Hindawi
Advances in Civil Engineering
Volume 2018, Article ID 1096282, 9 pages
https://doi.org/10.1155/2018/1096282

Research Article

Modeling of Corrosion Rate and Resistivity of Steel Reinforcement of Calcium Aluminate Cement Mortar

Cristina Argiz,[1] Miguel Ángel Sanjuán,[2] Pedro Castro Borges,[3] and Emiliano Álvarez[4]

[1] *Civil Engineering School, Polytechnic University of Madrid, C/ Profesor Aranguren, s/n, Ciudad Universitaria, 28040 Madrid, Spain*
[2] *Spanish Institute of Cement and Its Applications (IECA), C/ José Abascal 53, 28003 Madrid, Spain*
[3] *Centro de Investigación y de Estudios Avanzados del IPN, Unidad Mérida, km 6 Antigua Carretera a Progreso, 97310 Mérida, YUC, Mexico*
[4] *I.E.S. "Enrique Tierno Galván", C/ Camino de los Frailes, s/n, Leganés, 28911 Madrid, Spain*

Correspondence should be addressed to Miguel Ángel Sanjuán; masanjuan@ieca.es

Received 3 August 2017; Accepted 26 December 2017; Published 5 March 2018

Academic Editor: Constantin Chalioris

Calcium aluminate cement (CAC) is a binder whose hydrated compounds change over time from cubic phases to hexagonal phases, producing an increase of porosity in reinforced concretes. Thereby, chloride ions, among other steel corrosion promoters, can enter the concrete more easily leading to an increase of the reinforcement corrosion process. When such a transformation of phases is completed, a characteristic value regarding both corrosion intensity (I_{corr}) and resistivity (related to the ohmic drop of the cementitious material) is reached, which depends mainly on the mix proportions of the material and the curing procedure. This paper presents the characteristic corrosion intensity values of steel embedded in mortars made of CAC after five years of exposure to either a 0.5 mol/l or 1.5 mol/l NaCl solution in order to be applied to estimate the service life of reinforced concrete made of calcium aluminate cement (CAC) which is used in real construction structures. Ohmic drop measurements are also presented to support the values obtained. The aim of this paper is to model the corrosion rate and resistivity of the steel reinforcement of calcium aluminate cement mortar with regard to environmental factors (temperature and chloride content) and mortar quality (water/cement ratio).

1. Introduction

Steel reinforcement corrosion is one of the major problems for a reinforced concrete structure exposed to a chloride environment. The passivation layer is removed locally by the chloride ions when the critical chloride threshold level is achieved. Corrosion process imposes rebar cross-sectional area reduction and internal expansion promoted by the corrosion products which results in the cover concrete cracking. Particularly, corrosion of steel-reinforced concrete made of calcium aluminate cement (CAC) has been reported in Europe [1, 2]. For instance, in Spain, a block of flats collapsed in November 1978, resulting in several persons injured. It is estimated that about 200,000 dwellings were built in Spain between 1950 and 1970 using calcium aluminate cement (CAC) concrete.

It has been reported [3] that the lower the level of C_3A in Portland cements, the lower the chloride ion binding capacity is. Also, the binding capacity depends on the type of the calcium aluminate hydration products such as C_3A, C_4AF, and $C_{12}A_7$ [4]. This binding capacity also reduces the chloride diffusion through the pore system [5]. Therefore, calcium aluminate cement (CAC) might provide a high binding capacity due to the high Al_2O_3 content and reduce the corrosion rate [6]. Moreover, the chloride binding capacity increases by the curing time [7]. The high efficiency of CAC regarding chloride binding is also found in other ion immobilization [8].

Calcium aluminate hydrate phases (e.g., CAH_{10}, C_2AH_8, and C_3AH_6), that typically form in CAC systems, are prone to phase conversion phenomena [6]. Then, a chemical process in which hexagonal phases of the cement, CAH_{10} and C_2AH_8, turn into cubic phases, C_3AH_6, leads to an increase of porosity [5], and the corrosion initiation increases together with the porosity. The above-mentioned

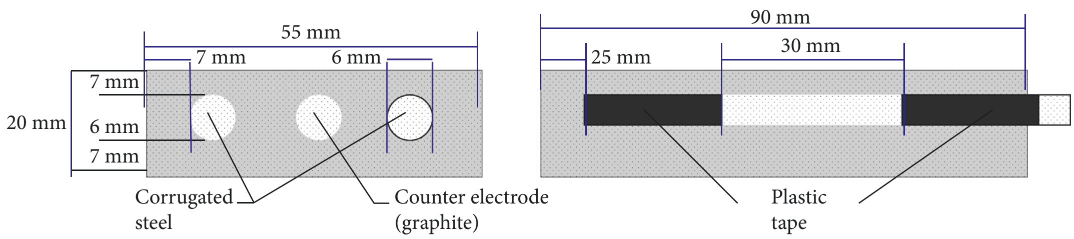

Figure 1: Specimen dimensions.

hydrates in CAC could be converted into stable hydrates by means of a carbonation curing process without the instance of increased porosity; then, the volumetric instability of CAC is avoided [9].

As it is well known, the presence of chloride ions in the environment (sea water, salty fog, deicing salts, salty solutions, etc.) is the main promoting factor of corrosion initiation [5–7]. Although aluminous hydrates can react with chloride ions forming chloroaluminates, the amount of remaining chloride ions in the pore solution in equilibrium could be enough to initiate significant reinforcement corrosion along the time [10]. Currently, new corrosion protection coatings based on chloride immobilization are being studied [11]. Also, bound chlorides may be released by changes in the pore solution such as pH lowering or free-chloride reduction [6]. It is remarkable that the corrosion rate level was found to be directly influenced by the degree of conversion from hexagonal to cubic phases which was achieved by increasing the curing temperature [10, 12].

