Pergamon

Cement and Concrete Research, Vol. 26, No. 10, pp. 1593-1599, 1996
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0008-8846/96 $15.00 + .00

PII S0008-8846(96)00139-1

THE PREDICTION OF CORROSION RATES OF REINFORCING STEELS IN CONCRETE

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(Refereed)
(Received August 1, 1995; in final form July 23, 1996)

ABSTRACT

The effect of chloride and acetate ions on corrosion of steel in concrete was studied. The reinforcement corrosion was evaluated by measuring the corrosion potentials and corrosion current density using linear polarization resistance technique. The initial corrosion rates (i_o) of reinforcing steel in concrete containing either chloride or acetate ion were found to be higher as compared to concrete without admixture. The corrosion rate is very high at early days and decreases by time.The corrosion rate vs time curves for reinforcements in all three types of concrete blocks follow the same pattern. The following exponential quantitative relation between the corrosion rate (i_{cor}) and time (Θ) was proposed: $i_{cor} = i_0 \exp(-C\Theta)$ where C was termed as concrete corrosion constant having a value of 1.1×10^{-3} day^{-1} for the types of concrete samples under consideration.

Introduction

Concrete is a porous solid containing an alkaline pore solution that promote passivation of reinforcing stell (1, 2) provided its protective capacity is not overwhelmed by contamination by aggressive anions such as Cl^- ions. In offshore and coastal structures, chlorides are supplied to the concrete by direct sea water immersion or by seawater splashing. Sodium chloride, used as a deicing agent on bridge decks, is also a source of chloride. When sea-dregged sand or admixtures which contain chlorides are used chloride ions exist in concrete from the start. Thus the chloride ions enter concrete from a variety of sources. The deterioration of reinforced concrete structures caused by chloride - induced corrosion of the steel reinforcement has become a matter of significant importance all over the world (3-6).

Many of the commonly available electrochemical techniques have been used to determine the corrosion rate (7-9). Corrosion of steel-in-concrete systems was extensively studied by using pore solutions (of pH = 12, 6 or more) (3, 10). However such experiments give very limited information about the corrosion rate as the diffusion of ions is far slower in concrete than in pore solutions. Also, there is no convective transport in concrete, as is possible in pore solutions.

Decrease in pore saturation degree has two opposing effects on the corrosion of reinforcing steel (1). Decrease in the corrosion rate as a result of increase of concrete resistivity, (2) an increase in corrosion rate as a result of increased rate of diffusion of gaseous oxygen in partly dry concrete. Both are markedly influential on the corrosion kinetics at the steel/concrete interface. Which one of these two opposing effects will tend to prevail over the other depends on the pysical structure of concrete, age and the cement cover thickness of concrete.

There are quantitative relations between the corrosion rate of reinforcement and the degree of pore saturation.There is a critical pore saturation value that results in a concrete resistivity of $10^5\ \Omega$ cm, below which i_{cor} values are too small. Below the critical pore saturation value, the resistivity of concrete prevents the corrosion of reinforcements as effectively as passivating layers of steel in mortars without chloride (11, 12).

Efforts and researches to find an alternative to sodium chloride as deicer has gained great attention in recent years and calcium-magnesium acetate seems to have an important potential to be used for this purpose. This study is therefore planned to study the effect of acetate and chloride ion on the corrosion of reinforcing steel when mixed with fresh concrete and to find a quantitative relation between i_{cor} and time.

Experimental Program

Materials. The chemical composition of the cement used in the preparation of concrete samples and the concrete mix ratio are given in Table 1 and in Table 2 respectively.

A number of Concrete blocks were made. Some of these (group A) were prepared with no salt added to the mix. Group B concrete blocks were made with the cement in which NaCl was used as admixture in an amount corresponding to 6 kg $Cl^-/1\ m^3$ concrete. In the preparation of the other concrete blocks calcium acetate was used instead of sodium chloride in chemicaly equivalent amount. Cylindrical molds of 15cm diameter and 15cm height were used for concrete samples. The concrete blocks contained three identical embedded steel bars, one was used as a counter electrode, the other one as the working electrode and the last one as counter electrode. The upper end of the mild steel electrode was coated with polyethylene bandage leaving an exposed surface area of $10cm^2$.

