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Effect of the Type of Concrete with Mineral Additions on the Reinforcement Corrosion Induced by Chlorides - Analysis in the Same Mechanical Strength Class

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Abstract. *The environment in which the concrete structure is inserted has a great influence on its durability and its service life. Thus, the present work aims to study of the performance of 5 types of concretes of same compressive strength (35 MPa at the age of 28 days) and considers kinetic and thermodynamic aspects of the corrosion induced by chlorides. The 5 types of concretes studied were produced with the use of mineral additions in partial replacement on cement mass (10% of silica fume, 30% of fly ash and 20% of metakaolin), besides the control situation (without mineral addition). The water-to-cementitious materials ratio was different for the concretes ranging from 0.30 to 0.55. Specifically, for the concrete with fly ash, two water/binder ratios were studied (0.30 and 0.40) with the goal of verifying if there are or not significant differences on properties of corrosion with little change of water quantity in the mix. The chloride attack consisted by 308 days (44 weekly cycles) in immersion in aggressive solution rich in chlorides and subsequent drying in a laboratory environment. During this period, the corrosion potentials (E_{corr}) and corrosion rate (i_{corr}) from polarization resistance (R_p) of steel bars were monitored. As a general result, it was possible to compare the performance of concretes at the same class of compressive strength to denote which systems have the longest durability in view of attack by chloride. The results have shown that the concretes produced with mineral additions did not show steel bar corrosion, thus configuring major service life for them. Control concrete presented depassivation of reinforcing steel, E_{corr} more electronegative and higher i_{corr} over time.*

Keywords: *Concrete, Mineral Additions, Chlorides, Corrosion, Durability.*

1 Introduction

Brazilian energy matrix is composed of approximately 60.8% of hydroelectric power plants that have vulnerability in periods of drought (Gomes *et al.*, 2019). The energy policy covers tax incentives for the generation of energy from alternative sources, such as wind energy that shows its low environmental impact, low gas emissions and towers deployment.

The Brazilian northeast region was the first to house these wind farms in the country and a large number of towers are being deployed in these coastal. The wind potential of other regions of the country has been studied. In these wind farms, the base of the wind towers is made of reinforced concrete and both humidity and chloride ions may be present. This combination is extremely deleterious for concrete, since chloride ions, when in critical concentration level near the reinforcement, they can trigger the corrosion process.

For preventing corrosion at the base of wind towers, concrete of high performance can be designed. The concrete improved composition makes difficult for aggressive agents to enter from exterior to its internal structure, increasing the material's service life, safety and durability and reducing maintenance costs (Oliveira and Cascudo, 2018).

In this sense, concretes of the same strength class, with or without supplementary materials, can have different durability and service life, when exposed to harsh environments, especially containing chlorides. The use of supplementary materials, i.e. mineral additions in the composition of concretes and their benefits, has been extensively studied in recent years by literature (Ferreira, 2003; Ramezamianpour *et al*., 2012; Figueiredo *et al.*, 2014, Shi *et al.*, 2017; Rattanashotinunt *et al.*, 2018). These materials can increase concrete durability making the ingress of aggressive agents, such as chloride ions, more difficult. On the other hand, these materials can also change the pH´s pore solution, leading to a reduction of its alkalinity, which can make the steel bars in the concrete vulnerable to corrosion. However, among the mineral additions, some of them may present better performance and increase the service life of the structures, specially the so-called super pozzolans of high reactivity and fineness.

In Brazil, concretes are specified and purchased based on compressive strength, maximum water/binder ratio and environmental aggressiveness class (ABNT NBR 6118: 2014). Thus, the C35 compressive strength class is an intermediate class for most constructions and also meets the construction of wind tower concrete bases.

The aim of the present paper is to evaluate the protection ability of concretes against the steel bar corrosion. The compared concretes have the same compressive strength (C35 MPa) at the age of 28 days and the same exposure condition in harsh environment, containing chlorides. Concrete with fly ash (FA), silica fume (SF), metakaolin (Mk) and without mineral addition – Control (CR) were studied. Additionally, for the concrete with fly ash, the influence of a water/binder ratio also were measured (0.30 and 0.40). Thermodynamic (E_{corr}) and kinetic (i_{corr}) parameters of reinforcement corrosion were evaluated.

