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Determination of Corrosion of Steel Embedded in Alkali Activation of a Binary Mixture

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In order to evaluate the use of structural concrete conventional different mixtures with different components were made to Portland cement, such as fly ash and steel slag, cementitious materials were mixed in binary form and in different percentage. Degradation was determined against corrosion phenomena due to permanent chloride attack by wetting and drying cycles. Electrochemical techniques used for evaluation corresponding to potential corrosion and electrochemical impedance spectroscopy. The results indicate the trend of concrete mixed with fly ash and steel slag, to present potential of anodic oxidation corrosion. The results of the electrochemical characterization comparatively describe concrete containing Portland cementing a slightly more porous and permeable material, which makes it more susceptible to attack by chlorides.

Keywords: fly ash, steel slag, chloride ion, corrosion.

1. INTRODUCTION

The study of lightweight aggregates and their use in structural concrete, it is part of an interesting application of concrete technology representing some advantages over conventional concrete [1-2]. The previous studies have performed theoretical and experimental characterization process material respects; involving the lightweight aggregate thermally expanded clay (AET) [3]. Also they have determined the parameters of corrosion in steel structural concrete, subject to permanent chloride attack by wetting and drying cycles, using electrochemical techniques polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) [4].

Fly ash are byproducts from power generation processes by calcination of pulverized coal in power plants. Over 20 million tons of fly ash are generated annually in Colombia mostly Class F type, and their use is generally only 10% to 15% [4-5]. According to their morphology chemical and

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mineralogical composition and particle size fly ash have a varying pozzolanic activity [6]. That is, the ash particles are reacted with an alkali activator (eg calcium hydroxide) in the presence of water to produce a cementitious material characteristics [7]. Additionally, the use of fly ash as partial replacement of cement has beneficial effects such as reduced demand for water in the mixture decreased segregation lower heat of hydration and crack control at an early age. Therefore, its use as an addition results in a cost-effective alternative and useful for improving the properties and concrete performance in both fresh and cured state [8].

On the other hand, Blast furnace slag is a byproduct of the manufacture of pig iron or cast iron, which is separated from it in liquid (molten) in the blast furnace process. When cooled rapidly (warm) with water (granulation) or air (pellet) a glassy product is obtained which produces a finely ground powder of potentially hydraulic cementitious properties [9]. The hydraulic activity of slag mainly depends on its mineralogical structure which it is related to the chemical composition and influences the glass phase thereof [10]. The activating embedded solutions should accelerate the solubilization of the slag; and favoring the formation of stable hydrates of poor solubility and the formation of a compact structure with these hydrates. The activating compounds may be alkali or alkaline earth hydroxides, salts of weak acid (R_2CO_3, R_2S, RF), strong acid salts (Na_2SO_4, $CaSO_4.2H_2O$) and silicic salts R_2O type (n) SiO_2 wherein R is an alkaline ion type of Na, K or Li. Between these, sodium silicate and sodium hydroxide, have been reported as the most effective activators, taking into account the mechanical and durability properties obtained in the final products [11]. The main hydration product that forms in this material is calcium silicate hydrate (CSH); this gel phase differs from that of Portland cement paste having a smaller C / S. The formation of other phases or hydrated compounds, it will depend on the type and amount of activating employee the structure and composition of the slag and curing conditions under which it will develop hardening [12].

Alternatively, the development and application of cementitious materials by alkaline activation of aluminosilicate such as blast furnace slag Metakaolin wheel and ash it is gaining importance by the need for sustainable building materials [13]. Alkali activated cements also they called geopolymers, they can be synthesized by mixing an alkaline solution with a source of aluminosilicates such as metakaolin, fly ash or blast furnace slag, and these have proven to be a valuable alternative for use in the production of concrete [14]. Among the alkali activated cementitious systems fly ash and granulated blast furnace slag, they have been the most studied materials. This is due to optimal activation process presented; and the formation of cementitious products they generate in the slag by the gelation C- (A) -S-H and ashes by gelation N-A-S-H and zeolites as side reaction products. In cured state, the mechanical performance of the fly ash and mixtures of alkali activated slag, it depends primarily on the chemical composition of the alkaline agents nature and quality of pozzolanic materials and curing type performed [15-16]. As a result, these cementitious materials exhibit comparable mechanical properties with those presented by traditional Portland cement concrete and adequate durability in service.

