Comparison of Electrochemical Properties Between Portland Cement, Ground Slag and Fly Ash

W. Aperador[*]*, J. Duque, E. Delgado*

School of Engineering, Universidad Militar Nueva Granada, Bogotá-Colombia
[*]E-mail: g.ing.materiales@gmail.com

With the aim of generating solutions against the deterioration of the steel embedded in the concrete are studied three cementitious systems obtained from: Portland cement, steel blast furnace slag and fly ash from coal-fired power plants. The main objective was to compare the mechanical performance and durability of each of the systems independently. The cement with steel slag and fly ash alkali activated by combining alkali activators: sodium silicate and sodium hydroxide. The characterization of the powdered raw materials and products formed reaction was performed by analysis of X-ray diffraction. The evaluation of mechanical properties was performed in compression then the concrete will be exposed to the entry of aggressive agents such as chloride ions during 24 months, time when their electrochemical properties were evaluated. The results for various mixtures indicate that these alternative materials (fly ash and steel slag) generate adequate mechanical and durability performance.

1. INTRODUCTION

Alternative concrete obtained by mixing different types of minerals, waste and industrial byproducts. Many times, these materials do not meet the specifications to be classified as suitable materials for incorporation into cement and concrete. By applying alkali activation technology, they can be properly harnessed and transformed into new energy-saving materials, characterized by presenting high durability and excellent mechanical performance [1-2].

Actually they have conducted research to actively participate in the development of world problems, both socially and in technology, environmental and economic [3]. A breakthrough to new technologies, materials and environmental conservation is achieved through the contribution they make to innovation processes and the development of alternative building materials to traditional

Portland cement in the manufacture, non-polluting gases are emitted. Is obtained a considerable energy saving and the service life of the structures increases [4-5].

The incorporation of industrial wastes as raw materials in these fields of construction and encourages the development of new industries and the possibility of increased competition in the markets [6-7]. The steel slag and fly ash; is one of the world waste materials with the greatest potential to be used as raw material in the production of concrete with alternative technologies lower power consumption for processing and preparation over traditional Portland concrete [8-9].

The steel slag and the fly ash is used as a partial replacement for Portland cement rather than when aggregate volume due to the high cost of Portland cement, that is attributable to high energy consumption for the production of Portland cement [10-11]. The traditional way to use the slag and fly ash is partially replace Portland cement which normally it produces a low compressive strength at early ages [12]. The presence of an activator can accelerate dissolution of structure; and hydration of the steel slag and fly ash. Some research results have indicated that the steel slag and fly ash mixtures made separately and activated with Portland cement exhibit increases in compressive strength denser structure and good durability compared with Portland cement [13].

At the global level research has been conducted in which mixtures made of coal ash and slag in different fields of engineering [14-15]. Nevertheless, they have not been evaluated properties corrosion or suitability for construction. Slag and fly ash they have some significant impact on the performance of reinforced concrete structures [16]. Considered the most important the huge reduction in the rate of penetration of chloride ions into the concrete and increasing the critical concentration of chloride to the induced corrosion [17-18].

Therefore, this research was performed in order to replace Portland cement is within the sustainable development, economic growth comprising ecological balance and social progress. The concrete of steel slag and fly ash, part of these materials. As well as meet the required mechanical properties during manufacture using waste materials from other processes.

2. EXPERIMENTAL DETAILS

To study the mechanical and electrochemical properties is used specimens with and without steel bars embedded in three types of concrete were used those based on alkali activated slag (AAS), those obtained with fly ash and Portland cement made from Type I (OPC) commonly used in construction. Cylindrical specimens of 10 cm diameter and 20 cm length were prepared. Mixtures of alternative cementitious materials used as granulated activated furnace slag and fly ash "sodium silicate" (Na_2SiO_3) at a concentration of 5% expressed as Na_2O weight percent to incorporate in slag, with a ratio SiO_2/Na_2O of 2.4. The commercial Portland cement mixtures used without any additive. The manufacture of concrete mixtures in the three cases containing a dosage of cementitious material of 380 kg / m^3. It is assumed that the water / cement + activator solution and water / slag are equivalent; in the three mixtures that ratio was 0.5 in order to obtain proper seating (92 mm).

The type, composition, size of the fine and coarse aggregate was the same for different types of concrete. Corresponded to a gravel maximum size of 19 mm, specific gravity of 2.94 g/cm^3, compact unit mass of 1.86 kg/cm^3, loose unit weight of 1.70 kg/cm^3, and absorption of 1.3%.

