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PHYSICAL MODEL FOR STEEL CORROSION IN CONCRETE SEA STRUCTURES— THEORY

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NATURE OF PROBLEM

Serviceability and durability of concrete structures exposed to sea water can be seriously affected by corrosion. This is of particular concern for large offshore oil storage tanks, because leaks of oil into the sea must be avoided. The electrochemistry of the processes of corrosion of steel in general (13,35,36) and of reinforcing steel embedded in concrete in particular (9,14,23,26,29-31) has been extensively studied and is reasonably well understood at present. Although some useful empirical methods for predicting the time to cracking have been formulated (8,10-12), the present knowledge is essentially qualitative. It is therefore difficult to estimate the relative importance of the diverse factors affecting the corrosion rate to make possible predictions of corrosion damage. The problem is very complicated and many processes intervene; in such situations a mathematical analysis usually can be of great help. Thus, it is desirable to develop a complete mathematical model of the corrosion process as a basis for calculations, for which the finite element method may, in general, be contemplated. The present state-of-the-art seems to be ripe for such efforts. An approach toward meeting this goal was considered in Ref. 5; however, a complete set of equations for the problem was not formulated at that time. This will be the main purpose of this study, which is logically subdivided in two parts.

In this paper, after outlining the chemical reactions involved, we will formulate the transport of oxygen and chloride ions through the concrete cover, the mass sinks and sources of oxygen, ferrous hydroxide, and hydrated red rust due to chemical reactions, the depassivation of steel due to critical chloride ion concentration, the cathodic and anodic electric potential with the concentration polarization of electrodes, and the flow of electric current through the electrolyte

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in pores of concrete. To enable numerical calculations we will deduce the values of various necessary coefficients using indirect arguments when direct experimental measurements are lacking. Our final aim in this paper will be to achieve a complete formulation in the form of an initial-boundary-value problem. In the companion paper, which follows in this issue, we will then apply this general mathematical formulation to the calculation of the corrosion rates and times to cracking in various basic cases and present a host of simple numerical examples.

The mathematical formulation to be attempted is based on a more in-depth description of the processes involved than has been carried out so far. We hope that this will improve our understanding of the problem and indicate the gaps that need to be filled in the existing body of experimental information.

ELECTROCHEMICAL PROCESSES CAUSING CORROSION

Normally, steel in concrete is highly resistant to corrosion. In one view (14,24,29), steel is protected from corrosion by a surface film (approx 10,000 Å thick) that consists chiefly of ferric oxide, Fe₂O₃. This oxide film is thought to passivate steel against corrosion. For the corrosion to begin, the film must be broken or depassivated. The depassivation could happen if the alkalinity (basicity) of the water solution (electrolyte) in the pores of concrete decreased. This can be caused by carbonation, especially near cracks, or by water dilution, which accompanies cracking. In this work, concrete that is cracked due to effects other than corrosion will not be considered, and in such a case a depassivation due to a basicity decrease is unlikely because the reserve basicity of concrete due to the presence of crystalline Ca(OH)₂ is so high that pH is essentially constant even when a great amount of chloride ions penetrate into concrete (17). Rather, the depassivation must be caused directly by corrosive anions, of which the case of Cl⁻ is most important. Depassivation is then induced directly by reaching a threshold concentration of Cl⁻ in concrete in the immediate vicinity of the steel surface. In another more recent view (2,37), no protective oxide film might exist (in the anodic area) and corrosion might be initiated by formation of a chloride-ion film at the steel surface. Because the walls of pores in cement paste adsorb great amounts of Cl⁻, the Cl⁻ film can form at the steel surface only if the Cl⁻ concentration exceeds a certain threshold value.

For our mathematical modeling, both views are essentially equivalent since in both cases it is the attainment of a certain Cl⁻ concentration that initiates the corrosion process. This process consists of dissolution of iron in pore water, i.e., iron is oxidized, iron ions passing into the solution:



in which e⁻ = electron. This reaction, which makes steel electrically negative, occurs first at tiny anodic areas and leads to the formation of narrow pits in the surface of steel (37). Soon these anodic areas become densely and uniformly distributed, forming a large anodic area. In this study, the processes on the microscopic scale leading to the formation of tiny corrosion pits will not be considered, and only the later, global stage of corrosion will be analyzed.

The areas of steel surface that are adjacent to anodic ones begin to function as cathodes (and the oxide film will certainly exist there). The electrons liberated

in the anodic area (Eq. 1) move through steel toward the cathodic area, creating in steel an electric current, *I*, which flows from the cathodic to the anodic area. Simultaneously, with chloride ions, oxygen that is dissolved in sea water diffuses through concrete toward the steel. In the cathodic region, oxygen dissolved in pore water reacts with the incoming electrons, e, from the steel bar in the presence of water to form hydroxyl ions, OH⁻ (reduction of oxygen)



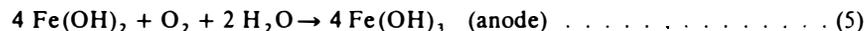
The electric current passes through the electrolyte in the pores of concrete by means of a transfer of negative hydroxyl ions, OH⁻, toward the anode (15). Although the transfer of OH⁻ is a transfer of mass (15), it need not be formulated as a diffusion process, because this is equivalently done by writing the Ohm's law for the electrolyte in the pores of concrete. The hydroxyl ions that arrive at the anodic area electrically neutralize the Fe⁺⁺ dissolved in pore water (Ref. 13, p. 12), forming a solution of ferrous hydroxide as described by the equation



The total cell reaction, summarizing the result of Eqs. 1-3, is



The ferrous hydroxide further reacts with available oxygen and water (Ref. 13, p. 13)



The Fe(OH)₃ constitutes hydrated red rust (Fe O OH + H₂O), the final product that precipitates from the solution.

The foregoing relations represent a simplified picture of the essential electrochemical reactions. The detailed reactions and the microscopic processes within the interface layer between steel and concrete are much more complicated (37) and not yet fully understood. One should also be aware that there are many different ions in concrete, not just Ca⁺⁺, Cl⁻, and OH⁻. Moreover, Fe(OH)₃ is not the only product of corrosion. Other compounds may form; e.g., FeO(OH), HFe O OH, HFeO₂, FeSO₄, and especially black rust, Fe₃O₄; 3Fe + 8OH⁻ → Fe₃O₄ + 8e⁻ + 4H₂O (1). In fact, the production of black rust (thickening of oxide film) seems to be the only form of rusting at continuous very deep water immersion (28,33) for which the oxygen supply is restricted. For brevity, however, the stoichiometry of all the following analysis will be based on red rust, although conversion to black-rust analysis would be straightforward. In any case, it is the red rust that is more dangerous for cracking concrete because its volume is four times as large as that of steel while the black-rust volume is twice as large (33).

It is obvious from Eqs. 2 and 5 that the supply of oxygen is essential for corrosion to proceed. Oxygen is consumed both at the cathodic area and the anodic area, and cessation of its supply at either place blocks further corrosion. The supply of water, as required by Eqs. 2 and 5, is not a controlling factor because it is abundant. Nevertheless, it indirectly influences the corrosion process in at least two ways: (1) The degree of water saturation affects the electrical resistivity of concrete; and (2) it probably also affects the mobility of oxygen

(diffusivity) in concrete and the mobility of chloride ions.

One objective of the analysis is to predict the rate of production of red rust. The volume expansion due to rust production causes tensile stresses in concrete, which ultimately result in cracking. This starts a "chain reaction," in that cracked concrete allows oxygen, chlorides, and water to enter faster, thereby accelerating corrosion and causing further cracking. The same acceleration is, of course, obtained when cracking is induced by shrinkage and thermal stresses or applied loads.

ELECTRODE POTENTIALS

The electric current of the corrosion process is determined by the electrode potentials (voltages) at the cathode and anode. The electrode potential, $\Delta\phi$, represents the potential difference between the electrode and the adjacent electrolyte and is, in general, determined by Nernst equation (13,21,25,36)

$$\Delta\phi = \Delta\phi_1 + \frac{RT}{nF} \ln \left(\frac{Q_{oxid}}{Q_{red}} \right) \dots \dots \dots (6)$$

in which T = absolute temperature; R = gas constant (8.314 J/°K); F = faraday [96,500 c (coulombs) or 6.02×10^{23} electrons]; n = ionic valence of the substance that passes into the solution, also equal to the number of electrons involved in the reaction at the electrode, e.g., $n = 2$ for Eq. 1 at the anode and $n = 4$ for Eq. 2 at the cathode; Q_{oxid} and Q_{red} = oxidation and reduction rates, respectively, at the electrode; and $\Delta\phi_1$ is called standard electrode potential and is measured with respect to the standard hydrogen electrode (20).

For the anodic reaction, Eq. 1, $n = 2$ and $\Delta\phi_1 = -0.440$ v (25). According to Eq. 1, $Q_{oxid}/Q_{red} = [Fe^{++}]/[Fe]$ in which $[Fe^{++}]$ = activity of Fe^{++} , which roughly equals molarity of Fe^{++} (concentration of Fe^{++} in moles per liter of electrolyte) and $[Fe] = 1$, $[Fe]$ being the activity of an Fe molecule in the steel bar. Substitution into Eq. 6 and conversion to decadic logarithms yields, for the anodic potential (in volts at 25° C)

$$\Delta\phi^A = -0.440 + 0.0296 \log [Fe^{++}] \dots \dots \dots (7)$$

in which superscript A refers to anode. As the electric charge in the solution ought to be in balance, $[Fe^{++}]$ should equal $1/2 [OH^-]$; this follows from the dissociation relation of ferrous hydroxide, $Fe(OH)_2 = Fe^{++} + 2 OH^-$. This relation also indicates that the molarity of Fe^{++} equals the molarity of $Fe(OH)_2$, which may further be expressed in terms of the mass concentration, u_f , of $Fe(OH)_2$ (per unit volume of concrete)

$$[Fe^{++}] = \frac{55.85 u_f}{88.87 u_w} \left[\frac{\text{mole}}{\text{liter}} \right] = 628.6 \frac{u_f}{u_w} \left[\frac{\text{mole}}{\text{liter}} \right] \dots \dots \dots (8)$$

in which 88.87 = molecular weight of $Fe(OH)_2$; 55.85 = molecular weight of Fe; u_w = amount of electrolyte in concrete = amount of capillary water (mass) in grams per cubic meter of concrete; and $u_w/1,000$ = amount of capillary water in liters per cubic meter of concrete. Substituting Eq. 8 into Eq. 7, we have (in volts at 25° C)

$$\Delta\phi^A = \phi_1^A + 0.0296 \log u_f \quad \text{with} \quad \phi_1^A = 0.357 - 0.0296 \log u_w^A \dots \dots \dots (9)$$

Note that u_w is less than the total evaporable water content. We exclude the adsorbed water because it has a strongly reduced mobility and does not allow uninhibited ion interactions. The fraction of capillary water in total evaporable water may be estimated according to Powers, but the precise value is questionable; perhaps 0.7 is a reasonable guess in many cases. Restriction of u_w to capillary water would be, however, excessive for low w/c -ratio concretes that contain a negligible amount of capillary water. For such concretes, at least some adsorbed water must be included within u_w .