Therefore, in order to help reduce the emission of gases into the atmosphere and increase the durability of concrete properties it was carried out this investigation, by which they were developed and evaluated through tests of half-cell potential and electrochemical impedance spectroscopy, concrete mixtures of these features do not generate as high energy consumption; also they do not emit greenhouse gases.

2. EXPERIMENTAL DETAILS

2.1 Materials

In this study commercial Type I Portland cement is used Class F fly ash from thermal power plant Sochagota and granulated blast furnace slag from the plant of Paz del Rio. Characterization of these materials was conducted by fluorescence assays and their chemical composition are summarized in Table 1.

Table 1. Chemical composition of the used cementitious materials.

Compound	Portland cement, %	fly ash, %	Blast furnace slag, %
SiO_2	18.15	54.30	33.70
Al_2O_3	4.65	20.8	12.80
Fe_2O_3	3.80	5.30	0.48
CaO	60.03	6.40	45.40
MgO	2.50	0.80	1.00
Na_2O	0.80	0.90	0.12
K_2O	0.50	0.70	1.50
P_2O_5	-	0.70	-
TiO_2	-	1.20	0.50
MnO	-	0.01	-
SO_3	2.40	0.92	-
SiO_2/Al_2O_3	3.90	2.67	2.63
Unburned		8	

Stone material was used as fine aggregate type of river sand with fineness modulus of 3.04 and absorption of 0.81%. Fine gravel as coarse aggregate of 12 mm is used. To ensure the settlement of the mixtures; and workability; a super plasticizer additive called Sika ViscoCrete 2100 per dosage weight of cementitious material used. The characteristics and mixture proportions are summarized in Table 2.

Table 2. Proportions of concrete mixtures.

identification	PC (kg/m^3)	FA (kg/m^3)	BFS (kg/m^3)	coarse aggregate (kg/m^3)	fine aggregate (kg/m^3)	Water (kg/m^3)	Sodium silicate (kg/m^3)	Sodium hydroxide (kg/m^3)	Plasticizers (%)
B8F2S0	358.4	89.6	-	997.3	830.4	224	-	-	1.0
B8F0S2	358.4	-	89.6	997.3	830.4	224	-	-	0.8
B6F4S0	268.8	179.2	-	997.3	830.4	224	-	-	1.2
B6F0S4	268.8	-	179.2	997.3	830.4	224	-	-	1.0
B0F8S2	-	358.4	89.6	997.3	830.4	-	33.6	190.4	2.0
B0F6B4	-	268.8	179.2	997.3	830.4	-	33.6	190.4	2.0
B0F4S6	-	179.2	268.8	997.3	830.4	-	33.6	190.4	2.0
B0F2S8	-	89.6	358.4	997.3	830.4	-	33.6	190.4	2.0

2.1.1 Cement-ash - cement- steel slag

Binary mixtures of Portland cement-fly ash Portland-cement and blast furnace slag, they were used as the main cementitious material Type I Portland cement and fly ash additions and blast furnace slag in different percentages. Also in these mixtures sodium silicate (Na_2SiO_3) is used at a concentration of 5% Na_2O, expressed as a percentage by total weight of the cementitious materials. In the manufacturing process of the mixtures aggregate and cementitious materials were dry mixed for a time five minutes later on dry materials enough water was added sodium silicate and plasticizer and the mixing was continued for five minutes.

2.1.2 Fly ash- steel slag

Binary mixtures of fly-ash, blast furnace slag were activated by combining 85% NaOH 14M and 15% sodium silicate. As main cementing materials it was used and additions of fly ash, blast furnace slag in different percentages. In the manufacturing process of the mixtures aggregate and cementitious materials were dry mixed for a time five minutes then on the dry materials enough and activating said liquid plasticizer and the mixing was continued for five minutes. Each fresh mixture was poured into molds; appropriately rammed and compacted by traditional methods. Mixtures with different contents of fly ash were cured under a regime of 85 ° C for 24 hours and specimens were demoulded later; and housed in a storage room with room temperature until the day of test. Particularly, specimens of the mixture with 100% slag (PC0-FA0-BFS10) were demoulded and stored under humid conditions (90% RH) until the test day.

