Int. J. Electrochem. Sci., 11 **(2016)** 2994 - 3006

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Evaluation of a Stainless Steel as Reinforcement in Sustainable Concrete Exposed to Chlorides

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Received: 11 September 2015 / *Accepted:* 8 February 2016 / *Published:* 1 March 2016

Corrosion of steel reinforcement is one of the top three causes of deterioration of reinforced concrete structures. For this research three concrete mixtures were produced, the first concrete was made with 100 % cement CPC 30R, the second mixture was considered sustainable concrete because using 80 % of cement CPC 30R and 20 % of silica fume and the third mixture was elaborated with 80 % of cement CPC 30R and 20 % of fly ash, these mixtures were designed according to the method ACI 211.1, in the specimens were embedded bars of AISI 304 stainless steel and AISI 1018 steel, the specimens were exposed in a solution at 3.5 % of NaCl, simulating a marine environment, for to evaluate the corrosion resistance were used electrochemical techniques of Half-Cell Potential, standard ASTM C-876-09 and the Linear Polarization Resistance, standard ASTM G59, results E_{corr} and I_{corr} after 180 days of exposure show that, the best performance was presented concrete specimens produced with 20 % silica fume and reinforced with AISI 304 stainless steel, with corrosion potential (E_{corr}) indicating a 10 % probability of corrosion and I_{corr} values that indicate a passivity level of corrosion.

Keywords: Sustainable Concrete, Corrosion, Marine Environment, Fly Ash, Silica Fume

1. INTRODUCTION

Currently and historically, the world's most widely used building material is hydraulic concrete, which in conjunction with AISI 1018 carbon steel rods, form a system known as reinforced concrete. The structures of this system are known for their long-lasting and low maintenance characteristics. However, one of the most important issues for the maintenance of the structural integrity of civil projects such as: bridges, tunnels, roads, docks, etc., from a country, are untimely maintenance requirements costing billions of dollars due to the corrosion of the steel reinforcement embedded in the concrete [1-6].

In Mexico there are no data to give us an idea of the problem, however, has more than ten thousand kilometers of coastline, where there are many reinforced concrete structures susceptible to damage by corrosion. External causes of non-structural nature that usually affect the durability of a concrete structure, they result, primarily on their exposure conditions and service [7-9].

Chloride ions are the main cause of corrosion of reinforcing steel, these ions can be provided by the components of the concrete mixture (Coarse Aggregate, Cement, Water, Additives), or because they penetrate from the outside to be located the structure concrete in a marine environment, or because they come from deicing salts, chloride ions are causing severe damage to reinforced concrete structures around the world [10-12].

Another important aspect of this study of the process of corrosion in reinforced concrete has been the replacement in Portland cement mixes of certain percentages of alternative materials such as silica fume, fly ash and in the last 20 years by bagasse of sugar cane, and ash from rice husks rice among other materials in order to reduce the problem of corrosion and create greater concrete integrity and sustainable [13-18].

From the above concerns and the importance of studying the electrochemical behavior of AISI 304 stainless steel, as reinforcement embedded in concrete made with industrial wastes as a partial replacement of cement, specifically looking for an alternative sustainable, environmentally friendly and has a high durability in harsh environments as it is the marine environment, helping to increase the sustainability of reinforced concrete structures, along with a reduction in environmental pollution by using industrial wastes as silica fume and fly ash.

2. EXPERIMENTAL

For this research three concrete mixtures were made, two of them are considered as sustainable concrete, because they have a partial replacement of Portland Cement by industrial wastes according to different research [19-21], the first mixture was prepared with 100 % CPC 30R cement, the second mixture with 80 % cement CPC 30R and 20 % of silica fume, the third mixture with 80 % CPC 30R and 20 % fly ash, the three mixtures were designed according to the method ACI 211.1 [22], for a compressive strength $f'c=350\ kg/cm^2$.

2.1 Physical characteristics of the aggregates.

Was performed physical characterization of coarse and fine aggregates, according to the standards of the ONNCCE, the results obtained are showing in table 1, these parameters are required for the design of the concrete mixture.

Table 1. Physical characteristics of the aggregates used in mixture

Physical characteristic	Coarse Aggregate	Fine Aggregate
Specific Gravity (gr/cm^3)	2.32	2.66
Volumetric Weight Dry Compacted (kg/cm^3)	1391	- - -
Absorption (%)	5.45	1.97
Fineness modulus	- - -	2.62
Maximum Aggregate Size (mm)	19	- - -

2.2 Design and proportioning of concrete mixture

With the results of the physical characterization of the aggregates, calculation or proportioning of the necessary quantities of each material for a cubic meter of concrete was performed, as indicated above the method used to mix proportioning was the ACI 211.1. The following table shows the amounts used to manufacture 1 m^3 of concrete, for each concrete mixtures used in this investigation.

