( z-y \) vector map is the projection on the plane \( x = 0 \) (metal surface). The biofilm position is shown by a gray shade.

Processes (growth/detachment/decay) are much slower than the relatively fast physical and chemical processes considered in this model (diffusion/migration/reactions).

2. The mass flux of each species contains transport terms by molecular diffusion in a concentration gradient, and, for charged species only, also migration in the electric field. Convection of species by a moving electrolyte was neglected.

3. In the approximation of infinite dilute solution, the ionic mobility was related to the more convenient diffusion coefficient by the Nernst-Einstein equation.

4. Physical parameters (e.g. diffusion coefficients) were assumed constant, and the system was isothermal.

With these assumptions, material balances for a small liquid volume element are written for all seven chemical species

\[
D_i \nabla^2 C_i + D_{zi} \frac{F}{RT} \nabla(C_i \nabla \Phi) + \sum_{j=1}^{1} s_{ij} r_j = 0 \quad i = 1, 2, \ldots, 7 \quad [23]
\]

where \( \Phi \) is the electric potential (V), \( D_i \) the diffusion coefficient (m² s⁻¹), \( z_i \) the charge (e⁻/mol), \( F \) is Faraday’s constant (96487 C/e⁻), \( R \) the universal gas constant (J mol⁻¹ K⁻¹), \( s_{ij} \) is the stoichiometric coefficient of species \( i \) in the \( j \)th homogeneous reaction with rate \( r_j \) (mol m⁻³ s⁻¹), and \( \nabla \) is the divergence operator written in 3D Cartesian coordinates. Because there are seven partial differential
equations with eight unknowns (besides concentrations \( C_i \), the field of potential \( \Phi \) in the solution has also to be determined), the set of equations is closed with the equation of local electroneutrality

\[
\sum_i z_i C_i = 0 \quad \text{[24]}
\]

This equation for conservation of charge (when applied outside the few nanometers thick double layer close to the metal surface) replaces in fact with a very good approximation the more troublesome Poisson’s equation of electrostatic potential.

**Boundary conditions.**—1. The concentrations at the boundary layer-bulk liquid interface \((y = L)\) were set equal to those in the bulk solution

\[
C_i = C_{i,b} \quad \text{[25]}
\]

The bulk concentrations also obeyed the electroneutrality condition. The absolute value of potential in the bulk liquid (i.e., on a plane far from the metal surface) is arbitrary and therefore it was set to zero on this outside boundary\textsuperscript{27}

\[
\Phi = 0 \quad \text{[26]}
\]

2. At the metal-liquid interface \((x = 0)\), the normal component of the total flux of each species is related to the normal component

\[
\text{Figure 7.} \quad \text{Distribution of (a) anodic and (b) cathodic current densities normal on the metal surface, for biofilm structure no. 3 with 0.75 g biomass/m}^2. \quad \text{Bulk concentrations are } \left[O_2\right] = 0.5 \text{ g/m}^3, \left[\text{Cl}^-\right] = 0.1 \text{ M, and pH 7. Contour levels are in both plots equally spaced at 0.001 A/m}^2. \quad \text{Note the much stronger gradients in the cathodic current intensity.}
\]

\[
\text{Figure 8.} \quad \text{Distribution of anodic density of current, } i_1, \text{ on the metal surface, at different fractions of metal covered with biofilms (structures 1-6). Bulk concentrations for this simulation case are } \left[O_2\right] = 0.5 \text{ g/m}^3, \left[\text{Cl}^-\right] = 0.1 \text{ M, and pH 7. Gray levels indicate the corrosion rate on a logarithmic scale ranging from the lowest corrosion rate (10}^{-3} \text{ A/m}^2, \text{ white) to the strongest corrosion (6} \times 10^{-3} \text{ A/m}^2, \text{ black).}
\]
of the current density, \(i_j\). That is, the rate of superficial production of a species on the metal surface must equal the flux transported away by diffusion and migration. With each electrode reaction written in the general form

\[
\sum n_jM_i^j \rightarrow n_pe^- \quad j = 1, 2
\]  

the boundary condition for each reacting species is

\[
D_i \frac{\partial C_i}{\partial x} + D_z \frac{\partial \Phi}{\partial x} + \sum n_jF_i j = 0
\]  

where \(n_j\) is the number of electrons transferred in electrode reaction \(j\) and \(M_i\) is a symbol for the chemical formula of species \(i\). For nonreacting species (such as Cl\(^-\) and Na\(^+\)), the normal total flux is zero. To close the problem, the electroneutrality equation, Eq. 24, is also applied.