Corrosion intensity measurements have been used over time as an 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 $\mu A/cm^2$ should be considered of significance in concrete reinforcement made of portland cement [13] and 0.1 $\mu A/cm^2$ for concrete reinforcement made of CAC cement [14].

Characteristic values of corrosion intensity (I_{corr}) and resistivity serve to establish the corrosion state. Therefore, the knowledge of the corrosion level will be very helpful when corrosion assessment is made. The conversion process was induced by the increase of the curing temperature. The characteristic values of corrosion intensity and resistivity (expressed as ohmic drop data) of calcium aluminate cement (CAC) mortars exposed to chloride-containing environments are presented.

The scope of the present work is to set such limiting values in steel-reinforced calcium aluminate cement-based materials exposed to a wet chloride contaminated environment. The final scope of this study is to obtain a mathematical model which lead to know the relationship between the corrosion intensity and the ohmic drop of the steel reinforcement with the water-cement ratio, curing temperature, and the environmental chloride content.

2. Experimental Method

2.1. Sample Elaboration. Prismatic ($20 \times 55 \times 90$ mm) reinforced mortar specimens (0.35:0.50 water-cement ratio and 1:3 cement-sand ratio) were made (Figure 1) and cured at 100% RH. Curing was performed at 20°C, 40°C, and 60°C for two weeks. Then, they were immersed in either 0.5 M or 1.5 M NaCl solution for 255 days [10], and afterwards, subjected to a sheltered from rain environment for five years.

2.2. Electrochemical Measurements. Steel rebars embedded in CAC mortars (Figure 1) were electrochemically monitored after 5 years of exposure to either a 0.5 mol/l or 1.5 mol/l NaCl solution. Thereby, corrosion intensity and ohmic drop values were measured according to [13].

2.3. XRD. Solid-phase *analysis* was performed by XRD by means of a Philips PW 1730 diffractometer equipped with a graphite monochromator, and Cu $K_{\alpha 1}$ radiation was used over a 2θ angular range of 5–65°, with a step size of 0.04° at 2 s per step.

3. Results and Discussions

3.1. XRD Analysis. X-ray diffractograms shown in Figure 2 demonstrate that, after five years, all the specimens suffered the complete conversion from hexagonal phases to cubic phases which are the most stable forms, and then, it is not expected any significant change along the time. Therefore, the electrochemical parameters recorded during this period could be considered as the characteristics values of such material, which are only dependant on the mix proportions (water-cement and cement-aggregate ratios) and the environmental conditions (e.g., chloride content and temperature).

The semiquantitative determination of the crystalline compounds, calculated from the intensity of reflections at 11.2 (2θ) for Friedel's salt, 12.35 (2θ) for CAH_{10} and 17.27 (2θ) for katoite (C_3AH_6), is presented in Figure 2. After five years, the reflections of hexagonal Friedel's salt ($Ca_4Al_2O_6Cl_2 \cdot 10H_2O$) remain high, whereas hexagonal CAH_{10} ($CaAl_2O_4 \cdot 10H_2O$) appeared much smaller. The intensity of the cubic katoite ($Ca_3Al_2(OH)_{12}$) and gibbsite γ-$Al(OH)_3$ reflections was detected. The intensity of the cubic phase reflections increases with time, while that corresponding to hexagonal CAH_{10} decrease [6, 10]. The chloride binding capacity is increased not only by the curing time for calcium aluminate cements [7] but also by the curing temperature and compactness of the mortar as shown in Figure 2.