Table 2. Proportioning of three concrete mixtures 1 m^3

Content in kg	Compressive Strength f´c=350 kg/m^2		
	CPC 30R	Silica Fume	Fly ash
Cement	410	328	328
Partial Substitute	0	82	82
Water	205	205	205
Coarse Aggregate	890	995	995
Fine Aggregate	838	562	562

2.3 Characterization of concrete in fresh and hardened state.

The physical and mechanical characterization of concrete mixes fresh and hardened state, was performed according to ONNCCE and ASTM standards, established for each test, table 3 shows the results obtained for the three mixtures were used in this study.

Table 3. Physical and mechanical properties of concrete mixture

Test	CPC 30R	Silica Fume	Fly ash
Slamp [23]	4 cm	3 cm	3 cm
Temperature [24]	24 ºC	21.7 ºC	22.4 ºC
Density [25]	2150 kg/m^3	2188 kg/m^3	2173 kg/m^3
Compressive Strength [26]	352 kg/cm^2	364 kg/cm^2	359 kg/cm^2

2.2 Features and specifications of study specimens

The Figure 1 shows the dimensions and arrangement of the specimens with AISI 1018 steel and AISI 304 stainless steel bars embedded as reinforcement, both have 3/8" of diameter, also placed in the center a stainless steel sheet as auxiliary electrode, all concrete specimens were prepared and stored for 24 hours, to be subsequently subjected to humidity lost, which was for a period of 28 days. The manufacture, storage and curing of the specimens was performed according to standard NMX-C-159-2004 [27].

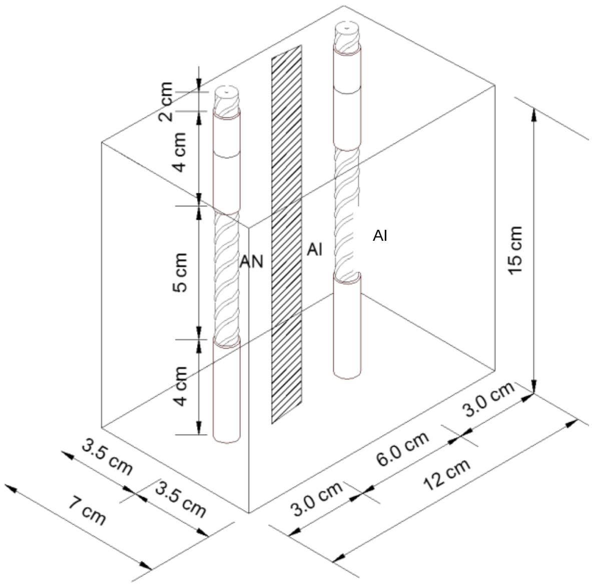

Figure 1. Dimensions of test specimens.

In order to identify the specimens used in the electrochemical study, each specimen was identify with a nomenclature based on the experimental set up parameters.

Table 4. Nomenclature of test specimens.

Nomenclature used		
4AI	4BI	4CI
4AN	4BN	4CN

Signification:

- The number 4 indicates the exposure medium (solution at 3.5% of NaCl).
- The second term indicates partial replacement or cement used for concrete, in A (CPC 30R), B (20 % silica fume) and C (20 % Fly Ash).
- The third term indicates the reinforcement, I (AISI 304 Stainless Steel), N (AISI 1018 Steel).

After the humidity lost step, the specimens were placed in the simulated marine environment, 3.5 % NaCl solution. They were evaluated for a period of time of 180 days by electrochemical techniques as: corrosion potential (E_{corr}) and corrosion kinetics (I_{corr}). Figure 2 shows the experimental arrangement, where it was carried out according to standard ASTM G59. This arrangement constitutes the electrochemical cell used in all electrochemical measures. The CuSO4 electrode was used as reference electrode (RE) and two rod of the 304 stainless steel (SS 304) samples were used as auxiliary Electrode (AE) and work electrode (WE) respectively.

