Study of the Influence of Cement Type, Cement Content and Concrete Cover Thickness on the Resistance and Durability of Concretes Subjected to Chloride Ion Aging.

by Alex Joukoski, Kleber F. Portella, Carlos M. Garcia, Almir Sales, Orlando Baron and Juliano F. de Paula

Synopsis:

Reinforced concrete structures constructed in coastal zones have constantly been threatened by environmental damaging elements. The chloride ion is known as one of the most aggressive of these elements, causing, among other damages, corrosion of the steel reinforcement and degradation of concrete. The goal of this work was to determinate the influence of the cement type and cement content, as well as the concrete cover thickness, in the resistance and durability of reinforced concrete elements exposed to aging in a 3.4 % sodium chloride aqueous solution. Many concrete mixtures were made using CPII-F 32 (with filler), CPII-Z 32 (pozzolanic mixture) and CPV-ARI RS (sulfur resistance) portland cements, with contents of about 290 and 350 kg/m^3 (490 and 590 lb/yd^3), and with the concrete cover thicknesses of 10, 15, 25 and 30 mm (0.394, 0.591, 0.984 and 1.18 in). The evaluation of the concrete behavior was taken from the results of physical and mechanical tests of cylindrical concrete samples and electrochemical tests – mainly the electrochemical impedance spectroscopy (EIS) – of small prismatic reinforced concrete samples. The results are presented for each combination of cement type and content, in terms of the aging time. Half cell potential measurements show that concretes made with CPV-ARI RS cement presented the best results, with longer periods necessary to produce electrical change in the samples. The concrete made with CPII-Z 32 cement and cement content of 288 kg/m^3 (485 lb/yd^3) was the mixture with the worst durability, with some samples showing fracture after 110 days of aging.

Keywords: Chloride ion, corrosion of steel reinforcement, degradation of concrete, electrochemical impedance spectroscopy.

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INTRODUCTION

The serious problem of service life reduction of reinforced concrete structures located at coastal zones, caused by the corrosion of its steel reinforcement and by the degradation of concrete, is already well-known by the world technical and scientific community (1). Special care is required from concrete components used for electric energy distribution and public illumination systems, such as light poles and crossarms (2), due to the risk of injuries or even death of pedestrians caused by failure of the deteriorated structures.

Most cases of corrosion and degradation of reinforced concrete of coastal structures are the consequence of electrochemical reactions started by the presence of chloride ions (Cl^-) (3). After its contact with the poles and crossarms surfaces, the chloride ion can diffuse through the concrete cover and reach the steel reinforcement before the end of the planned service life of the structure (4).

Significant concentrations of chloride ion in the concrete can produce depassivation of steel, a phenomenon which manifests itself in a polarization curve as a strong increase in the electrical current, at the passivity potential zone (4).

The corrosion of the steel reinforcement in concrete, as well as the methods for its detection, are the subject of many studies all over the world, mainly using non-destructive techniques. The electrochemical impedance spectroscopy (EIS) technique is one of the most important and useful methods in evaluating the behavior of many construction materials, as much for determining corrosion speed as detecting the ingress of aggressive elements into the concrete to the reinforcement steel (5).

EXPERIMENTAL PROCEDURE

Materials Used

All materials used in the concrete mixtures were submitted to physical and chemical analysis. The cements used were CPII-F 32 (addition of carbonate filler), CPII-Z 32 (addition of pozzolan) and CPV-ARI RS (high-early-strength cement, with resistance to sulfate attack) types, and a few of its properties are shown in Table 1. No chemical alteration was observed in the cement, and its compressive strengths are in agreement with the requirements of the corresponding Brazilian technical specification (6,7).

Table 1—Physical properties and chemical composition of cement

	CPII-F 32	CPII-Z 32	CPV-ARI RS
Chemical analysis, %			
Aluminum oxide (Al_2O_3)	4.1	6.9	6.7
Silicon dioxide (SiO_2)	18.0	22.6	22.4
Ferric oxide (Fe_2O_3)	2.64	2.96	3.00
Calcium oxide (CaO)	59.6	52.6	54.7
Magnesium oxide (MgO)	5.42	4.54	3.66
Sulfur trioxide (SO_3)	2.75	2.77	3.33
Sodium oxide (Na_2O)	0.25	0.21	0.23
Potassium oxide (K_2O)	0.86	0.77	0.84
Equivalent alkali ($Na_2O + 0.658\ K_2O$)	0.82	0.72	0.78
Loss on ignition	5.63	5.75	3.81
Physical tests			
Specific surface, Blaine, m^2/kg (ft^2/lb)	303 (1479)	339 (1655)	432 (2109)
Specific gravity	3.10	2.94	3.00
Compressive strength, MPa (psi)			
3-day	21.9 (3176)	19.7 (2857)	32.2 (4670)
7-day	27.3 (3960)	25.2 (3655)	34.1 (4946)
28-day	-	31.3 (4540)	45.8 (6643)

Both fine and coarse aggregates used are from the Curitiba region, in the south of Brazil, and consist of crushed limestone with a maximum nominal size of 19 mm (0.75 in), and natural sand (washed). Some results of the physical analysis of these aggregates are given in Table 2. Potential reactivity test of the aggregates was also made, and the results (Fig. 1) show that only the sample with CPII-Z 32 cement had acceptable expansibility, according to the specification ASTM C1260-94 (8).

