EVALUATION OF CORROSION OF STEEL EMBEDDED IN GEOPOLYMER CONCRETE IN CONTACT WITH ACIDIC SOILS

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ABSTRACT

In this article, electrochemical tests concrete cylinders obtained in a mixture of ground granulated blast furnace slag is studied. Assays were performed by stabilizing the half-cell potential measurement and then using electrochemical impedance spectroscopy, in a solution which simulates an acidic soil (variation pH = 4.0 to 5.5), test were performed for 12 months. In addition to the mechanical properties compared to the results of corrosion, it is characterized. After the evaluation period steels were extracted to determine the morphology and corrosion products through the techniques of scanning electron microscopy and X-ray diffraction.

Key words: Geopolymer, Blast furnace slag, Corrosion, Acid soils.

INTRODUCTION

Corrosion of steel embedded in concrete has limited industrial atmospheres or salts that characterize the marine atmosphere, nevertheless, there is very little information analysed corresponding to rural atmospheres in which there are a variety of inorganic chemicals that are used in farming; these include fertilizers, herbicides, insecticides and fungicides. Many of these compounds are corrosive and some are hygroscopic[1,2]. Organic materials include manures and crop residues. The fertilizer is usually acid coatings such compounds increase the time of wetting of surfaces. Ammonia from manure or fertilizers, it can also be aggressive. Steel and its alloys are particularly susceptible to corrosion by ammonia compounds[3].

One factor that increases the intensity of corrosion phenomenon in the atmosphere is the same chemical composition[4]. Sulphur dioxide (SO_2) and sodium chloride (NaCl), are the

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most common and significant corrosive agents in the atmosphere, although particles and hydrogen sulphide (H_2S) in particular cases are also important. NaCl is added to the atmosphere from the sea while far from it, air pollution depends on the presence of industries and population centers. It is the main pollutant by their frequency and impact on the corrosive process SO_2 from the burning of solid and liquid fuels containing sulphur[5].

The deterioration by high concentrations of sulphur dioxide (SO_2); it occurs more quickly in reinforced concrete, because of the content of SO_2, even considering that the presence of this pollutant volume is small[6]. About the cyclical process of formation of rust sulphur dioxide, this deterioration is due to the presence of two mechanisms: acid cycle regeneration, due to moisture and sulphur dioxide they are absorbed in the metal surface and thus the process of electrochemical oxidation of sulphur dioxide in the presence of dissolved oxygen occurs, when it accumulates enough on the metal surface corrosion product mainly oxide and ferrous sulphate, conditions are favourable for the existence of an electrochemical cell exchange[7]. With this mechanism, the amount of oxide and the corrosion rate increases and corresponds to the studies of the structure of the corrosion product layer on steel[8]. Therefore, sulphate ions react with hydrated calcium aluminates the cementitious ettringite forming, which it is very poorly soluble in water and causes a large increase in volume. This expansion that produces large internal tensions as usual. They cannot be absorbed by the material and triggers a series of cracks and surface material detachments.

Degradation mechanisms without a doubt the most difficult to understand are the chemical nature, because it is not only necessary to understand the behaviour of concrete as a single material, but also, the relationship of this with the steel that reinforces and different environments is subject[9]. List each of the substances or devices that are not compatible with concrete is a very extensive work and includes a number of variables. A large number of destructive processes due to salt formation may be related to the aggressiveness of sulphates. Causing the sulphate ion specific degradation may be present in soil or groundwater or ground water in aqueous solutions of sulfuric acid or salt forms sulphates are identified as anion SO_4. Salts of sulphates damaging the concrete are present mostly in selenite gypsum soils and groundwater of the same soil, it is worth mentioning that apart from water sulphate salts contain is made up of other salts whose chemical work together as well as exposure make medium to be severely harmful[10]. In humid environments, the sulphur is usually present in form of organic compounds. Sulphates can be readily dissolved to the ground while the combined sulphur as inorganic compounds provides increased resistance to being dissolved and transformed into it is gradually sulphates[11]. This transformation of organic sulphur in sulphate decomposition requires nitrogen content albumins in nitrates increasing the acidity of the soil. According to research conducted in different countries using artificial

fertilizers and manure significantly increase in the sulphate content in the soil, added to this it promotes soil cultivation soil aeration whereby at certain depths sulphur oxidation are increased in large areas why in cultivated soils sulphate concentrations can increase up to 100% on uncultivated soils[12].