An arena with specific surface area of 2.47 g/cm^3, compact unit mass of 1.67 kg/cm^3, loose unit weight of 1.58 kg/cm^3, absorption of 2.9%. Additionally, located in the center of the bore and parallel to the length direction of the specimen with a coating of 2 cm measured from the underside of the cylinder, in each specimen structural steel bar ½ " and of length equal to 20 cm is imbibed in this way, with the coating adopted, the steel rod 2 cm protruded on the upper face of the cylinder so that could be used as a working electrode for electrochemical measurements. Finally, the specimens were cured under various conditions for a period of 28 days, the setting of Portland cement specimens was achieved by immersion under water to achieve adequate curing and activated slag specimens were conditioned for curing a controlled environment with 90% relative humidity and constant temperature of 25 ° C. Fly ash mixtures were cured under a regime of 85 ° C for 24 hours and subsequently their specimens were demolded and housed in a storage room at ambient temperature until the day of test.

The mixture proportions are related to the abbreviations; B, F and S, They were used to identify Portland cement materials (B), fly ash (F) and blast furnace slag (S) respectively, for its acronym in English. Also, They were introduced to the nomenclature replacement percentages principal cementitious material: for example, B0F10S0 represents the mixture of 0% Portland cement, 100% fly ash and 0% blast furnace slag; B1F0S0 represents the mixture of 100% Portland cement, 0% fly ash and 0% blast furnace slag; and B0F0S1 represents 0% the mixture of Portland cement, 0% fly ash, and 100% blast furnace slag.

2.1. Testing Method

The study was performed characterization tests of electrochemical and mechanical properties of plain concrete; and concrete reinforced with steel bar. These tests were performed in order to determine the effect of the corrosive environment on the mechanical properties, ie, degradation of its strength and performance.

2.2. Mechanical test

For mechanical testing an automated system that controls a hydraulic press with 2000 kN capacity was used, which it was used for compression tests on cylinders.

2.3. Chloride Ion Permeability

To evaluate the performance of concrete added with fly ash, Portland 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.

2.4. X-ray powder diffraction (XRD)

To determine the crystal structure type PW1710 diffractometer was used the Ka line of copper (1.540998 Å). Measurements were performed with a current of 30 mA a potential difference of 40 kV, and with a sweep of 30° to 90° (2θ) configured with a time step of 0.50 s and a step size of 0.02 ° (2θ) in continuous mode, XRD measurements were performed in Bragg-Brentano geometry.
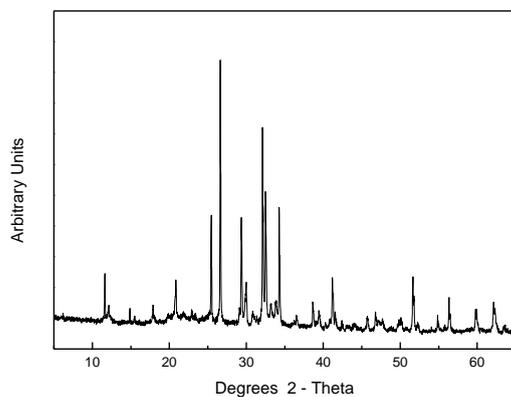
2.5. Electrochemical test

The electrochemical characterization was performed in a potentiostat / galvanostat model Gamry PCI 4 (circuit potential measurements and electrochemical impedance spectroscopy) using a cell consisting of a stainless steel counter electrode, a reference electrode saturated calomel working electrode and as structural steel (UNS G10200) was used. All electrochemical tests were performed under immersion in a solution of distilled water. The corrosion potential tests were performed in a time 12000 seconds until it reached the stabilization. Tests Electrochemical impedance spectroscopy is performed by applying a potential of 5 mV, the range of frequencies applied in the test was between 10^{-2} and 10^5 Hz and measures for different specific, were made in a period of 6 months for 2 years. The specimens were subjected to a corrosion process 24 months immersed in a solution of 3.5% NaCl.
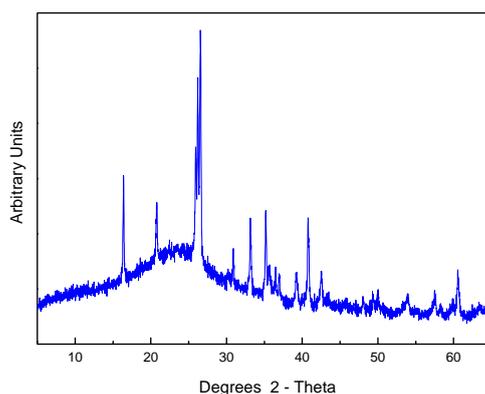
3. RESULTS