3. A periodic space was made in \(y\) and \(z\) directions. That is, concentrations and potentials on the domain side at \(y = L_Y\) equal those at \(y = 0\), and similarly, values at \(z = L_Z\) equal values at \(z = 0\).

Zero-current condition.—In a corrosion system, electrochemical reactions on the metal surface do not generate a net current. In other words, the total (over the full metal surface) anodic current must be balanced by the total cathodic current at the corrosion potential \(E_{\text{corr}} = \Delta \Phi_{\text{corr}} = (\Phi_M - \Phi)_{\text{corr}}\). The unknown metal potential, \(\Phi_M\), which appears in equations for densities of current \(i_1\) and \(i_2\), is calculated so that the zero net current condition on the metal surface is satisfied

\[
\int_0^{L_Y} \int_0^{L_Z} (i_1(\Phi_M) + i_2(\Phi_M))d\zeta dy = 0
\]  

Method of solution.—By simple arithmetical manipulations, the mass balances, Eq. 23 written for ferric and for proton ions were replaced with equilibrium equations for the fast iron precipitation and water dissociation. By substituting the potential \(\Phi\) with a non-dimensional potential \(\varphi = \Phi F/RT\), the mass and charge balances in volume become

\[
\begin{align*}
\text{O}_2 & - \nabla^2 C_1 - [r_1(C_1) + 0.25r_2(C_1, C_2, C_4)]/D_1 = 0 \\
\text{Fe}^{2+} & \nabla^2 C_2 + 2\nabla(C_2 \nabla \varphi) - r_2(C_1, C_2, C_4)/D_2 = 0 \\
\text{HO}^- & D_3 \nabla^2 C_3 - D_3 \nabla(C_3 \nabla \varphi) - 3D_3 \nabla^2 C_3 - 9D_3 \nabla(C_3 \nabla \varphi) - 2r_2(C_1, C_2, C_4) = 0 \\
\text{Na}^+ & \nabla^2 C_6 + \nabla(C_6 \nabla \varphi) = 0 \\
\text{Cl}^- & \nabla^2 C_\gamma - \nabla(C_\gamma \nabla \varphi) = 0 \\
\text{Fe}^{3+} & K_3 - C_3/C_\gamma = 0 \\
\text{H}^+ & K_4 - C_\gamma C_3 = 0 \\
\text{Charge} & 2C_2 + 3C_3 - C_4 + C_5 + C_6 - C_\gamma = 0
\end{align*}
\]

Similar treatment of model equations can be found in the literature.\textsuperscript{27-30} In this way, the system to be solved was reduced to five second-order partial differential equations (PDEs) Eq. 30-34, plus three algebraic equations [two nonlinear (Eq. 35 and 36) and one linear (Eq. 37)], plus the integral equation (Eq. 29). The PDEs are also strongly nonlinear due to the reaction terms, either in volume or on the metal surface. Equations 30-34 were discretized with a seven point centered finite difference scheme in each point of the computational domain. The boundary conditions at the metal surface (Eq. 28) were also discretized by centered finite difference with interior point at the boundary.\textsuperscript{31}

The finite difference equations are coupled with equilibrium constraints and charge balance equations written in each grid node (Eq. 35-37), and with the zero-current condition (Eq. 29) evaluated by the trapezoidal rule. The result is a highly nonlinear system of algebraic equations that has to be solved to find the spatial distribution of concentrations \(C_1\) - \(C_\gamma\) and potential \(\varphi\), and the metal potential \(\varphi_M\). This system was solved by a classical Newton-Raphson procedure.\textsuperscript{31} The convergence rate and stability of the nonlinear algorithm are significantly improved by providing an analytical Jacobian matrix. For this task, the analytical derivatives were computed with the symbolic package from MATLAB. The linear system involved in the Newton-Raphson routine was solved by the biconjugate gradient method (BiCG) with Jacobi preconditioning, an iterative method adequate for large systems of linear equations with a sparse matrix of coefficients.\textsuperscript{32} The nonlinear numerical solution greatly depends on the initial guess of the concentration and potential fields. A multigrid method\textsuperscript{33} was used to refine the solution obtained on the course initial grid (2 \(\times\) 4 \(\times\) 4 nodes) to the finest grid (16 \(\times\) 32 \(\times\) 32 nodes) by a succession of mesh size doubling and bilinear interpolations to find the initial approximation at each grid level. The initial guess on the coarsest grid is a uniform distribution of concentration and potential at the values from the bulk liquid. The program written in standard C needs <1 h to find the solution of this system on a 16 \(\times\) 32 \(\times\) 32 grid, running on a Pentium III PC (800 MHz).