The purpose of this study was to evaluate the reaction of the sulfate ions with geopolymeric concrete by electrochemical tests in a sulphate content, which may be contained in the soil and groundwater that could come into contact with the concrete they may have a certain amount of sulfur released sulfur dioxide in the presence of oxygen and moisture form sulfuric acid.

EXPERIMENTAL

The steel blast furnace slag was used for the manufacture of concrete specimens, based on the results of mechanical properties obtained in preliminary studies, indicating the proper performance of these materials. Cementitious mixtures used as granulated blast furnace slag activated "Sodium Silicate" (Na_2SiO_3) at a concentration of 5% expressed as Na_2O weight percent to incorporate slag with a SiO_2/Na_2O ratio of 2.4. The manufacture of concrete mixtures in both cases containing a dosage of cementitious material $350 kg/m^3$. It was assumed that the water/cement + activator solution and water/slag are equivalent this ratio was 0.5 in order to obtain proper seating (70 to 100 mm). As stone material fine aggregate was used river sand type of fineness modulus of 3.04 and absorption of 0.81%. As coarse aggregate fine gray gravel was used Nominal Maximum Size (TMN) of 12 mm.

Commercial structural steel ASTM A706 reference commonly used in earthquake-resistant construction was used with a diameter of 1/8" and without any pretreatment, during corrosion test steel was used as working electrode[13].

For the development of electrochemical tests, it is used as the external reference electrode Silver-silver chloride (Ag/AgCl) BAS Electrochemistry analytical type (MF-2052 RE-5B). A graphite electrode immersed in the test tubes served as counter electrode in all the tests.

To study the effect of degradation, it was performed in the aqueous solution that simulated the influence of sulphur dioxide in the concrete (SO_2) and nitrous oxide (NOx) and which sought sulphated the concrete structure we chose to saturate water with gas SO_2 and NOx. This was achieved by injecting both SO_2 and steadily, in the controlled atmosphere chamber, thereby obtaining a saturated solution of sulfuric acid where the function of the sealed chamber is justified due to the elimination in the form of gas SO_2.

The behaviour of steel was monitored using electrochemical techniques obtaining the values of corrosion potential and characteristics of the steel-concrete interface using electrochemical impedance spectroscopy. These procedures provide quantitative measurements of corrosion rates as a parameter of the activity or passivity of steel embedded in concrete. Potential measurements they were carried out using a commercial potentiostat-galvanostat Gamry PCI-4 taking measures for 1200 seconds to allow an equilibrium potential is established between the three electrodes. Spectroscopy for electrochemical tests impedance's a sinusoidal signal of 10 mV is applied in a sweep at different frequencies between 300 kHz to 0.1 mHz. Modelling electrochemical equivalent circuit was performed using commercial program Echem analyst.

Once completed electrochemical studies the specimens were opened longitudinally using a diamond blade cutter to visually study the concrete-steel interface. With the technique of X-ray diffraction corrosion products they were established formed and by scanning electron microscopy morphology of the products formed analysed concrete steel interface and other sites of interest in the specimens. The characterization was done with a software PANalyticalX'Pert PRO using Cu-Ka radiation with $\lambda = 1.54060$ Å, 40 mA and 40 kV, in the Bragg Brentano mode. The technique is performed in order to observe the surface morphology of the coatings, for this a scanning electron microscope Jeol 5000 with features in the filament 15 kV, 1.2 nA and chamber pressure equal to 9.8 x 10^{-6} was used Torr, using a secondary electron detector.