2.2 Characterization

2.2.1 Electrochemical characterization

The electrochemical characterization was performed on a potentiostat / galvanostat, through the techniques of half-cell potential and electrochemical impedance spectroscopy using a cell consisting of a graphite counter electrode, a reference electrode, Cu/CuSO4 electrode and as structural steel work NTC 2289 was used with an exposed area of 10 cm2. Electrochemical measurements were performed for the concrete at 0, 3, 6, 9 and 12 months exposure to a solution composed of 3.5% Sodium Chloride Solution [16].

2.2.2 Chloride Ion Permeability

To evaluate the performance of concrete added with fly ash and steel slag against the penetration of chloride ions, the test was performed rapid chloride permeability based on the ASTM C1202 standard. These tests were performed after 28 days of curing.

3. RESULTS

3.1 Chloride Ion Penetrability

Among the main causes of the premature deterioration of the concrete from the effects of corrosion, it is framed in the penetration of chloride ion because their income generating chemical oxidation and reduction reactions with the metal can be present for several purposes should further consider the porosity of the cement mixture that can indicate the status of each of the mixtures rapid Chloride Permeability Testing.

In Figure 1, the result of step load to each of the mixtures analyzed is observed values are the average of the mixtures studied adjusted in accordance with the ASTM C1202 test RCPT These values are expressed as load in Coulombs (C) and they are the result of the numerical integration of current versus time curves.

The results indicate that the permeation of chloride ion is high in all mixtures containing Portland cement, this is characteristic in particular with high Portland cementing relationships. However, mixtures of concrete with fly ash and steel slag they have lower load magnitudes with respect to a concrete with Portland cement content. For each type of concrete as the ratio of cementitious Portland is increased the load values are increased proportionally. In this particular case the change in magnitude of load became more pronounced in the concrete by varying the ratio of fly ash [17]. This is because a pozzolanic action is achieved when the added expanded rich in silica is combined with the calcium hydroxide released during cement hydration. This decreases the permeability and minimizes leaching of soluble compounds which reduce the possibility of action of sulphates however, the quality of the matrix of Portland cement paste, it presents high levels of air and low cement content and offers greater resistance to chloride intrusion.

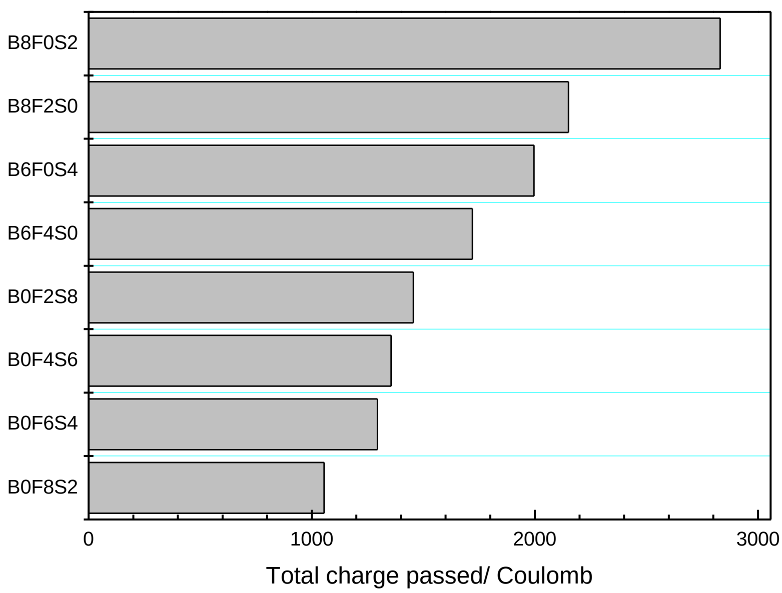

Figure 1. Measurement of the total charge passed in each of the binary mixtures.

3.2 Half-cell potential

In Figure 2, the corrosion potential versus time is determined, variations were measured within 3 months where the corrosion potential sets a trend according to the cementitious mixture. This value is obtained by taking a corresponding two trends to consider that an active state of corrosion and the other in a state of corrosion probability [18-19]. The behavior of concrete mixtures to be part of an electrochemical cell so high variation in each system analyzed is observed. The potential decreased considerably to increase the ratio of Portland cementing. Relations with a corresponding high percentage to 80% of portland cement generate corrosion states further deterioration when compared to other mixtures tested. Not so with the mixture you have no cementing Portland since the potential values are higher taking a trend to protection of steel so you can establish a relationship so that materials with better performance against corrosive phenomena [20].