Consider now the cathodic reaction. Eq. 2 provides $n = 4$, and from measurements (24), $\Delta\phi_1 = 0.401$ v. According to Eq. 2, $Q_{oxid}/Q_{red} = [O_2] [H_2O]^2 / [OH^-]^4$, in which brackets denote, again, molarity; and $[H_2O] = 1$. Substituting $\log [OH^-] = pH - 14$, we obtain from Eq. 6 the cathodic potential (in volts)

$$\Delta\phi^C = 1.229 + 0.0148 \log [O_2] - 0.0591 pH \dots \dots \dots (10)$$

The molarity of oxygen, $[O_2]$, may be calculated as

$$[O_2] = \frac{u_o}{32} \frac{1,000}{u_w} \left[\frac{\text{moles}}{\text{liter}} \right] \dots \dots \dots (11)$$

in which u_o = concentration of oxygen in kilograms per cubic meter of concrete; and 32 = molecular weight of oxygen.

Considering concrete with a water-cement-sand-gravel ratio 0.45:1:3.08:3.29 and a weight of 2,300 kg/m³ and assuming that after a prolonged hydration the weight of chemically combined water is about 22% of the weight of cement, we further have $u_w = 2,300 \times 0.7(0.45 - 0.22)/(0.45 + 1 + 3.08 + 3.29) = 48$ kg/m³, neglecting moisture exchange by diffusion. For smaller degrees of hydration, u_w is, of course, higher.

The pH of the electrolyte in the pores might be expected to be affected by penetration of various ions (Cl^- , Mg^{++} , K^+ , Na^+ , SO_3^- , CO_3^{--} , etc.) or by leaching of others (Ca^{++}). There is generally also a tendency for the pH to equalize with that of sea water, pH = 8 (15). However, these effects are, in a good quality concrete, negligible because of the large reserve of basicity due to $Ca(OH)_2$, and, according to recent investigations, pH is essentially constant and equal to 12.5 or 12.6 (17). (The reserve basicity is absent when corrosion of steel is tested in a solution, and this is why in such tests pH is found to have a large effect.) In a poor quality concrete or in a cracked concrete, pH could be, however, significantly lowered by possible penetration of sea water, because $MgCl_2$ contained in sea water combines with $Ca(OH)_2$ to produce a highly insoluble hydroxide, $Ca(OH)_2 + MgCl_2 \rightarrow CaCl_2 + Mg(OH)_2$. In a good quality concrete, on the other hand, $MgCl_2$ might inhibit corrosion, since it probably penetrates only a thin surface layer of concrete and the almost insoluble $Mg(OH)_2$ produced in this layer may be expected to clog the pores (Gjørsv, O. E., personal communication). Carbonation, i.e., $Ca(OH)_2 + CO_2 \rightarrow Ca^{++} + CO_3^{--} + H_2O$, $Ca^{++} + CO_3^{--} \rightarrow CaCO_3$, which can penetrate deep in poor quality concrete exposed to air, could also significantly reduce pH, which is an important mode of corrosion initiation in concrete exposed to air. On the other hand, $CaCO_3$ also has a low solubility and may clog the pores, thus inhibiting corrosion.

Eq. 10 was given by Hausmann (24); however, he wrote this equation for the anode because he considered an electrolytic cell instead of a voltaic cell, in which the cathode and the anode are reversed. Also, his constant term was different from 1.228 in Eq. 10 because he used for reference the saturated calomel electrode (20) rather than the standard hydrogen electrode.

Substituting pH = 12.5 and Eq. 11 into Eq. 10, we obtain (in volts)

$$\Delta\phi^C = \phi_i^C + 0.0148 \log u_o^C, \text{ with } \phi_i^C = 1.18$$

in which $1.187 = 1.229 + 0.0148 \log (1,000/32) - 0.0591 \log 12.5$.

The values of $\Delta\phi^A$ and $\Delta\phi^C$ represent the potentials ϕ_{st}^A and ϕ_{st}^C of steel at the surface of anode and cathode when no current flows through the steel bar. Then the potentials in concrete near anode and cathode (at the outside face of the electrolytic layer at steel surface) are $\phi_{con}^A = \phi_{con}^C = 0$. When electric current flows, the potential differences $\Delta\phi^A$ and $\Delta\phi^C$ must be preserved, but the potentials themselves change according to Ohm's law. We have $\phi_{st}^C - \phi_{st}^A = R_{st}I$ and $\phi_{con}^C - \phi_{con}^A = RI$, in which R_{st} = ohmic resistance of the steel bar and R = ohmic resistance of concrete. In case of a power cell, the electronic conductor (steel) has a much higher resistance (R_{st}) than the electrolytic conductor (R), thus ϕ_{con}^C and ϕ_{con}^A are then almost equal and $\phi_{st}^A \approx \Delta\phi^A$, $\phi_{st}^C \approx \Delta\phi^C$. The opposite happens in the corrosion cell. Here, R is much larger than R_{st} . Consequently, $\phi_{st}^C \approx \phi_{st}^A = \phi_{st}$ (although, actually, ϕ_{st}^C and ϕ_{st}^A must have very small positive and negative values, respectively). By virtue of this argument we have $\phi_{con}^A = \phi_{st} - \Delta\phi^A$, $\phi_{con}^C = \phi_{st} - \Delta\phi^C$. Thus, when current flows, concrete at anode is positive and concrete at cathode is negative, $\phi_{con}^C > \phi_{con}^A$. This is also clear from the fact that positive ions enter concrete at anode (Eq. 1) and negative electrons enter concrete at cathode (Eq. 2). The electric potential difference (electromotive force) that drives the current through the electrolyte in concrete from anode to cathode is $\Delta\phi = \phi_{con}^A - \phi_{con}^C = \Delta\phi^C - \Delta\phi^A$. Substituting Eqs. 9 and 12, we obtain (in volts)

$$\Delta\phi = \phi_i = + n^C \log u_o^C - n^A \log u_f, \text{ with}$$

$$\phi_i = 0.829 - n^C \log u_w^C + n^A \log u_w^A \dots \dots \dots (13)$$

in which $n^C = 0.0148$ v; and $n^A = 0.0296$ v. Superscripts *A* and *C* are affixed to distinguish between concentrations at anode and cathode. If negative $\Delta\phi$ is obtained, the anode and cathode must be interchanged, and if again $\Delta\phi < 0$, we must set $\Delta\phi = 0$.

From Eq. 13 we might be tempted to conclude that the electric potential difference at anode is independent of the supply of oxygen at anode. However, this is not true because u_f depends on the supply of oxygen at the anode. Note also that $\Delta\phi$ can be made zero by a sufficiently small oxygen concentration or by a sufficiently large value of u_f or $[Fe^{++}]$ at anode.

Furthermore, we must take into account the depassivation of anode surface. The electromotive force in Eq. 13 develops as a result of the electrochemical reactions in Eqs. 1 and 2. For these reactions to take place, the chloride concentration must surpass a certain threshold, u_c^* . Thus, we must set

$$\Delta\phi = 0 \text{ if } u_c^A < u_c^* \dots \dots \dots (14)$$

i.e., $\Delta\phi$ exhibits a discontinuous jump as the threshold is passed.

To estimate the threshold, we might use the measured value of chloride concentration at which passivity is broken when a steel bar is submerged in a water solution; in this type of test, corrosion begins when pH drops to about 11.5. The data points from Refs. 9 and 17 yield $pH = 12.4 - 14.6 u_c/u_w$, which indicates that $pH = 11.5$ is reached for $u_c = u_c^* = 0.062 u_w$. More directly, we might perhaps estimate u_c^* from the fact that about 0.6% NaCl in water-saturated concrete is known to break passivity (22). By atomic weights, this corresponds to the Cl content of 0.364% of the weight of concrete, and for a concrete that contains 5.87% of capillary water by weight (which is a reasonable value for concretes of higher *w/c* ratios), we obtain the same as before, $u_c^* = 0.062 u_w$. From recent tests, though, it appears that the critical NaCl concentration may decrease with the duration of exposure (33,34). (At zero impressed voltage, the NaCl concentrations in Ca(OH)₂-solutions that initiated corrosion within 18 hr, 60 hr, and 400 hr were 1 mole/l, 0.1 mole/l, and 0.01 mole/l, respectively.)

Still another estimate could be based on the concentration of CaCl₂ (in concrete) needed to break passivity; it is between 0.78% and 1.56% of CaCl₂, which corresponds to 0.50%-1.00% of Cl⁻ in concrete. [On the other hand, in solution, lower concentrations, 0.0165 to 0.0495 of Cl⁻, were found to break passivity (26).] Note that u_c^* would also depend on the type of steel.

EQUATIONS GOVERNING DIFFUSION PROCESSES

The surface region of a reinforced concrete wall or slab submerged in the sea (Fig. 1) may be idealized as a half space made of concrete, with a surface, $x = 0$, exposed to sea water. The diffusion through the pores is characterized by mass fluxes J_w , J_o , J_c , and J_f (all of dimension kg/m² sec) and mass concentrations u_w , u_o , u_c , and u_f (all in kg per m³ of concrete) in which subscript *w* refers to the capillary water; *o* to oxygen, O₂; *c* to chloride ions, Cl⁻; and *f* to ferrous hydroxide, Fe(OH)₂. Calcium hydroxide undoubtedly also diffuses through concrete, but its concentration is so high that changes in its concentration should be insignificant for pH. Although hydrated red rust might be also mobile to small extent, it may be assumed that it precipitates where it is formed (which is near the surface of steel) and stays there.