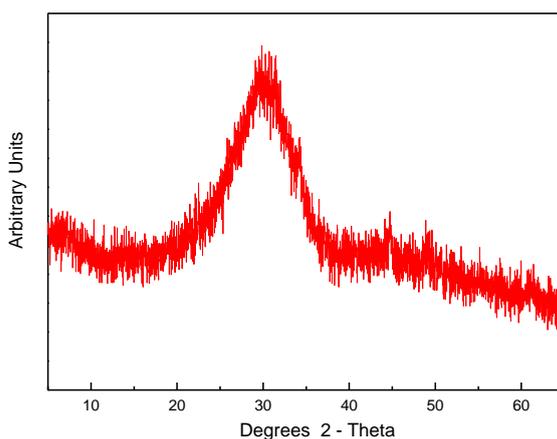*3.1 Characterization by X-ray diffraction measurement*

X-ray powder diffraction pattern for the three original materials studied are show in Fig. 1. Both slag, fly ash and Portland. Mineralogical analysis carried out through XRD on the pastes at 28 days of reaction showed clear differences in the identified phases of the activated raw materials, see Fig. 1a, 1b and 1c. In the activated slag paste with the alkaline solution, consisted mainly of an amorphous phase, indicated by a wide and diffusive reflection in the interval of 20-35º angles 2θ , in the case of the fly ash and in the unreacted slag between 2θ = 25-35º [19-20]. The differences in the location of this hump were associated with the structural differences in the amorphous glasses present in the two raw materials. However, the spectra also contained a series of minority crystalline phases such as $Ca_2Al_2SiO_7$ (JCPDS 00-034-1236) for the slag and quartz (SiO_2, JCPDS 00-033-1161), mullite ($3Al_2O_3.2SiO_2$, JCPDS 00-015-0776) and hematite (Fe_2O_3, JCPDS 00-001-1053) for the fly ash, phases identified were sodium aluminosilicate hydroxide hydrate ($Na8(AlSiO_4)6(OH)24H_2O$, JCPDS 00-041-0009) and a C-S-H gel (JCPDS 00-033-0306) [21]. In the activated fly ash paste, the halo attributed to the vitreous phase in the initial ash to slightly higher angular values (2θ = 25-40º). This effect is indicating the formation of a sodium aluminosilicate hydrate (N-A-S-H) gel of amorphous nature and three-dimensional network. The crystalline phases (quartz, mullite and hematite) detected in the initial material remained apparently unaltered with the activation.

A

B

C

Figure 1. XRD patterns of concrete mixtures, corresponding to: a) the specific Portland is displayed after performing curing for 28 days, in part b) is represented by mixtures of fly ash, where an amorphous part is obtained and other crystalline, section c) has the spectrum for the mixture of steel slag wherein the alkali activate a purely amorphous structure is generated.

X-ray powder patterns for the alkali activated mixtures showed the formation of different reaction products, which varied depending on the percentage of each raw material, see Fig. 1a, but no new phases were detected. In the F2S8 mixture (with 80% of slag and 20% of fly ash), C-S-H gel and

aluminosilicate hydrate were clearly detected, whereas diffraction lines corresponding to quartz and mullite from the ash were very small. On increasing the content of the fly ash (from 40% to 80%) implied: i) a decrease in the amount of C-S-H gel and aluminosilicate hydrate, which were not detected in the F6S4 and F8S2 mixtures; ii) an increase in the amount of quartz and mullite; and iii) the width of the halo at 25-40º in 2θ became larger, meaning that the F8S2 mixture presented the highest proportion of N-A-S-H gel [22].