RESULTS AND DISCUSSION

Evolution of porosity

Obtaining geopolymers based on steel slag, it has been initially studied to obtain materials with compressive strength up to 70 MPa. This mechanical performance is largely due to its porosity, additionally, evaluated its performance against attack by acids. In Fig. 1, the type of concrete used in this study based on the volume of permeable pores is observed, this graph can be noted that; comparing the specific function of pH[13]. Those with higher pH value are those with least amount of permeable pores, however, the difference is minimal in all cases that is, to say which they are good quality concrete. A lower percentage to 10% in all cases indicating a significant decrease in porosity, which it may be due to the hydration products and to further densification of the paste, due to hydration products obtained at short times a lower percentage of pores. Concrete subjected to acid solution show an increase in the percentage of permeable pores income due to SO_2, which generates pores are interconnected and% porosity is increased.

As evidenced in the extent permeable pores the effect of the steel slag on pore connectivity is evident with the pH, since pozzolan reaction products and thus, they develop porosity decreases producing a refinement of the porous structure, this factor is linked with the durability of concrete, especially of reinforced concrete as by reducing the pore size capacity transporting liquids and aggressive gases through its limited porous system[14].
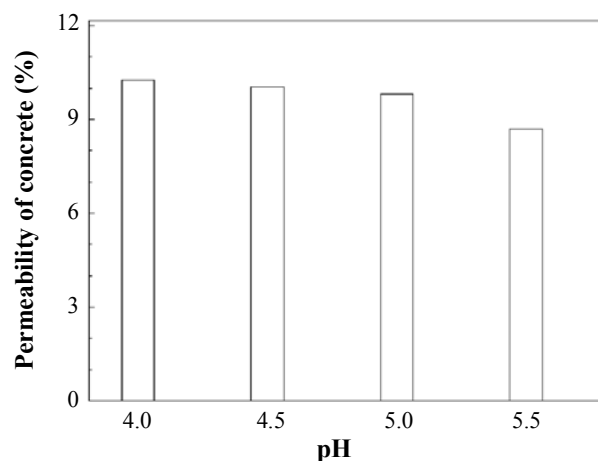

Fig. 1: Percentage of permeable pores function of pH, the alkali-activated cements subjected to sulphur dioxide

As it was established in this investigation, at the beginning of curing conditions 90% relative humidity the concrete has the same porosity values but after the year of assessment percentages decrease, this due to the effect of the acid solution.

Electrochemical evaluation

The technique of electrochemical impedance spectroscopy (EIS) is useful for evaluating corrosion of steel embedded in concrete alternative, it allows describing the various mechanisms, that have also allowed to precisely to give some important in each of the months where deterioration of steel bars embedded in concrete was assessed values the AC impedance method involves measuring the impedance while scanner frequencies is performed[15]. A diagram of the absolute values of the imaginary against the real component of impedance values several form semicircles. The frequency ranges used were between 0.1 mHz to 300 kHz, 300 kHz was found that 300 Hz are the frequencies at which it is possible to characterize the interface. The impedance spectra exhibit two arcs, the high frequency is the solution in contact with concrete and medium frequency are the cement matrix, the polarization resistance of the concrete increases, with evolution the pH[16]. The conductivity of the cement matrix pore in the alkaline concrete increases rapidly with time during the 6 months evaluated and then remains constant at 9 months.

The equivalent circuit of Fig. 2 has been proposed to model the electrical response of the systems analysed from chemical and microstructural considerations given by the entry of the acidic solution, the individual characteristics and microstructures have been considered in the context of its electrical responses[17]. This circuit has the following meaning: (Cf) the connected porosity, (Rf) blocked porosity (Cdl) hydration product generated by contact of the acidic solution, (Rct) resistance generated chemical reaction by alkaline activation (Ca) capacitance of ions entering the concrete and steel interface (Ro) non-reaction with hydration products.