Being highly nonlinear, the system may have multiple solutions, as shown even for a simpler system.\textsuperscript{3} However, it was beyond our goal to deal with multiplicity of steady states. In that case, stability analysis should also be performed, or dynamic simulations must start with a realistic initial condition. If the corrosion model, as it is presented in this study, were included in the model for biofilm development in time,\textsuperscript{34} then it should be easier to find realistic stable states of corrosion system. Such an application, however, will be the object of future work.

Results and Discussion

Although we tried to use realistic parameters for the model, simulation results should serve only for orientation on possible effects, but not as ultimate quantitative data. This is because electrode kinetic data found in the literature differ very much and they are often unreliable. A possibility would have been to make use of di-
mensionless groups in studying diverse environmental effects on corrosion rates. However, we feel that this would have abstracted too much an already complex problem, and one could easily lose grip on the real parameters like pH, oxygen concentration, or salinity.

Biofilm geometry and simulation plan.—Six biofilm geometries were considered, with characteristics listed in Table II (cases 1-6). These structures were generated with the diffusion-reaction-growth (DRG) model we reported earlier.13 The objective was to obtain different biofilm compactness and fraction of metal covered by the biofilm, but having finally the same maximum biofilm thickness (120 μm). To do this in the frame of the DRG model, biomass was inoculated in 1, 3, 5, 20, 40, and 100 grid elements adjacent to the metal surface. From these seed points, colonies of bacteria as shown in Fig. 3 grew after some time. The more elements inoculated with biomass, the more compact the emerging biofilm develops. The biofilm structural measures shown in Table II are explained in detail in another publication.13 In addition, calculations were done also for two limiting cases: a bare metal surface (case 0 in Table II) and a compact biofilm with uniform thickness of 120 μm (case 7 in Table II).

For each biofilm geometry, simulations were done with variation of three parameters: aeration, acidity, and chloride concentration. At normal aeration, dissolved oxygen concentration in the bulk was 5 g/m³, and at reduced aeration, it was 0.5 g/m³. Two acidity conditions, pH 7 and 8, and three NaCl concentrations in the bulk 1, 0.1, and 10⁻¹ M were considered in all combinations with each other.

Concentration, potential, and current distributions.—Solution of the system of Eq. 29-37 gives the three-dimensional spatial distribution of concentrations $C_1$-$C_7$ and potential $\Phi$ in solution and also the metal potential $\Phi_M$. In addition, the vector field of total ionic currents at each point in the solution can be computed as

$$i = -\frac{F^2}{RT} \nabla^2 \Phi \sum_{i=2}^7 z_i^2 D_i C_i - \frac{F}{\sum_{i=2}^7 z_i D_i} \nabla C_i$$

[38]

Contour maps of the oxygen distribution (Fig. 4) indicate substantial differences of concentration between different locations on the metal surface. There can be an order of magnitude difference in the oxygen concentration between the bare areas and the biomass-covered areas. These differences are caused by the nonuniformity and patchi-
ness of bacterial colonies repartition, which allows formation not only of strong vertical (x-y plane) gradients of concentration but also significant in horizontal direction (y-z plane). By comparing these oxygen gradients in vertical direction with those resulted in case 0 (no biofilm), it can be concluded that reaction $r_1$ (oxygen consumption by bacteria) and not reaction $i_2$ (oxygen reduction on the metal surface) is mainly responsible for generation of these gradients.