2 Experimental Program

2.1. Materials

The concrete mix proportions were based on previous studies from the durability´s study group of the Federal University of Goiás (Carasek and Cascudo, 2001; Ferreira, 2003). The composition was a combination of Portland Brazilian cement (composed by 6–10% in mass of limestone filler and by 90–94% of clinker – with a small amount of calcium sulfate), whose mechanical strength requirement is a minimum of 32 MPa of compressive strength of the age of 28 days – similar to European CEM II/A-L, mineral additions (silica fume, fly ash or metakaolin), fine sand aggregate (river sand) and coarse aggregate (stone from mica schist metamorphic rock), plasticizer, superplasticizer and tap water (potable water from the public distribution network). In the concrete mixtures, 10%, 30% and 20% of cement (by weight) were replaced by silica fume, fly ash and metakaolin, respectively. Furthermore, a control concrete (without mineral additions) was studied.

The water-to-cementitious materials ratio was different for the concretes ranging from 0.30 to 0.55. However, all concretes showed compressive strength at the age of 28 days of 35 MPa. Specifically, for the concrete with fly ash, two water/binder ratios were studied: 0.30 and 0.40.

Table 1 shows the compositions of the concretes and Table 2 shows the compressive strength of concretes at the age of 7, 28 and 91 days. The slump test was fixed in (80±10) mm. Steel bars with a nominal diameter of 10 mm (0.4 in.) were used to evaluate the corrosion.

Table 1. Composition of concretes used under this investigation.

Materials	Concretes*				
	Control	Silica Fume	Fly Ash		Metakaolin
Portland cement (kg/m^3)	552	331.2	525.0	487.5	294.4
Water/binder ratio	0.40	0.55	0.30	0.40	0.55
Mix Unit (kg) (cement: mineral addition: sand: stone)	1,0: 0.0:0.8:2.1	1.0:0.1:1.9:3.5	1:0.3:0.7:2.1	1:0.3:0.7:2.3	1:0.3:2.1:3.9
Plasticizer (%)	0.03	0.05	0.03	0.03	0.05
Superplasticizer (%)	0.00	0.15	0.08	0.01	0.00

*10%, 30% and 20% of cement (by weight) were replaced by silica fume, fly ash and metakaolin, respectively.

Table 2. Average of compressive strength of concretes studied at the ages of 7, 28 and 91 days.

Age (days)	Average compressive strength and water/binder ratio				
	Control	Silica Fume	Fly Ash		Metakaolin
	0.40	0.55	0.30	0.40	0.55
7	27 (0.8)	25 (0.4)	29 (1.0)	27 (0.1)	28 (1.3)
28	36 (1.4)	36 (0.4)	36 (1.9)	33 (1.4)	32 (1.3)
91	41 (0.3)	42 (0.6)	49 (0.9)	44 (1.8)	39 (1.7)

*Standard deviation is given in parentheses.

From Table 2, it was possible to observe that although all concretes have the same mechanical strength at 28 and 91 days (except fly ash concretes at the age of 91 days, in which their values of strength are slightly higher, in the order of 45 MPa to 50 MPa), they have different microstructure and porosity characteristics. As the water/binder ratios are different (among some of these concretes), the global porosity and the pore size distribution are, in fact, different among them. This interferes with important aspects related to durability, such as: interconnectivity and tortuosity of pores, in addition to the compactness characteristics of the paste - aggregate interfacial transition zone (Oliveira and Cascudo, 2018). Although the mechanical strengths are similar (premise of the present work), it is important to note that there are different cementitious systems being compared.

The steel bar used in the specimens was of a single type, having been used a Brazilian CA-50 carbon steel (for reinforced concrete structures). This steel meets the Brazilian standard of steel for reinforced concrete structures (ABNT NBR 7480: 2007) and it featured a yield strength higher than 500 MPa.