3.2. Characteristic Value of Corrosion Intensity. Figure 3 presents the characteristic values of corrosion intensity

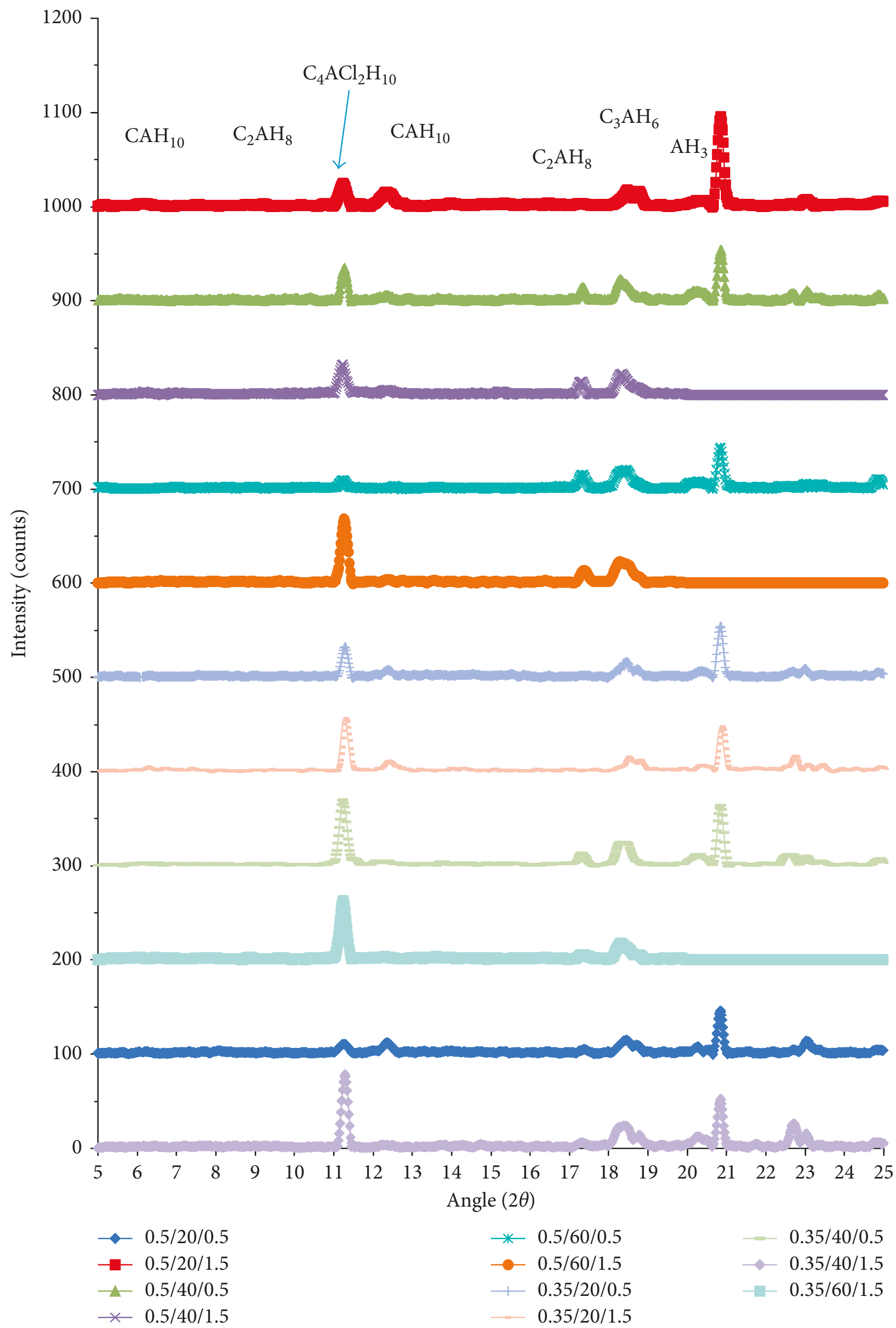

FIGURE 2: XRD diffractograms after five years of exposure.

found for CAC mortars for different mix proportions and conservation conditions. As expected, higher water-cement ratios lead to higher porosities in the cases of 40°C and 60°C and, therefore, lead to a higher characteristic corrosion intensities. Also, it was found that the higher the chloride content, the higher the corrosion intensity is.

Corrosion intensity measurements are the most accurate electrochemical measurements related to the corrosion state of the steel reinforcement [13]. Therefore, a characteristic value of corrosion intensity, I_{corr}, can be quite helpful when service life estimations are required. This parameter is presented as the most appropriate one because it provides very useful estimations for designing in order to establish a safe service life calculation. By using this technique, some authors have observed an inhibition effect on the steel corrosion in CAC mortars subjected to a chloride environment [14]. Also, a higher corrosion resistance in marine environments as compared to Portland cement has been found [15].

3.3. Characteristic Value of Corrosion Potential. Corrosion potential is an electrochemical parameter related to the corrosion state of the steel (Figure 4). However, regarding the steel reinforcement of the reinforced concrete, this parameter is only useful when the real history of the

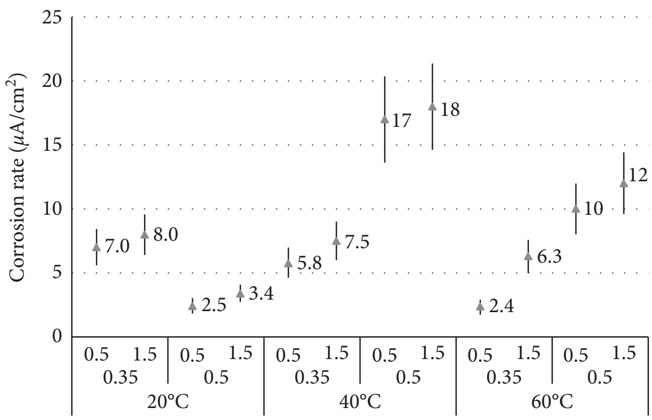

Figure 3: Characteristic values of corrosion intensity.

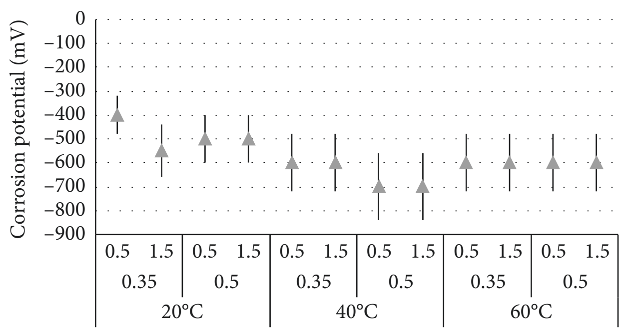

Figure 4: Characteristic values of corrosion potential.

reinforced concrete structure is well known. If not, the measurements could be misinterpreted due to the influence of the conditions of the surrounding mortar or concrete. The negative values of corrosion potential show that the steel rebars are corroding (Figure 4) [16]. Nevertheless, this parameter cannot be used to differentiate the relative performance of the steel in the environmental conditions considered in the present study.

3.4. Characteristic Value of Ohmic Drop. Ohmic drop data, which are related to the resistivity of the mortar or concrete embedding the steel rebar, are influenced by the microstructural and humidity changes in the mortar. Therefore, first of all, this parameter is affected by the conversion reaction and the subsequent increase of porosity [5] and then by the increase of humidity in the pores and the possible penetration of some ions from the exterior. After the conversion process, resistivity or ohmic drop values tend to reach a more stable level if the environmental conditions remain constant [17], such value is the characteristic resistivity which is presented in Figure 5 as ohmic drop value, expressed as ohm·cm.