3.2 Testing for chloride permeability of concrete

The specimens after the curing process were subjected to a process of inclusion of chloride ions where the concrete with Portland load values presented in Coulombs greater than 4000. So having high chloride ion permeability, as an indicator of the susceptibility of the material to attack by chlorides [23-24]. This behavior indicates that the Portland such that reduce the quality of concrete. In terms of results with respect to mixtures of fly ash it can be seen that the samples had the lowest load values, compared with samples of concrete and steel slag Portland.
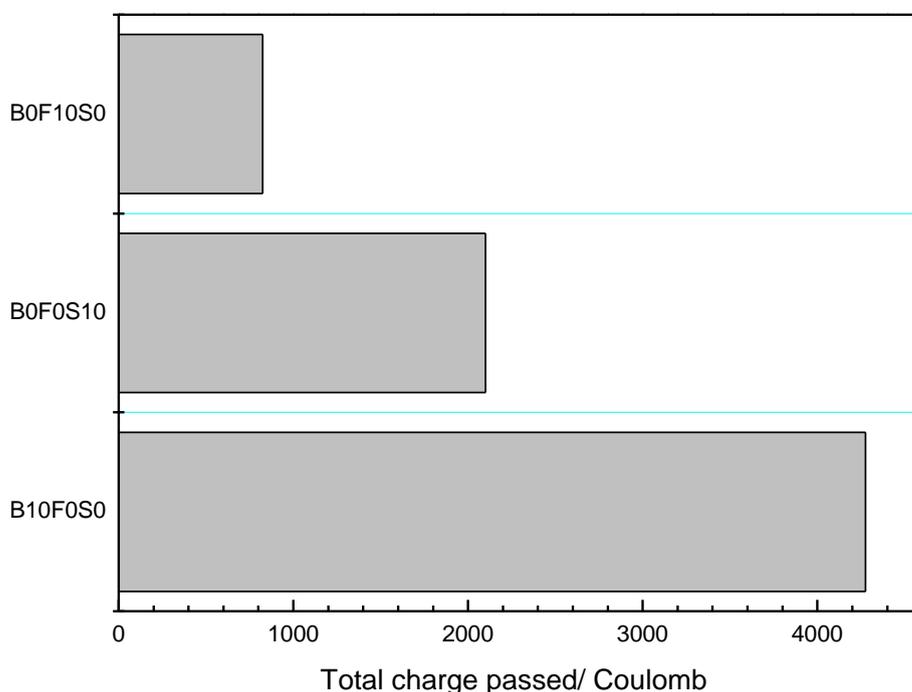

Figure 2. Total charge that passed through the specimen of the three mixtures evaluated, which is calculated relative to the current response after a potential is applied, this test is required because the charge is related to the resistance of concrete.

This is because the pozzolanic reaction due to the content of silica is combined with the calcium hydroxide released during cement hydration [25]. This decreases the permeability and minimizes leaching of soluble compounds which reduce the possibility of action of the chlorides, further the quality of the cement matrix it offers greater resistance to chloride intrusion, so the

transport is controlled by the permeability of concrete when there is a pressure differential between adjacent sections result in a movement of the fluid, this type of concrete to be denser less porous and dry concrete, it is less permeable [26-27]. Concrete obtained with steel blast furnace slag allows a higher income of chloride ions on the concrete compared to the fly ash aluminate phases react with chlorides to form an insoluble compound, this salt formation stops the transport of chloride ions; however, this incorporation produces damage and produce volume changes in concrete.

The figure 3 relates measuring half-cell potential with the condition of corroded steel in concrete system relative to the charge transferred in the material revenue product of chloride ion for 24 months [28-29]. It is noted that for the system obtained with fly ash presented the best performance since a greater amount of potential is reflected in the entire study period concrete with steel slag obtained also presents a similar behavior but with lower potential these two behaviors are associated with the load transmitted during evaluated, reacts with the cement matrix generating suitable values of corrosion potential, as a measure of corrosion compared with Portland where measurements show decreased potential for 9 months and this potential decreases, indicating a lower corrosion resistance so that the effect of chloride ion generated a decrease of the electrochemical properties [30].
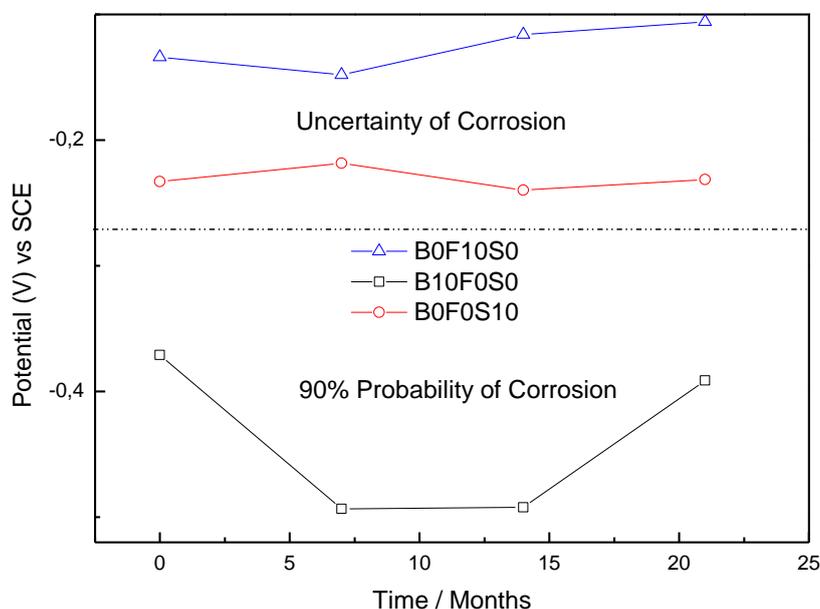