Table 2—Physical properties of aggregates

	Fine aggregate	Coarse aggregate
Specific gravity (dry)	2.61	2.68
Absorption, %	0.65	0.46
Maximum nominal size, mm (in)	2.4 (0.0945)	19.0 (0.748)

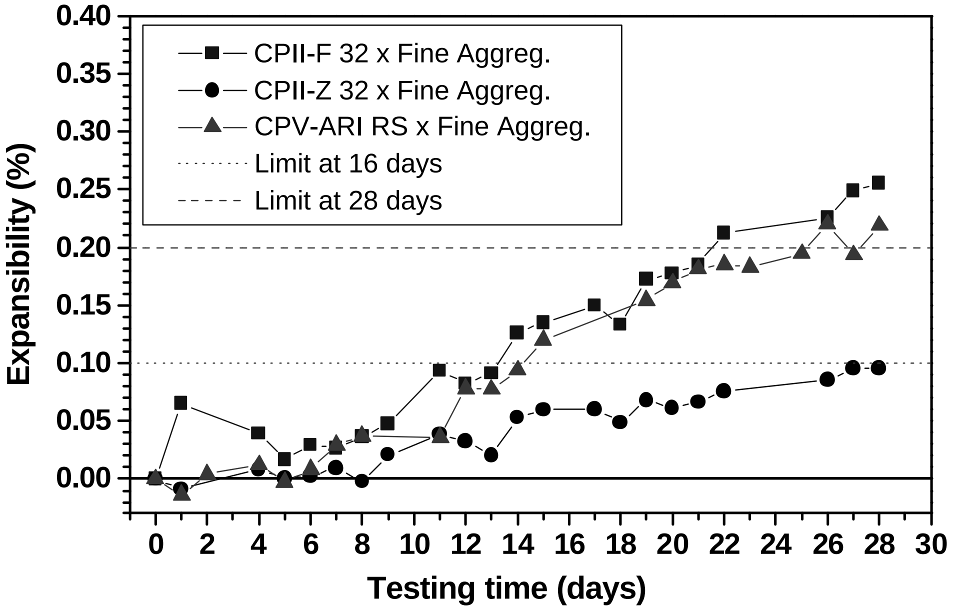


Fig. 1—Potential reactivity of cement and fine aggregate

Concrete Mixtures

Six different concrete mixtures were made using the three cement types described above, and using two cement contents for each type, as shown in Table 3. The slump for all mixtures was fixed at 40 mm ± 10 (1.57 in ± 0.394). No plasticizer, superplasticizer or air-entraining admixture were used.

Table 3—Mixture proportions and some properties of fresh concrete

Mixture	1	2	3	4	5	6
Cement type	CPII-F 32		CPII-Z 32		CPV-ARI RS	
Quantities, kg/m³ (lb/yd³)						
cement	293 (494)	347 (585)	288 (485)	345 (582)	292 (492)	344 (580)
fine aggregate	733 (1236)	656 (1106)	720 (1214)	656 (1106)	730 (1231)	654 (1102)
coarse aggregate	1172 (1975)	1218 (2053)	1152 (1942)	1215 (2048)	1168 (1967)	1211 (2041)
water	190 (320)	200 (337)	199 (335)	184 (310)	190 (320)	186 (314)
w/c	0.65	0.58	0.69	0.53	0.65	0.54
Slump, mm (in)	35 (1.38)	50 (1.97)	50 (1.97)	40 (1.57)	40 (1.57)	35 (1.38)
Temperature, C (F)	18.5 (65.3)	17.8 (64.0)	17.5 (63.5)	17.6 (63.7)	15.7 (60.3)	14.2 (57.6)
Unit weight, kg/m³ (lb/yd³)	2390 (4028)	2427 (4091)	2357 (3973)	2402 (4049)	2383 (4017)	2395 (4037)
Air content, %	0.0	0.0	0.8	0.8	0.8	0.8