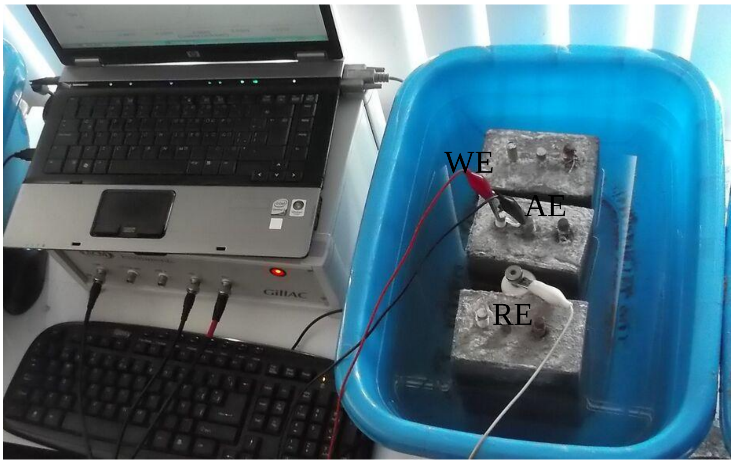

Figure 2. Electrochemical cell for to evaluation of specimens in solution at 3.5% NaCl.

3. RESULTS AND DISCUSSION

3.1 Corrosion Potential

Monitoring and interpretation of corrosion potential of the test specimens was performed according to the standard ASTM C876-09 [28], adding a rank according to literature [29], see table 5.

Table 5. Corrosion probability according to E_{corr} in reinforced concrete

E_{corr} (mV vs Cu/$CuSO_4$)	Probability of Corrosion
< - 500	Severe corrosion
-500 a -350	90% Probability of Corrosion
-350 a -200	Uncertainty
> -200	10% Probability of Corrosion

Figure 3 shows the results of the corrosion potential (E_{corr}) obtained by the SS 304 sample immersed in concrete. 4 AI specimen was elaborated with concrete without nothing added. The 4BI specimen was elaborated replacing Portland cement by 20% of silica fume; finally, the 4CI was elaborated replacing Portland cement by 20% of Fly Ash.

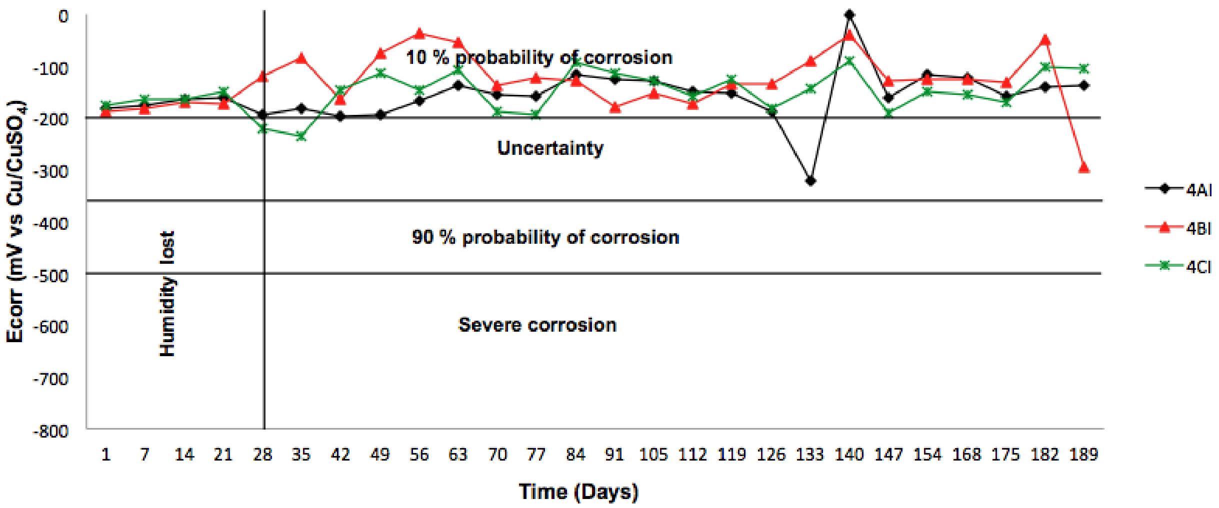

Figure 3. E_{corr} of the SS 304 concrete specimens immersed in 3.5 % NaCl solution

Figure 3 shows that the E_{corr} behaviour of 4AI specimen is slightly homogeneous during the exposure time. In the curing step (first 28 days), the E_{corr} values oscillate between 150 and 195 mV indicating a passivation process in the SS 304 sample. The E_{corr} value decreased to -130 approximately in day 84 and, in day 133 of the exposure time, the potential increased considerably to get a value of -330 mV. In last 50 days of the exposure time the E_{corr} values was -200 mV approximately. According to standard of ASTM C876, these E_{corr} values indicate that the probability of the corrosion in the SS 304 sample localized in the 4AI specimen was of 10%.