For intermediate frequencies of 100 Hz to 0.1 Hz, information microstructure carried cement during hydration is obtained, here ranges spectra are mentioned and related components of the microstructure in this range you can be related to the distribution of pore sizes and thickness of the layers that separate pores, the conductivity is related to the volume fraction of porosity, the conductivity of the solution pore interconnectivity and porosity.
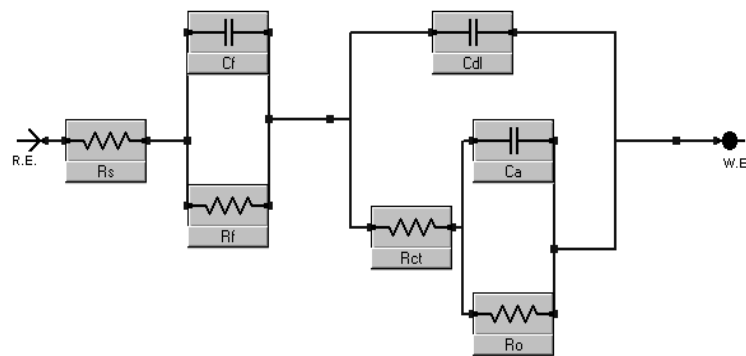

Fig. 2: Equivalent circuit model proposed concrete subjected to different concentrations of acid medium, varying pH

In Fig. 3, the effect of gas consisting of a sulphur atom and two oxygen (SO_2) chlorine ions on the breakdown of passivity of the steel in the simulation solution pore and reinforced concrete is observed[18]. In this case, the results clearly show that decreasing the pH influences the electrochemical properties. In all cases studied must be resistance Rs is given by the electrolyte (acid solution) through the pores of the matrix. However, since the content of the solution changed to achieve different pH; indicates that this resistance corresponds to that caused by the electrolyte but in the pores that maintain a direct connection, in this case, inside the specimen where the steel, i.e. the pores not present obstructions. Impedance generated for this reason, is at high frequencies greater than 100 kHz, which it depends on just how closed the pores of the matrix are hindering the ion flow.

In Figs. 3a, b, c and d, major discrepancies presented is relevant to the area of the matrix (The first semi dome generated in the curve of Nyquist) instead of taking a capacitor for this area replaces it with an element of constant phase called Cf1, also to function as a capacitor characteristics into account as roughness a normal capacitor, would not take account as it considers flat surfaces. Cf1 and Rf correspond to the capacitance and resistance caused by the interfacial zone and the cementitious matrix aggregates; however due to pH change can represent this film hydration products generated chemical reactions in the matrix are caused by these elements any obstructions the pores[18]. In any case, this capacitance and resistance correspond to elements present in the matrix and thus obtained values are attributable to it and not the steel. It obtained as other parameters correspond to the resistance to charge transfer, i.e. reactions consuming the protective layer of the rod by the corrosion process as time progresses assessment, being equivalent to the polarization resistance, and the capacitor formed by the passive layer that protects the steel, which it is also treated as an element of constant phase that takes into account the roughness of the layer.