The time indicates the evolution of the corrosion process with the variation of corrosion potential. Reinforcing steel in concrete with a composition of 80% and 20% Portland fly ash or steel slag increases its corrosion rates to moderate levels generally higher than in concrete containing industrial byproducts. The electrochemical measurements in early instances of corrosion are described by their tendency application of criteria and speed ranges of corrosion processes that their exact numerical values. This is observable due to the complexity of the methods and because dispersions are presented to nine months of evaluation. However, they are very good indicators of the corrosion behavior of metal on concrete. On the other hand, determining the corrosion potential depends on the measure of the strength of concrete, as with the EIS is a well-known non-destructive electrochemical technique for measuring the impedance of a system at different frequencies [21-22].

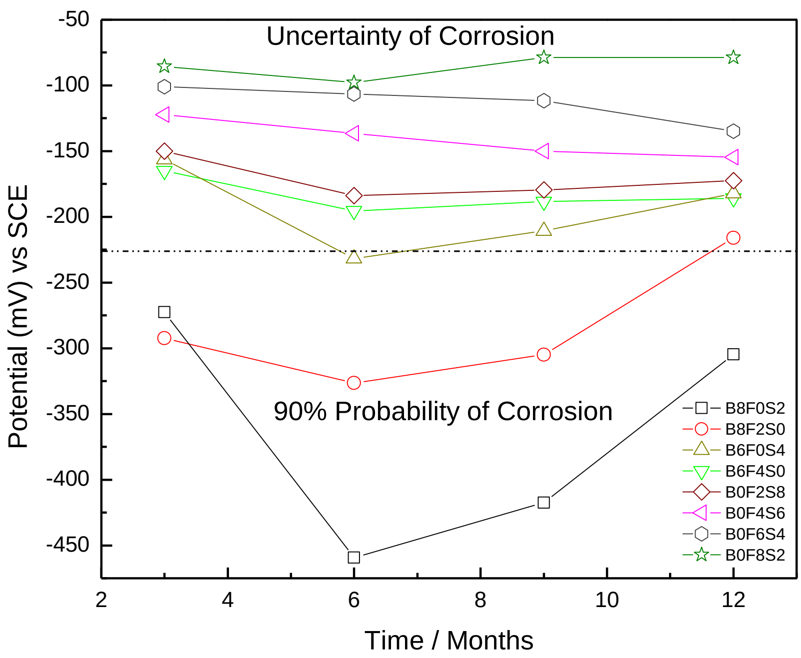

Figure 2. Half-cell potential of the different binary mixtures evaluated for 12 months in a system containing chloride ions.

3.3 Electrochemical Impedance Spectroscopy

In Figure 3 and 4, Nyquist plots where behavior obtained in the frequency range applied in the trials is observed, was between 10^{-2} and 10^{5} Hz. The high frequencies greater than 104 Hz, describe the behavior of the cementitious matrix, intermediate frequencies; between 10^{1} and 10^{4} Hz, describe the behavior of the porous film formed on the steel-concrete interface and low frequencies lower than 10^{1} Hz, define the processes of charge transfer and diffusion of the interface steel-corrosion products.

In Figure 3, 90 days after a curing period of 28 days in untreated water and air dried for 7 days the first measurement taken to the specimens shown in potentiostat. In the Nyquist diagram for high and middle frequencies namely from 10^{1} Hz to 10^{5}, corresponding to the mortar matrix (>10^{4} Hz) and to the porous layer formed by hydroxides (between 10^{1} and 10^{4} Hz), samples with fly ash and steel slag shows that the points form a circle while the no fly ash and steel slag, are disorganized about the real axis [23]. This indicates that while in the spiked samples without the presence of Portland cement a system of capacitance and resistance is best glimpsed resulted in greater obstruction of pores in the matrix in samples without the addition of cementitious Portland is less interference in the pores (less capacitance) virtually only generated ion flow resistance through the pores unobstructed, namely, ion flux is more direct in mixtures high in Portland.