The E_{corr} values of the first 180 days are agree with the results reported by Garcia-Alonso [30]. This study showed the corrosion resistance of the 304 and 306 stainless steel where these were used as reinforcement in a concrete specimen and then they were exposed to 3.5% NaCl solution during two years.

The E_{corr} values of the 4BI specimen shown that in the curing step and in the first 7 days, the E_{corr} was -180 mV and after 35 days of the exposure time, the E_{corr} decreased to -100 mV to finally after 56 days decreased to -50 mV. This behaviour is attributed to the properties in the microstructure of the concrete matrix with silica fume, such as the decrement of the permeability attributed mainly to particle size and the hydration reactions generated [31]. In the period of time between 70 to 126 days, the E_{corr} showed a stable behaviour from -150 to -190 mV but in the last days of the exposure time, the E_{corr} value increased to -300 mV. The behaviour observed at almost end of the exposure time indicate uncertainty of corrosion.

In case of the specimen with 20% of fly ash (4CI specimen) and in the first 21 days of curing, the E_{corr} showed a similar behaviour that the 4AI and 4BI specimen. This behaviour is attributed to the fact that in the curing step, the hydration process of the concrete is similar in concrete with fly ash and silica fume; where this fact is attributed mainly to pozzolanic characteristics [32,33]. In period of time between 28 to 35 days of the exposure time, the E_{corr} values of the 4CI specimen showed potentials that they have related with an uncertainty of corrosion in the system. Since 42 days to 189 days of exposure, the E_{corr} values fluctuated between -140 to -180 mV, indicating with these E_{corr} values that the probability of the corrosion was 10%. It is according to ASTM C876.

Figure 4 shows the results obtained by the E_{corr} monitoring of the specimens produced with the same concentration of the concrete analyzed in figure 3, but these specimens are reinforced by AISI 1018 steel. 4AN specimen is the concrete without additions. This specimen shows E_{corr} values that indicate severe corrosion since the first day of the exposure time. The E_{corr} value in the period of time between 35 and 77 days oscillate in -600 mV approximately, but in the period of 84 to 105, the E_{corr} values decreased to -470 mV approximately, indicating with this decrement that the specimen had a 90% of corrosion probability. This fact is according to the Norma ASTM C876. In the last 80 days of the exposure time, the E_{corr} value was -500 mV keeping the severe corrosion behavior

On the other hand, in case of specimens with silica fume and fly ash, 4BN and 4CN respectively, the E_{corr} is approximately -500 mV in both conditions. This E_{corr} values indicate a severe corrosion in the reinforced consequently is possible to say that the concrete proportionated a nule protection. According with the E_{corr} values presented in figure 3 and 4 is possible to point out that the highest corrosion resistance was showed by the specimens with SS 304.