Comparatively the Figs. 3a to 3d, sequence impedance diagrams samples relative pH shown, qualitative analysis was done on all samples to a period of 12 months. The deterioration suffered samples from previous ages is seen, presenting, at low frequencies, smaller impedances at the interface steel-matrix, i.e., greater destroy or damage slowly by chemical action, by the deterioration of the passive layer. Even at high and intermediate frequency matrix is immersed in the higher pH value is severely compromised with lower impedances over previous generations, however, when comparing with the lower value of pH = 4, these impedances increased, i.e., continued to reduce pores, while those with lower pH, sulphur dioxide forced their way. Therefore, further corrosion is confirmed in the samples with decreasing of pH.
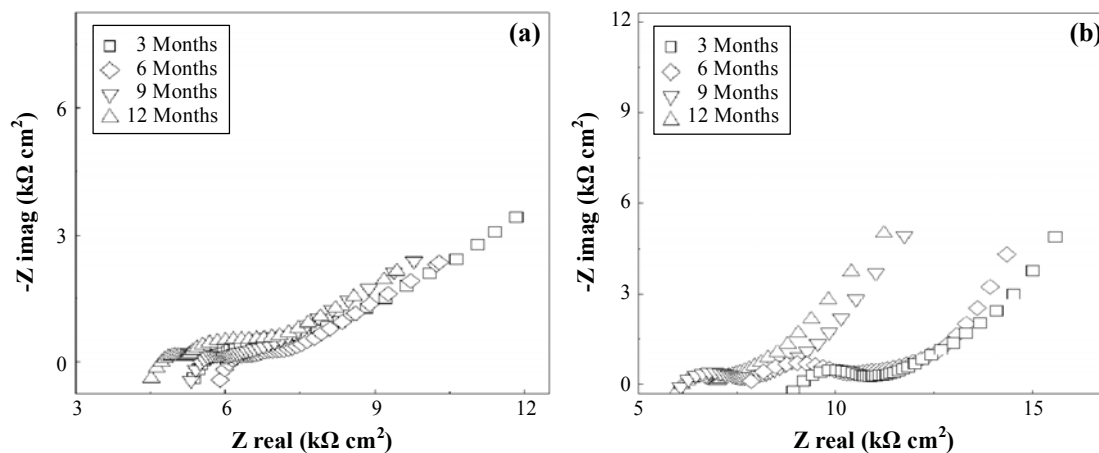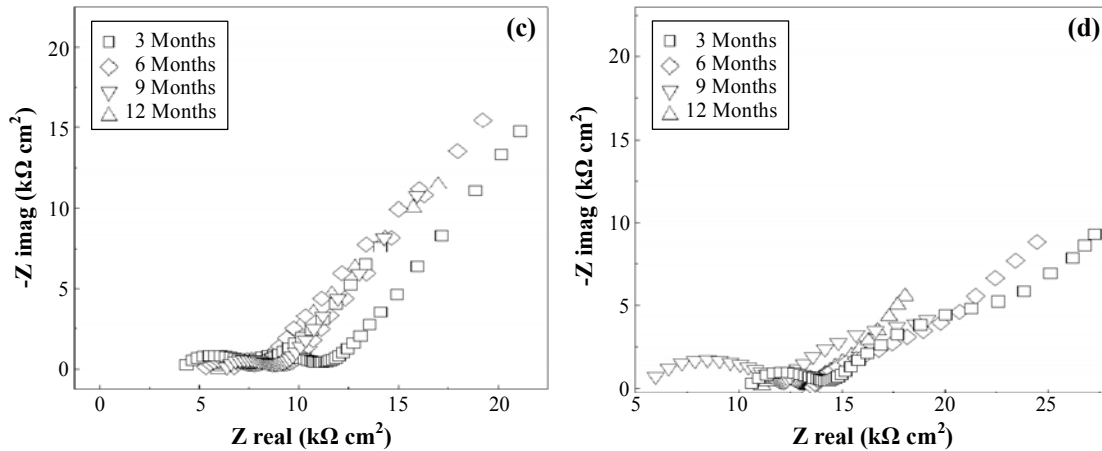
Fig 3: Diagrams Nyquist to geopolymer subjected to different concentrations of SO$_2$, varying the pH and evaluated over a period of 12 months

It is concluded that to 365 days the samples subjected to higher pH values. They have higher clogging pores offer more resistance to ion flow through the matrix, providing increased protection to the reinforcement embedded in the medium, reducing the instability of its protective layer product of the steel passivation[19].