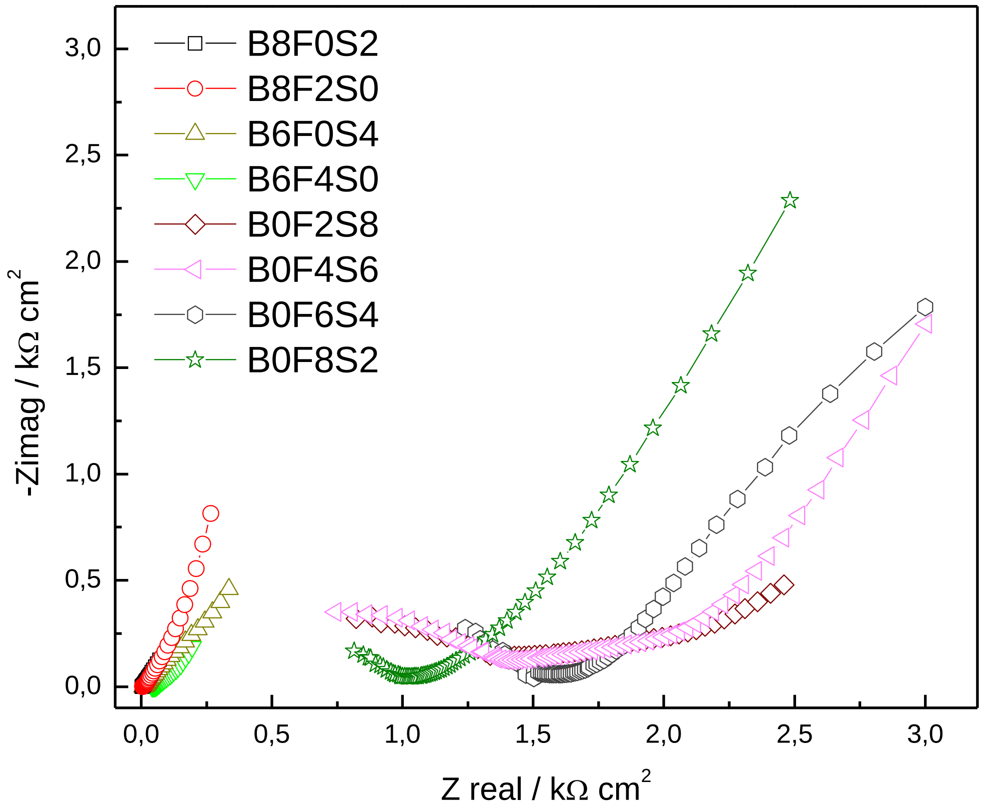

Figure 3. Diagram of Nyquist binary mixtures evaluated after of the curing and for 90 days subjected to the chloride ion penetration.

In addition, points of high and medium frequencies, for samples with mixtures of fly ash and steel slag,they are further displaced on the real axis with respect to the matrix with only Portland, indicating a greater resistance to the passage of ions in mortars with fly ash, this is consistent with the foregoing [24]. For low frequencies, that is lower than 101 Hz representing the interface of the steel and corrosion products (gray area) in both cases with a similar slope lines they are appreciated no tendency to close at the lower frequencies indicating predominance of passive behavior on the rods, namely, when the specimens were pickled melted without the protective oxide film and thus active, after the curing period have such protection, therefore, the curing time necessary to passivate the rod is estimated at around 6 days [25]. Therefore, at 90 days the samples with additions to have higher clogging their pores offer more resistance to ion flow through the matrix samples Portland only ensuring greater protection for the embedded reinforcement in the middle reducing the instability of the protective layer product steel passivation. In Figure 4, it shows that at 12 months of immersion in a solution of 3% NaCl, Notably, high and intermediate frequency the capacitive behavior of the samples with Portland cement is diminished (compared to that observed in Figure 3) and resistance to ion flow (displacement of the points to the left) which can be interpreted as the involvement of chlorides to add mortar generating reactions that lead to the breakup of the obstructions that prevent ion flux, due to a passivation (deterioration of the protective film) of steel [26].

In Figure 4, it shows that at 12 months of immersion in a solution of 3% NaCl, Notably, high and intermediate frequency the capacitive behavior of the samples with Portland cement is diminished (compared to that observed in Figure 3) and resistance to ion flow (displacement of the points to the left) which can be interpreted as the involvement of chlorides to add mortar generating reactions that lead to the breakup of the obstructions that prevent ion flux, due to a passivation (deterioration of the protective film) of steel. Not so in the samples with fly ash and steel slag, where a significant drop is not seen in the flow resistance, otherwise by an increase in impedance, at high and middle frequencies, the impedances remain higher in the matrix with alternative cementitious mixtures [27-28].