In order to standardize the surface conditions of the bars, they were initially chemical cleaned using a solution of (Hexamethylenetetramine) (Figure 1a). The general appearance of steel bars after chemical cleaning can be seen in Figure 1 (b). However, this procedure did not allow the complete removal of visible oxides from the bars. So, it was necessary to perform a mechanical cleaning performed with a circular brush attached to emery, as shown in Figure 1 (c). The appearance of the bars before and after mechanical cleaning can be seen in the Figure 1 (d). Finally, the steel bars were identified (Figure 1 e). These bars had a total length of 15 cm (6 in.) and they were partially inserted into of concrete´ specimens, constituting 2.5 cm (1 in.) of cover thickness. Just a portion of steel, as showed Figure 1 (f) (5 cm = 2 in.) was exposed to corrosion induced by chloride ions (Figure 1 f). The surface area of rebar exposed to corrosion was 12.88 cm^2 (5.15 in^2) (Figure 1 g).

Cubic concrete specimens of 1500 mm side were produced and they were reinforced with four longitudinal rebars of 10 mm of nominal diameter. These test specimens were designed for the electrochemical tests, while for the electrical resistivity test, the same cubic specimens were used, but without steel bars. Oliveira and Cascudo (2018) used the same specimen shape. After manufacturing, the test specimens were under cure for 28 days in a controlled room (temperature of 22±2ºC and a minimum relative humidity of 95%). Thereafter, the specimens remained until the age of testing in the laboratory environment, which corresponded to the age greater than 91 days.

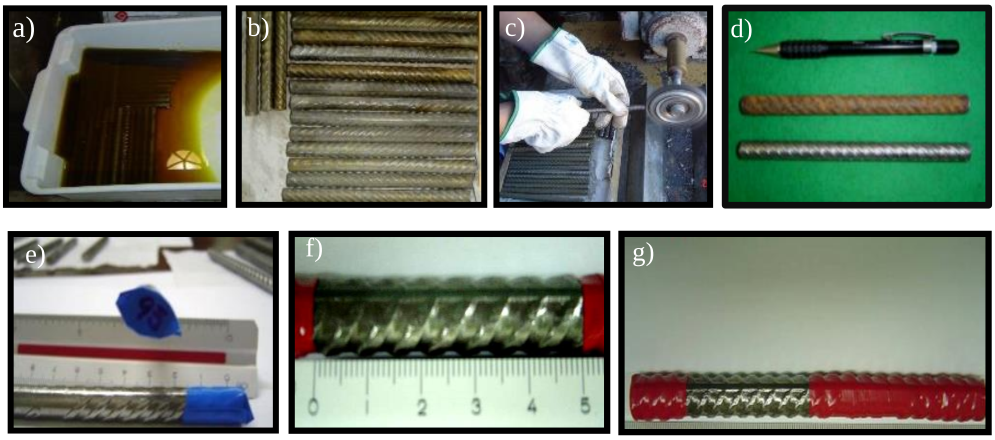

Figure 1. Preparation of steel bars: (a) chemical cleaning with (Hexamethylenetetramine), (b) final appearance of the bars after chemical cleaning, c) mechanical cleaning, (d) before and after mechanical cleaning, (e) bar identification, (f) bar ends wrapped with electrical tape and (g) bar center detail (5 cm) ready to be placed in the molds.

2.2. Methods

The corrosion was induced by wet–dry cycles in NaCl solution (NaCl diluted to 5% by mass or 0.855 M). The weekly cycles were 2 days of partial immersion of the specimen until 15 cm of its height in NaCl aggressive solution and subsequent drying during 5 days in a controlled environment (40ºC of temperature and 50 ± 5% of relative humidity).

The NaCl solution was replaced every four cycles (28 days) to facilitate aeration in a sufficient level so that the corrosion could develop. Specimens were subjected to total of 44 cycles or 308 days of attack in aggressive solution containing chlorides. The definition of the cycles was based on the studies of Cascudo (2000), considering the fact that concrete absorbs water much faster than it loses (during drying), reason why it was adopted 2 days of wetting and 5 days of drying. The importance of cycles to accelerate the phenomenon of corrosion was explained by Oliveira and Cascudo (2018).

The techniques of half-cell potential - E_{corr} (ASTM C 876: 2015) and polarization resistance (R_p) were used, the latter making it possible to estimate the instantaneous corrosion rate (i_{corr}).

These electrochemical measurements were performed by means of a three-electrode arrangement using a Voltalab 40 PGZ potentiostat, managed by Voltamaster software.

