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A Study on Corrosion of Reinforcement in Concrete and Effect of Inhibitor on Service Life of RCC

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Abstract

Cement concrete has clearly emerged as the material of choice for the construction of a large number and variety of structures in the world today. Literature on reinforcement corrosion in concrete structures, its mechanism and factors affecting corrosion of steel in concrete are available. Extensive research work has been devoted to develop models that predicts the time for corrosion initiation. The study reveals that though Calcium palmitate and its combination with calcium nitrite reduces the concrete strength but inhibition to the corrosion of the rebar increases the service life of the Reinforced concrete by 8 to ten times.

1. Introduction

Cement concrete has clearly emerged as the material of choice for the construction of a large number and variety of structures in the world today. This is attributed mainly to low cost of materials and construction for concrete structures as well as low cost of maintenance. Use of high water cement ratio (w/c) in a high early strength cement led to serious problems with durability of structures, especially those subjected to severe environmental exposures **[1]**. . Corrosive species become available when the concrete is exposed to environment where engrossment of chlorides, CO_2 or H_2S is a common occurrence. The level of chloride ions required to initiate corrosion in concrete corresponds to 0.10% soluble chloride ion by weight of cement [2-3]. The chloride threshold concentration is generally within 0.9 to 1.1 kg of chlorides per cubic meter of concrete. [4] Corrosion of the Reinforcement is a serious problem not only because of the reduction of the effective area of reinforcement and the corresponding strength reduction, but also due to the volume of the rust products in the form of Ferric oxides/hydroxides whose volume is 3-6 times more than the volume of steel. These rust product cause internal stresses and consequently the cracking and spalling of the concrete surrounding the reinforcement.[5-6] Factors influencing the ability of the reinforcing steel to remain passivated are the water to cement ratio, permeability and electrical resistance of concrete. For the enhancement of service life of reinforced concrete structures exposed to corrosive environments, the use of corrosion-inhibiting admixtures, epoxy-coated reinforced steel, and cathodic protection are among the better known technological advancements.

Literature on reinforcement corrosion in concrete structures, its mechanism and factors affecting corrosion of steel in concrete are available. In this paper various aspect of the reinforcement corrosion, service life of the structure and role of inhibitors as listed have been discussed :

- Factors affecting reinforcement corrosion
- Service life prediction of corroded structure
- Role of inhibitors on service life of reinforced concrete

2. Factors affecting reinforcement corrosion

Corrosion of reinforcement in concrete structure is an electro-chemical process and is similar to the action which takes place in a flash battery [7]. The ‘anodic reaction’ which is the oxidation process and is dependent on the pH of interstitial electrolyte, presence of aggressive anions and the existence of an appropriate electrochemical potential at the reinforcing bar surface, results in dissolution or loss of metal whilst the ‘cathodic reaction’ which is a reduction process and is dependent on the availability of O_2 and the pH in the vicinity of re-bar. These anodic and cathodic reactions are broadly referred to as ‘half cell reactions’ and the corresponding electrode potential can be derived by Nernst equation. The electromotive force (e) of reinforcement corrosion cell which is the difference of E_C and E_A drives the corrosion current through the electrolyte from anode and cathode and is expressed by Eq.(1) [8]:

$$e = 1.669+0.0418 \log[O_2]-0.0591pH-0.0296\log[Fe^{2+}] \quad (1)$$

It is evident from Eq. (1) that corrosion rate is dependent on

(i) The pH surrounding the rebar
(ii) The availability of oxygen and capillary water and
(iii) Concentration of Fe^{2+} near the rebar.

- *Effect of carbonation and entry of gaseous pollutants*

The pH of the concrete is reduced by the carbonation and entry of acidic gaseous pollutants such as SO_2 and NO_2. The fall in pH to certain levels may cause commencement of reinforcement of corrosion, loss of passivity of concrete against rebar corrosion and catastrophic corrosion [9] as indicated in table 1

Table 1 State of reinforcement corrosion at various pH[9]

pH of concrete	State of reinforcement corrosion
Below 9.5	Commencement of steel corrosion
At 8.0	Passive film on the steel surface disappears
Below 7	Catastrophic corrosion occurs

- *Effect of aggressive anions*

Chloride in concrete may be present as Acid soluble chloride, chemically bound chloride with hydration products of cement and free or water soluble chloride within the pore solution of concrete. Generally, the concentration of free chloride ions (Cl^-) influences the corrosion process [10]. It is reported that the corrosion rate increases with an increase in chloride content. However, the change in pH is insignificant due to change in chloride content of concrete [11].The risk of reinforcement corrosion associated with the level of chloride content in both uncarbonated and carbonated concrete is presented in table 2 [12].