Nonuniform oxygen concentration on the metal surface implies a lower rate of oxygen reduction under the biofilm (shown as a gray shade on the potential map in Fig. 4) than in the areas free of biofilm. As a result, a higher alkalinity is created on the areas uncovered by bacteria. This can be clearly seen on the pH contour maps shown in Fig. 4. Actually, the pH gradients were very much diminished by the iron precipitation reaction that consumes hydroxyl ions. Simulations done without including the equilibrium Eq. 5 yielded stronger pH variations, about 4-5 units of pH, instead of the maximum 1-2 units resulting from the present model.

At high salt concentrations, such as 0.1 M, the solution is highly conductive. Therefore, there are almost no potential gradients in the solution (Fig. 4c). Ionic transport is then determined by the rate of molecular diffusion, driven by concentration gradients. Migration can play a more important role at low salinity (case $10^{-7}$ M), when sensible potential gradients may form (Fig. 5).

The vectorial plots of total current density clearly indicate the formation of anodic and cathodic areas on the metal surface (Fig. 6). The current vector (by definition, the flux of positively charged ions, defined by Eq. 38) points outward metal (plane $x = 0$) under the biofilm and it reverses in outside areas. Overall, the ionic current flows from the biofilm to the open regions. The vertical cross section from Fig. 6 shows a gradual change in the magnitude of normal current densities, from a positive value in the biofilm area to a negative value in the open zones. However, the total normal current on the surface must be zero, as already imposed by Eq. 29. The normal current is the algebraic sum of anodic current generated by iron dissolution (Fig. 7a) and cathodic current produced by oxygen reduction (Fig. 7b). As Fig. 7 indicates, there are much stronger gradients of cathodic current between open and biofilm-covered areas than the gradients of anodic current. This is because the superficial reaction rate $i_2$ is much more sensitive to variations of oxygen concentration than is rate $i_1$ to variations of pH. The result is that the cathodic areas (places of oxygen reduction) are much better delimited than what we call “anodic areas” (places of iron oxidation), which appear to be more diffuse.
Local corrosion currents.—In certain situations, the differences between corrosion rates at different locations on the metal surface can be quite important. Model results indicate that the degree of metal coverage with bacteria significantly influence the heterogeneity of the corrosion pattern. Results for the test case at 0.5 g O₂/m³, pH 7, and 0.1 M NaCl are presented in Fig. 8. Dark areas in Fig. 8 indicate places of high corrosion rate on a gray scale correlated with the logarithm of anodic current density, the same scale for all six images. At the lowest coverage (~16%), there is less corrosion because the potential and pH are high enough to assure uniform passivation of the metal surface. As more bacteria cover the metal, the corrosion potential is decreased toward the active-passive region because less oxygen becomes available. It is therefore possible that zones covered by bacteria become active, while regions free of bacteria are still passivated (Fig. 8, coverage 38 and 47%). This is the parametric domain when the differential aeration mechanism works: high oxygen concentration and high pH passivate bare metal, while low oxygen and lower pH increase corrosion under the biofilm. When the metal is covered with even more bacteria, then uniform corrosion replaces again the localized corrosion, since all the metal surface becomes active. However, if the biofilm becomes compact (95% coverage), then the corrosion rate decreases greatly because of oxygen depletion at the metal surface.

The onset of differential aeration cells at different biofilm distribution is a function of aeration. It is shown in Fig. 9 that at higher dissolved oxygen concentration the heterogeneous corrosion appears only at higher coverage (74 and 86%). This shift of localized corrosion domain toward higher surface coverage is due to the higher oxygen availability.

Total average corrosion currents.—The total average anodic density of current is given by

$$\bar{i}_1 = \frac{1}{L_yL_z} \int_0^{L_y} \int_0^{L_z} i_1(\Phi_M)dzdy$$

and it has been computed for different surface coverages, at different oxygen concentrations, pH, and salinity (see Fig. 10 and 11). Depending on all these factors, the total average corrosion current on iron covered with biofilms can be either higher or lower than the current in a similar but sterile system.

An increased concentration of salt has the effect of amplifying corrosion by promoting pitting, but also by increasing conductivity of the solution (Fig. 10a and b). In seawater, for example, the high concentration of Cl⁻ prevents passivation of the steel, and under these circumstances the more aerated metal corrodes at a higher rate.

