JOURNAL OF MATERIALS SCIENCE **35** (2000) 105–108

Overview on electrochemical parameters to assess the corrosion state of steel reinforcement in CAC mortar and concrete

M. A. SANJUÁN
Instituto Español del Cemento y sus Aplicaciones (IECA), C/ José Abascal, 53, 28003 Madrid, Spain

Calcium Aluminate Cement (CAC) can be used successfully in mortars and concretes for special applications such as refractory and sulphate-resistant materials. However, some failures have been reported when used in reinforced concretes exposed to wet environments in presence of chloride ions. Chloroaluminates formation in either reinforced CAC mortar or concrete could be a way to reduce chloride ions in the pore solution of this material, thereby, decreasing the risk of corrosion. This paper presents the characteristic values of corrosion rate, corrosion potential and resistivity and the relationship between them. Assuming a significant corrosion state at corrosion rate values over 0.1 μA/cm^2, we can establish a threshold level for corrosion initiation in reinforced mortar or concrete of -250 mV and 10^4 Ω·cm. Therefore, lesser values constitue important corrosion rates.

1. Introduction

Corrosion of steel reinforcement in CAC reinforced concretes have arisen in several countries in the past 30 years [1, 2]. The corrosion initiation increases together with the porosity [3] which is a result of a chemical process in which hexagonal phases present in the cement, CAH_{10} and C_2AH_8, turn into cubic phases, C_3AH_6. One of the main factors affecting the development of such a corrosion process is the action of chloride ions which either can be present in the raw material (mixing water, aggregates or additives) or can enter from the environment (sea water, when de-icing salts are used and so on).

Aluminous hydrates reacted highly with chloride ions leading to chloroaluminates formation. Nevertheless, the amount of remaining chloride ions in the pore solution was enough to initiate significant reinforcement corrosion over time [4]. Bound chlorides may be released by changes in the pore solution such as pH lowering or free-chloride reduction, and then, they contribute after time to increase the corrosion risk. Corrosion rate was found to be directly influenced by the degree of conversion from hexagonal to cubic phases which were achieved by increasing the curing temperature.

Electrochemical methods to determine the corrosion state of reinforcement are non-destructive and demonstrate to be quicker compared to gravimetric measurements, among them, corrosion rate measurement is shown as the most effective [5]. Following this method, values over 0.1 μA/cm^2 were presented as indicative of an important corrosion state. On the contrary, corrosion potential values were not so confident to asses the corrosion state of steel reinforcement as it depended strongly on the humidity of the concrete, amongst other factors. That is to say, this measurement could not reflect accurately the corrosion state of steel. Only when the environmental conditions are well known can this method be useful. For instance, in wet and chloride-contaminated surroundings the corrosion potential values can be established in relation to a certain corrosion activity. On the other hand, resistivity measurements seem to be more reliable to determine the corrosion state of the reinforcement. In both cases, the threshold values to establish either low or high corrosion rates must be known. This point is the scope of the present work which is focused in CAC materials exposed to an humid chloride-contaminated environment.

In this paper, CAC mortars performance was studied when exposed to sodium chloride solutions. The typical corrosion levels, which may be achieved by the steel reinforcement embedded in CAC mortars, are shown; it is possible these would be quite similar to those in concrete. The conversion process of these materials was promoted by the use of several curing temperatures which when increased accelerated the conversion reaction [6]. The relationship between corrosion rate, corrosion potential and resistivity of CAC mortars and concretes in chloride-containing environments is discussed later.

2. Experimental methods

2.1. Samples elaboration

Reinforced mortar specimens (0.35 and 0.50 water-cement and 1/3 cement-sand ratios) were made either

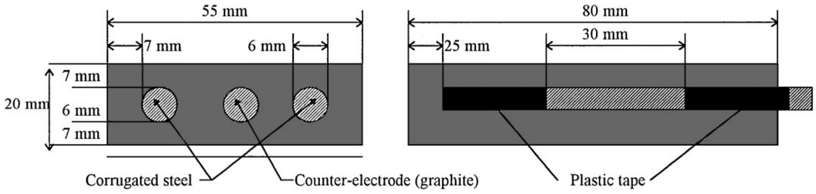

Figure 1 Specimen dimensions.

TABLE I Standard conductivities of KCl solutions

KCl Concentration	Conductivity at 20 °C (mS)	Conductivity at 25 °C (mS)
0.01 N	1.278	1.413
0.02 N	—	2.819
0.1 N	11.67	12.88
1 N	102.07	111.8

premixed with 4% NaCl, cured and kept in plastic bags or without NaCl, cured and immersed in either a 0.5 or a 1.5 M NaCl solution for eight months [4]. Curing was performed at 20, 40 and 60 °C for two weeks.