In mortars made with a water/cement ratio of 0.5, it is evident that the increase of NaCl in the solution leads to a decrease of the ohmic drop. On the contrary, the increase of temperature for every NaCl solution seems to result in a decrease of the ohmic drop. With regard to mortars made with a water/cement ratio of 0.35 and cured at 20°C or 40°C, these two conclusions are not clear. This fact seems to be

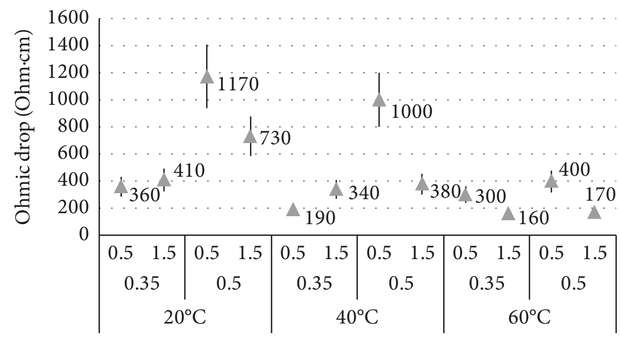

Figure 5: Characteristic values of ohmic drop.

a consequence of the more dense structure obtained in mortars made with a lower water/cement ratio. Only when these mortars (water/cement ratio of 0.35) are cured at 60°C, the general trend observed in mortars made with water/cement ratio of 0.5 is found again.

3.5. Modeling. A relationship between the electrochemical parameters (corrosion intensity and ohmic drop), the mix proportions (w/c ratio), and temperature and the storage conditions (0.5 M or 1.5 M NaCl solution) is obtained in the present research program. This relationship was achieved by using a factorial design of experiments, which provides an approach to the study of a process with a large number of variables involved such as reinforcement corrosion in reinforced concrete mortar or concrete. Also, it allows determining the variables having significant effects on the corrosion process. The traditional experimental method changes a variable which remains constant the rest of the time, and then, data variation is attributed to the shift in that variable. Therefore, this method is very time consuming, and it does not measure the interaction between several variables at a time [18–20].

3.5.1. Factorial Design of Experiments. The variables chosen for studying the characteristic values of the corrosion intensity and ohmic drop formed eight combinations with water-cement ratios of 0.35 and 0.50, chloride contents of 0.5 M and 1.5 M, and curing temperature of 20°C and 60°C. This choice was made taking into account the actual values which can be found in real cases.

Then, the modified Box-Hunter statistical method was applied in order to have a relationship between the corrosion intensity and the ohmic drop of the steel reinforcement with the curing temperature, water-cement ratio, and the environmental chloride content. Thus, the designed experiment includes three variables: curing temperature, water-cement ratio, and chloride content. This kind of design includes eight experiences on the cube presented in Figure 6 (numbered spheres at the corners). Then, it is formed by 8 experimental combinations corresponding to a 2^3 factorial design.

The variables were coded in order to obtain the three levels of −1, 0, and +1. The levels or values of the coded variables X_1, X_2, and X_3 were obtained from (1), where X_1 is the curing temperature, X_2 is the water-cement ratio, and X_3 is the chloride content:

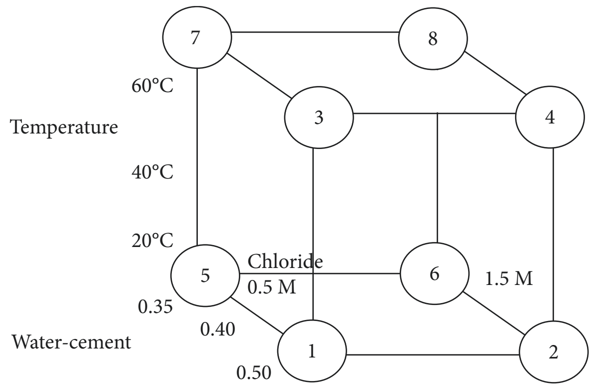

Figure 6: Schema of the factorial design of experiments: 2^3 factorial design.

Table 1: Variable levels.

Level parameters	Lower value (−1)	Central value (0)	Higher value (+1)
$X_1 = T$ (temperature)	20°C	40°C	60°C
$X_2 = w/c$ (water-cement ratio)	0.35	0.42	0.50
$X_3 = Cl^-$ (chloride concentration)	0.5 M	1 M	1.5 M

$$X_i = \frac{X_i' - X_0}{\delta}, \quad (1)$$

where X_i is the value or level to code, X_i' is the uncoded variable, X_0 is the central value (mean value of the matrix composition), and δ is the distance between the central value and the +1 and −1 levels. The scope is to sample a reasonable range of the values of interest. If a variable is significant and the results show that extreme values are desirable, subsequent experiments can explore this new range.

The corresponding values of the three variables were calculated considering chloride concentrations from 0.5 M to 1.5 M, curing temperatures from 20°C to 60°C, and water/cement ratios from 0.35 to 0.50. These values represent the working range proposed to study the effect of these variables on the corrosion intensity and ohmic drop. Table 1 shows the variables used in this study, where X_1 is the curing temperature, X_2 is the water-cement ratio, and X_3 is the chloride content. Therefore, the 2^3 factorial design of experiments has been defined.