Figure 3. Variation of corrosion potential versus time of exposure required to probabilistically determine the state of the steel structure embedded in the concrete.

In Figure 4 mechanical strengths they are between 14 MPa and 32 MPa. As factors influencing the concrete strength is the content of cementitious and reaction time of the additives and curing, the ratio water / cement, properties of coarse and fine aggregate, the maximum size of lightweight aggregate, remained constant for three mixtures tested. The cementing must be controlled so that the mixture composition give better quality; that is to say; not always the most concrete offers greater resistance and this can be reflected in higher heat of hydration and cracking. The quality, shape, texture, grain size, maximum size, strength and absorption of lightweight aggregate thickness affects

the strength of concrete, because of this these relationships were left equally in each of the mixtures. Alternative curing concrete is quite rigorous, but has the advantage of presence of alkalies in the pores of activators added prolonging internal curing, this is one reason why the chloride ion no income to where the steel at the time of evaluation. The compressive strength is closely related to its density and unit weight, also depends on the size of the cementitious and shape so the more spherical as possible is recommended, thus, in this case it corresponds to the fly ash it is the most suitable since the resistance can be determined by several individually broken grains by slow compression in a cylindrical concrete.

The use of alkaline activators contributes to the properties of strength and durability. Because of this the concrete has high strength steel slag in concrete for their pozzolanic properties. Fly ash and slag have more extensive applications. They are used to improve the properties of durability and increase early compressive strength. Mixtures of fly ash and slag, is capable of initiating rapid hydration at early ages. Conventional concrete is a material that is often the weakest compared to the other systems components.
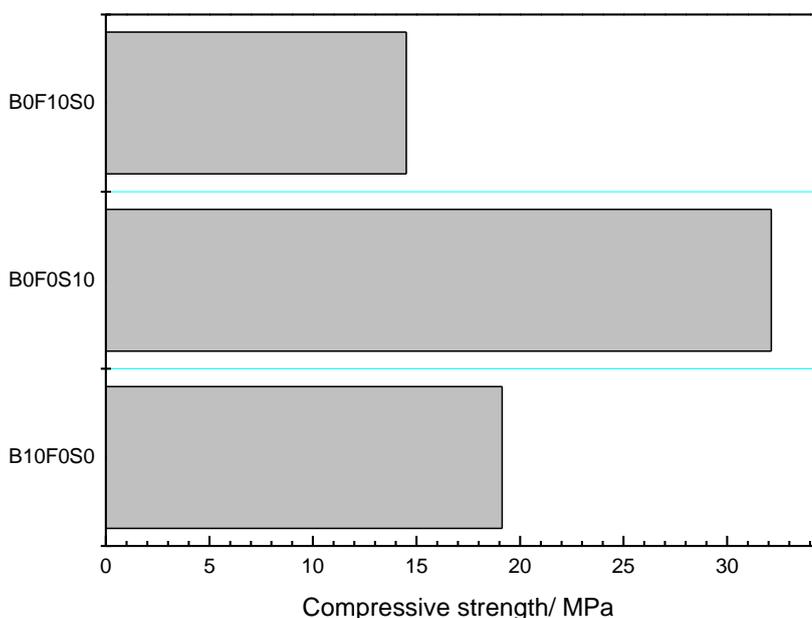

Figure 4. Determination of resistance to compression, wherein the average value of each series was conducted in nine cylindrical specimens following standard procedure ASTM C39 ; three cylindrical test specimens of each mixture were subjected to compression test at 28 days of curing. The specimens used were cured each in different conditions of temperature and relative humidity. Differences are framed in reactions by the alkaline activator and the total porosity.