2.2. Electrochemical measurements

Steel rebars embedded in CAC mortars (Fig. 1) were electrochemically monitored throughout the experiment. In particular, corrosion potential, corrosion intensity and resistivity values were recorded. A saturated calomel electrode was used as reference to measure corrosion potentials (E_{corr}). Corrosion rate (I_{corr}) data were obtained from Polarisation Resistance measurements, R_{p} [5]. An Amel Model 2053 potentiostat with electronic compensation of the ohmic drop (R_{ohm}) between reference and working electrodes was used. A polarisation sweep from −10 to 10 mV, with the corrosion potential value as centerpoint, was applied to the steel electrode at a rate of 10 mV/min to measure the ohmic drop value. The corrosion rate value was calculated by Equation 1 assuming values of B equal to 26 mV for the corroding steel and 52 mV for the passive one.

$$I_{\mathrm{corr}} = \frac{\Delta I}{\Delta E} xB = \frac{B}{R_P} \qquad (1)$$

Resistivity values were calculated according to Equation 2 where the distance-area ratio (l/A), called geometric factor, was calculated using several standard dissolutions of known conductivities (Table I). Assuming parallel lines of current between two plates of an area equal to A which are separated by a length equal to l, the calculated geometric factor was 0.25.

$$R_{\Omega} = \rho \cdot \left(\frac{l}{A}\right) \qquad (2)$$

3. Results

3.1. Corrosion potential vs. corrosion rate relationship

Corrosion rate data is the most accurate electrochemical parameter related to the corrosion state of the steel reinforcement in concrete. It was established that corrosion rates over a band ranged between 0.1 and 0.2 μA/cm^2 should be considered of significance [5]. With this starting point in mind, active corrosion potentials for CAC mortars or concretes would be those below −250 mV as shown in Fig. 2.

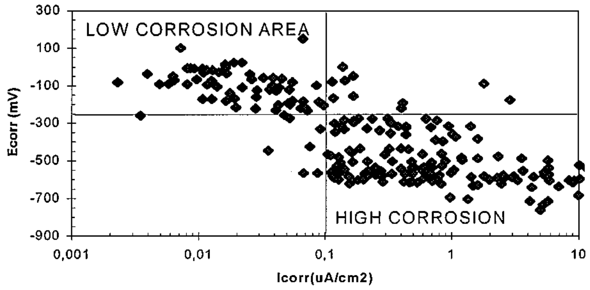

Figure 2 Corrosion potential vs. corrosion rate for all the tested specimens.

3.2. Corrosion potential vs. resistivity relationship

Resistivity values are dependent on the microstructure of the mortar and ionic concentration in the pore solution. A high resistivity of about 32,000 Ω·cm (0.5 M) or 3,200 Ω·cm (1.5 M) means a more dense material and a lesser ionic conductivity (20 °C curing) while a low resistivity of 2,000 Ω·cm (0.5 M) or 400 Ω·cm (1.5 M) means a lesser dense material and a higher ionic conductivity (40 & 60 °C curing). All these data are shown in Fig. 3 in comparison with the corrosion potential data. As can be seen, there is an undefined area between 10,000 and 100,000 Ω·cm in which assessing a significant corrosion level of the steel is difficult.

3.3. Resistivity vs. corrosion rate relationship

Fig. 4 shows the relationship between corrosion rate and resistivity. An undefined area can be observed again between 10,000 and 100,000 Ω·cm corresponding to the 0.1 μA/cm^2 (over this limit significant corrosion is stated) and 0.01 μA/cm^2 (low corrosion level of the steel) respectively.

4. Discussion

The failure reported in CAC concrete structures has been attributed in most cases to a loss of strength due to steel reinforcement corrosion. The increase of porosity with time in CAC mortar and concrete leads to an easier external aggressive agents penetration. This process is

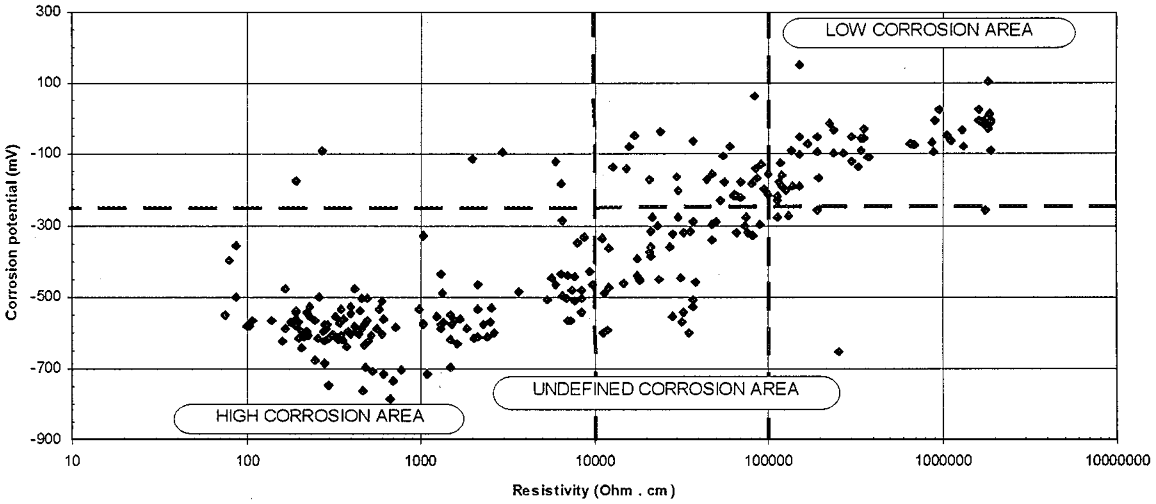

Figure 3 Corrosion potential vs. resistivity for all the tested specimens.