Table 2 Corrosion risk in concrete containing chlorides[12]

Total chloride (wt% of cement)	Condition of concrete adjacent to reinforcement	Corrosion risk
Less than 0.4%	Carbonated	High
	Uncarbonated, made with cement containing less than 8% C_3A	Moderate
	Uncarbonated, made with cement containing 8% or more C_3A	Low
0.4% - 1.0%	Carbonated	High
	Uncarbonated, made with cement containing less than 8% C_3A	High
	Uncarbonated, made with cement containing 8% or more C_3A	Moderate
More than 1.0%	All cases	High

- *Effect of Bacterial action*

Aerobic bacteria may aid in the formation of differential aeration cell which will lead to corrosion. In sewer concrete, the anaerobic bacteria produces iron sulfides which too enables the corrosion reaction to proceed even in absence of oxygen[9]. The bacteria decrease the amount of cover by disintegration of cementitious material [13].

- *Effect of w/c ratio*

Basically w/c ratio control strength, durability and permeability of concrete and does not control the rate of corrosion but 'permeability' which is a function of w/c ration affects the corrosion of rebar. The depth of penetration of particular chloride threshold value increases with an increase in the w/c ratio [14]. Carbonation depth has been found to be linearly increasing with an increase in w/c ratio [15]. The oxygen diffusion coefficient is also found to be increasing with an increase in the w/c ratio [16]. In a study it is observed that the permeability of hardened cement paste is increased 100 fold by increasing the w/c ration from 0.35 to 0.45 [17] and the time of initiation of reinforcement corrosion in a sample with a w/c ration 0.4 is 2.15 to 1.77 times more as compared to a sample with a w/c ratio of 0.55, under accelerated corrosion testing [18].

- *Effect of cover over reinforcing steel*

Risk of reinforcement corrosion with low cover thickness, has been reported by various researchers. The cover thickness has a remarkable effect on rebar corrosion due to penetration of chloride or carbonation [19]. This effect of corrosion is limited within the time of casting to the time at which the rebar is depassivated and corrosion is started. The rate of corrosion, once it has started, is independent of the cover thickness [20].

3. Service life prediction of structure

The state of corrosion of steel in concrete is a function of time. Corrosion process of Reinforcement in concrete starts with depassivation i.e loss of oxide layer over the rebar and then propagate to reach at a critical stage at which corrosion would produce spalling of concrete cover or cracking through the whole concrete as depicted in fig. 1[8]. Hence the service life of concrete may be expressed as:

$$t_{cr} = t_p + t_{cor} \qquad (2)$$

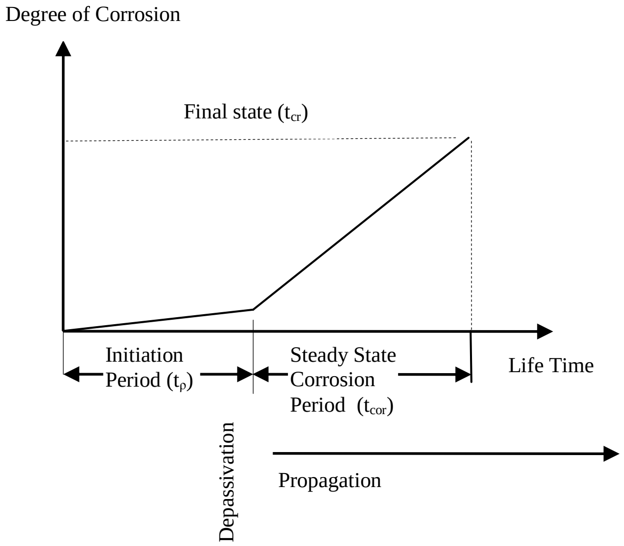

Fig. 1 The stages of rebar corrosion

A careful visual survey for any sign of cracking, spalling and rust staining provides valuable information as to whether the corrosion of reinforced steel is really a cause of concern or there is some other cause of distress. Usually (i) half-cell potential(E_{corr}), (ii) concrete resistivity (ρ) and (iii) corrosion current density (I_{corr}) are the three measure parameters which are correlated with the degree of reinforcement corrosion. Half-cell potential (E_{corr}) and concrete resistivity(ρ) is a qualitative index while the corrosion current density(I_{corr}) is a quantitative index. A brief review of available monitoring techniques and service life prediction model is given by Ahmad [8]. Among all the methods of I_{corr} the 'linear polarization method' [20,21,22] is fastest, simplest, non-destructive, relatively inexpensive and most widely used. However, the main difficulties observed were; (i) the high resistance of concrete between the working electrode (rebar) and the reference electrode offers a potential drop [23] (ii) the distribution of the electrical signal applied for polarization of rebar is non-uniform throughout the cross-section of beam [24] and (iii) accuracy of Tafel constant.