Conservation of the mass of each substance requires

$$\frac{\partial u_w}{\partial t} + \nabla \cdot J_w + \dot{m}_h = 0 \dots \dots \dots (15a)$$

$$\frac{\partial u_o}{\partial t} + \nabla \cdot J_o - J_w \cdot \nabla u_o + \dot{m}_o = 0 \dots \dots \dots (15b)$$

$$\frac{\partial u_c}{\partial t} + \nabla \cdot J_c - J_w \cdot \nabla u_c = 0 \dots \dots \dots (15c)$$

$$\frac{\partial u_f}{\partial t} + \nabla \cdot J_f - J_w \cdot \nabla u_f + \dot{m}_f = 0 \dots \dots \dots (15d)$$

in which *t* = time. Fluxes J_w , J_o , J_c , and J_f do not include the convective fluxes expressing the masses carried by the water as it moves through the

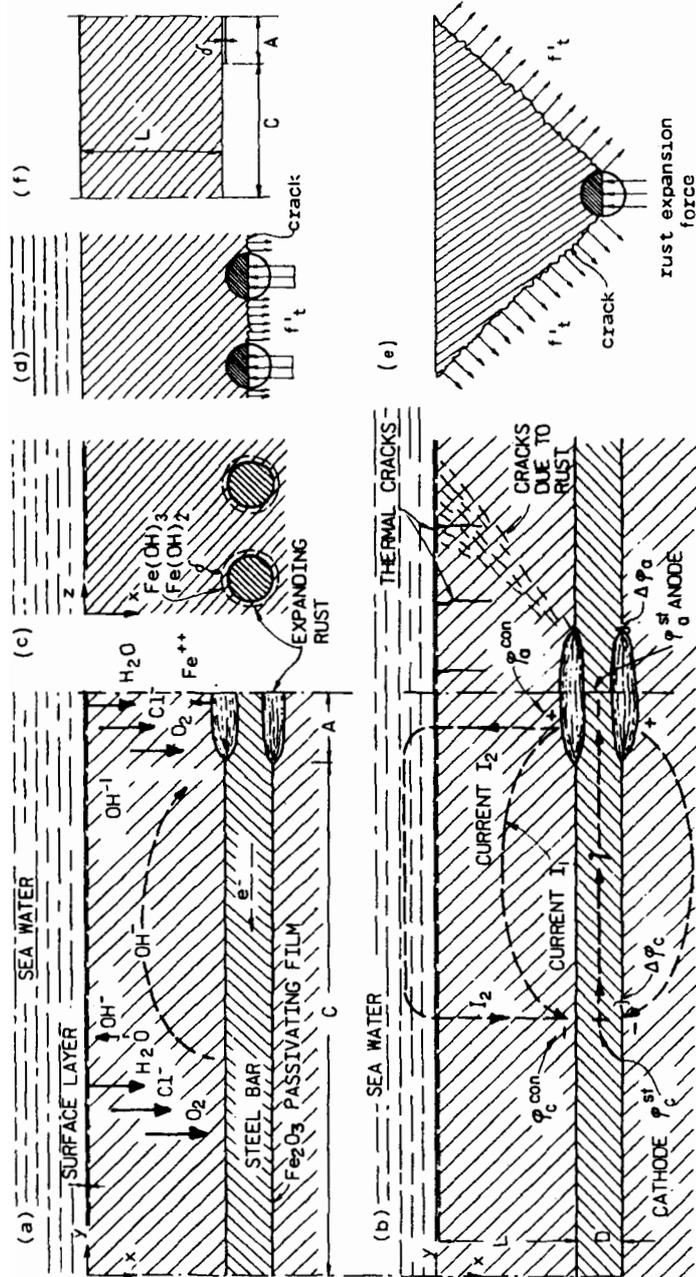


FIG. 1.—Main Processes Involved in Corrosion (a-c). Balance of Internal Forces at Crack Formation Due to Rust (d-e), and Domain on which Idealized Corrosion Problem Is to Be Solved (f)

pores. These fluxes are $J_w \nabla u_w, \dots, J_w \nabla u_f$, and they appear in Eq. 6 as separate terms. The term \dot{w}_h is a distributed sink of capillary water, due to the progress of hydration (see especially Ref. 4; also Refs. 3 and 6). For crude calculations it can be neglected. Terms \dot{m}_o and \dot{m}_f represent distributed sources or sinks of oxygen and ferrous hydroxide due to chemical reactions. Except at anode very near the surface of steel, we have $m_o = m_f = 0$.

Flux J_w represents diffusion of capillary water through the pores, while fluxes $J_o, J_c,$ and J_f represent diffusion of oxygen, chloride ions, and ferrous hydroxide through capillary water (with regard to water, not the pore walls). They are related to concentration gradients according to Fick's law of diffusion

$$J_w = -c_w \nabla u_w; \quad J_o = -c_o \nabla u_o; \quad J_c = -c_c \nabla u_c + c_{cl} \nabla \phi; \\ J_f = -c_f \nabla u_f \dots \dots \dots (16)$$

in which $c_w, c_o, c_c,$ and c_f are the diffusivities. A possible coupling between diffusion fluxes (27) is here neglected. However, Eq. 16 for J_c includes a coupling to the electric field because Cl^- has an electric charge. We thus express the fact that Cl^- must move in response to the gradient of electric potential ϕ . This must cause the concentration of Cl^- at cathode to become higher than at anode when the electric corrosion current flows. Before the current starts, $\nabla \phi$ in Eq. 16 is zero (unless cathodic protection is considered). Flux J_c must be, of course, electrically balanced by fluxes of other ions that do not directly participate in the corrosion process; perhaps $OH^-, Ca^{++}, Mg^{++},$ etc.

The diffusivity of water, c_w , at pore saturation can vary from $10^{-4} \text{ m}^2/\text{s}$ to $10^{-10} \text{ m}^2/\text{s}$, depending on the type of concrete (4). In unsaturated concrete, c_w decreases about 20 times as pore relative humidity decreases from 90% to 60% (3,6). The effective values of $c_w, c_o,$ and c_c for concrete cover might be largely reduced by clogging of pores near the surface due to deposition of $Mg(OH)_2$ (from sea water) or $CaCO_3$ (carbonation due to air exposure) (O. E. Gj\o rrv, personal communication). Progress of hydration (aging) reduces c_w by orders of magnitude (3,6).

The diffusivities of oxygen, chloride ions, and ferrous hydroxide could be thought to be estimated as (7) $c_o = c_w (\mu_w / \mu_o), c_c = c_w (\mu_w / \mu_c), c_f = c_w (\mu_w / \mu_f)$ in which $\mu_w, \mu_o, \mu_c,$ and μ_f are the dynamic viscosities of the substances (their values at 25°C are $\mu_w = 3.24 \text{ kg/m hr}, \mu_o = 0.072 \text{ kg/m hr},$ and $\mu_c = 0.0504 \text{ kg/m hr}$). However, this did not give good results, probably because water flow is controlled by adsorbed water migration, which is not a viscous process. By fitting the concentration profile at 27 yr after exposure to sea water, as reported by Gj\o rrv (17) (Fig. 2) and using the measured value for the surface ($u_c^s = 22 \text{ kg/m}^3$) as the boundary condition, it was determined that for this concrete $c_c \approx 1.0 \times 10^{-11} \text{ m}^2/\text{s}$. (This is approx 20 times less than μ_c would give.) Oxygen permeabilities have also been reported (19): $c_o = 17.3 \text{ mm}^2/\text{day}, 23.3 \text{ mm}^2/\text{day},$ and $29.4 \text{ mm}^2/\text{day}$ for $w/c = 0.4, 0.5,$ and $0.6,$ respectively. (This is only a little less than μ_o would give.) In more recent measurements (33,34) it was found that for saturated concrete $c_o \approx 0.04 \text{ mm}^2/\text{day}$, which upon first drying to 80% and 50% saturations increased to $250 \text{ mm}^2/\text{day}$ and $2,500 \text{ mm}^2/\text{day}$; this value remained essentially constant on subsequent saturation up to 95%. (Interestingly, the dependence upon water saturation is thus opposite to that of $u_w,$ and can be explained only by the effect of microcracks.)

The greatly increased value of c_o in resaturated concrete, along with the low resistivity and high oxygen availability, and perhaps the possibility of carbonation, might explain why in the splashing zone the corrosion rates are much higher.

The law of chloride diffusion might be more complicated than Eq. 16 indicates, for a certain significant fraction of Cl ions u_c^o appears to be physically bound in the pores and only that portion of u_c that is in excess of u_c^o can move freely. This would mean replacing Eq. 16 for J_c by

$$\begin{aligned} \text{for } u_c \geq u_c^o: J_c &= -c_c \nabla(u_c - u_c^o) + c_{cl} \nabla \phi; \\ \text{for } u_c \leq u_c^o: J_c &= 0 \end{aligned} \quad (17)$$

Diffusion predictions according to this theory (for $c_{cl} = 0$) as well as before to the limited data points in Fig. 2. To decide which approach is correct, concentration profiles for many different times would be needed.

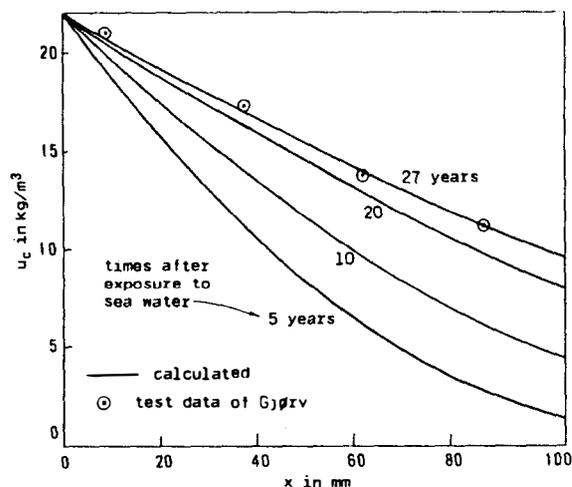


FIG. 2.—Fit of Gjørv's Measurements of Chloride Concentration

Because $Fe(OH)_2$ is rather insoluble, one might doubt the assumption that $Fe(OH)_2$ can diffuse through concrete. However, if this diffusion was not included, then the dependence of voltage on u_f (Eqs. 8 and 13) introduced. Therefore, it is inevitable that $Fe(OH)_2$ diffuses away from the steel surface, although possibly to an extremely small distance. As a simplifying alternative, though, it might be practically acceptable (16) a constant representing the maximum amount of Fe^{++} ions, which is given by the solubility product of $Fe(OH)_2$, i.e., $L_{Fe(OH)_2} = 10^{-15}$. At pH = 12.6, this value would give $[Fe^{++}]_{max} = 10^{-12.2}$ moles/l (16) or $u_f = 5.7 + 10^{-11} u_w$ g/m³ of concrete.