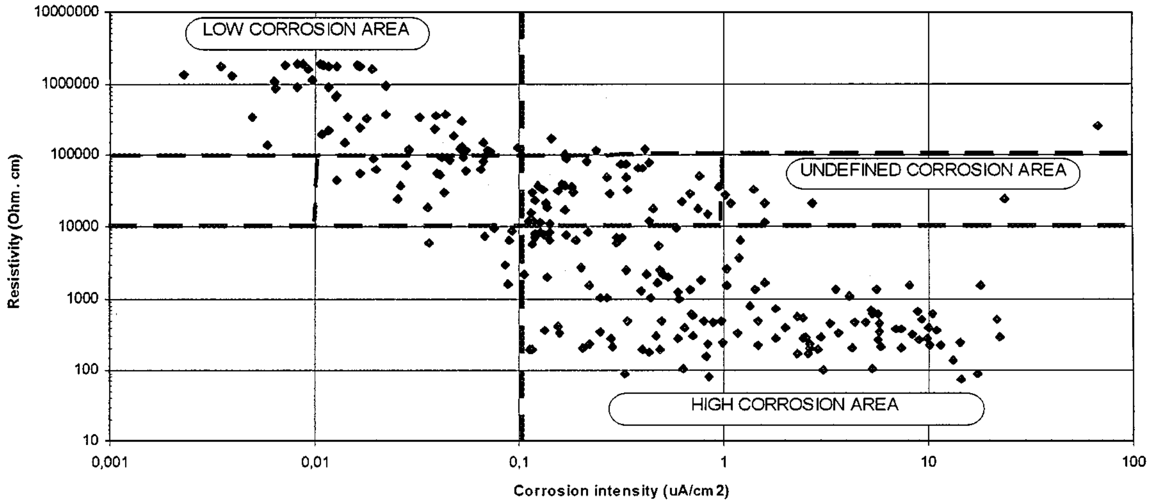

Figure 4 Resistivity rate vs. corrosion for all the tested specimens.

of particular importance in chloride-contaminated environments [7]. Therefore, the knowledge of the peculiar threshold levels of corrosion potential and resistivity values in these materials, and for the studied environment to identify reinforcement corrosion initiation, is of great importance.

A clear line can be defined between insignificant and high corrosion with regard to the corrosion potential. This is to say, negative values of more than −250 mV represent significant corrosion rates of the reinforcement embedded either in concretes or mortars made of CAC.

On the contrary, there is not an unique value of resistivity to establish such a limit. In the considered environment, it can only be said that values above 100.000 Ω·cm correspond to an insignificant corrosion level, whereas below 10.000 Ω·cm means a high corrosion state. Values between 10^4 and 10^5 Ω·cm are not clearly related to the reinforcement corrosion. In this case, it is recommendable to follow the evolution of the resistivity over time, but checking the structure using another electrochemical parameter during the inspection would be better. In contrast, resistivity measurements only becomes important if the chloride threshold level for corrosion is exceeded. The employment of several electrochemical parameters to get a complementary analysis is of interest from the point of view of assessing the actual corrosion state of the reinforcement and, therefore, this information would be very helpful in durability and service life calculations.

TABLE II Corrosion level

	Low corrosion	Undetermined corrosion	High corrosion
Corrosion potential, mV ⟨SCE⟩	>-250	—	<-250
Resistivity, Ω·cm	$>10^5$	10^4–10^5	$<10^4$
Corrosion rate, μA/cm^2	<0.1	—	>0.1

Finally, Table II gives approximate values to set the corrosion state of the tested steel rebars embedded in CAC mortars.

5. Conclusion

Threshold values of electrochemical parameters between insignificant corrosion and a high corrosion level have been stated. Considering a corrosion rate value of $0.1\ \mu A/cm^2$ as a limit for significant corrosion, the values of corrosion potential and resistivity, which show high corrosion for CAC reinforced mortars exposed to chloride environments, are -250 mV and 10,000 Ω·cm respectively. However, values of resistivity between 10^4 and 10^5 Ω·cm could also mean an active corrosion state.

Corrosion rate of the steel depends significantly on the conversion degree of the CAC mortar and it increases from mortars cured at 20 °C (hexagonal phases) to those cured at 60 °C (cubic phases) as result of a more compact microstructure.

Acknowledgements

The author thanks the Directorate-General for Science, Research and Development of the European Commission for the receipt of a Fellowship under the Human Capital and Mobility program. The author is also grateful to K. L. Scrivener and colleagues of the Imperial College of Science, Technology and Medicine of London (U.K.).

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Received 5 August 1998
and accepted 5 May 1999