Study the steel surface after the electrochemical evaluation

Scanning electron microscopy

In Fig. 4, the steel surfaces after 12 months of evaluation of corrosion resistance and subjected to acid solutions are observed, with pH between 4 and 5. The form to evaluate corrosion in this study the measurement of the depth of corrosion was done. They found that the concrete forming a protective layer consisting mainly of FeS$_2$, which provided a barrier to corrosion. With observations in the evaluation by EIS, it is determined that the resistance of concrete to corrosion depends on the protective layer and the nature of the hydration products and to a lesser extent to the porosity or permeability of hardened cement.

In Fig. 4a, the study focused on the interface located between the steel and cement alkaline slag, the micrograph shows a transition zone or interface, however there is a wide region where it has a dense area and uniform interface this can be attributed to several factors, such as those mentioned above. In Figs. 4b to 4d, a degree of deterioration in steel is obtained, this is even more evident with the formation of oxides around the corrugated steel[20].

The final appearance of the specimens more change in the past evaluations and at

lower pH, due to the presence of gases SO_2, which in contact with water, made the most aggressive means, a gas with water form acids. That is, the attack by sulfation is most evident, because it starts from the outside inward. Clearly displayed on the rods with lower pH values, which are the most deterioration presented. Nevertheless, these do not penetrate into the concrete, that is, low porosity appeared in the concrete so the rod into the concrete showed no deterioration. Therefore, one can conclude that the concrete produced appears good barrier sulfation processes. It is noteworthy that the curing time also helped improve the quality of concrete.
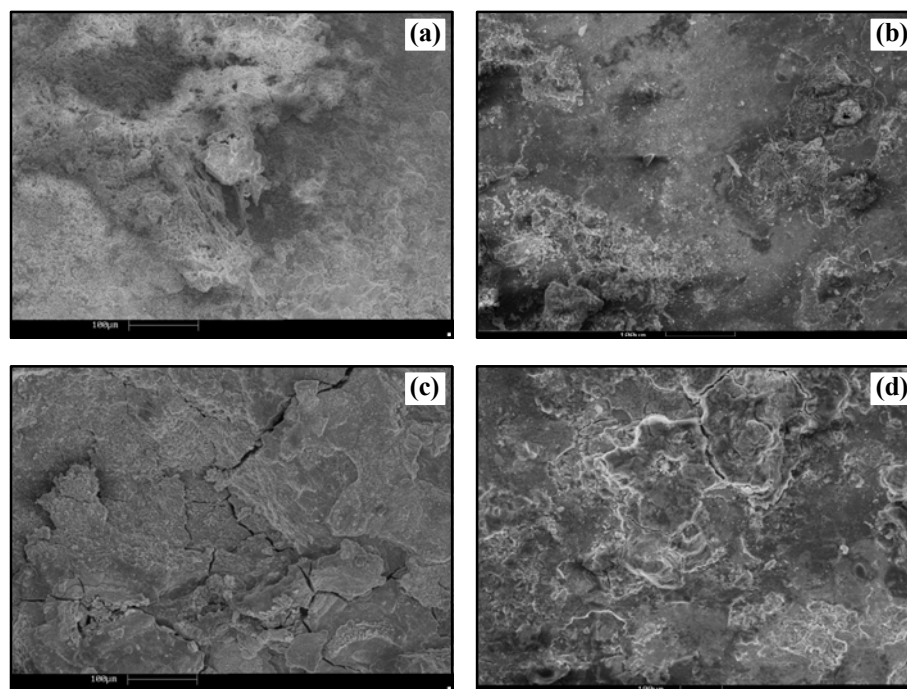
Fig. 4: SEM images that indicate the degree of deterioration present after 12 months of evaluation, in the Fig., the image of steel exposed to a pH of 5.5 is obtained, Fig. b shows the surface pH = 5, the image c indicates pH = 4.5 and micrograph d, pH =4

X-ray diffraction (XRD)