In the light of above difficulties, Ahmad and Bhattacharya [25] suggested an arrangement and calculation procedure, for in situ measurement of E_{corr}, ρ and I_{corr} of rebar embedded in the concrete. Using the observation taken from this arrangement, the ohmic resistance and resistivity of concrete, the polarization resistance of rebar, Tafel slopes and corrosion rate can be determined

The time required for corrosion initiation corresponds to the time required for CO_2 or Cl^- ions to diffuse to the steel-to-concrete interface and activate corrosion. Extensive research work has been devoted to develop models that predicts the time for corrosion initiation. Different models, validated in the field studies, for the rate of carbonation propagation and chloride ingress which predict the time for corrosion initiation can be found in literature [26-31]. Bazant [29] suggested a mathematical model to calculate the time between corrosion initiation and corrosion cracking of RC bridge decks. Bazant's model assumes that all corrosion products create pressure on surrounding concrete and related the duration of steady-state corrosion period (t_{cor}) as follows:

$$t_{cor} = \rho_{cor}\,(D\Delta D/pJ_r) \qquad (3)$$

where: ρ_{cor} is combined density factor for steel and rust, D is diameter of rebar, ΔD is increase in diameter of rebar due to rust formation, p is the perimeter of rebar, J_r is instantaneous corrosion rate given as

$$J_r = (W/F)I_{corr} \qquad (4)$$

Where:

J_r = instantaneous corrosion rate ($gm/cm^2/s$)
W = equivalent weight of steel = 55.85/2 = 27.925 gm
F = Faraday's constant = 96487 C
P_r = penetration rate (cm/s)

Liu and Weyers [30] extended the work of Bazant [29] taking same parameters as used in Bazant's model along with time required for corrosion products to fill a porous zone around the re bar before creating an internal pressure on surrounding concrete. In Liu-Weyer's mdel, the rate of steel mass loss was assumed to be directly proportional to the square root of the product of the corrosion current and the time of corrosion exposure. This assumption significantly underestimates the amount of steel weight loss compared with that obtained by Faraday's law [32] , consequently overestimating the time to corrosion cracking.

Morinaga [31] proposed the following empirical equation based on the field and laboratory data to predict the time from corrosion initiation to corrosion cracking (t_{cr}):

$$t_{cr} = [0.602D\{1+2(C/D)\}^{0.85}]/i_{cor} \qquad (5)$$

where: t_{cr} is time from corrosion initiation to corrosion cracking(days), D is the rebar diameter (mm), C is the clear concrete cover(mm), and i_{cor} is the corrosion rate (10^{-4} g/cm^2)day). Empirical equation proposed by Morinaga [31] does not consider the mechanical properties of concrete which may significantly affect the time of corrosion.

Considering the primary deficiencies of the previous models, Maaddawy and Soudki [33] presented a mathematical model in which a relationship between the steel mass loss and the internal radial pressure caused by corrosion was developed accounting the mechanical properties of concrete. According to it, the time from corrosion initiation to corrosion cracking, t_{cr} is given as

$$t_{cr} = [7117.5(D+2\delta_0)(1+\upsilon+\psi)/iE_{ef}][(2Cf_{ct}/D)+ 2\delta_0 E_{ef}/\{(1+\upsilon+\psi)(D+2\delta_0)\}] \qquad (6)$$

where: $\psi = D'^2/2C(C+D')$, $D' = D+2\delta_0$, and E_{cf} (effective elastic modulus of concrete) = $[E_c/(1+\phi_{cr})]$ in which E_c is elastic modulus of concrete and ϕ_{cr} is concrete creep coefficient, D is the diameter of rebar(mm), δ_0 is thickness of porous zone typically in a range of 10–20μm, υ is Poisson's ratio of concrete (0.18), C is clear concrete cover (mm) and i is current density. Eqs. (7) and (8) may be used to calculate tensile strength and Young's Modulus of concrete where f_c' is characteristic strength of concrete