3.5.2. Influence Calculation. Main effects are calculated from the data d_i obtained at the eight corners ($i = 1, \ldots, 8$) as follows:

$$\begin{aligned} T &: \frac{d_3 + d_4 + d_7 + d_8}{4} - \frac{d_1 + d_2 + d_5 + d_6}{4}, \\ \frac{w}{c} &: \frac{d_1 + d_2 + d_3 + d_4}{4} - \frac{d_5 + d_6 + d_7 + d_8}{4}, \\ [Cl^-] &: \frac{d_2 + d_4 + d_6 + d_8}{4} - \frac{d_1 + d_3 + d_5 + d_7}{4}. \end{aligned} \quad (2)$$

However, the interactions between each of the two factors have been calculated according to the following equations:

$$\begin{aligned} T * [Cl^-] &: \frac{d_1 + d_4 + d_5 + d_8}{4} - \frac{d_2 + d_3 + d_6 + d_7}{4}, \\ T * \frac{w}{c} &: \frac{d_1 + d_2 + d_7 + d_8}{4} - \frac{d_3 + d_4 + d_5 + d_6}{4}, \\ \frac{w}{c} * [Cl^-] &: \frac{d_1 + d_3 + d_6 + d_8}{4} - \frac{d_2 + d_4 + d_5 + d_7}{4}. \end{aligned} \quad (3)$$

Finally, the interaction between all the three parameters considered is given by the following equation:

$$t * \frac{w}{c} * [Cl^-] : \frac{d_2 + d_3 + d_5 + d_8}{4} - \frac{d_1 + d_4 + d_6 + d_7}{4}. \quad (4)$$

The confidence interval (CI) is calculated by using (5) and considering a standard deviation, s, equal to 2.5 for the corrosion rate study and 150 for the ohmic drop study when an active corrosion process is onset, whereas these values are much higher if the corrosion process is not produced. The student coefficient, t, is 2.306 for 8 experiments, n, considering a confidence level of 95%:

$$CI = t \frac{s}{\sqrt{n}}. \quad (5)$$

Main effects and interactions between variables are shown in Table 2, where the curing temperature and the combined factor (T) (w/c) are higher than the experimental error, while the chloride content is slightly lower. This means that these two parameters (curing temperature and $T \times w/c$) are the most important with regard to the corrosion rate of the reinforcement. In relation to the ohmic drop study, it is observed the great influence on this parameter of the curing

Table 2: Main effects and interactions.

Parameters	Main effects and interactions for the I_{corr} study	Main effects and interactions for the ohmic drop study
T (curing temperature)	2.45	−410
w/c (water/cement)	1.55	310
Cl (chloride content)	1.95	−190
(T) (w/c)	−5.6	255
(T) (Cl)	1	4
(w/c) (Cl)	0.5	145
(T) (w/c) (Cl)	1.375	−100
Confidence interval	2.04	122
Curvature effect	−3.3	10
Confidence interval of the curvature effect	3.53	212

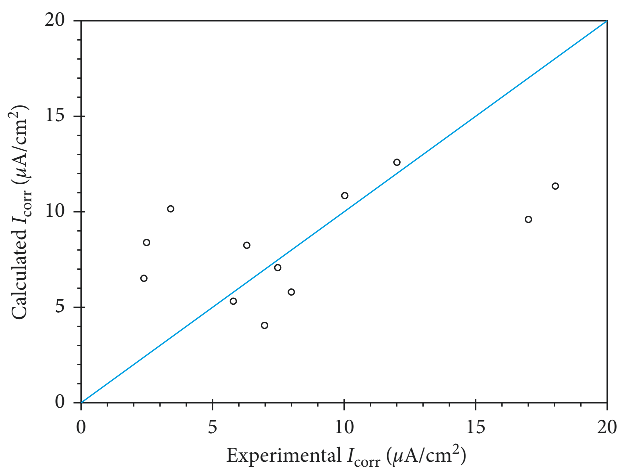

Figure 7: Calculated I_{corr} results applying (8) versus experimental I_{corr}.

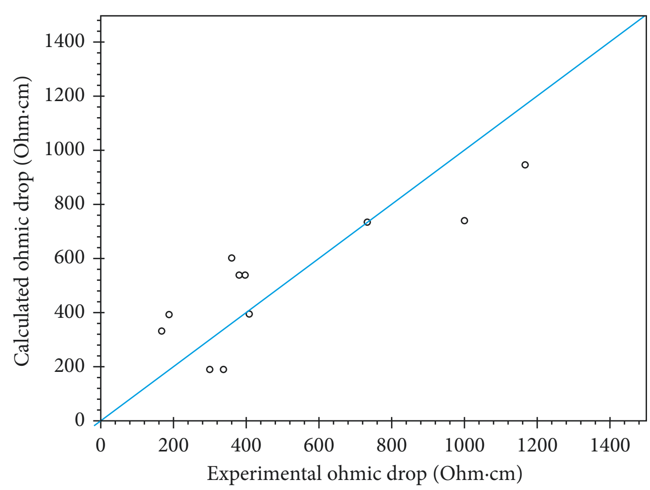

Figure 8: Calculated ohmic drop results applying (9) versus experimental ohmic drop.

temperature and the water-cement ratio, considered isolated and also combined. The effect of the chloride content is of less important when compared with the other two variables.

The curvature effect, C, is the difference of the average of the data at the central points and the average of the factorial design experiment data, which was calculated according the following equation:

$$C : \frac{d_a + d_b + d_c + d_d}{4} - \frac{d_1 + d_2 + d_3 + d_4 + d_5 + d_6 + d_7 + d_8}{8}. \tag{6}$$

The confidence interval of the curvature effect (CICE) was calculated taking into account the total number of experiments, N, according to the following equation:

$$\mathrm{CICE} = t \cdot s \cdot \sqrt{\left|\frac{1}{N} + \frac{1}{n}\right|}. \tag{7}$$

The values considered in this case were $s = 2.5$ for the I_{corr} study and $s = 150$ for the ohmic drop study, $t = 2.306$, $N = 4$, and $n = 8$.