For low frequencies, relaxation is seen in the passive film specimens containing Portland (decrease in phase angle), reducing its impedance, whereas those added with sub industrial products impedance indicates an increase. Impedance, representing resistance to reactions that form corrosion products, it remains higher on the rod embedded in mortars with mixed with Portland cement a percentage which can be seen in Figure 4, where the time constant is less frequently than with cementitious mortar of steel slag and fly ash. This can be explained as a predominance of the reactions that tend to form the passive film in mortars added and a predominance of the reactions tend to consume the passive film in added with Portland, ie, in both cases two reactions occur, but at some point one of the two prevails over the other. Measurements at 6 and 9 months, in high and middle frequencies, substantially increased resistance to ion flow is zero, it is a little higher in the samples without Portland, However, does not exceed the impedances presented in matrix. Likewise, despite increases in impedance in mortars with Portland, you never get to overcome presented at 28 days of curing and 3 months of evaluation before permanent exposure to chloride attack by immersion in solution of sodium chloride (NaCl) to 3%. At low frequencies, the passive film on the samples is achieved without adding stabilize, while those with Portland continues rupture of the passive layer and for the first time the impedance presented by these samples is less than the one containing the pozzolan. The above, it is understood as the breaking filtered chloride added through the matrix products as internal reactions within the matrix altered the protective layer of the steel.

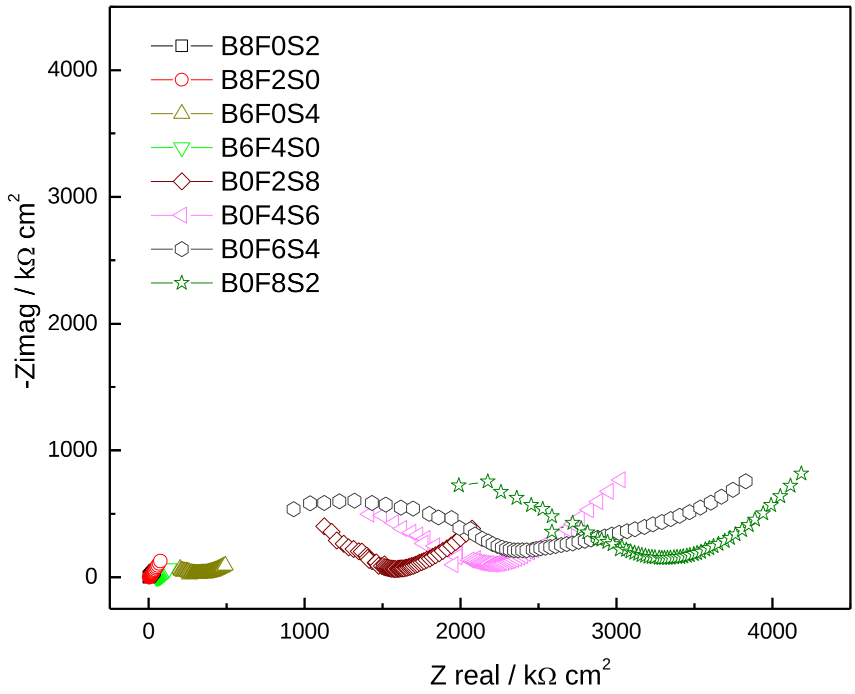

Figure 4. Nyquist diagram of binary mixtures subjected to processes of wetting and subsequent drying with saline solution simulating sea conditions, for 12 months.

4. CONCLUSIONS

The impedances in the matrix with cementitious material with high content of fly ash and steel slag they are higher in all ages to the concrete added with Portland, therefore, chlorides attack affected more specimens spiked with traditional concrete the least affected correspond to higher resistance to Ionoflux. At low frequencies, where corrosion products are generated samples with fly ash and steel slag present time constants greater than non-additions resulting in higher impedance than that of Portland only samples in most cases. However, in the last measurement the impedance at the interface of the steel-mortar is lower in specimens with metakaolin with respect to those without, which, as it cannot be due to leakage of chlorides through the pores of the matrix, which is greater in the matrix with Portland, but to a product caused by internal reactions in the mortar added with fly ash and steel slag which is not presented in the added with Portland.