TABLE 1

Chemical Composition of Cement

Constituent	Weight(%)
Pouzzolane	10
Sulfur Trioxide	2.5
Total Alkalies	2.2
Free Calcium Oxide	0.5
Magnesium Oxide	2.5
Ignition Loss	2.2
C_3S	46
C_2S	12
C_3A	8
C_4AF	14

TABLE 2

Concrete Mix Ratio (kg)

Portland Cement (10 % pouzzolane)	Sand (Natural)	Gravel	Water (w/c = 0.60)	Admixtures (*)		
				A	B	C
5	10	15	3	-	0.15	0.20

* (A): none, (B) : NaCl , (C) : Ca $(CH_3COO)_2$

Experiment were performed with the concrete blocks prepared under the same conditions.Concrete blocks were removed from the molds after 24 hours and are allowed to stand in laboratory atmosphere of 40% relative humidity till the time at which the polarization measurement has been carried out. The corrosion rate of the reinforcing steel in concrete was determined by the use of polarization resistance measurements after 1, 7, 28, 60 and 90 days.For each age a new block was used for the determination of the corrosion rate at this age. All electrochemical determinations were carried out in duplicate.

Polarization Measurements. Anodic and cathodic polarization curves were obtained at different times for the steel in these concrete blocks by the use of galvanostatic method. A diagram of the experimental set-up is shown in Figure 1. External anodic and cathodic currents were applied to the electrodes from 0.1 mA/cm^2 up to 100 mA/cm^2 so as to cover the linear region of the Tafel plots and the overvoltages were recorded corresponding to the applied currents. From cathodic and anodic Tafel plots, β_a and β_c values were determined. For the calculation of the corrosion rates of steel bars in concrete, Stern-Geary equation was used:

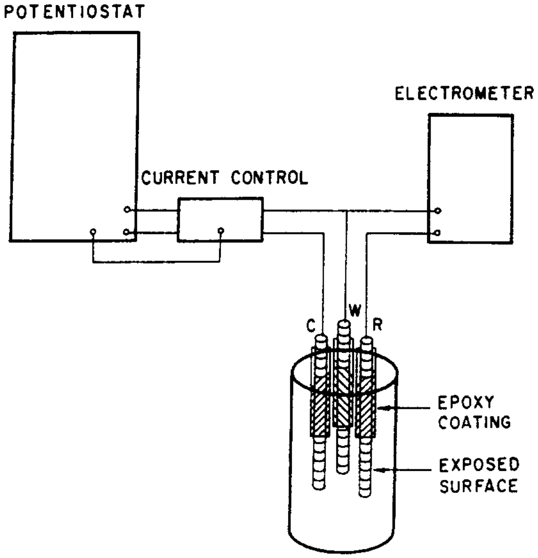

FIG. 1.
Diagram of galvanostatic polarization apparatus.

$$i_{cor} = \frac{1}{R_p} \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)}$$

where R_p denotes the polarization resistance which was evaluated using the slope of the linear part of the measured polarization curve.

Results and Discussion

For the calculation of the corrosion rates, three factors should be determined according to Stern-Geary equation. These are the slope of the polarization resistance curves, β_a and β_c. Figure 2 shows the results of polarization resistance tests which were conducted for a ±10 mV shift from the corrosion potentials in concrete samples containing chloride ion. All the slopes have been determined graphically and are listed in Table 3 together with the calculated corrosion rates. The initial corrosion rates obtained in these experiments were somewhat high in comparison with the reported values in literature (6,14). These high values are probably due to the preparation conditions of concrete samples. To make a better compari-

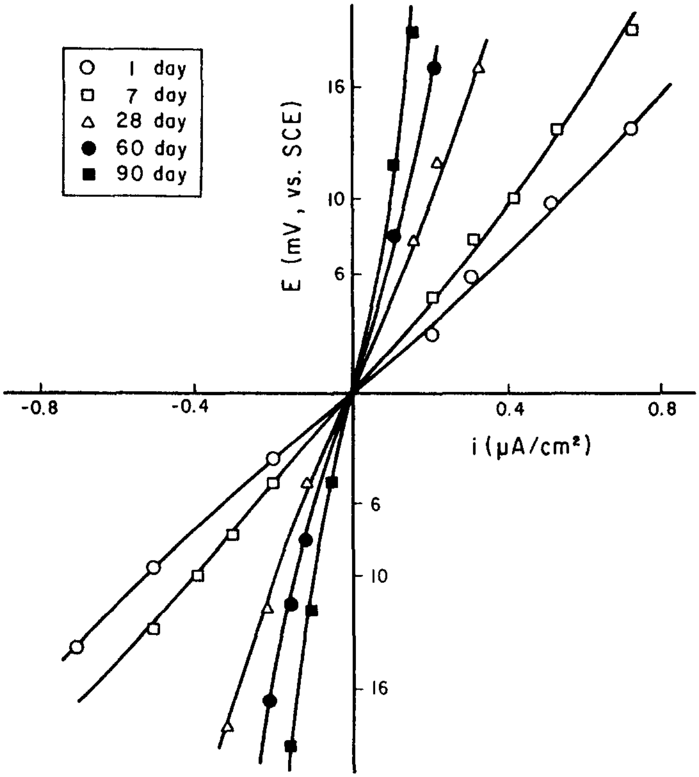

FIG. 2.