The curvature value is lower than the interval of confidence of the curvature effect. Thus, a linear model to determine the influence between variables can be chosen; this means that it is not necessary to take into account such curvature effect.

3.5.3. Modeling. The data obtained in the corrosion intensity and ohmic drop of mortar were fitted to a polynomial function ((8) and (9), resp.), which allows a prediction of the experimental data as Figures 7 and 8 show:

$$I_{corr} = -8.11 + 0.61(T^a) + 1.75(\mathrm{Cl}^-) + 28.78\left(\frac{w}{c}\right), \tag{8}$$

$$R_\Omega = 95.56 - 10.25(T^a) - 205(\mathrm{Cl}^-) + 2322.22\left(\frac{w}{c}\right). \tag{9}$$

The R^2 coefficient was calculated according to (10) to evaluate the reliability of the proposed models. Such coefficient gave a reliability of about 20% for the corrosion intensity estimation and 70% for the ohmic drop one. The simulation results were compared with the experimental data, and correlation was found to be good for ohmic drop. On the contrary, a worse prediction has been found for corrosion intensity:

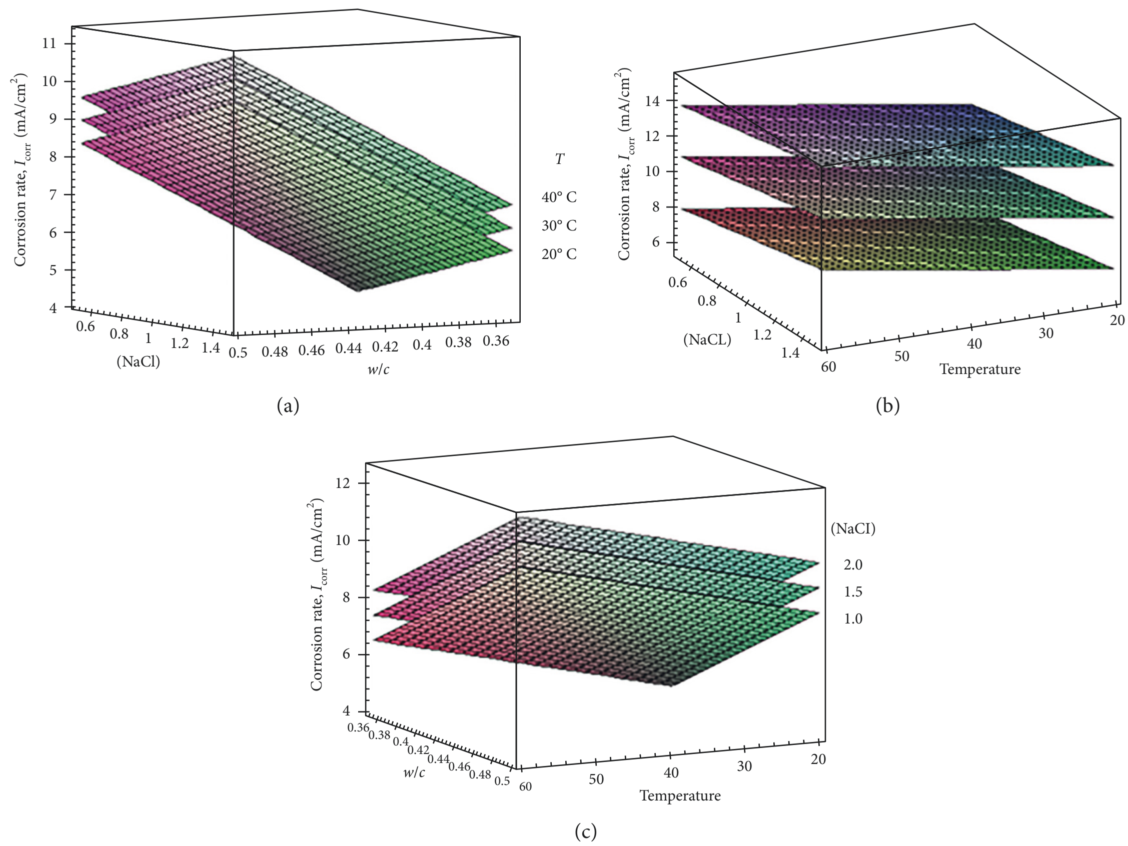

Figure 9: Calculated I_{corr} from (8): influence chart (response surface). (a) Constant curing temperature of 20°C, 30°C, and 40°C, (b) constant water-cement ratio of 0.40, 0.50, and 0.60, and (c) constant chloride content of 1 M, 1.5 M, and 2 M.

$$R^2 = \frac{\sum_{i=1}^{n} (z_i^* - \overline{z}_i)^2}{\sum_{i=1}^{n} (z_i - \overline{z}_i)^2}, \tag{10}$$

where z_i is the experimental data, z_i^* is the calculated data using the model, and $\overline{z}_i$ is the average value, whereas n is the number of data.

3.5.4. Response Surfaces. The mathematical model allows the simulation of the corrosion intensity (Figure 9) and ohmic drop (Figure 10) response in function of the variables studied. Once the system has been described with the model equation, the computer and the software facilitate the solving the model and plot the results. For example, Figure 9 shows the surfaces of response for three cases considered: (a) constant curing temperature of 20°C, 30°C, and 40°C, (b) constant water-cement ratios of 0.40, 0.50, and 0.60, and (c) constant chloride content of 1 M, 1.5 M, and 2 M.