$$f_{ct} = 0.94\sqrt{f_c'}\ \text{MPa} \qquad (7)$$

$$E_c = 4500\sqrt{f_c'}\ \text{MPa} \qquad (8)$$

Role of inhibitor on service life of reinforced concrete

Literature survey reveals that various researchers have studied the inhibiting behavior of many organic and inorganic substances on concrete properties and its inhibition effect on embedded steel. Berke and Weil [43] presented a comprehensive review of corrosion-inhibiting admixtures in concrete. Gaidis and Rosenberg [35] showed that the addition of 2 percent calcium nitrite by mass raised the threshold chloride concentration to levels that were high enough to inhibit the corrosion of steel.[35] Considering the toxicity and adverse effect on concrete properties shown by the most of the commercially available inhibitors, environmentally benign green inhibitors are being developed. Quraishi et. Al[36] reports the inhibiting effect of calcium palmitate and its combination with calcium nitrite.

Due to insufficient experience, there are no hard data on the cost-benefit analysis of technologies that have been recently developed for the enhancement of service life of reinforced concrete structures exposed to aggressive environmental conditions. Gerwick [37] reports that the use of a corrosion-inhibiting admixture or epoxycoated reinforcement increases the cost by 8 percent. Role of the inhibitor on the service life of concrete has been studied by using Eq (5) and (6) and the experimental data reported for calcium palmitate (CP), its combination with calcium nitrite(CN)[36] and microsilica [38] given in table 3.

Table 3 Parameters of the experimental data [36, 38] used for prediction of total corrosion period

Sample	Name and % (by weight) the inhibitor used	28 days Compressive Strength of concrete $f_c^{/}$(N/mm^2)	Weight loss of 8 mm dia 50 mm length rebar in 60 days (gm)	%age weight loss of rebar (m_l)
C	Control	41.47	0.136	0.689
P_2	2% CP	27.57	0.018	0.090
P_3	3% CP	24.62	0.014	0.070
P_1N_1	1% CP+1%CN	32.86	0.021	0.107
P_2N_1	2% CP+1%CN	28.28	0.017	0.088
P_1N_2	1% CP+2%CN	33.21	0.018	0.089
$P_{1.5}N_{1.5}$	1.5% CP+1.5%CN	30.44	0.018	0.089
$P_3N_{1.5}$	3% CP+1.5%CN	25.73	0.013	0.068
$P_{1.5}N_3$	1.5% CP+3%CN	31.11	0.014	0.070
$M_{7.5}$	7.5% Microsilika	40.89	0.037	0.188
M_{10}	10% Microsilika	40.15	0.033	0.169

Using the data given in table 3, the total corrosion period is calculated by the empirical equation proposed by Morinaga [31] and mathematical model suggested by Maaddawy and Soudki [33] taking thickness of porous zone δ_o = 10μm and result is given in table 4

Table 4 Predicted service life

Sample	Corrosion rate i_{cor} (10^{-4} g/cm^2/d)	Current Density i^a (μA/cm^2)	Effective elastic modulus of concrete E_{ef}	Predicted Service Period (yrs) by	
				Morinaga Empirical formula	Maaddawy mathematical model
C	1.675	7.195	8650	26	54
P_2	0.217	0.938	7053	199	417
P_3	0.17	0.735	6665	254	533
P_1N_1	0.258	1.116	7700	167	351
P_2N_1	0.213	0.919	7143	203	426
P_1N_2	0.215	0.929	7741	201	422
$P_{1.5}N_{1.5}$	0.215	0.930	7411	201	421
$P_3N_{1.5}$	0.164	0.709	6814	264	552
$P_{1.5}N_3$	0.168	0.728	7492	257	538
$M_{7.5}$	0.453	1.960	8590	95	200
M_{10}	0.41	1.769	8512	106	221

i^a calculated by eq. $i = 78.3\text{x}\ m_l \text{ x D/T}$, where: D= diameter of rebar in mm and m_l is percentage steel mass loss in time T(days)

Conclusion

From Tables 1 and 2 it is clear that though the use of 3% Calcium Palmitate reduces the compressive strength of the concrete by 41% but enhance the inhibition capacity of reinforced concrete considerably increasing the service life of RC structure almost ten times. Same service life of a RC structure may be expected by using of 1.5% Calcium Palmitate in combination with 3% Calcium Nitrite in such case reduction in compressive strength of the concrete is only 25%. The service prediction tested herewith is based on the experimental data of a shorter duration and no load condition. Therefore, the results are indicative.

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