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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

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

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 $\text{Fe}(\text{OH})_2$ 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.

$$k_{f1} \frac{\Delta\phi}{a_b A^2 R} = c_f \frac{u_f}{\delta} \dots \dots \dots (5)$$

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

$$j_r = \frac{k_{r1}}{a_b A^2 R} \Delta\phi \dots \dots \dots (6a)$$

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

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

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

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

$$\text{in which } k_1 = k_{f10} \frac{c_o^c C^2}{c_o^a A^2}; \quad k_2 = \frac{k_{o1}^c L}{c_o^c R a_b C^2};$$

$$k_{f10} = \frac{k_{f1}}{k_{f0} k_{o1}^c} = 0.5000 \dots \dots \dots (8)$$

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

$$j_r = \frac{k_{r1}}{k_2} \frac{u_o^s}{a_b A^2 R} = 6.66 \frac{C^2 u_o^s}{A^2 L} c_o^c; \quad u_o^c = 0; \quad u_f = 0;$$

$$u_o^a = (1 - k_1) u_o^s; \quad \Delta\phi = \frac{u_o^s}{k_2}; \quad \delta = \frac{c_f u_f}{k_{f1} \Delta\phi} a_b A^2 R \dots \dots \dots (11)$$

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

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

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

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

$$\frac{C^2}{A^2} \geq k_{f10} \frac{c_o^a}{c_o^c} = 0.5000 \frac{c_o^a}{c_o^c} \dots \dots \dots (13)$$

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 $k_2 AR$ 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_r 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 $D + \Delta D$. Expressing the increase in volume per unit length of bar by means of M_r and also by means of ΔD we have $M_r/\rho_r - M_{st}/\rho_{st} = [(D + \Delta D)^2 - D^2] \pi/4$, in which ρ_r, ρ_{st} = mass densities of steel and of $Fe(OH)_3$; $\rho_{st} = 7.85 \text{ g/cm}^3$; and $\rho_r = \rho_{st}/4$ (Ref. 33 of companion paper, Ref. 1). Putting all together we have $(D + \Delta D)^2 = D^2 + 2 s j_r t_{cor}/\rho_{cor}$, in which $\rho_{cor} = [(1/\rho_r) - (0.583/\rho_{st})]^{-1} \pi/2 \approx 3.6 \text{ g/cm}^2$ and noting that $\Delta D \ll D$, we may obtain

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

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, $\Delta D = \delta_{pp} p_r$, in which the bar hole flexibility δ_{pp} is bounded by $(1 + \nu)D/E_c$ from below (thick-wall cylinder) and by $[1 + \nu + D^2/2(L^2 + LD)] D/E_c$ from above (infinite space); here ν = Poisson ratio of concrete (≈ 0.18) and E_c = effective elastic modulus of concrete = $E/(1 + \phi_{cr})$, 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 $2p_r D^3/s^2 E_c$ 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 $\delta_{pp}^0 = \frac{D}{E_c} (1 + \nu) + \frac{2D^3}{s^2 E_c}$;

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

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'_c , equilibrium requires that $2L f'_c = p_r D = D \Delta D / \delta_{pp}$. Thus, the critical value of ΔD that produces inclined cracks emanating from a single bar is

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

(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'_c , we may write the equilibrium condition $(s - D)f'_c = p_r D$, which yields

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

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., $u_c \approx u_c^s (1 - x/H)^2$ for $x \leq H$. For concrete surface ($x = 0$) this gives $\partial u_c / \partial x = 2u_c^s / H$. The mass of Cl^- ions in concrete is $M_c = \int_0^H u_c dx = u_c^s H/3$. The flux of Cl^- into concrete at $x = 0$ must equal dM/dt , i.e., $2c_c u_c^s / H = (dH/dt) u_c^s / 3$. Integration of this differential equation yields the approximation $H = \sqrt{12c_c t}$, 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 $c_{c_i} = 0$. 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 $u_f = 8.5$ 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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APPENDIX.—REFERENCES

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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