**Figure 12.** Decrease of metal potential, $\Phi_M$ (V, SHE), as a function of the degree of metal coverage with biofilms at (a) pH 7 and (b) pH 8. Dissolved oxygen concentration ($\circ$, $\bullet$) 0.5 and ($\triangle$, $\Delta$) 5 g/m³. ($\Delta$, $\circ$) $[\text{Cl}^-] = 1$, ($\triangle$, $\bullet$) $[\text{Cl}^-] = 0.1$ M, and (gray symbols) $[\text{Cl}^-] = 10^{-7}$ M.
This is why bare metal corrodes faster than that covered with biofilm. This is clearly seen also from Fig. 11b, where at high aeration the density of anodic current is one order of magnitude higher than at poor aeration (Fig. 10b). The exception is the case when in the absence of chlorides, the whole metal is in passive state, with \( i_\text{corr} = 5 \times 10^{-4} \text{A/m}^2 \). Although these predicted trends can be correct for carbon steel, the situation is quite different for stainless steels in natural seawater. In the latter case, the biofilm-covered material corrodes faster than the bare alloy.\(^{34}\)

At higher pH, the height of the peak in the active region of current density decreases, thus the metal passivates easier (Fig. 2a). This can be seen by comparing current densities in Fig. 10a (pH 7) with those from Fig. 10b (pH 8). There are two consequences. First, in all simulations done at pH 8 the average corrosion current was smaller than in similar conditions but at pH 7. Second, by comparing the interval of variation of anodic current density around the average value, variation shown in Fig. 10 by error bars, we can conclude that at pH 8 there is a more uniform corrosion. Thus, formation of differential aeration cells is greatly diminished by an increasing pH. This can be seen also by comparing the error bars corresponding to the black symbols from Fig. 11a and b. It is worth noting that at pH 8 the shape of the current-coverage curves is similar to the shape of anodic current-potential function, with active, passive, and pitting regions (compare Fig. 10b, supposedly having a reversed x axis, with Fig. 2b). Because of the uniform corrosion rate, the curve is simply determined by the oxygen concentration at the metal surface, which decreases with surface coverage.

As expected, a higher concentration of dissolved oxygen generally leads to an increased corrosion (see Fig. 11a, and also compare Fig. 10b with 11b). A second effect is, as already mentioned, the shift of nonuniform corrosion range to higher surface coverage with biofilm, when oxygen concentration increases. The latter effect can be clearly visualized from the position of the large error bars in Fig. 11a, at 5 g O\(_2\)/m\(^3\) (○) and 0.5 g O\(_2\)/m\(^3\) (□). In most of the simulated situations, a higher percentage of metal surface covered with bacteria led to a decrease in corrosion due to less oxygen available and less surface of the “cathodic” area. This result suggests that indeed, an aerobic biofilm covering the metal surface can be protective. The best corrosion protection was achieved when a compact biofilm with 120 \( \mu \text{m} \) thickness was used (case 7 in Table II). In this case, the corrosion rate is several orders of magnitude lower than in the bare surface case. It was also shown that, theoretically, sometimes it is not needed to have 100% coverage of the surface, because the dissolved oxygen concentration in the spaces between colonies can be low enough to prevent a significant corrosion (e.g., Fig. 11b). However, there is another point of concern here. A patchy biofilm can create favorable niches for attachment and growth of anaerobic bacteria (like sulfate-reducing bacteria), which usually produce corrosive agents. If this is the case, sulfate-reducing bacteria must be inhibited, for example, with antimicrobial peptides generated in the biofilm.\(^{39}\)

**Corrosion potential.**—The corrosion potential was defined as the potential \( E_\text{corr} = (\Phi_\text{M} - \Phi_\text{cal}) \) at which the zero-total-current condition (Eq. 29) is satisfied. If the reference potential \( \Phi \) is taken to be zero, then an indication of biofilm activity on the metallic surface can be found by plotting the metal potential \( \Phi_\text{M} \) as a function of surface coverage. Our simulations show without exception that the metal potential decreases with increasing surface coverage (Fig. 12). This is undoubtedly caused by bacterial respiration that reduces the concentration of oxygen at the metal surface by respiration. The trend shown by this model is comparable with experimental data reported in the literature.\(^2\) These researchers measured a decrease of the corrosion potential in time, as the metal is gradually covered by a more compact and thick (fully grown) biofilm. It can be considered as an experimental indication that aerobic biofilms can inhibit corrosion through oxygen depletion. Moreover, there are reports of a lack of corrosion inhibition with a dead biofilm as compared to a living biofilm.\(^{1,2}\) Model results present also a shift toward more positive potentials at higher aeration of the medium (5 g compared to 0.5 g O\(_2\)/m\(^3\)). In contrast with model predictions is the behavior of passive metals in real seawater, where natural biofilms produce an ennoblement (positive shift) in the open-circuit corrosion potential.\(^{40}\)