A working electrode (rebars embedded in concrete), a saturated calomel electrode – SCE (as the reference electrode) and a counter electrode of stainless steel (externally in contact with one of the faces of the concrete test specimen) were used connected to the potentiostat. In order to avoid interferences from external electric field, the measuring set up (i.e. the concrete test specimen with the 3 electrodes) were inserted inside a Faraday cage, where all the electrochemical measurements were taken. The criteria of ASTM C 876: 2015 were considered to evaluate the results of E_{corr} (mV). These criteria consider that if E_{corr} is more positive than -126 mV (SCE), the steel is passive and the probability of corrosion is smaller than 10%. Also, if E_{corr} is more negative than -276 mV (SCE), they consider that active corrosion is developing. Finally, there is a range of uncertainty with potentials between -126 mV and -276 mV (SCE).

From polarization resistance or linear polarization (R_p), it was possible to assess corrosion current density (i_{corr}). The Stern–Geary equation (Equation 1) and the proportionality factor (B Stern-Geary constant) were used.

$$i_{corr} = B/Rp \tag{1}$$

It was adopted a value of 26 mV for corroding steel and a value of 52 mV for passive steel, as established by Andrade and Alonso (2001). The criteria were adopted, which associate corrosion rates with the intensity of corrosion on corrosion levels.

3 Results and Discussion

Figure 2 (a and b) shows E_{corr} and i_{corr} against the number of cycles, respectively. The results are the average results of 4 rebars for each type of concrete. Table 3 shows the magnitude of the corrosion potentials for the studied concretes.

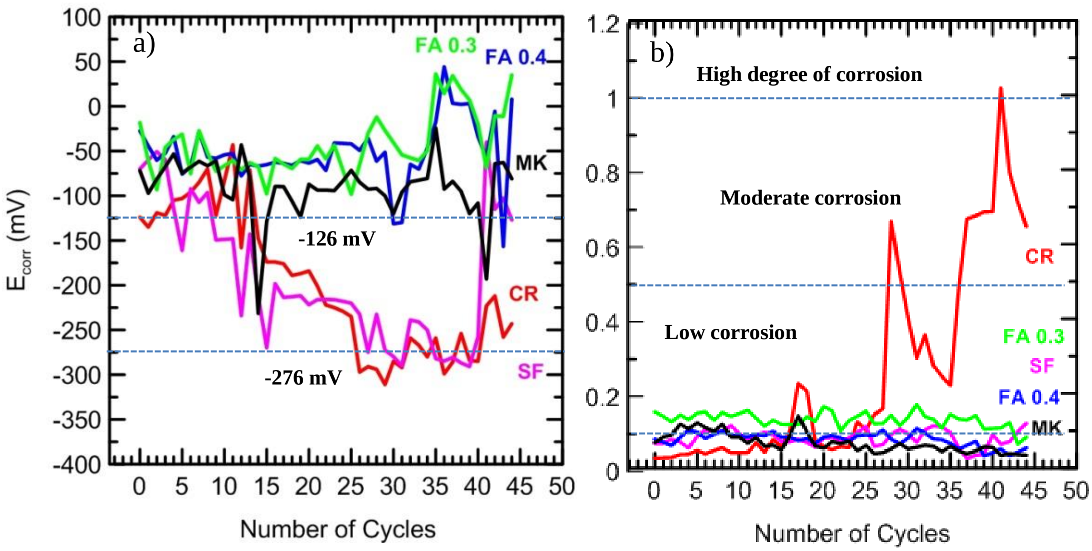

Figure 2. Influence of the type of concrete in terms of initiation and propagation of corrosion induced by chlorides on the concretes performance: representative curves of (a) E_{corr} (SCE) and (b) i_{corr} *versus* attack time by chlorides (number of wet-dry cycles in NaCl solution) according to ASTM (ASTM C 876: 2015) and Andrade

and Alonso (2001) criteria, respectively.

Table 3. Magnitude and average of E_{corr} during the 44 cycles of immersion in aggressive chloride-containing solution.