In Figure 5 Nyquist curves at 90 days was observed after a period of 28 days cure, it is noted that tends to form a semicircle at high and intermediate frequency samples with steel slag and fly ash, but there were differences in samples with only ordinary Portland which points to high frequency (greater than 10^4 Hz) are scattered in a disorderly way. This indicates that samples with alternative cements have fewer pores that act as input to ion flow better behaving like a capacitor making it forced

the entry of ions over conventional mortar where more pores are presented and therefore ions are more entries into the specimen not clearly defining a semicircle to represent a good capacitor [31].

In the Nyquist plot, at low frecuency, corresponding to the interface steel-concrete specific frequencies, the tendency to form semicircles made lower frequencies which are outside the range of measurement comprising a capacitive behavior by the presence of the protective film is observed the steel. It is higher, if extrapolated, the semicircle on the specimens with fly ash suggest better protection in the steel shown. In the curve of the specimen with steel slag it is also seen an inflection point at low frequencies indicating concentration changes electrochemically active species by diffusion processes processes representing mass transfer at the interface which is defined as Warburg impedance. In the specimen with Portland this does not happen simply stating no opposition from the layer [32].
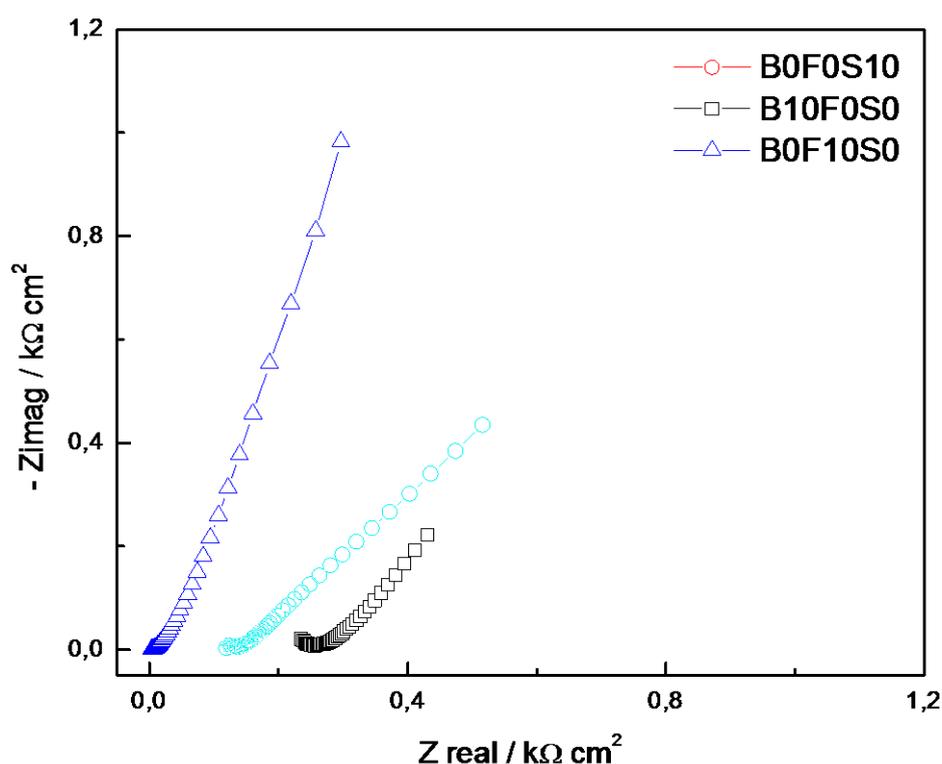

Figure 5. Nyquist diagrams for concrete-steel systems of the three mixtures evaluated at 3 months of exposure of the chloride ion penetration.

In the Nyquist plot of Figure 6 the behavior of the samples analyzed is displayed to 24 months, something like that in the 90 days analyzed system, because for high intermediate frequency (greater than 10^1 Hz) impedances are significantly higher in samples with fly ash and steel slag is identified in Portland, which is transmitted at low frequencies, representing the steel-concrete interface, where the impedance is higher in the rods embedded in mortar with fly ash, although the difference is not as marked with the steel slag [33]. The slope presented at low frequencies in both cases indicates a protective film occurs at the interface. Points higher frequencies to 10^4 Hz in the mortar without addition they correspond to an area where a resonance frequency occurs (phase angle zero, in which

capacitive and inductive behavior cancel) actually indicating resistance in the electrolyte solution, where the current flows freely.