At the concrete surface exposed to sea water there is a thin layer of concrete, perhaps up to 1 mm thick, which might deserve special treatment (O. E. Gjørv, personal communication). The $Mg(OH)_2$ (brucite) that forms due to penetration of sea salts ($MgCl_2, CaCl_2$) is rather insoluble and must clog the pores of a concrete of good quality. This could substantially reduce diffusivities $c_w, c_o,$

and c_c (O. E. Gjørv, personal communication), except at the splashing zone where deposition of $Mg(OH)_2$ is unlikely.

The electric current passing through the electrolyte in the pores of concrete is governed by the Maxwell's equations of electrostatics, i.e., Ohm's law and the condition of conservation of electric charge

$$\lambda \mathbf{l} = -\nabla \phi \quad (18a)$$

$$\nabla \cdot \mathbf{l} = 0 \quad (18b)$$

in which \mathbf{l} = vector of the current density; and λ = electrical resistivity of concrete. For $w/c \approx 0.5$, $\lambda = 40$ ohm m at 100% saturation, 90 ohm at 80% saturation, 400 ohm m at 60% saturation, and 90,000 ohm m at 40% saturation by water; for $w/c = 0.7$, the values reduce to 1/2 (for 100%) (for 40%);

The electrical resistivity in Eqs. 18 should correspond to the effective value of the current resulting from diffusion of various ions, such as $OH^-, Cl^-,$ and Ca^{++} . (However, the movement of Cl^- depends also on the gradient of Cl^- concentration, ∇u_c , therefore, it might be more appropriate to limit $\nabla \phi$ in Eqs. 18 strictly to the transfer of OH^- and add terms proportional to the flux J_c of Cl^- as well as to the flux of Ca^{++} .)

CALCULATION OF MASS SOURCES AT ELECTRODES AND RUST PRODUCTION

Oxygen is consumed by the corrosion process at cathode at the rate:

$$j_o^c = -k_{oi}^c i^c \quad (\text{cathode}) \quad (19)$$

in which the minus sign is used because the plus sign is chosen to correspond to production (a source) of mass. According to Eq. 2, four electrons react with one molecule of O_2 , thus 4 faradays or $4 \times 96,500$ c react with one mole or 32 g of oxygen. Thus, $k_{oi}^c = 8.290 \times 10^{-5}$ g/c.

Passage of electric current at anode causes a flux of Fe^{++} ions into a diffusion layer, δ , thought to exist near the anode surface. This amounts to a source of $Fe(OH)_2$ in this layer

$$j_f = k_{fi} i^A \quad (\text{anode}) \quad (20)$$

According to Eqs. 1 and 3, two electron charges produce one molecule of $Fe(OH)_2$, therefore, 2 faradays or $2 \times 96,500$ c produce one mole of $Fe(OH)_2$, which is 89.67 g. Thus, $k_{fi} = 89.67 / (2 \times 96,500)$ or $k_{fi} = 4.646 \times 10^{-4}$ g/c. Furthermore, if all $Fe(OH)_2$ is immediately transformed to hydrated red rust according to Eq. 5, the rates of consumption of oxygen and production of rust are

$$j_o^A = -k_{of} j_f = -k_{oi}^A i^A \quad (\text{anode}) \quad (21a)$$

$$j_r = k_{rf} j_f = k_{ri} i^A \quad (\text{anode}) \quad (21b)$$

in which the minus sign indicates that oxygen is consumed rather than produced. According to Eq. 5, one mole or 32 g of O_2 combines with four moles or 4×89.67 g of $Fe(OH)_3$, so $k_{of} = 0.08922$; one mole or 89.87 g of $Fe(OH)_2$ produce one mole or 106.87 g of $Fe(OH)_3$, so $k_{rf} = 1.189$. Furthermore, $k_{oi}^A = k_{of} k_{fi} = 3.478 \times 10^{-5}$ g/c, $k_{ri} = k_{rf} k_{fi} = 5.524 \times 10^{-4}$ g/c.

If all oxygen diffusing to anode is immediately converted to hydrated red rust, the rates of consumption of Fe(OH)₂ and production of Fe(OH)₃ are

$$j_f = -k_{fo}j_o^A \quad (\text{anode}) \quad \dots \dots \dots (22a)$$

$$j_r = k_{ro}j_o^A \quad (\text{anode}) \quad \dots \dots \dots (22b)$$

According to Eq. 5, $k_{fo} = 4 \times 89$.

$$106.87/32 = 13.3$$

The boundary conditions at the surface of steel bars must describe the balance of mass and of electric charge in the electrochemical reactions. To avoid three-dimensional calculations for the surface of round bars, it is convenient to imagine that the layer of steel reinforcement is "smeared out," having a planar surface $x = L$. The consumption of oxygen at cathode and the production of Fe(OH)₂ at anode may be regarded as concentrated mass sources (or sinks). The jump in their mass fluxes J_o and J_f across the plane $x = L$ must equal the rate of mass sink, thus, for $x = L$

$$(J_o)_{L+} - (J_o)_{L-} = -j_o^C = k_{oi}^C i^C = k_{oi}^C \{ [i_x]_{L+} - [i_x]_{L-} \} \quad (\text{cathode}) \quad \dots \dots (23)$$

$$(J_f)_{L+} - (J_f)_{L-} = -j_f = -k_{fi}^A i^A = k_{fi}^A \{ [i_x]_{L+} - [i_x]_{L-} \} \quad (\text{anode}) \quad \dots \dots (24)$$

in which i_x is the x component of i ; and current densities i^C and i^A flowing out of cathode and into anode exhibit jumps in i_x across the plane $x = L$.

Production of rust occurs within concrete beyond the electrolytic layer, although still very close to the surface of steel. According to reaction kinetics (the rate law of reaction)

$$\dot{m}_r = Z_r u_f u_o \quad (\text{near anode}) \quad \dots \dots \dots (25)$$

in which $Z_r = Ze^{-U/RT}$, Z = collision number = constant, U = activation energy = constant. The rate of this reaction is undoubtedly much faster than the corrosion process as a whole, provided that both $u_f > 0$ and $u_o > 0$. So, the value of β_r is immaterial as long as it is chosen sufficiently large so as to effectively represent an immediate reaction. To make such a choice, consider the reaction in Eq. 25 for $u_o = \text{constant}$ and assume that the supply of Fe(OH)₂ by diffusion is negligible; then $\dot{m}_r = -k_{rf}\dot{u}_f$, so that $k_{rf}\dot{u}_f + Z_r u_f u_o = 0$. This differential equation has the solution $u_f \sim e^{-t/\tau}$ in which $\tau = k_{rf}/Z_r u_o$. For the reaction to be fast with regard to the entire corrosion process, τ may be set equal to 100 days, which yields $Z_r = (k_{rf}/u_o)0.01/\text{day}$ in which $k_r = 1.189$.

$u_o = 0.001 \text{ g/m}^3$, we conclude that a reasonable choice would be $Z_r \geq 10 \text{ m}^3/\text{g day}$.

The distributed mass sinks of oxygen and ferrous hydroxide due to rust production are

$$\dot{m}_f = -k_{fr}\dot{m}_r, \quad \dot{m}_o = -k_{or}\dot{m}_r \quad \dots \dots \dots (26)$$

in which $k_{fr} = 1/k_{rf} = 0.841$;

ELECTRODE POLARIZATION

The values of electrode potentials are known to be lowered very significantly (by orders of magnitude) as the density of electric current increases. This

phenomenon is called polarization of the cell (20). Denoting the drop in electromotive force due to polarization as η , one has $\Delta\phi = \Delta\phi_o - \eta$ in which $\Delta\phi_o$ is the value of $\Delta\phi$ at negligible current. According to the physical source, polarization is of two kinds: (1) Activation polarization η_A ; and (2) concentration polarization η_C , i.e., $\eta = \eta_A + \eta_C$.

Concentration polarization is due to the fact that the current depletes the ions available near the electrode surface, which, in turn, reduces the voltage and inhibits the current. For the current to continue, further ions must be supplied by diffusion (diffusion of oxygen and of Fe⁺⁺ ions in the present case), and the rate of this diffusion determines the equilibrium ion concentration and the steady-state or limiting current i_L that will eventually be reached. This is usually described (13) by the equation $\eta_c = (RT/nF) \ln(1 - i/i_L)$, which is based on an approximate expression for the rate of ion diffusion through an idealized diffusion layer near the electrode, derived from the assumption of a linear concentration profile across the layer (see Ref. 20, p. 446). So if this equation were used, it would be a substitute for solving the diffusion of O₂ and Fe⁺⁺ ions from the foregoing field equations.

Activation polarization is a drop in electrode potential due to changes caused by the current magnitude in the mechanism of ion transfer through the steel-concrete interface. In electrolytes in which the ion concentration is high (as in concentrated acids), concentration polarization is negligible and activation polarization prevails. Diffusion cannot transport ions to the electrode too rapidly, thus the opposite happens when ion concentration is low. In concrete, the concentration depends on the diffusion of oxygen through concrete, and this is a very slow process. Thus, for the purpose of simplification, it is reasonable to expect that the concentration polarization would prevail, and the activation polarization may then be neglected. At any rate, since the role of concentration polarization increases with the thickness L of the concrete cover while the activation polarization is independent of L , there must exist a certain value of L beyond which the activation polarization becomes negligible. Furthermore, the activation polarization, having its source in a very thin surface layer, takes place very rapidly, whereas in concrete it is the long-term changes in behavior that are of interest. Therefore, activation polarization will be neglected.

Concentration polarization is automatically accounted for by the effect of changes in oxygen and Fe⁺⁺ concentrations upon electrode potentials, as given by Eqs. 9, 12, and 13. For example, if the corrosion current is too high, oxygen at cathode will be depleted, i.e., u_o^C will decrease; by Eq. 13 this will reduce $\Delta\phi$ and diminish the current, thus allowing u_o^C to build up again and cause an increase in $\Delta\phi$. Or, if electric current produces a high concentration of Fe⁺⁺, $\Delta\phi$ will be reduced (by Eq. 13), and this would allow the Fe⁺⁺ concentration to diminish and cause an increase in $\Delta\phi$.

STATEMENT OF INITIAL-BOUNDARY VALUE PROBLEM

$$\text{and } k_{or} = 1/k_{ro} = 0.0$$

The electric boundary condition at the surface of concrete and at electrode surfaces (Fig. 2) are

$$\text{For } x = 0: \quad \phi = 0 \quad (\text{submerged}), \text{ or } i_x = 0 \quad (\text{exposed to air}) \quad \dots \dots (27)$$

$$\text{For } x = L: \quad \phi = \phi_{rr} - \Delta\phi^A \quad (\text{anode}); \quad \phi = \phi_{rr} - \Delta\phi^C \quad (\text{cathode}) \quad \dots (28)$$

The boundary condition at the surface of concrete submerged in sea water expresses the fact that the conductivity of the sea may be considered perfect (as compared to concrete). On the other hand, when the concrete surface is exposed to air no current can be transmitted to the air. The bars are assumed to be free of any direct connection to sea water ($\phi = 0$). Steel bar potential ϕ_s is one unknown to be solved. In the case of concrete exposed to air, we may set $\phi_s = 0$. For some structures, more complex electric boundary conditions might be required, e.g., to account for impressed currents from cathodic areas that are very remote from anodic areas.