Specimens Casting

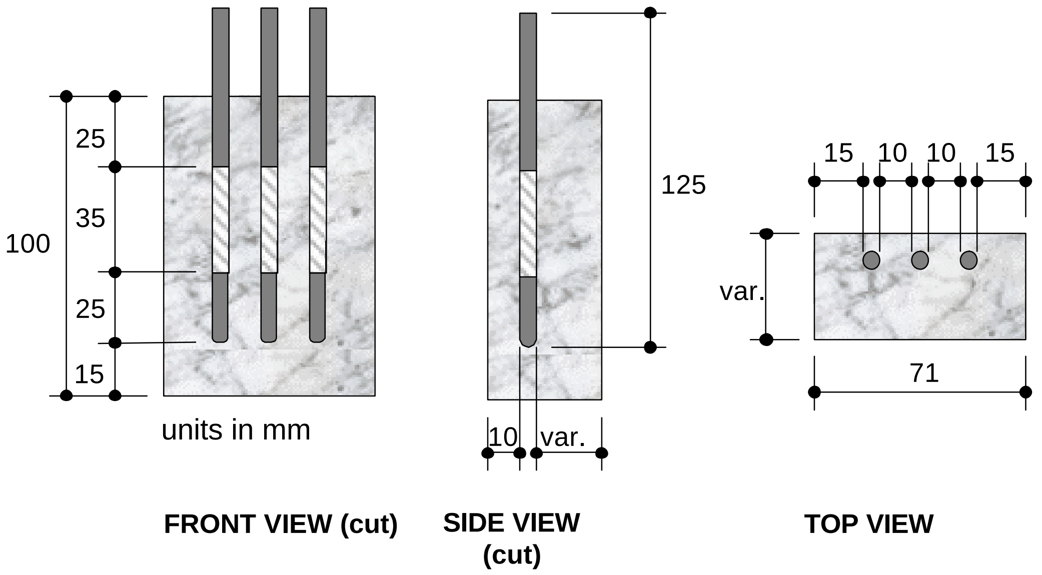
For each mixture, three types of specimens were cast:

Concrete Cylindrical Specimens – 100 x 200 mm (3.94 x 7.87 inches) in size, for determining compressive strength at 3, 14 and 28 days after casting, and after 30 and 90 days of aging by immersion in a 3.4 % Sodium Chloride (NaCl) aqueous solution.

Concrete Cylindrical Specimens (large) – 150 x 300 mm (5.91 x 11.8 inches) in size, for permeability tests and determination of specific density, absorption and porosity of concrete (after 28 days from casting).

Reinforced Concrete Prismatic Specimens – with two dimensions equal to 71 and 100 mm and a variable third dimension. Thus, it was possible to cast samples with four different concrete cover thickness: 10 mm (0.394 in), 15 mm (0.591 in), 25 mm (0.984 in) and 30 mm (1.18 in).

The reinforcement of the prismatic specimens consisted of three bars of class CA-50 steel (carbon-steel, with 500 MPa [72,519 psi] of tensile strength), 6.3 mm (0.248 inch) in diameter and 125 mm (4.92 in) long. Both extremities of each bar were protected by a tar-based painting, resulting in only a central steel-exposed region of the bar with about 35 mm (1.38 in) of length. Figs. 2,3 show more details about the prismatic specimen.



FRONT VIEW (cut) **SIDE VIEW (cut)** **TOP VIEW**

Fig. 2—Prismatic specimen sketch.(Note: 1 mm = 0.0394 in).

After casting, all specimens were left covered in the casting room for 24 hours, then demolded and placed in a moist curing room, at 23 C ± 2 (73.4 F ± 4) and 100 % relative humidity, for 28 days.

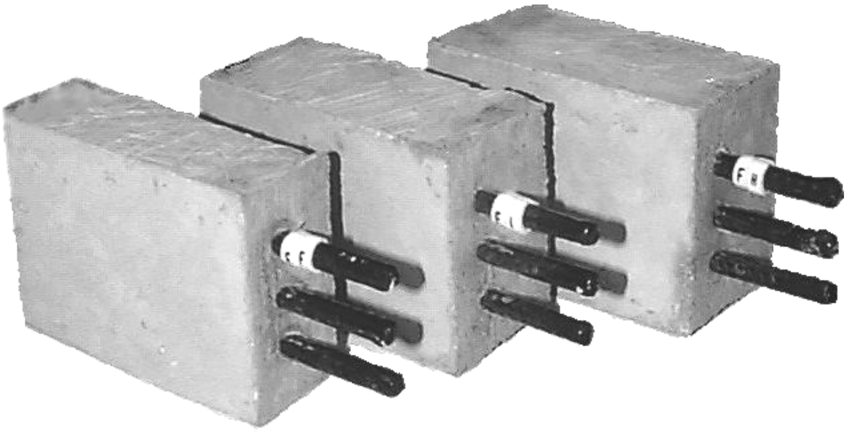


Fig. 3—Prismatic specimens photograph.

Electrochemical Impedance Spectroscopy (EIS)

After 28 days of curing, the aging process of prismatic specimens by the NaCl solution started, as well as the EIS testing. "Aging cells", consisting of two PVC piping caps, were fastened to each specimen, as shown in Figs. 4,5. The container at the side of the concrete cover was filled with the saline solution, whereas the other one was filled with distilled water.