Linear polarization curves measured after different LIfe times in concrete samples containing Cl^- ion.

TABLE 3

Tafel Parameters and Corrosion Rates of Reinforcing Steel at Different Life Times

Concrete	Life Time Days	Tafel Constants		Corrosion Rates, μ A/cm^2
		β_a,mV	β_c,mV	
Without admixture	1	524	160	0.53
	7	481	203	0.45
	28	421	219	0.25
	60	370	220	0.11
	90	306	289	0.07
6 kg NaCl/m^3	1	338	309	4.60
	7	365	339	3.80
	28	406	393	2.20
	60	423	391	1.20
	90	480	394	0.64
10 kg Ca(CH$_3$COO)$_2$/m^3	1	195	375	1.40
	7	222	257	1.19
	28	304	236	0.60
	60	321	261	0.25
	90	397	142	0.09

son between the admixtures, the concrete blocks were prepared with high W/C ratio and low vibration on purpose to increase the corrosion rates of reinforcing steel.

Figure 3 represents the change of corrosion rates with respect to time for three different concrete samples. The corrosion rates decrease exponentially with time most probably due to the lack of electrolyte. From the similarity between the curves for the steel in concrete with and without admixture, the following relation can be suggested for corrosion rate of reinforcing steel: $i_{cor} = i_o \exp(- C \Theta)$ where i_{cor} is the corrosion rate at time Θ, i_o is the initial corrosion rate; Θ, is the life time, C denotes a constant which can be termed as concrete corrosion constant. The value of C evaluated from the corrosion rate curves in Figure 3, was found to be approximately the same for all three concrete samples. The average of those three C values is equal to to 1.1×10^{-3} day^{-1}. The value of C depends on the structure and the properties of concrete, namely concrete pore saturation degree, pH, permeability and the cover thickness of concrete.

The corrosion rates of reinforcing steel in concrete depend on various factors. The most important ones, are moisture content of concrete, access to oxygen (permeability of concrete), and especially the presence of chloride ions in concrete. The presence of chloride ions in concrete provides mainly two effects: (1) It increases the conductivity of electrolyte, (2) the protective oxide layer may be broken because of the formation of a soluble complex of iron chloride with the chloride ions (15-17). These two effects facilitate the dissolution of metal ions. As it can be seen from Figure 3, the corrosion rates for concrete samples with chloride anion are higher in comparison to the corrosion rate values in the other concrete samples.

For the time period of experiments the corrosion rates of reinforcement in both Cl- containing concrete and acetate containing concrete are higher at all the time than that in the concrete with no admixture. This indicates that both Cl^- and acetate anions also promote the corrosion but the effect of acetate is less than that of Cl^- anion. More detailed studies are required to elucidate the reinforcement corrosion mechanism involving cements of varying amount of acetate and differing exposure conditions.

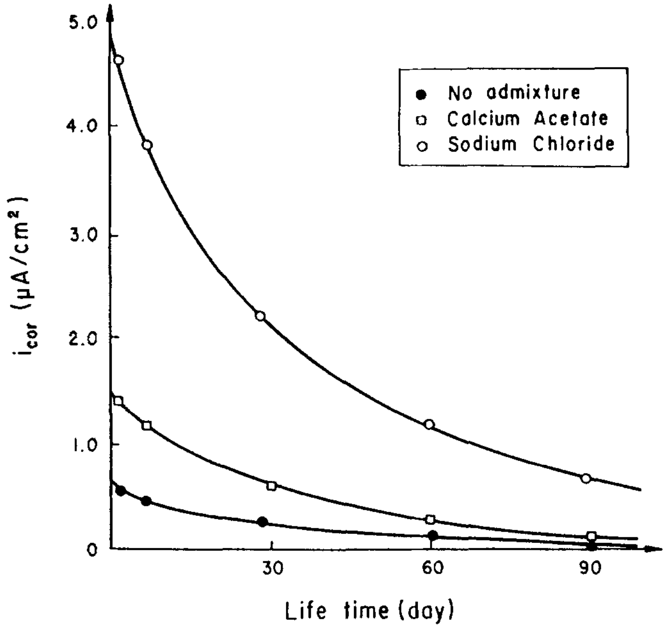

FIG. 3.

Changes in corrosion currents with time in concrete with and without admixtures.

Conclusions

The corrosion rate of the reinforcing steel is high at the early days. But it decreases exponentially as time progresses due to drying of concrete according to the following expression: $i_{cor} = i_o \exp(-C\Theta)$. Concrete corrosion constant (C) value was found to be equal to 1.1×10^{-7} day^{-1} for all of the concrete samples of specific concrete mixture and curing conditions. By the use of C and proposed equation corrosion rate can be predicted.

Acetate anion is not as aggresive as chloride ion. So, from the point of view of corrosion calcium acetate seems to be more reliable deicer than sodium chloride.

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