However, in our opinion, measuring potential alone is not reliable enough, because local and total corrosion currents can have nonmonotonic variations; as shown in Fig. 10 and 11. Consequently, for metals having an active-passive behavior, a decreasing corrosion potential is not equivalent with a decreasing corrosion rate, and therefore, any experimental result showing this kind of correlation must be examined with care.

**Conclusions**

1. A spatially three-dimensional model was developed for investigating the interactions between biofilms and a metal surface. It is an attempt to interpret microbiologically influenced corrosion by simple physical and chemical processes in the frame of a mathematical model. The model includes transport of seven important chemical species by diffusion and migration, electrochemical reactions at the metal surface, and homogeneous reactions in the liquid volume. Solution of the model equations gives the three-dimensional spatial distribution of concentrations and potential in solution and also the metal potential. In addition, the vector field of total ionic currents in the solution and corrosion current distribution on the metal surface can be computed.

2. Because of the large number of phenomena (physical, chemical, and biological) that influence a biocorrosion system it is difficult to predict its overall behavior on the basis of intuition alone. The mathematical model is therefore needed because it permits testing of different hypotheses and compares the relative importance of various processes in certain regions of parameter space.

3. The applicability of the model lies in clarifying conditions under which the onset of localized corrosion is likely to occur. Although we tried to use realistic parameters for the model, simulation results should serve only for orientation on possible effects and not as ultimate quantitative data. This is because electrode kinetic data found in the literature differ very much and they are often unreliable. Moreover, we used a quite simple chemical system, where a few reactions only from oxygen and iron systems were permitted. Under natural biofilms, phenomena are far more complex, requiring at least inclusion of manganese and sulfur chemistry in a future model.\(^{51}\)

4. This model can be used to test the effect of changing different operational parameters (e.g., pH, aeration, salinity) and biofilm characteristics (e.g., surface coverage, density, thickness) on the extent of metal corrosion. Model simulations show that a metal surface largely covered with aerobic biofilms can be protected against corrosion. If the biofilm consists exclusively of aerobic bacteria and the metal does not show the active-passive peak of anodic current, it is in principle not needed to have full surface coverage for an appreciable corrosion inhibition. However, model results indicate that the degree of metal coverage with bacteria significantly influence the heterogeneity of the corrosion pattern.

5. Oxygen concentration at the metal surface plays a key role in the establishment of corrosion current and corrosion potential. There are cases when although the total average corrosion rate decreases by decreasing oxygen concentration, there is a localized enhancement of corrosion under the biofilm colony. This can be explained by formation of a differential aeration cell between active zones under the biofilm (anodes) and passive zones on the bare metal (cathodes) experiencing higher O\(_2\) concentration and higher pH. In addition, the onset of differential aeration cells at different biofilm distribution is a function of aeration. At higher dissolved oxygen concentration the heterogeneous corrosion appears only at higher coverage.

6. System behavior in highly saline environment can also be explored. An increase in chloride concentration amplifies the corrosion by decreasing the electrical resistance in the solution, and also...
by destroying the passive layer, especially under the colonies of bacteria.

7. An important characteristic of the model is that it does not require a priori specification of where the anodic and cathodic regions exist. These regions develop as a result of interactions between biofilm and metal. Overall, the ionic current flows from the biofilm to the open regions.

8. Measurements of corrosion potential alone as an indication for corrosion intensity may not be reliable enough. For metals presenting an active-passive behavior, a decreasing corrosion potential is not equivalent with a decreasing corrosion rate, and therefore, any experimental result showing this kind of correlation must be examined with care.

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