The boundary conditions for the diffusion processes at the surface immersed in sea water are

$$\text{For } x = 0: \quad u_w = u_w^{sat}; \quad u_o = u_o^s = nu_o^{sea}; \quad u_c = u_c^s \dots \dots \dots (29)$$

in which u_w^{sat} = saturation concentration of capillary water = amount of capillary water in the pores in kilograms per cubic meter of saturated concrete; u_o^s , u_c^s are concentrations of oxygen and chloride ions in pores of concrete at the surface ($x = 0$); and n = ratio of pore volume to total volume of concrete = capillary porosity. Unlike u_o^s , u_c^s is not expressible as nu_c^{sea} and is probably much higher than this value because chlorides from sea tend to enter the concrete surface layer to react with Ca(OH)_2 in concrete. Perhaps $u_c^s \approx nu_c^{sat}$ in which u_c^{sat} is the saturation concentration of Cl^- in pore water. This is, however, the most unfavorable estimate. If the pore water near concrete surface is considered as a saturated solution of CaCl_2 , it would contain about 86 g of CaCl_2 or 55 g of Cl^- per 100 g of pore water. This would give $u_c^{sat} = 550 \text{ kg/m}^3$, and for the aforementioned concrete with 48 kg of capillary water per cubic meter of concrete $u_c^s = 550 \times 48/2,300 = 11.5 \text{ kg/m}^3$.

Oxygen concentration in sea water depends on the depth of sea to the point of interest. The degree of mixing by surface waves is of paramount importance. As a result of mixing, the concentration of dissolved oxygen in the North Sea is not substantially reduced even at the depth of 100 m. Characteristic values are $u_o^{sea} = 7.16 \text{ g/m}^3$, $u_c^{sea} = 20 \text{ kg/m}^3$ (9,15).

Deep in concrete, behind the reinforcement layer, we may postulate conditions of zero current densities and zero mass fluxes across some plane $x = l \gg L$. In the y direction, one can imagine boundaries $y = y_1$, $y = y_2$ on which either the same boundary conditions or periodicity conditions (anode-cathode-anode, etc.) apply.

The initial conditions when exposure to corrosive environment begins are

$$\text{For } t = 0: \quad \phi = 0, \quad u_w = u_w^{sat}, \quad u_o = 5n \frac{\text{g}}{\text{m}^3}, \quad u_c = 0;$$

$$\text{For } 0 \leq t \leq t_p: \quad u_f = 0 \dots \dots \dots (30)$$

in which the value of u_o refers to concrete that was mixed with typical fresh water, which normally contains 5 g of oxygen per cubic meter. The condition $u_f = 0$ obviously persists until the time, t_p , when steel is depassivated due to u_c reaching critical value u_c^* .

Since the initial value of u_f is zero, Eqs. 12 and 13 give $\Delta\phi^C = \Delta\phi = -\infty$ because $\log u_f = -\infty$. This is, of course, beyond the range of applicability of these equations. However, theoretically, this makes no difficulty because

the infinite voltage would last only for an infinitely short time. According to the equations, the large voltage yields a large current, which generates a rapid supply of Fe^{++} ions, which in turn causes a rapid drop in voltage and a rapid depletion of oxygen available at anode. In fact, the concentration of oxygen at the steel surface must be reduced to zero immediately after depassivation, because the source of Fe^{++} is a concentrated one.

Mathematically, we have now completed formulation of an initial-boundary-value problem. Its field equations are Eqs. 18 (electric field) and Eqs. 15 and 16 (mass diffusion), complemented by algebraic equations in Eqs. 25 and 26 (distributed mass sources) and Eq. 25 (reaction rate). This represents a system of 13 field equations for 13 unknowns (ϕ , i , u_w , u_o , u_f , u_c , J_w , J_o , J_f , J_c , \dot{m}_f , \dot{m}_o , and \dot{m}_c). So, the equations should suffice for solving the problem. The initial conditions are Eqs. 30, and the boundary conditions are Eqs. 27-29, with Eqs. 9 and 12 (voltages), complemented by interface jump conditions in Eqs. 23 and 24 (mass balance). The problem is nonlinear because of Eqs. 9, 12, and 25 and because diffusivities depend on concentrations as well as pore-water saturation (and possibly on corrosion-induced cracking as well).

Solution of the complete problem is well feasible at present with a computer, using the finite element method. Some preliminary work in this direction has already been done at Northwestern University (W. Klud-um, personal communication), but this approach is beyond the scope of this study.

SUMMARY

In view of the multitude of factors and processes involved in the corrosion problem, development of a physical-mathematical model is necessary. This is attempted herein for concrete exposed to sea water. The model describes: (1) Diffusion of oxygen, chloride ions, and pore water through the concrete cover of reinforcement; (2) diffusion of ferrous hydroxide near steel surface; (3) the depassivation of steel due to critical chloride ion concentration; (4) the cathodic and anodic electric potentials depending on oxygen and ferrous hydroxide concentrations according to Nernst equation; (5) the polarization of electrodes due to changes in concentration of oxygen and ferrous hydroxide; (6) the flow of electric current through the electrolyte in pores of concrete; (7) the mass sinks or sources of oxygen, ferrous hydroxide, and hydrated red rust near the electrodes, based on Faraday law; and (8) the rust production rate, based on reaction kinetics. To enable calculations, numerical values of all coefficients are indicated. Many of them are deduced by indirect arguments since direct measurements are unavailable. The theory is completed by formulating the problem as an initial-boundary-value problem.

Although the present mathematical formulation will undoubtedly be revised in the future, we hope it will lead to an improved understanding of the problem and give useful guidance for further experimental work. The complete equation system presented herein is complicated, but it would lend itself readily to a computer step-by-step solution in time using the finite element method. This should be one objective of further development.

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JOURNAL OF THE STRUCTURAL DIVISION

PHYSICAL MODEL FOR STEEL CORROSION IN CONCRETE SEA STRUCTURES— APPLICATION

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INTRODUCTION

The theoretical physical model for corrosion of steel in concrete exposed to sea water, developed in the companion paper (1) that immediately precedes in this issue, will now be applied to a simplified calculation of corrosion rates and times of corrosion cracking of concrete cover. First, we derive approximate estimates of the effective ohmic resistance of the corrosion cell. By treating oxygen and chloride ion transport through the concrete cover as quasistationary and one-dimensional, the corrosion problem will be reduced to ordinary differential equations in time. This will allow us to analyze various steady-state corrosion processes as special cases. Finally, after developing approximate formulas for the time of steel depassivation due to chloride ions and for cover cracking due to rust expansion, we will give some illustrative numerical examples.

Note that the notation introduced in the preceding companion paper (1) will continue to be used herein and that reference will be made to figures, equations, and references cited in that paper.

SIMPLIFIED PRACTICAL TREATMENT OF ELECTRIC CIRCUIT

To avoid three-dimensional calculations, the electric currents may be calculated from their assumed effective cross sections and simple paths. For this purpose, we must distinguish whether or not the cathodic or anodic area is large with respect to the concrete cover thickness, L , and the bar diameter, D . Let the anodic and cathodic areas be A^2 and C^2 , while A and C roughly characterize their linear dimensions on the plane $x = L$; see Fig. 1(b) of (1). The electric current densities at anode and cathode then are

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$$i^A = \frac{\Delta\phi}{a_b A^2 R}; \quad i^C = \frac{\Delta\phi}{a_b C^2 R} \quad \dots \dots \dots (1)$$

in which R = total ohmic resistance of the circuit; and a_b = steel surface per unit area of the plane $x = L$.

Case I: Large Scale Corrosion.—Let either A or C be larger than L but smaller than the thickness of concrete below the reinforcement layer. Then, if concrete surface is immersed in water [Fig. 1(b) of (1)], the total electric current through the electrolyte in concrete consists of two parts, $I = I_1 + I_2$ (A/m or amperes per meter), in which I_1 is the current passing exclusively through concrete, essentially parallel to the steel bar; and I_2 is the current that goes from the anode through the concrete cover to sea water, then through sea water, and then from sea water through the concrete cover to the cathode and further through the steel bar back to the anode. The mean cross sections through which current I_1 passes near the anode and cathode are roughly $AL + A^2/2$ and $CL + C^2/2$, respectively. The corresponding effective lengths of current passages are $A/2$ and $C/2$. Since the ohmic resistance of steel bars is negligible, the total ohmic resistance for this current is $R_1 \approx \lambda(A/2)/(AL + A^2/2) + \lambda(C/2)/(CL + C^2/2) = \lambda[(A + 2L)^{-1} + (C + 2L)^{-1}]$, in which L = the thickness of the cover [Fig. 1(b) of (1)]. The effective length of passage for current I_2 is $L + L$ because the ohmic resistance of sea water is negligible, and the mean cross sections are A^2 and C^2 , giving the resistance $R_2 = \lambda(L/A^2 + L/C^2)$. Thus, the total current $I = I_1 + I_2$ is $I = \Delta\phi/R_1 + \Delta\phi/R_2 = \Delta\phi/R$ with R being the total resistance of the circuit in ohms,

$$\frac{1}{R} \approx \frac{1}{\lambda} \left[\frac{1}{\frac{1}{A+2L} + \frac{1}{C+2L}} + \frac{1}{L \left(\frac{1}{A^2} + \frac{1}{C^2} \right)} \right] \quad \text{(immersed)} \quad \dots \dots \dots (2a)$$

However, if the concrete surface is exposed to air [Fig. 1(b) of (1)], current I_2 is zero while current I_1 is the same. This gives

$$\frac{1}{R} \approx \frac{1}{\lambda} \frac{1}{\frac{1}{A+2L} + \frac{1}{C+2L}} \quad \text{(exposed to air)} \quad \dots \dots \dots (2b)$$

Note that for $C \rightarrow \infty$, R tends to a constant, $R = \lambda/(A + 2L)$, while for the previous case $R = \lambda/(A + 2L + A^2/L)$.