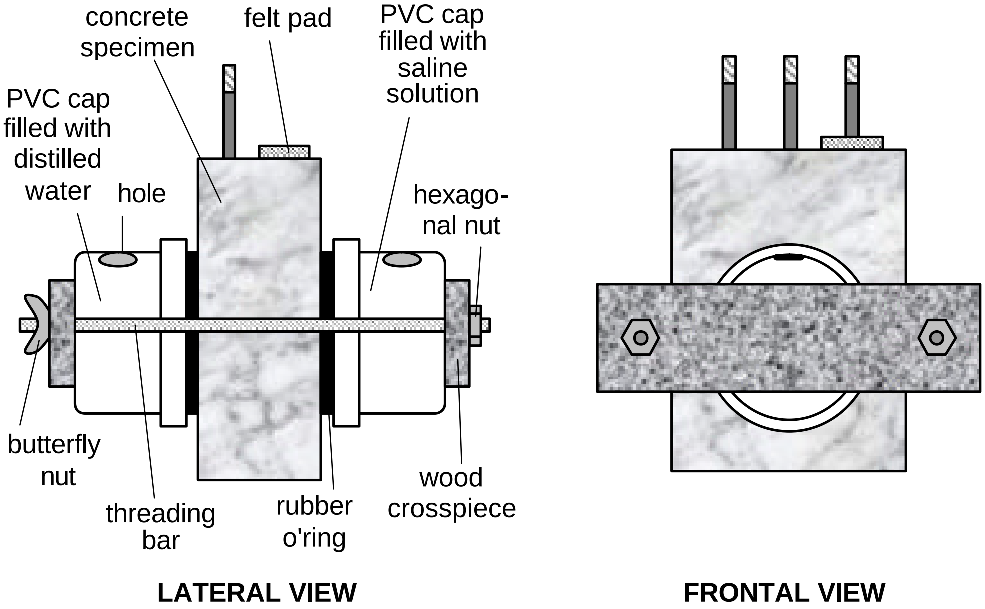


Fig. 4—Aging cell sketch.

The steel bars of the specimen functioned as working and auxiliary electrodes. A saturated calomel reference electrode was also used.

Fig. 5—Aging cell photograph.

The corrosion potential measurements and the impedance tests were performed, according to the orientations of ASTM C876-91 (9), after many aging times. This standard test method also indicates the relative probability of corrosion activity as function of the half-cell potential reading, for a $Cu/CuSO_4$ reference electrode (Table 4).

Table 4—General guidelines for half-cell potential interpretation

Half-cell (oxidation) potential reading versus $Cu/CuSO_4$	Half-cell (reduction) potential reading versus Hg/Hg_2Cl_2	Corrosion activity
Less negative than –200 mV	Less positive than +275 mV	90 % probability of no corrosion
Between –200 mV and –350 mV	Between +275 mV and +425 mV	Corrosion activity uncertain
More negative than –350 mV	More positive than +425 mV	90 % probability of corrosion

The guidelines described in ASTM C876 provide basic principles for evaluation of the reinforcing steel corrosion in concrete. These values are referred to oxidation potentials, and to convert them to reduction potentials, changing the signal is all is needed. The standard reduction potential versus that of standard hydrogen electrode (SHE) of $Cu/CuSO_4$ and saturated calomel (Hg/Hg_2Cl_2) electrodes is +316 and +241 mV, respectively. Thus, the difference of the two reference electrodes is 75 mV. So, for the calomel electrode, the guidelines of the ASTM C876 become the values positioned at the middle column of the Table 4.

Compressive Strength

The cylindrical concrete specimens with dimension of 100 x 200 mm (3.94 x 7.87 in) were tested for compressive strength at 3, 14 and 28 days of curing. Additional specimens were immersed for aging in the saline solution for about 30 and 90 days, and then were also tested.

Other Tests or Analysis

Additional testing was performed, trying the evaluation of concrete behavior to durability conditions. Besides absorption, specific gravity, porosity and permeability determinations, others techniques were applied, such as: differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray diffratometry (XRD) and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Electrical Properties

The plots presented in Figs. 6 to 9 show the half-cell potentials (or corrosion potentials) obtained from EIS measurements, for all six concrete mixtures, as function of the aging time. Each plot is referred to a different concrete cover thickness.