In the diagram, at high frequencies more negative phase angles can be seen in the concrete of fly ash and steel slag, confirming their best behavior as capacitor, resulting in its time constant (represented by the peak of the curve or inflection point) by above 10^5 Hz, while for the specimens of Portland peak is low (angles close to zero phase) and is between 10^4 and 10^5 Hz, indicating a less capacitive behavior. This also indicates that the frequency ranges to study the concrete with fly ash and steel slag are wider and higher at 10^5 Hz than just Portland, up to 10^5 Hz, which must be related to the greater difficulty of income ion current in the first sample [34]. For three mixtures after the evaluation at 24 months of inducing corrosion at high and middle frequencies are still appreciating the increase in impedance, however low, these are reduced, indicating instability in the passive film, being most noticeable in specimens with Portland.

The stability of the passive film remains stable in the samples of fly ash and steel slag, this because fewer pores occurs and thus reduced transmission of chloride ions; somehow affirming that products that seal the pores in the samples with Fly Ash and Steel Slag affect the pH in the interface increasing it; and decreasing corrosion processes (the relationship Cl^- / OH^+ apparently greater in samples with Portland).
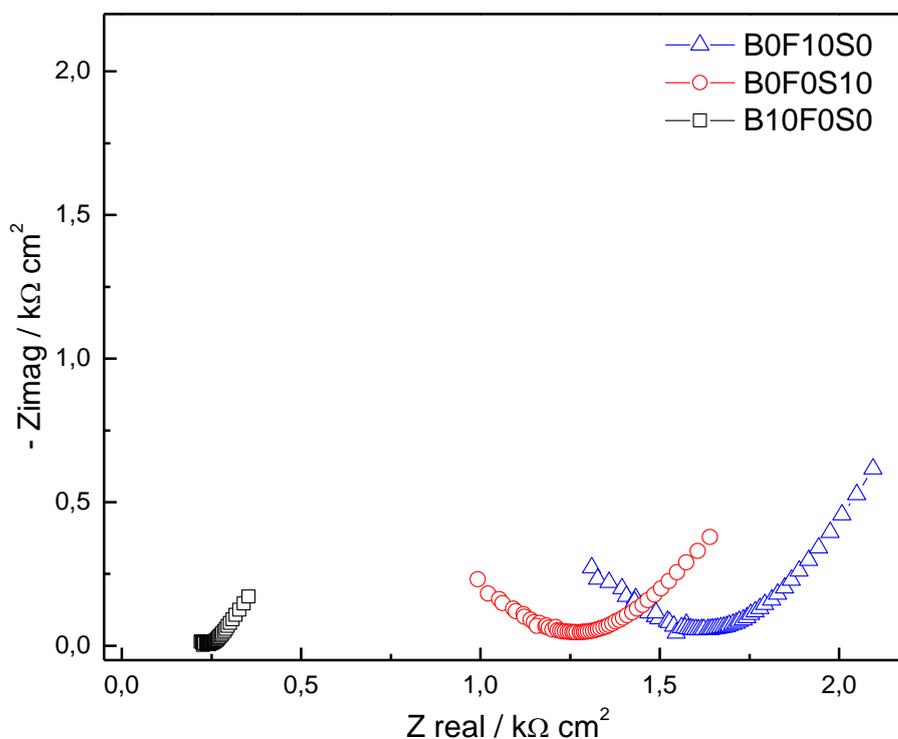

Figure 6. Nyquist diagrams corresponding to the electrochemical properties of the steel-concrete evaluated 12 months' exposure systems. These can be seen in the difference because the cementitious mixtures containing fly ash and steel slag has values very high corrosion resistance.

4. CONCLUSIONS

The behavior between samples with fly ash and steel slag it is similar to that presented to the 24-month assessment, ie an improved performance in the samples with pozzolans. However, in the course of 90 days immersion in sodium chloride solution of 3% (3% NaCl), the impedances at high and intermediate frequencies were low, something which is suitable for this type of concrete, because 28 days curing was performed measurement, by which the samples were completely saturated in its pores, representing less resistance to ion flux, while the long age, after the period of immersion for two years chloride ion, ions they can flow more easily through the pores saturated solution. Although the foregoing, capacitive behavior is maintained in the samples with alkali activated mixtures and improved in this. Indicating that the samples are in solution of 3% NaCl, the cementitious material present which has not been hydrated does, closing pores in the matrix this is most notable in the fly ash samples. For specimens with Portland the flow resistance of chloride ions is greater in these samples, due to rupture of the passive layer in Portland concrete and can be caused by chemical factors by lowering the pH by any product generated by reactions of the cementitious material with Portland.