The electrical behavior of the concrete in the electrochemical cell could simulate a capacitor or capacitor capable of storing and releasing electrical energy containing an electric field and it is having two surfaces the metal reinforcing steel and saline testing. In processes of load and electric shock, when there is a capacitor in a circuit current flows there are current flows the dependent logarithmic functions dependent logarithmic functions. Not enough to make the test for resistance to polarization parallel tests such as electrochemical impedance spectroscopy must be done with which one can determine the resistivity of the concrete. The determination of the half-cell potential determine the corrosion potential and is related to the state of corrosion.

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References

1. T. Ruan, N. Spandley, C. Johnson, A. Poursaee, *Fire Saf. J.*, 78 (2015) 196
2. N.M. Ahmed, M.G. Mohamed, M.R. Mabrouk, A.A. ELShami, *Constr. Build. Mater.*, 98 (2015) 388
3. V. Maruthapandian, S. Muralidharan, V. Saraswathy, *Constr. Build. Mater.*, 107 (2016) 28
4. J. Ožbolt, G. Balabanić, M. Kušter, *Corros. Sci.*, 53 (2011) 4166
5. S. Muthulingam, B.N. Rao, *Corros. Sci.*, 82 (2014) 304
6. R.G. Duarte, A.S. Castela, R. Neves, L. Freire, M.F. Montemor, *Electrochim. Acta*, 124 (2014) 218
7. A. Michel, A.O.S. Solgaard, B.J. Pease, M.R. Geiker, H. Stang, J.F. Olesen, *Corros. Sci.*, 77 (2013) 308
8. Y.G. Du, A.H.C. Chan, L.A. Clark, X.T. Wang, F. Gurkalo, S. Bartos, *Eng. Struct.*, 56 (2013) 8
9. K.G. Papakonstantinou, M. Shinozuka, *Eng. Struct.* 57 (2013) 306
10. T.T.H. Nguyen, B. Bary, T. de Larrard, *Cem. Concr. Res.*, 74 (2015) 95
11. J.L.S. Ribeiro, Z. Panossian, S.M.S. Selmo, *Constr. Build. Mater.*, 40 (2013) 40
12. S. Muthulingam, B.N. Rao, *Corros. Sci.*, 93 (2015) 267
13. M. Shafqat Ali, Chenhui Ji, M. Saeed Mirza, *Constr. Build. Mater.*, 93 (2015) 317
14. A. Królikowski, J. Kuziak, *Electrochim. Acta*, 56 (2011) 7845
15. M. Tapan, R.S. Aboutaha, *Constr. Build. Mater.*, 25 (2011) 2596
16. L. Hariche, Y. Ballim, M. Bouhicha, S. Kenai, *Cem. Concr. Compos.*, 34 (2012) 1202
17. J. Wei, X.X. Fu, J.H. Dong, W. Ke, *J. Mater. Sci. Technol.*, 28 (2012) 905
18. A. Kaya, M. Dawood, B. Gencturk, *Constr. Build. Mater.*, 94 (2015) 20
19. S. Soleimani, P. Ghods, O.B. Isgor, J. Zhang, *Cem. Concr. Compos.*, 32 (2010) 360
20. L. E. Narváez, R.I. Rosales-Martínez, L. Narváez-Hernández, L.S. Hernández- Hernández, J. M. Miranda-Vidales, *Int. J. Electrochem. Sci.*, 10 (2015) 10003
21. A. Bautista, S.M. Alvarez, E.C. Paredes, F. Velasco, S. Guzman, *Constr. Build. Mater.*, 95 (2015) 186
22. T. Wells, R.E. Melchers, *Cem. Concr. Res.*, 61–62 (2014) 1
23. W. Aperador, A. Delgado, J. Carrillo, *Int. J. Electrochem. Sci.*, 8 (2013) 7713
24. M.C. García-Alonso, M.L. Escudero, J.M. Miranda, M.I. Vega, F. Capilla, M.J. Correia, M. Salta, A. Bennani, J.A. González, *Cem. Concr. Res.*, 37 (2007) 1463
25. N.K. Brown, M.J. Kowalsky, J.M. Nau, *J. Constr. Steel Res.*, 107 (2015) 111
26. E.A. Flores-Johnson, Q.M. Li, *Compos. Struct.*, 94 (2012) 1555
27. W. Aperador, R. Mejía de Gutiérrez, D.M. Bastidas, *Corros. Sci.*, 51 (2009) 2027
28. H. Nahali, L. Dhouibi, H. Idrissi, *Constr. Build. Mater.*, 78 (2015) 92