Once a characterized the electrochemical mechanism the morphology of corrosion products and concrete steel interface so proceeded to determine whether the type of generated oxide had influence in protecting the metal. Diffraction analysis was performed with the same pieces of steel (extracted concrete) used for microscopy studies. The diffractograms obtained experimentally show the presence of surface oxides iron typical processes corrosion of steel when it is in concrete. The steel surface, presents species formed

by iron oxides and some silicates. In environments, untreated iron oxides corresponding to phases are predominant, in particular by the hydroxide Goethite ($Fe_3 + O (OH)$) formed in the electrochemical reactions[21]. The compounds Magnetite ($FeO \cdot Fe_2O_3$, $Fe_2 + Fe_3 + 2O_4$) and Hematite (α-Fe_2O_3) they come from steelmaking process, these are known as "steel hulls" and have lower properties against corrosion. Some silicates such as quartz (SiO_2) and Andradite ($Ca_3Fe_2 (SiO_4)$) is also present. That is presumed to correspond waste concrete (cement and sand) that they were not eliminated and which are generated during the manufacture of the ceramic paste lesser extent is Lepidocrocite (γ-$Fe_3 + O (OH)$), hydroxide with the same stoichiometry that goethite composition but different crystal structure.

Passing high environments pH of 5.5 to 4 in the same concrete compounds appears most previously reported. However, it may be noted that the peaks so sharply is not present compared with the diffractogram obtained in the above environment. This fact is supported by the complexity (chemical) compounds formed on the metal. Thus the protective layer consists mainly of goethite becomes a mixture of various hydroxides and wustite (FeO). This iron oxide but has high chemical stability, has an irregular morphology that does not protect the steel against electrochemical attack[22].

Moreover, in particular steel embedded activated slag, was generated the same kind of products at different pH values (Fig. 5). In both cases the same components found iron, goethite, magnetite, hematite and lepidocrocite. That is to say, conditions in which the steel is no influence on the corrosion products formed. This indicates that in this material oxides (hydroxides) of the passive layer of steel tend to "re-combined" with pore water and ferrous ions present therein to form the same type of compounds.
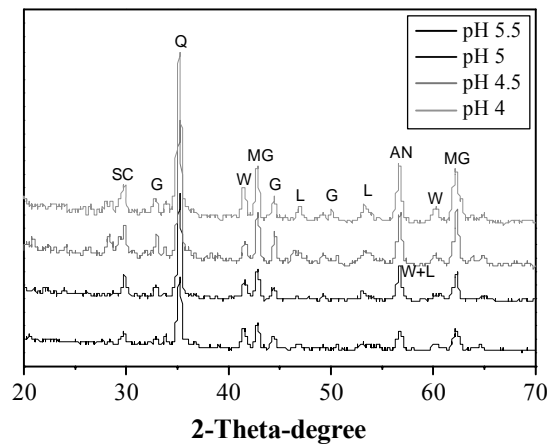

**Fig. 5: XRD of the steel surface where corrosion products, such as identified;
G: Goethite, W: Wuestita, MG: Magnetite, L = lepidocrocite, Q: Quartz**

CONCLUSION

The pH of the acid solution has an important role in the formation or pore interconnection. This is because it reacts with the hydration products for these materials are given long ages that can lead to one year, therefore, it states that the proportions of evolution of heat of hydration it is lower for systems that have the lowest values of pH.

This indicates that while in samples indicate a system capacitance and resistance resulted in greater obstruction of pores in the matrix. In samples without addition are less interference in the pores (less capacitance) virtually only generated ion flow resistance through the pores unobstructed, that is, the flow of ions is more direct in mixtures without addition. In addition, points of high and medium frequencies, for specimens with steel slag, are more displaced in the real axis indicating a greater resistance to the passage of ions in the concrete with steel slag.

With corrosion products, it is established there is no mechanism of chemical protection of the metal in these materials. Conversely the system tries to increase the thickness of the oxide layer forming the same type of compounds to create a mechanical barrier (small scale). Finally by combining a thick passive layer formed with compounds of low protection and electrochemical stability on steel, combined with low porosity of the concrete, an effect that results in greater protection against corrosive phenomenon of metal on concrete based activated slag.

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