Case II: Small-Scale Corrosion.—In the early stage of corrosion, both A and C would probably be much smaller than $L/2$ and much smaller than the bar diameter D as well. In that case, current I_2 , passing through sea water, would contribute little; thus it would be immaterial whether concrete is immersed or exposed. Current I_1 will have an effective cross section less than L (i.e., it does not reach all the way to the concrete surface) and the situation can be regarded as a half space of concrete in contact with a half space of steel. Then the cross sections of current I_1 will be roughly $A^2/2$ and $C^2/2$, and the corresponding lengths of passage will be $A/2$ and $C/2$, giving

$$\frac{1}{R} \approx \frac{1}{\lambda} \frac{1}{\frac{1}{A} + \frac{1}{C}}, \quad \text{with } a_r = 1, A, C \ll L, D \quad \text{(immersed or exposed)} \quad (2c)$$

In the intermediate case when still $A \leq L/2$ and $C \leq L/2$ but A and C are of comparable size to bar diameter D , the bar must be regarded as round and the flow of the current would be roughly parallel to the bar [Fig. 1(d) of (1)]. The anodic and cathodic areas on the surface of steel now are πDA and πDC . The cross sections of electric current at anode and cathode will then be roughly circles of diameters $D + A$ and $D + C$ less the cross section of steel bar, $\pi D^2/4$, and the corresponding lengths would be $A/2$ and $C/2$. This yields

$$\frac{1}{R} \approx \frac{\pi D}{4 \lambda}, \quad \text{with } a_r = 1, A, C \approx D \ll L \quad \text{(immersed or exposed)} \quad \dots (2d)$$

TRANSIENT CORROSION WITH QUASISTEADY ONE-DIMENSIONAL DIFFUSIONS

Restricting our attention to large-scale corrosion, we may now consider the cathodic and anodic areas to be large enough to permit considering the diffusions of oxygen at cathode and anode as mutually independent and one-dimensional. Moreover, the distributed mass sources and sinks may be removed from the field equations (setting $\dot{m}_o = \dot{m}_f = \dot{m}_r = 0$ in Eq. 15 of Ref. 1) and they may be replaced by total mass sources and sinks j_r, j_f, j_o^A , which are imagined to take place within a certain "diffusion" layer or "rusting" layer of thickness δ near the anode surface, $L - \delta \leq x \leq L$. This layer is assumed to roughly indicate the depth of penetration of Fe^{++} ions from the electrode into concrete.

Analysis can be further facilitated by assuming that the diffusion processes are in quasisteady states, such that the diffusion fluxes are essentially constant throughout the cover thickness, which means that the concentration profiles are linear. Let u_o^C and u_o^A denote the unknown oxygen concentrations at the surfaces of cathode and anode, and c_o^C, c_o^A the respective oxygen diffusivities (usually equal). Then, for constant oxygen concentration u_o^S at the concrete surface (in the sea), the change of total oxygen content in cover L at cathode is $(du_o^C/dt)L/2$, which must equal the flux of oxygen into the concrete cover, less the rate of oxygen consumption at the cathode surface; thus

$$\frac{L}{2} \frac{du_o^C}{dt} = c_o^C \frac{u_o^S - u_o^C}{L} - k_{oi}^C \frac{\Delta\phi}{a_b C^2 R} \quad \text{(cathode)} \quad \dots \dots \dots (3)$$

At anode, the rate of change of oxygen content in cover L must equal the rate of diffusion into cover L , minus the rate, j_o^A , of consumption of oxygen for rusting; this yields $(du_o^A/dt)L/2 = c_o^A(u_o^S - u_o^A)L - j_o^A$. The rate of change of $Fe(OH)_2$ content of rusting layer δ must equal the rate of production, k_{fi}^A , by electric current $i^A = \Delta\phi/a_b A^2 R$, minus the rate of consumption by reaction with O_2 ; this gives $(du_f/dt)\delta/2 = k_{fi}^A \Delta\phi/a_b A^2 R - k_{fo} j_o^A$. Expressing j_o^A from here and substituting it into the preceding relation, we obtain

$$\frac{L}{2} \frac{du_o^A}{dt} - \frac{\delta}{2k_{fo}} \frac{du_f}{dt} = c_o^A \frac{u_o^S - u_o^A}{L} - \frac{k_{fi}^A}{k_{fo} a_b A^2 R} \Delta\phi \quad \text{(anode)} \quad \dots \dots \dots (4)$$

The rate of production of Fe(OH)₂ at the anode surface must equal the rate of its transport into rusting layer δ, i.e.

$$k_{f_i} \frac{\Delta\phi}{a_b A^2 R} = c_f \frac{u_f}{\delta} \dots \dots \dots (5)$$

Note that δ will normally vary with time. As a further simplification, it may be assumed that all Fe(OH)₂ that is supplied to layer δ reacts with oxygen practically immediately, compared to lifetimes of structures. This gives the rate of production of hydrated red rust in the whole layer δ as

$$j_r = \frac{k_{r_i}}{a_b A^2 R} \Delta\phi \dots \dots \dots (6a)$$

$$\text{with } \Delta\phi = \phi_1 + n^c \log u_o^c - n^a \log u_f \dots \dots \dots (6b)$$

Eqs. 3-6 represent a simplified formulation of the transient corrosion problem. It is a nonlinear system of five equations for five unknown functions of time: u_o^a , u_o^c , u_f , $\Delta\phi$, and j_r . By expressing $\Delta\phi$ from Eq. 5 and substituting it into Eqs. 3, 4, and 6b, and further expressing u_o^c from Eq. 6b and substituting it into Eqs. 3 and 4, we can further reduce the problem to a system of two nonlinear first-order ordinary differential equations for u_o^a and u_f , which is easily integrated step by step on a computer using standard subroutines.

STEADY-STATE CORROSION

The steady state is the easiest to analyze. In that case, $du_o^a/dt = du_o^c/dt = du_f/dt = 0$. Then, eliminating $\Delta\phi$ from Eqs. 3 and 4 and expressing u_o^c from Eq. 3 we may write

$$u_o^s - u_o^a = k_1 (u_o^s - u_o^c) \dots \dots \dots (7a)$$

$$u_o^c = u_o^s - k_2 \Delta\phi \dots \dots \dots (7b)$$

$$\text{in which } k_1 = k_{f_{io}} \frac{c_o^c C^2}{c_o^a A^2}; \quad k_2 = \frac{k_{oi}^c L}{c_o^c R a_b C^2};$$

$$k_{f_{io}} = \frac{k_{fi}}{k_{fo} k_{oi}^c} = 0.5000 \dots \dots \dots (8)$$

Eqs. 5-7 represent a nonlinear system of five algebraic equations for five unknowns with variables u_o^a , u_o^c , u_f , $\Delta\phi$, and j_r . However, in addition to these state variables, there are further unknowns, i.e., the geometrical parameters δ, A, and C/A. Thus, unless these can be determined by direct experimental observations, it is impossible to solve the problem without adding some further conditions. To obtain them, we may postulate the following principle, which could be deduced from irreversible thermodynamics (by using the principle of maximum entropy production, with entropy being produced by dissipative processes such as current flow and diffusions).

Principle of Maximum Corrosion Current Density.—Among all possible corrosion rates satisfying all conditions of balance of mass and electric charge, diffusion rates, and current densities, the actual corrosion rate maximizes the corrosion

current density i^A . This is equivalent to maximizing the rate of rust production per unit area, j_r .

Eqs. 5-6 include three indeterminate geometric parameters δ, A, and C/A. Thus, the principle may be written as

$$j_r \left(\delta, \frac{A}{L}, \frac{C}{A} \right) = \max \dots \dots \dots (9)$$

The maximization must be done with account of the obvious inequality restrictions

$$0 \leq u_o^a \leq u_o^s; \quad 0 \leq u_o^c \leq u_o^s; \quad u_f \geq 0; \quad 0 \leq \Delta\phi \leq \Delta\phi_{\max} \dots \dots \dots (10)$$

of which the first three are obvious and the last one gives a limiting voltage analyzed in the sequel. No restriction needs to be imposed upon δ, but if δ were obtained larger than L, it would mean that Fe(OH)₂ would be leaching through the concrete cover to the surface of concrete. For δ = L one could calculate u_f from Eq. 6b and solve all unknowns from Eqs. 3-5 without recourse to the extremum principle if A and C are given.

Case 1: Oxygen at Cathode Governs.—According to Eq. 7b, condition $u_o^c \geq 0$, and Eq. 7a, the condition of maximum $\Delta\phi$ yields $u_o^c = 0$, and so the solution is

$$j_r = \frac{k_{r_i}}{k_2} \frac{u_o^s}{a_b A^2 R} = 6.66 \frac{C^2}{A^2} \frac{u_o^s}{L} c_o^c; \quad u_o^c = 0; \quad u_f = 0;$$

$$u_o^a = (1 - k_1) u_o^s; \quad \Delta\phi = \frac{u_o^s}{k_2}; \quad \delta = \frac{c_f}{k_{f_i}} \frac{u_f}{\Delta\phi} a_b A^2 R \dots \dots \dots (11)$$

This stretches the Nernst equation for $\Delta\phi$ (Eq. 6) certainly beyond the range of its validity because $\log u_o^c \rightarrow -\infty$ and $\log u_f \rightarrow -\infty$. Nevertheless, let us assume that the Nernst equation is still valid when u_o^c is rather small but nonzero. Then, from Eqs. 6

$$u_f = [10^{\phi_1 - \Delta\phi} (u_o^c)^{n^c}]^{1/n^a} \dots \dots \dots (12a)$$

$$u_f \approx u_w^a \left(\frac{u_o^c}{u_w^c} \right)^{n^c/n^a} \dots \dots \dots (12b)$$

which is also a small but nonzero value. The second (approximate) expression ensues if we note that $\Delta\phi$ and ϕ_1 in the expression for $\Delta\phi$ (Eq. 12 of Ref. 1) become negligible compared to the logarithmic terms.

The present case applies only as long as the inequalities in Eq. 10 are fulfilled, in particular as long as $k_1 \leq 1$ or

$$\frac{C^2}{A^2} \geq k_{f_{io}} \frac{c_o^a}{c_o^c} = 0.5000 \frac{c_o^a}{c_o^c} \dots \dots \dots (13)$$

Obviously, this condition can be violated if the oxygen diffusivity at anode is too small, or the oxygen diffusivity at cathode is too large. However, if development of a large enough cathodic area is unrestricted, condition $k_1 \leq 1$ can be met for any specified nonzero oxygen diffusivities. Thus, it seems that Case 1 is the basic case which always develops, unless a sufficient cathodic area C is unavailable (see Case 2).