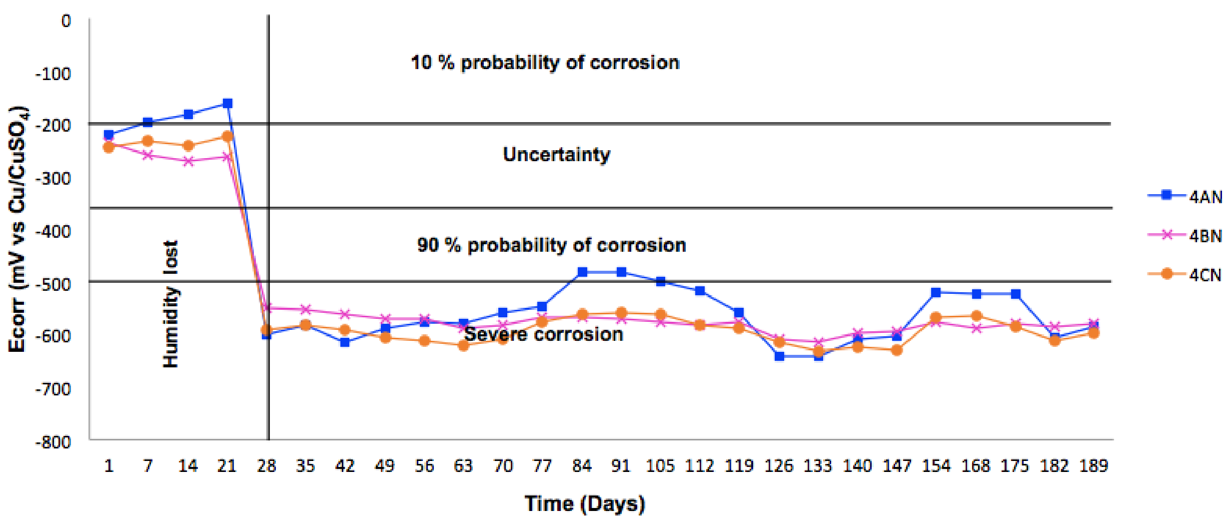

Figure 4. E_{corr} of the AISI 1018 steel in concrete specimens immersed in 3.5 % NaCl solution

In Figure 5 shows the behavior of all specimens of study, the performance obtained is compared for over 180 days exposure to aggressive marine simulated for both steels, this figure allows us to evaluate the difference between using stainless steel 304 and AISI 1018 steel, when they are embedded as reinforcements in sustainable concrete, according to the behavior of E_{corr}, it can be concluded that it is much less the probability of corrosion of stainless steel 304 as reinforcement in concrete sustainable exposed to a marine environment.

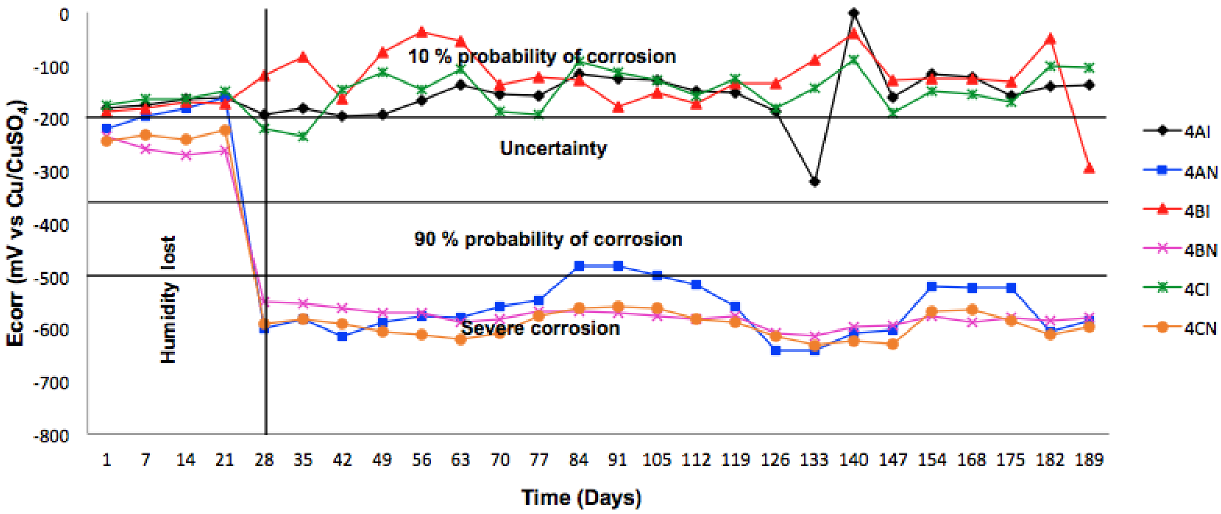

Figure 5. E_{corr} of the concrete specimens reinforced with SS 304 and AISI 1018 steel immersed in 3.5 % NaCl solution

3.2 Corrosion Kinetics

The linear polarization resistance (LPR), is an electrochemical technique that is widely used for monitoring the instantaneous corrosion rate in plant [34], and commonly used within the scientific community for laboratory tests [35]. The corrosion kinetics of specimens was evaluated at based on the standard ASTM G 59-97(2009) [36], using a typical scanning range of ± 20 mV around the E_{corr}, with scan speed of 0.1 mV/s. The criterion used for the interpretation of the results was noted in the Manual DURAR Network [37], which indicates four levels of corrosion; in table 6 can observer, such levels of corrosion.

Table 6. Levels of Corrosion rate according to i_{corr} values.