Corrosion intensity and ohmic drop data are used to assess the corrosion state of steel reinforcement in concrete. Both of them give an idea about the development of the corrosion process of the steel. This fact justifies that the same factors influence both of them. However, the magnitude of such influence is different for each property. That is, the ohmic drop is mainly affected by the effect of the curing temperature and the water-cement ratio, separately. Also, the combined effect of these factors is of importance. However, for the corrosion intensity study, it has been determined that such combined effect is the most relevant, and the effect of the curing temperature is also significant but not the isolated effect of the water-cement ratio. This result is due to the effect of the water-cement ratio on the capillary porosity of the material and the liquid phase contained in the pores [21], which affect greatly the measurements of the mortar, and then is reflected in the ohmic drop measurements.

On the contrary, once the corrosion process has been initiated, the higher or lesser porosity is of less importance to the corrosion intensity. This only could be affected in some cases by the access of oxygen from the exterior to the reinforcement.

With regard to the chloride content, it has a minor importance when the corrosion process is initiated. Only it has a significant influence on the ohmic drop as a result of a decrease in the resistivity of the material due to a hygroscopic effect and the presence of ions. The interaction of the water-cement ratio and the environmental chloride content is appreciable.

4. Conclusions

Based on the presented analysis, the following conclusions can be drawn:

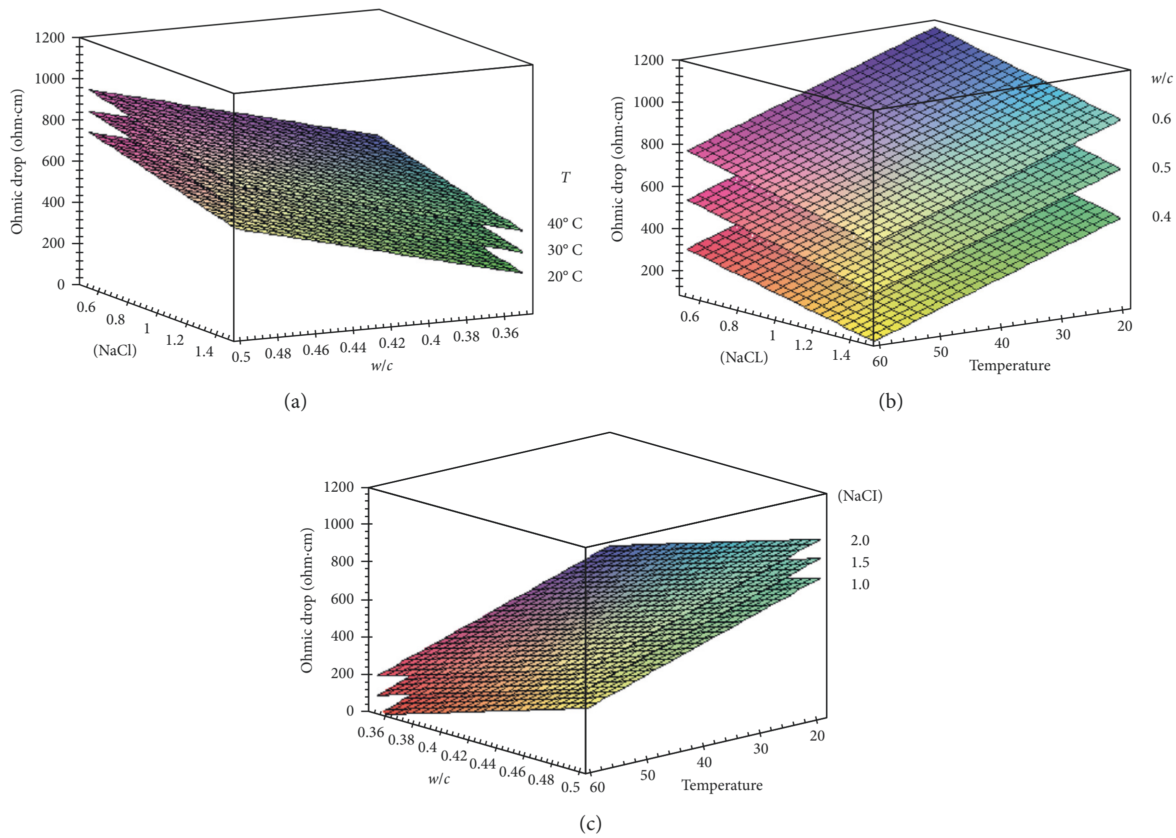

FIGURE 10: Calculated ohmic drop from (9): influence chart (response surface). (a) Constant curing temperature of 20°C, 30°C, and 40°C, (b) constant water-cement ratio of 0.40, 0.50, and 0.60, and (c) constant chloride content of 1 M, 1.5 M, and 2 M.

(i) The values of corrosion rate, and corrosion potential and resistivity, which show a steady-state plateau in corrosion data for CAC-reinforced mortars exposed to chloride environments, have been stated.

(ii) Very negative values of corrosion potential from −400 mV to −600 mV were recorded showing an active corrosion process of the steel reinforcement. However, this parameter did not allow distinguishing the magnitude of the process. By contrary, the characteristic corrosion rate of the steel depends on the combined effect of the curing temperature and the water-cement ratio showed the main effect interaction study and then by the isolated effect of the curing temperature and chloride content.

(iii) Factorial design methods are a useful tool to model the relation between characteristic values of I_{corr} and ohmic drop with curing temperature, water-cement ratio, and chloride content with a quite important saving in time. However, result utilisation is limited to the experimental range considered because of the high heterogeneity of the material.

(iv) High curing temperature, water-cement ratio, and chloride content ratios offer the maximum I_{corr}. Its interactions can play in a different way, which justify the statistical study. Therefore, further studies must be addressed to evaluate other variables or ranges.