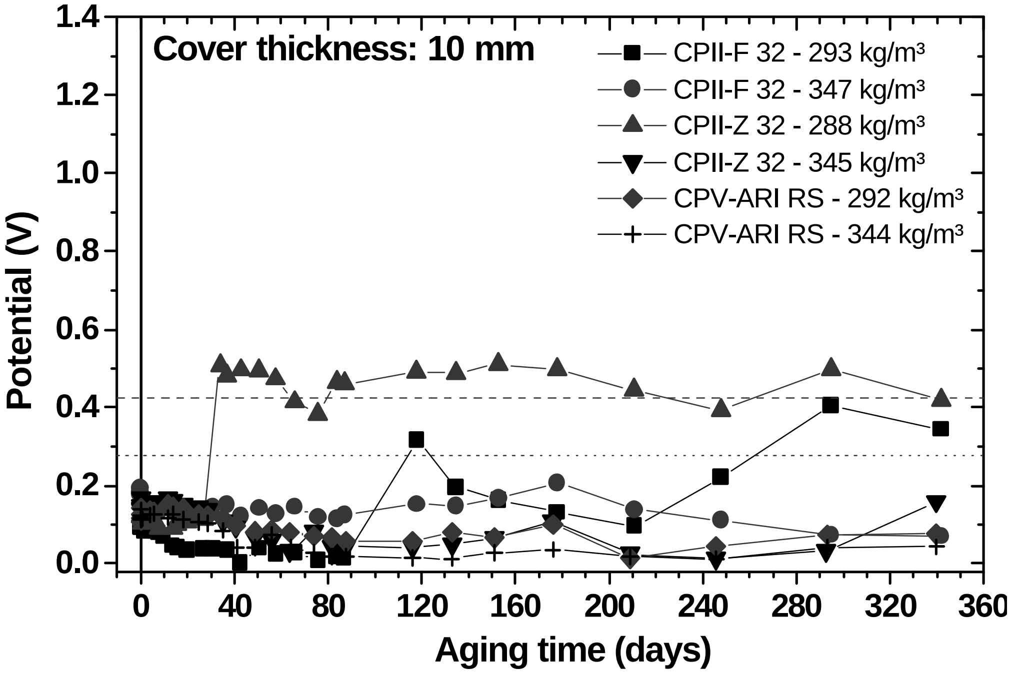


Fig. 6—Half-cell potential for specimen with cover thickness of 10 mm (0.394 in). (Note: 1 kg/m^3 = 1.69 lb/yd^3).

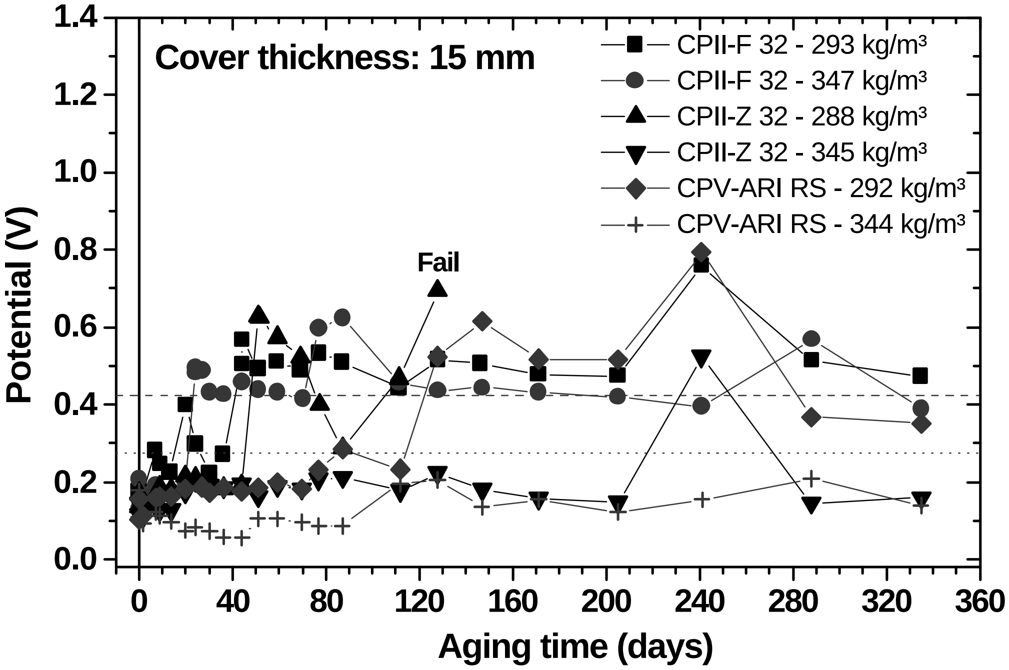


Fig. 7—Half-cell potential for specimen with cover thickness of 15 mm (0.591 in). (Note: 1 kg/m^3 = 1.69 lb/yd^3).