In this case, the voltage is governed by the rate of diffusion of oxygen at cathode. The corrosion rate is proportional to oxygen concentration at concrete surface (in the sea), to oxygen diffusivity at cathode, and to the inverse of cover thickness. Note, however, that the corrosion rate is independent of the resistivity of concrete and of the rate of supply of oxygen at anode. The only consequence of increasing resistivity is that a higher voltage develops as needed to sustain the corrosion current.

Further maximization of j_r is to be carried out with regard to cathodic and anodic areas, C and A . According to the expression for j_r in Eq. 6a, this is achieved if k_2AR is minimized. Eq. 8 shows that this happens for the minimum possible value of LA^2/C^2 , independently of R . This indicates that in large-scale corrosion the ratio of cathodic to anodic areas for Case 1 should be large.

As for the anodic area A per se, no condition is obtained from the extremum principle; but our assumption of one-dimensional diffusions does not allow A to be much less than the cover thickness, L . Probably, $A \geq L$ is required.

Case 2: Oxygen at Anode Governs.—If a large enough cathodic area C cannot develop (e.g., because of the reinforced concrete element being too small) or if the anodic (rusted) area is too large to begin with, then the supply of oxygen to the anode (Eq. 4) may govern the corrosion rate. This is the case for which the inequality in Eq. 13 is violated; we have $k_1 > 0$ and from Eqs. 5–6 it follows that

$$\text{For } k_1 > 1: j_r = \frac{k_{r1}}{k_1 k_2} \frac{u_o^S}{a_b A^2 R} = 13.33 \frac{u_o^A}{L} c_o^A;$$

$$u_o^C = \left(1 - \frac{1}{k_1}\right) u_o^S; \quad u_o^A = 0; \quad \Delta\phi = \frac{u_o^S}{k_1 k_2} \dots \dots \dots (14)$$

and u_f is given again by Eq. 12a but is not very small in this case. Comparing Eq. 14 with Eq. 11, we see that, for $k_1 > 1$, Eq. 14 always gives smaller j_r (slower rust production). The corrosion rate is proportional to oxygen concentration at the concrete surface (at sea), to oxygen diffusivity at anode, to inverse cover thickness, $1/L$, and to concrete conductivity $1/\lambda$; but, curiously, it is independent of C/A .

Maximization of j_r with regard to parameters of the problem requires that $k_1 k_2 a_b A^2 R / u_o^S$ be minimum, and substituting from Eq. 5 we see that we only need to maximize $c_o^A u_o^S / L$. From this we note that a higher oxygen concentration at the surface (at sea), a higher oxygen diffusivity at anode, and a thinner cover at anode mean (in this case) a faster corrosion, while previously the factors were the oxygen diffusivity at cathode or the cover thickness at cathode.

In contrast to the previous case, the corrosion rate is independent of concrete resistivity λ as long as this case holds, and areas A and C have no effect. The only effect of an increase in resistivity in this case is that a higher voltage develops as needed to sustain the corrosion rate.

Case 3: Limiting Voltage Governs.—It has been shown that Case 1 prevails when C/A is large enough, (Eq. 13) and that the corrosion rate then increases in proportion to C^2 and is unaffected by the increase in R . However, if $C \rightarrow \infty$ were possible, the corrosion rate would certainly not tend to infinity. Thus, there must be an upper limit. Noting that with increasing C or decreasing

k_2 the voltage increases ($\Delta\phi = u_o^S/k_2$, Eq. 11), there must be a limiting possible voltage $\Delta\phi_{max}$ that the mechanism of ion exchange at the steel surface can develop and sustain. Knowing this voltage, we can from Eq. 11 calculate $k_2 = u_o^S/\Delta\phi_{max}$ and the maximum of j_r :

$$j_r = \frac{k_{r1}}{a_b A^2 R} \Delta\phi_{max} \dots \dots \dots (15)$$

The value of C/L can be found from Eq. 8 for k_2 . If the value of C is still larger than that, Case 1 no longer applies and $u_o^C > 0$

$$u_o^C = u_o^S - k_2 \Delta\phi_{max}; \quad u_o^A = u_o^S - k_1(u_o^S - u_o^C) \dots \dots \dots (16)$$

Maximum j_r is obtained for minimum AR . For submerged concrete (Eq. 1), minimum AR (for $L \leq A \leq 2L$) is obtained for largest C/A and is approached asymptotically as $C/A \rightarrow \infty$. For concrete that is not submerged (Eq. 2), minimum AR is obtained for smallest C/A , which corresponds to the value of C/L found from Eq. 8 and $k_2 = u_o^S/\Delta\phi_{max}$.

In the earlier stage of large-scale corrosion while the percentage of rusted steel surface area is still small, it seems that a large cathodic-to-anodic-area ratio will always develop, and then the limiting voltage case might apply. The corrosion rate would then be for a while independent of oxygen diffusion and would depend on the ohmic resistance (which in turn depends on the degree of water saturation).

Case 4: Balanced Oxygen Flux (Small-Scale Corrosion).—Corrosion begins in the form of anodic and cathodic spots, which are much smaller than the concrete cover and the bar diameter. In that stage oxygen is drawn from the supply initially available in concrete. But this initial supply soon gets exhausted, so oxygen must be drawn from the environment. When a steady state is reached, the anodic and cathodic areas could remain small only if the diffusion fluxes are balanced in such a way that $u_o^A = u_o^C$. The maximum rate of corrosion may then be expected when $u_o^A = u_o^C = 0$. For this case Eq. 11 yields $k_1 = 1$, and because c_o^A must equal u_o^C , we have

$$\frac{C^2}{A^2} = k_{f10} = 0.5000 \quad (A, C \ll L) \dots \dots \dots (17)$$

while the rate-of-rust production and all other variables follow from Eq. 11. This C^2/A^2 ratio must get automatically established early in the corrosion process. According to the previous analysis of Case 1, C/A would later increase, for this gives a larger current. This is, however, possible if the areas which were initially anodic and already started to rust would subsequently begin acting as cathodic areas. In Case 1, it was tacitly assumed that this was possible.

CRACKING DUE TO RUST

Hydrated red rust has a smaller mass density than steel. Thus, rusting is accompanied by volume expansion; this may cause concrete to crack, which again induces faster corrosion. It is not clear whether the production of $Fe(OH)_2$ itself causes volume expansion. It will be assumed that only $Fe(OH)_3$ does,

but a simple modification of the analysis would be possible to account for the expansion due to Fe(OH)₂.

Consequently, prediction of corrosion damage requires the stress problem to be also solved. The volume expansion due to hydrated red rust may be introduced as a prescribed displacement at the surface of bars (although it might be better modeled as an inelastic volume strain distributed over layer δ). Let M_r denote the total mass of rust per unit length of one bar; assuming steady-state corrosion begins at depassivation time t_p, we have M_r = s j_r t_{cor}, in which s = spacing of bars; j_r = rate of rust production per unit area of plane x = L; and t_{cor} = duration of steady-state corrosion. The mass of steel that was consumed to produce M_r is M_{st} = 0.523 M_r, in which 0.523 = molecular weight of Fe divided by the molecular weight of Fe(OH)₃.

A bar having originally diameter D will increase its diameter to D + ΔD. Expressing the increase in volume per unit length of bar by means of M_r, and also by means of ΔD we have M_r/ρ_r - M_{st}/ρ_{st} = [(D + ΔD)² - D²] π/4, in which ρ_r, ρ_{st} = mass densities of steel and of Fe(OH)₃; ρ_{st} = 7.85 g/cm³; and ρ_r = ρ_{st}/4 (Ref. 33 of companion paper, Ref. 1). Putting all together we have (D + ΔD)² = D² + 2 s j_r t_{cor}/ρ_{cor}, in which ρ_{cor} = [(1/ρ_r) - (0.583/ρ_{st})]⁻¹ π/2 ≈ 3.6 g/cm² and noting that ΔD << D, we may obtain

$$t_{cor} = \frac{D \Delta D}{\rho_{cor} s j_r} \dots \dots \dots (18)$$

Stresses and cracking caused in concrete cover by this increase in diameter can be routinely solved by the finite element method. Assuming elastic behavior, one could also develop an analytical solution applying Guell and Dundurs' method (2) (but reformulating it in bipolar coordinates).

Nevertheless, it is worthwhile to make some simple, albeit crude, estimate of the stresses. Considering concrete to be a homogeneous elastic material, the pressure p_r at the surface of the bar is a pressure that is needed to expand a cylindrical hole of diameter D by ΔD; p_r would be smaller than the pressure for a hole in an infinite medium and larger than the pressure for a hole in a thick-wall cylinder of external diameter D + 2L. According to well known formulas, ΔD = δ_{pp} p_r, in which the bar hole flexibility δ_{pp} is bounded by (1 + ν)D/E_{cf} from below (thick-wall cylinder) and by [1 + ν + D²/2(L² + LD)] D/E_{cf} from above (infinite space); here ν = Poisson ratio of concrete (≈0.18) and E_{cf} = effective elastic modulus of concrete = E/(1 + φ_{cr}), in which φ_{cr} = creep coefficient (typically about 2.0).

If there is a row of parallel bars that all rust simultaneously, ΔD of one chosen bar may be appreciably influenced by the expansion of the two adjacent bars [Fig. 1(d) of Ref. 1]. If the displacement field due to the expansion of each adjacent bar is considered to be the same as the field for the expansion of a single bar in an infinite elastic space, the contribution to the expansion of one bar (normal to concrete surface) caused by applying pressure p_r at the surface of both adjacent bars would be approx 2p_r D³/s²E_{cf} in which s = spacing of the bars (on center). Adding this to the previous bounds on δ_{pp}, we obtain

$$\delta_{pp}^0 < \delta_{pp} < \delta_{pp}^1; \quad \delta_{pp} \approx \frac{1}{2} (\delta_{pp}^0 + \delta_{pp}^1) \dots \dots \dots (19)$$

in which $\delta_{pp}^0 = \frac{D}{E_{cf}} (1 + \nu) + \frac{2D^3}{s^2 E_{cf}}$;

$$\delta_{pp}^1 = \frac{D}{E_{cf}} \left[1 + \nu + \frac{D^2}{2L(L + D)} \right] + \frac{2D^3}{s^2 E_{cf}} \dots \dots \dots (20)$$

Failure may occur basically in two different modes. If spacing s of the bars is large (say, s > 6D), we may assume that the failure mode consists of planar cracks of 45° inclination, emanating from opposite points on the surface of the bar [Fig. 1(e) of Ref. 1]. If, at failure, the average tensile stress on the crack surfaces equals the tensile strength of concrete, f'_t, equilibrium requires that 2Lf'_t = p_rD = DΔD/δ_{pp}. Thus, the critical value of ΔD that produces inclined cracks emanating from a single bar is

$$\Delta D = 2f'_t \frac{L}{D} \delta_{pp} \text{ (inclined cracks)} \dots \dots \dots (21)$$

(This formula could be checked by setting up an analogous formula for conical bursting of the concrete cover caused by a fluid pressure within a penny-shaped cavity and comparing the prediction to test data from Ref. 3.)