Concretes	Partial replacement of cement, by weight (%)	Water/binder ratio	E_{corr} – magnitude* (mV)	Probability of corrosion - Criteria of ASTM C 876 (ASTM, 2015)	E_{corr} - average (mV)	Time for depassivation of reinforcing steel (cycles)
CR	0	0.40	-311	> 90%	-199	28
SF	10	0.55	-291	> 90%	-192	No**
FA	30	0.30	-157	Uncertain	-51	No***
		0.40	-98	< 10%	-42	No***
MK	20	0.55	-231	Uncertain	-90	No***

* Magnitude in the table means the maximum individual value obtained. ** There were no signs of depassivation of reinforcement. *** This concrete meets the criterion adopted to define the depassivation of reinforcement and is in the uncertainty range regarding the probability of corrosion. The kinetic aspects can confirm if the reinforced is really depassivated.

From the Figure 2 and Table 3, for concretes with the same compressive strength (35 MPa), it is clear the beneficial effect that the supplementary cementitious materials – SCMs (mineral additions) provide to the concretes, regardless of the water/binder ratio, promoting significantly more electropositive corrosion potential values in relation to the reference concretes. Thus, it can be seen that the control concrete, compared to the concretes with SCMs, exhibit a greater tendency to the depassivation of reinforcement when inserted in environments containing chloride ions. Silica fume, contrary to expectations, did not achieve the best corrosion potential performance. These results are in accordance with the literature (Andrade and Buják, 2013; Jin *et al.*, 2017).

It is worth mentioning the good performance of fly ash concretes, with behaviors close to concrete with metakaolin. The silica fume concrete did not present a good performance regarding E_{corr}, and the lowest performance was presented by the control concrete. Thus, the effectiveness of SCMs in physically and chemically protecting the rebar keeping it passivated as long as possible became evident. This result is important because even though the corrosion induction method used in this work is accelerated, it reports the time until the depassivation of reinforcement, which means that, comparatively, there is a very significant response concerning the differences in performance of the various concretes analyzed (in terms of their actual expectations of durability). Only control concrete gave unequivocal evidence of reinforcement depassivation over the 44 attack cycles. With the exception of the silica fume concrete, the other concretes with mineral additions presented regions with low probability of corrosion or uncertain probability. The E_{corr} average values for metakaolin (water/binder ratio of 0.55) and fly ash (w/b = 0.3) concretes were similar. This evidences the overperformance of metakaolin as a mineral addition, since the difference in terms of w/b ratios for these two concretes is very high.

The silica fume concrete showed E_{corr} magnitude more negative and an indication of active corrosion after some few cycles. In spite of this behavior, the silica fume system did not evidence active corrosion in the period of test, based on i_{corr} results (corrosion rates obtained by determining R_p). This can be seen in Figure 2b. This apparently different behavior for concrete with silica fume regarding the values of E_{corr} (compared to the concretes with metakaolin and fly ash) certainly reproduces some level of perturbation at the steel–concrete interface in terms of the passive layer (Oliveira and Cascudo, 2018). Probably due to local pH changes (because pore solution is different in silica fume modified systems), it is possible that thermodynamic changes occur at the interface, with changes in the state of electric charges on the electrode (reinforcement), perceived by drops in potential values (to more electronegative values).

Finally, the control concrete showed increase of values of i_{corr} (corrosion rates) in the beginning of dry-wet cycles. This denotes reduction of service life and durability. For the silica fume concrete, in terms of the corrosion rates, there was no increase in i_{corr} values over time, as well as there was no indication of depassivation of steel or significant corrosion for these concretes, within the test period. Thus, despite the negative E_{corr} values, there seems to be no depassivation and active corrosion in concrete with silica fume.

4 Conclusions

The following conclusions can be drawn from the present paper:

- More than one technique is important to diagnose the condition of the reinforcement and to assess the protection capacity of concrete.
- Control´s concrete protected less the steel bar against corrosion induced by chlorides, indicating E_{corr} more negatives and higher corrosion rates (i_{corr}).
- According to E_{corr} values, the concretes with mineral additions have showed similar performance among them (the silica fume concrete initially showed doubt, but later it was confirmed that there was no corrosion) and significantly better behaviors compared to control concrete.
- All concretes with mineral additions have not presented significant corrosion induced by chlorides for the 44 cycles (or 308 days - analyzed period).
- The influence of the small change in water/binder ratio on fly ash concretes was not significant, both for E_{corr} and i_{corr}.
- Metakaolin showed high performance as a supplementary cementitious material, even in a higher water/binder ratio.
- Among the concretes studied, those with mineral additions had higher durability and thus major service life.

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