References

1. L. Lei, J. Plank, *Cem. Concr. Res*, 60 (2014)1
2. A. Kanellopoulos, T.S. Qureshi, A. Al-Tabbaa, *Constr. Build. Mater.*, 98 (2015)780
3. J.F. Muñoz, T. Easton, J. Dahmen, *Constr. Build. Mater.*, 95 (2015) 86
4. E.K. Anastasiou, A. Liapis, I. Papayianni, *Resour. Conserv. Recycl.*, 101 (2015) 1
5. M.A. González-Ortega, S.H.P. Cavalaro, A. Aguado, *Constr. Build. Mater.*, 74 (2015) 169
6. M.K. Rahman, M.H. Baluch, M.A. Malik, *Constr. Build. Mater.*, 50 (2014)710
7. J. Ding, Y.C. Wang, *Eng. Struct.*, 29 (2007)3485
8. C.J. Moran, S. Lodhia, N.C. Kunz, D. Huisingh, *J. Cleaner Prod.*, 84 (2014)1
9. D. van Beers, G.D. Corder, A. Bossilkov, R. van Berkel, *Miner. Eng.*, 20 (2007)830
10. H. Merve Basar, N. Deveci Aksoy, *Constr. Build. Mater.*, 35(2012)508
11. O.A. Hodhod, G. Salama, *HBRC Journal*, 9 (2013)109
12. D. Kolokotsa, P. Maravelaki-Kalaitzaki, S. Papantoniou, E. Vangeloglou, M. Saliari, T. Karlessi, M. Santamouris, *Sol. Energy*, 86 (2012)1648
13. D.M.A. Huiskes, A. Keulen, Q.L. Yu, H.J.H. Brouwers, *Mater. Des.*, 89 (2016)516
14. E. Güneyisi, M. Gesoglu, N. Naji, S. İpek, *Arch Civ Mech Eng*, 16 (2016) 9
15. M.M. Villani, A. Scarpas, A. de Bondt, R. Khedoe, I. Artamendi, *Wear*, 320 (2014)179
16. B. Bournonville, A. Nzihou, P. Sharrock, G. Depelsenaire, *Process Saf Environ*, 84 (2006) 117
17. V. Corinaldesi, G. Moriconi, *J Bldg Eng*, 4 (2015)247
18. C. Lian, Y. Zhuge, *Constr. Build. Mater.*, 24 (2010)2664
19. N. Chousidis, E. Rakanta, I. Ioannou, G. Batis, *Constr. Build. Mater.*, 101 (2015)810
20. M.V. Diamanti, E.A. Pérez Rosales, G. Raffaini, F. Ganazzoli, A. Brenna, M. Pedeferri, M. Ormellese, *Corros. Sci.*, 100 (2015)231
21. M. Maslehuddin, F.R. Awan, M. Shameem, M. Ibrahim, M.R. Ali, *Constr. Build. Mater.*, 25 (2011)308

22. R.G. Duarte, A.S. Castela, R. Neves, L. Freire, M.F. Montemor, *Electrochim. Acta*, 124 (2014)218
23. T. Ruan, N. Spandley, C. Johnson, A. Poursaee, *Fire Saf. J.*, 78 (2015)196
24. A. Cañón, P. Garcés, M.A. Climent, J. Carmona, E. Zornoza, *Corros. Sci.*, 77 (2013) 128
25. M. Carsana, F. Tittarelli, L. Bertolini, *Cem. Concr. Res.*, 48, (2013) 64
26. P. Antonaci, C.L.E. Bruno, M. Scalerandi, F. Tondolo, *Cem. Concr. Res*, 51 (2013)96
27. A. Pérez, M.A. Climent, P. Garcés, *Corros. Sci.*, 52 (2010) 1576
28. C.C. Yang, C.H. Liang, *Mater. Chem. Phys*, 114 (2009) 670
29. M.M. Hossain, M.R. Karim, M.K. Hossain, M.N. Islam, M.F.M. Zain, *Constr. Build. Mater.*, 93 (2015)95
30. P. Garcés, M.J. Sánchez de Rojas, M.A. Climent, *Corros. Sci.*, 48 (2006) 531
31. A.J.J. van der Zanden, A. Taher, T. Arends, *Constr. Build. Mater.*, 81 (2015)120
32. S. Muthulingam, B.N. Rao, *Corros. Sci*, 93 (2015)267
33. 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
34. C.M. Hansson, A. Poursaee, A. Laurent, *Cem. Concr. Res*, 36 (2006) 2098