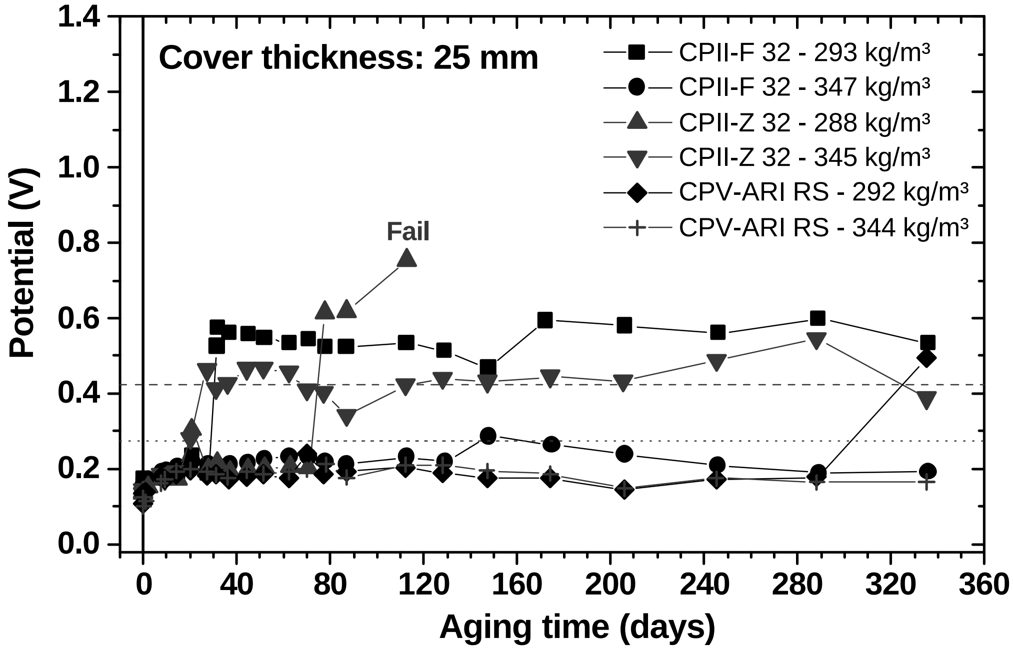


Fig. 8—Half-cell potential for specimen with cover thickness of 25 mm (0.984 in). (Note: 1 kg/m^3 = 1.69 lb/yd^3).

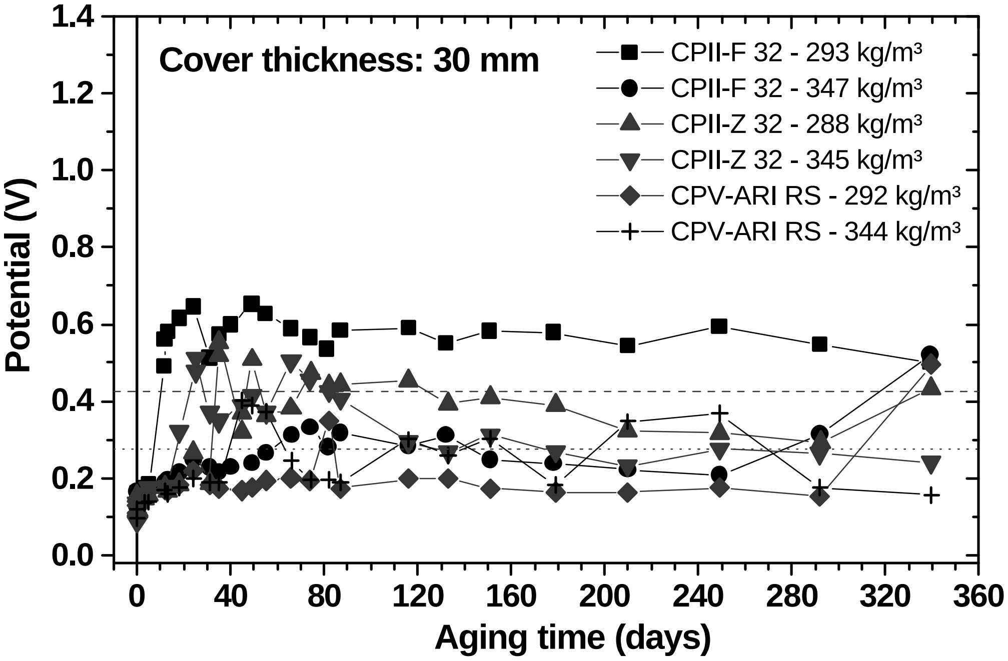


Fig. 9—Half-cell potential for specimen with cover thickness of 30 mm (1.18 in). (Note: 1 kg/m^3 = 1.69 lb/yd^3).

Comparing the curves of each plot, it's easy to realise that specimens representing concretes containing higher cement contents produced better performance, as expected. Concretes made with CPV-ARI RS cement produced, on average, the lowest potentials values. The worst results were obtained from the mixture made with CPII-Z 32 cement type and with a cement content of about 290 kg/m^3 (490 lb/yd^3), that is Mixture 3. The specimens with cover thickness of 15 and 25 mm of Mixture 3 showed cracking, peeling and scaling after approximately 120 days of aging.