Another basic failure mode consists of a crack that runs parallel to the surface from one bar to another. Assuming again the average tensile stress in concrete is equal to f'_t, we may write the equilibrium condition (s - D)f'_t = p_rD, which yields

$$\Delta D = f'_t \left(\frac{s}{D} - 1 \right) \delta_{pp} \text{ (cover peeling)} \dots \dots \dots (22)$$

This case obviously prevails whenever L > (s - D)/2. However, this type of cracking may often be less dangerous for two reasons: (a) Unlike the inclined cracks, it does not provide a flow channel connecting to the surface; and (b) the opening of the cracks parallel to concrete surface would be somewhat inhibited by stirrups or transverse ties in the reinforcing mesh.

The critical time t_{cr} at which corrosion would produce cracks through the whole cover is

$$t_{cr} = t_p + t_{cor} \dots \dots \dots (23)$$

in which t_{cor} may be solved from Eq. 18 if ΔD is estimated from Eq. 21 or 22; and t_p = the time of depassivation, which may be calculated from diffusion of Cl⁻ ions. Since this diffusion is uncoupled and can probably be considered to be linear, one could solve t_p using the well known solution in terms of the error function. However, like in other similar problems, it is possible to consider that the u_c profile is approximately parabolic up to the varying penetration depth x = H(t), i.e., u_c ≈ u_c^s(1 - x/H)² for x ≤ H. For concrete surface (x = 0) this gives ∂u_c/∂x = 2u_c^s/H. The mass of Cl⁻ ions in concrete is M_c = ∫₀^H u_c dx = u_c^s H/3. The flux of Cl⁻ into concrete at x = 0 must equal dM/dt, i.e., 2c_cu_c^s/H = (dH/dt)u_c^s/3. Integration of this differential equation yields the approximation H = √12c_ct, which is of a type often used in diffusion problems. Thus, the time when the critical Cl⁻ concentration at steel surface (x = L) will be reached is roughly

$$t_p = \frac{1}{12 c_c} \left(\frac{L}{1 - \sqrt{\frac{u_c^*}{u_c^s}}} \right)^2 \dots \dots \dots (24)$$

Simple formulas also exist for diffusion according to Eq. 18 of Ref. 1 with $c_c = 0$. The problem is analogous to spreading of hydraulic overpressure into unsaturated concrete dam (see Ref. 4 of companion paper, Ref. 1).

After corrosion causes the concrete cover to crack, diffusion of oxygen and chlorides toward the reinforcement may be greatly intensified and the degree of water saturation affecting its resistivity and diffusivities may be increased. All this may greatly accelerate the corrosion process. The average increase of effective diffusivities in cracked concrete will be proportional to w^3/a_c in which w = crack width; and a_c = crack spacing; the corrosion rate may then be calculated similarly as before. Cracking, however, may also cause $\text{Fe}(\text{OH})_2$ to leach out along the cracks, thus reducing the accumulation of rust at the surface of bars.

The determination of w and a_c will be of paramount importance for predicting lifetimes when the cracks are initiated by shrinkage or thermal stresses or by applied loads, especially fatigue loading. Such cracking, caused by repeated loads from wave action or by thermal stress from repeated filling with warm crude, is of concern for oil-storage tanks in the North Sea.

NUMERICAL EXAMPLES

To illuminate the effects of various factors, consider the wall of an offshore oil-storage concrete tank with cover thickness $L = 10$ cm and reinforcing bars 2 cm in diameter spaced at $s = 10$ cm. Assume the compressive strength, elastic modulus, and tensile strength of concrete to be $f'_c = 44.8$ N/mm²; $E = 31,700$ N/mm²; and $f'_t = 3.9$ N/mm². We have $a_b = \pi D/s = 0.63$, and taking the creep coefficient to be $\phi_{cr} = 2$, we obtain from Eqs. 19-20 the critical change of diameter of bars as $\Delta D \approx 0.093$ mm. [Tuutti (Ref. 33 of companion paper) observed that attainment of the value $\Delta D = 0.2$ mm due to rust caused the cover of 1 cm in thickness to crack, which is a very good correlation.] Let porosity n of concrete be relatively small such that the capillary water content at pore saturation is $u_w = 48$ kg/m³, yielding $n = 0.048$. Also assume that $u_o^{sea} = 7.16$ g/m³, giving $u_o^s = 0.15$ g/m³, and $u_c^s = 11.5$ kg/m³; $c_o^c = c_o^A = c_o = 10^{-12}$ m²/s; $c_c = 10^{-11}$ m²/s; $c'_f = c_c$, $\lambda = 40$ ohm m. Finally, let $A = 0.1$ m and $C = 1$ m (large-scale corrosion).

Example 1.—Considering that oxygen supply at cathode governs, we obtain, from Eqs. 11, 18, 8, and 2a: $j_r = 1.0 \times 10^{-9}$ g/m²s, $t_{cor} = 2,120$ yr, $R = 118$ ohm, $\Delta\phi = 0.0134$ mv; and taking $u_o^c \approx 0.01 u_o^s$ we also have from Eqs. 12 and 11 $u_r = 8.5$ g/m³ and $\delta = 0.4$ mm. Furthermore from Eqs. 24 and 23, $t_p = 11$ yr and $t_{cr} = 2,131$ yr. For deep immersion in the sea, this lifetime is not unrealistic (Ref. 13 of companion paper, Ref. 1).

Example 2.—It is now of interest to see the effect of changes in some parameters. For example, let all data be the same as in Example 1 except that $C = A = 10$ cm (limited cathodic area). Then $j_r = 1.0 \times 10^{-11}$ g/m²s, $R = 200$ ohm,

$\Delta\phi = 0.00037$ Mv, and $t_{cor} = 212,000$ yr.

Example 3.—If all data are the same as in Example 1, except that the cover is only $L = 2$ cm, we obtain $t_{cor} = 424$ yr.

Example 4.—If all data are the same as in Example 1, except that oxygen concentration is as low as $u_o^{sea} = 1$ g/m³ (deep, calm sea), we get $t_{cor} = 15,180$ yr.

Example 5.—If all data are the same as in Example 1, except that concrete has high oxygen diffusivity (to be expected e.g., in splashing zone) $c_o = 1.0 \times 10^{-8}$ m²/s, we have $t_p = 77$ days; $t_{cor} = 11$ yr (with $\Delta\phi = 0.13$ v). This time is unexpectedly short.

Example 6.—If all data are the same as in Example 1, except that concrete has a higher capillary porosity, $n = 0.15$, and a higher capillary water content, $u_w = 150$ kg/m³, we obtain $t_{cor} = 681$ yr.

Example 7.—In all previous examples, Case 1 (Eqs. 11 and 12) was assumed to apply. Consider now that a limiting voltage of $\Delta\phi_{max} = 1$ v is attained, all pertinent data being the same as in Example 1. Then we find from Eq. 15 that $j_r = 4.7 \times 10^{-3}$ g/m²s, $t_{cor} = 17$ days (with $C/A = 338$), which is a catastrophic case.

Example 8.—If all is the same as in Example 7, except that the ohmic resistance is typical of concrete exposed to dry air and having a 40% water saturation ($\lambda \approx 90,000$ ohm m), we have $R = 265,000$ ohm m and we find $R = 417$ ohm; $j_r = 2.08 \times 10^{-8}$ g/m²s; and $t_{cor} = 30$ yr. However, in case that limiting voltage is not attained, one must consider the drastic changes in c_o due to air exposure.

It is clear from these examples that diffusivities have a dominant effect on corrosion in many cases. Interestingly, oxygen supply in the cathodic (nonrusting) area (rather than anodic area) usually controls the process. Note that dramatic changes in effective diffusivities can be caused by cracking, decrease in water saturation, drying cycles, and carbonation.

SUMMARY AND CONCLUSIONS

The theoretical physical model for corrosion of steel in concrete exposed to sea water, developed in the preceding paper, is applied to a simplified calculation of corrosion rates and times to corrosion cracking of concrete cover. Setting up approximate estimates of effective resistance of the corrosion cell, and treating oxygen and chloride ion transport through concrete cover as quasistationary and one-dimensional, the corrosion problem is reduced to ordinary differential equations in time. For determining the extents of cathodic and anodic areas and the thickness of the rusting layer, a new principle stating that the actual corrosion current is maximum is postulated. Various steady-state corrosion processes are then analyzed, and after developing approximate formulas for the time of steel depassivation due to chloride ions and for cover cracking due to volume expansion of rust, a number of illustrative numerical examples illuminating the effects of various factors are given. The results are reasonable, but no test data for experimental verification of the model are known. Diffusivities for chloride ions and oxygen, not only at anodic (rusting) area but also and mainly at cathodic areas, are shown to be usually the controlling factors.

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14652 CORROSION IN SEA STRUCTURES—APPLICATION

KEY WORDS: Chlorides; Concrete deterioration; Concrete durability; Concrete structures; Constitutive equations; Corrosion; Corrosion currents; Cracking; Diffusion; Electrochemistry; Mathematical models; Offshore structures; Oxygen; Reinforcement; Rust; Sea water; Steel

ABSTRACT: The theoretical physical model developed in a companion paper, is applied to a simplified calculation of corrosion rates and times to corrosion cracking of concrete cover. Setting up approximate estimates of effective resistance of the corrosion cell, and treating oxygen and chloride ion transport through concrete cover as quasi-stationary and one-dimensional, the corrosion problem is reduced to ordinary differential equations in time. For determining the extents of cathodic and anodic areas and the thickness of the rusting layer, a new principle stating that the actual corrosion current is maximum is postulated. Various steady-state corrosion processes are then analyzed, and after developing approximate formulas for the time of steel depassivation due to chloride ions and for cover cracking due to volume expansion of rust, a number of illustrative numerical examples are given. Diffusivities for chloride ions and oxygen are shown to be usually the controlling factors.

REFERENCE: Bazant, Zdenek P., "Physical Model for Steel Corrosion in Concrete Sea Structures—Application," *Journal of the Structural Division*, ASCE, Vol. 105, No. ST6, Proc. Paper 14652, June, 1979, pp. 1155-1166