(v) The obtained equation can predict characteristic values of I_{corr} and ohmic drop in reinforced mortars. From the interaction, a study can be deduced that the parameters affecting mostly I_{corr} are the combined effect of the curing temperature and the water-cement ratio and then the isolated effect of the curing temperature and the water-cement ratio. However, for the ohmic drop, the isolated effects of the curing temperature and the water-cement ratio are the most important and a little lesser the combined effect. Also, the chloride content has a significant relevance but of lesser influence.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

Pedro Castro Borges acknowledges the financial support provided by the "Centro de Investigación y de Estudios Avanzados del IPN, Unidad Mérida." Miguel Ángel Sanjuán wishes to acknowledge 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. Miguel Ángel Sanjuán is also grateful to C. Andrade, K. L. Scrivener, and colleagues of the Instituto

Eduardo Torroja from Madrid (Spain) and Imperial College of Science, Technology and Medicine of London (UK).

References

[1] A. Neville, "History of high-alumina cement. Part 1: problems and the stone report," *Proceedings of the Institution of Civil Engineers Engineering History and Heritage*, vol. 162, no. 2, pp. 81–91, 2009.

[2] A. Neville, "History of high-alumina cement. Part 2: background to issues," *Proceedings of the Institution of Civil Engineers Engineering History and Heritage*, vol. 162, no. 2, pp. 93–101, 2009.

[3] C. L. Page, N. R. Short, and W. R. Holden, "The influence of different cements on chloride induced corrosion of reinforcing steel," *Cement and Concrete Research*, vol. 16, no. 1, pp. 79–86, 1986.

[4] C. Arya, N. R. Buenfeld, and J. B. Newman, "Assessment of simple methods of determining the free chloride content of cement paste," *Cement and Concrete Research*, vol. 17, no. 6, pp. 907–918, 1987.

[5] H. G. Midgley and A. Midgley, "The conversion of high alumina cement," *Magazine of Concrete Research*, vol. 27, no. 91, pp. 59–77, 1975.

[6] S. Goñi, M. T. Gaztañaga, J. L. Sagrera, and M. S. Hernandez, "The influence of NaCl on the reactivity of high alumina cement in water: pore solution and solid phase characterization," *Journal of Material Research*, vol. 9, no. 7, pp. 1533–1539, 1994.

[7] K. Y. Ann, T.-S. Kim, J. H. Kim, and S.-H. Kim, "The resistance of high alumina cement against corrosion of steel in concrete," *Construction and Building Materials*, vol. 24, no. 8, pp. 1502–1510, 2010.

[8] R. C. Ivanov, C. Angulski da Luz, H. E. Zorel Jr., and J. I. Pereira Filho, "Behavior of calcium aluminate cement (CAC) in the presence of hexavalent chromium," *Cement and Concrete Composites*, vol. 73, pp. 114–122, 2016.

[9] S. M. Park, J. G. Jang, H. M. Son, and H. K. Lee, "Stable conversion of metastable hydrates in calcium aluminate cement by early carbonation curing," *Journal of CO_2 Utilization*, vol. 21, pp. 224–226, 2017.

[10] M. A. Sanjuán, "Formation of chloroaluminates in calcium aluminate cements cured at high temperatures and exposed to chloride solutions," *Journal of Material Science*, vol. 32, no. 23, pp. 6207–6213, 1997.

[11] G. Falzone, M. Balonis, and G. Sant, "X-AFm stabilization as a mechanism of bypassing conversion phenomena in calcium aluminate cements," *Cement and Concrete Research*, vol. 72, pp. 54–68, 2015.

[12] A. Macías, A. Kindness, and F. P. Glasser, "Corrosion behaviour of steel in high alumina cement mortar cured at 5°, 25° and 55°C: chemical and physical factors," *Journal of Material Science*, vol. 91, no. 9, pp. 2279–2289, 1996.

[13] S. Goñi, C. Andrade, and C. L. Page, "Corrosion behaviour of steel in high alumina cement mortar samples: effect of chloride," *Cement and Concrete Research*, vol. 21, no. 4, pp. 635–646, 1991.

[14] S. H. Jin, H. J. Yang, J. P. Hwang, and K. Y. Ann, "Corrosion behaviour of steel in CAC-mixed concrete containing different concentrations of chloride," *Construction and Building Materials*, vol. 110, pp. 227–234, 2016.

[15] G. Li, A. Zhang, Z. Song, C. Shi, Y. Wang, and J. Zhang, "Study on the resistance to seawater corrosion of the cementitious systems containing ordinary Portland cement or/and calcium aluminate cement," *Construction and Building Materials*, vol. 157, pp. 852–859, 2017.

[16] L. G. Andión, P. Garcés, F. Cases, C. G. Andreu, and J. L. Vazquez, "Metallic corrosion of steels embedded in calcium aluminate cement mortars," *Cement and Concrete Research*, vol. 31, no. 9, pp. 1263–1269, 2001.

[17] M. A. Sanjuán, "Effect of curing temperature on corrosion of steel bars embedded in calcium aluminate mortars exposed to chloride solutions," *Corrosion Science*, vol. 41, no. 2, pp. 335–350, 1999.

[18] G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statitics for Experimenters*, John Wiley & Sons, New York, NY, USA, 1978.

[19] C. Argiz and M. A. Sanjuán, "Full factorial design to assess the concrete gas permeability," *Afinidad*, vol. 72, pp. 169–175, 2017, http://www.raco.cat/index.php/afinidad/article/download/.../419068.

[20] M. A. Sanjuán and C. Argiz, "Coal fly ash alkalis content characterization by means of a full factorial design," *Materials Letters*, vol. 164, pp. 528–531, 2016.

[21] H. F. W. Taylor, *Cement Chemistry*, Academic Press, New York, NY, USA, 1992.