It isn't hard to notice the relationship between durability and surface quality of specimens made with certain cement types, mainly CPII-F 32 and CPII-Z 32 with lower cement contents (Mixtures 1 and 3). A more detailed observation of the plots reveals that specimens with cover thickness of 10 mm showed, comparatively, better electrical performance. This, in a first look, may sounds contradictory, but can be explained. The side of these specimens related to the cover thickness under analysis presented better surface quality, because it was left at the bottom of the molds during the molding and vibrating processes.

Fig. 10 and Fig. 11 present, respectively, Nyquist and Bode plots obtained from electrochemical measurements of specimens made with CPII-Z 32 cement, 288 kg/m^3 (495 lb/yd^3) cement content and concrete cover 10 mm (0.394 in) thick, at four different aging times. It's interesting to observe that the alteration of the curves are coincident with the potentials changing, which happened between 27 and 34 days of aging, pointing to the start of a corrosion process.

In Fig. 12 is shown the model (equivalent electric circuit) used in the fitting, by non-linear least squares method, of the experimental results (10).

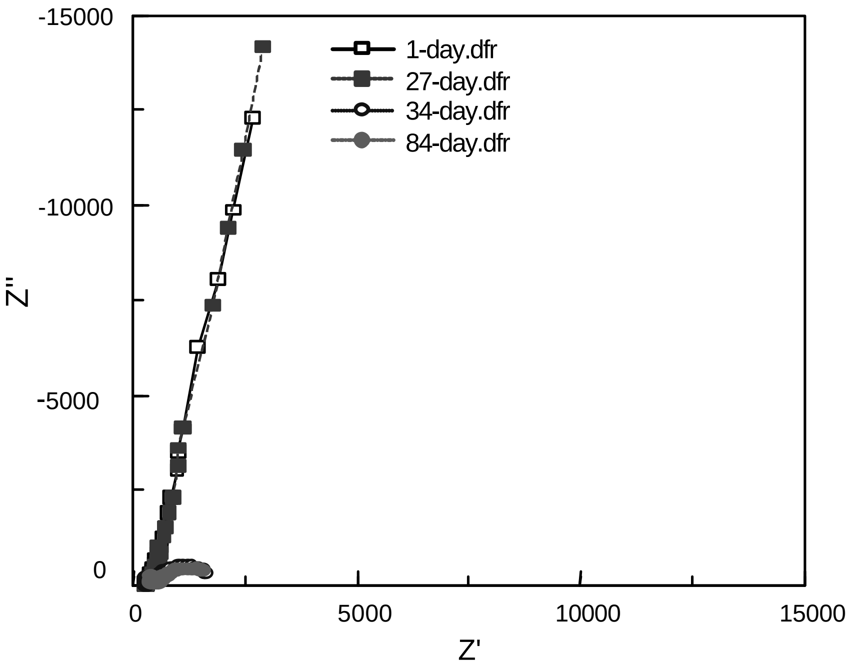


Fig. 10—Nyquist plot for specimen made with 288 kg/m³ (485 lb/yd^3) of CPII-Z 32 cement.

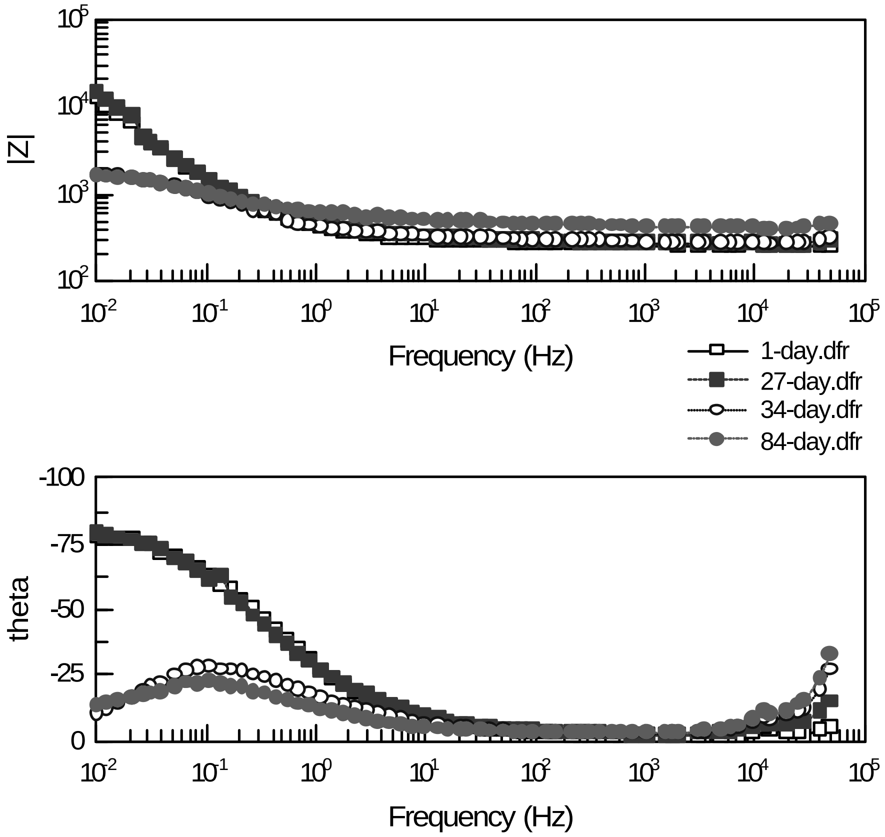


Fig. 11—Bode plots for specimen made with 288 kg/m³ (485 lb/yd^3) of CPII-Z 32 cement.

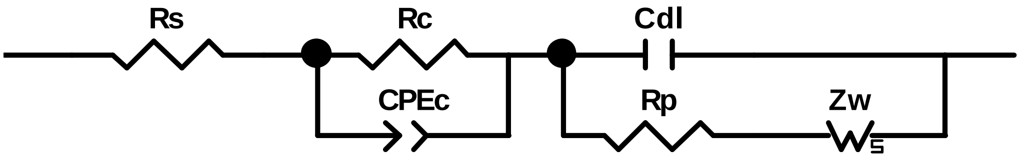


Fig. 12—Equivalent electric circuit used in the fitting of results.

Compressive Strength Results

The results obtained from compressive strength testing at 3, 14 and 28 days of curing and after 30 and 90 days on aging by a 3.4 % NaCl solution are shown in Fig. 13. It can be easily seen that concretes made with CPV-ARI RS cement type, as well as that ones made with higher cement contents, presented the highest resistance values, as expected (11).

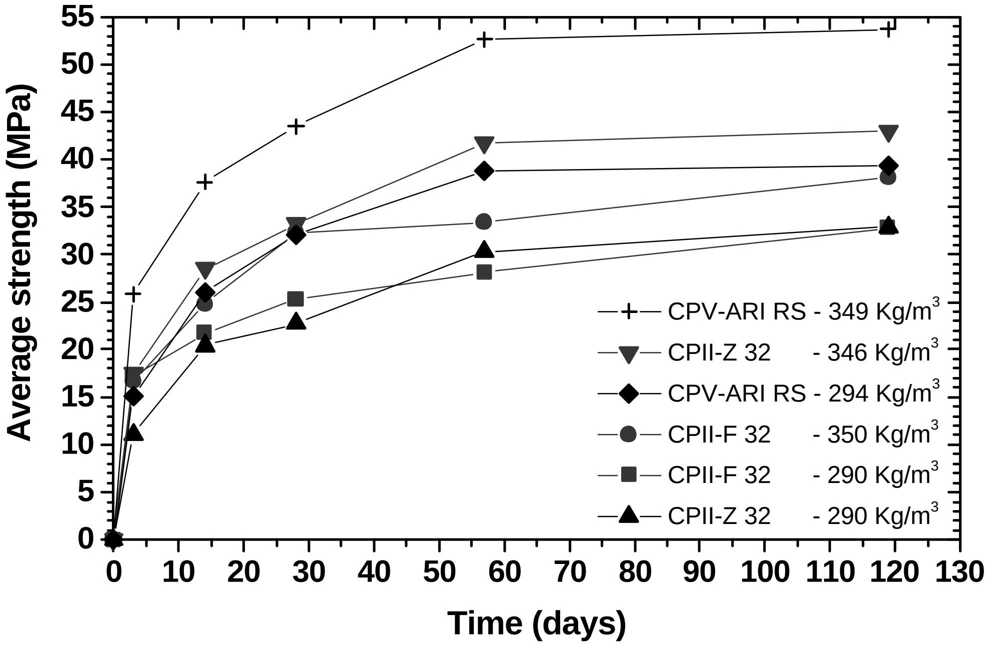


Fig. 13—Compressive strength of cylindrical specimens.
(Note: 1 MPa = 145 psi and 1 kg/m^3 = 1.69 lb/yd^3).

Other Results

The results of specific gravity and porosity are in the normal range, and the absorption values obtained are in agreement with the Brazilian standard NBR-8451 (2).

CONCLUSIONS

The results obtained from the study of electrical properties and half-cell potentials of concrete and reinforcement were presented. The variations occurred in the electrochemical system under analysis as a function of the aging by saline solution, that is steel bars corrosion. This was promptly detected by the alterations noticed in the impedance curves and in its respective electrical parameters. Thus, the electrochemical impedance spectroscopy technique is very useful for evaluating the corrosion level and the mechanisms involved in the degradation of concrete structures and parts.

It was possible to technically demonstrate the benefit of a concrete specimen containing good quality surface for durability, in relationship to its electrical behavior by aging with a saline solution.

The advantages obtained in the durability and resistance of concrete by using higher cement contents was obvious. The benefits of the use of CPV-ARI RS (high-early-strength with sulfate resistance) cement type were also proved. With this cement, it's easier to obtain concrete mixtures with higher mechanical resistance and better durability, especially in cases of aggressive environmental conditions.

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