Corrosion Rate (i_{corr}) µA/cm^2	**Level of Corrosion**
< 0.1	Passivity
0.1 – 0.5	Moderate
0.5 – 1	Elevated
> 1	Very high

The results showed in figure 6 indicate that the specimen since curing step, the corrosion rate (CR) is influenced by the concrete type. The 4AI specimen shows values of corrosion current density (i_{corr}) in a range between 0.03 y .02 µA/cm^2 while the 4CI specimen with 20% of fly ash shows values between 02 y 0.01 µA/cm^2, finally, the 4BI specimen with 20% of silica fume has the lowest values of the i_{corr}, values lower than 0.01 µA/cm^2. According to this fact is possible to point out that the best electrochemical behaviour correspond to the 4BI specimen. It is important to point out that the behaviour of 4BI specimen is attributed to the microstructure of the concrete matrix that it is impermeable due to the presence of the silica fume [38-41].

According to the analysis of the i_{corr} versus the total exposure time (more than 180 days) the best performance was presented by the 4BI with i_{corr} values lower than 0.01 μA/cm^2, followed by the 4CI specimen with 0.0 15 μA/cm^2 approximately. Finally, 4AI specimen with i_{corr} values close to 0.1 μA/cm^2 presented the worst performance. In agreement to table 6, the 4AI specimen has a trending to severe corrosion process.

The values of corrosion resistance obtained by the SS 304 used as concrete reinforced exposed to marine environment are agree with the results reported by Criado [42], where this author analyzed the SS 304 used as reinforced in mortars with activated fly ash immersed in alkaline solutions with chlorides and during 180 days. The i_{corr} value at this condition was approximately 0.02 μA/cm^2. The high corrosion resistance of the SS 304 was attributed to the increased alkalinity of the mortar provoked by the activated fly ash with pH values up to 13.

Some researchers, such as García-Alonso [43] have studies about SS 304 used as reinforcement of the Portland cement immersed in brine with 2 to 4 % of chlorides. After 180 days of exposure time at these conditions, the i_{corr} values were lower than 0.1 μA/cm^2 concluding with this fact that the SS 304 has high corrosion resistance. Other researcher about SS 304 in this brine [44] have concluded that SS 304 in marine environment is up to 100 times more resistance than AISI 1018.

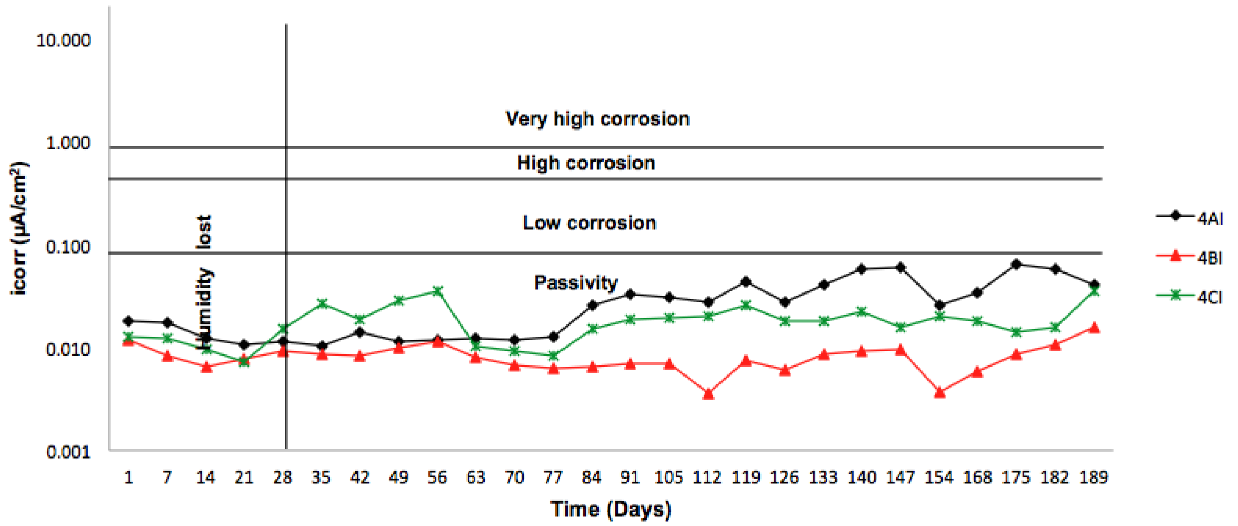

Figure 6. i_{corr} of the concrete specimens reinforced with SS 304 immersed in 3.5 % NaCl solution

Figure 7 shows the electrochemical measures of the concrete specimen synthetisized at iqual concentration that the specimens presented in figure 6; without added (4AN), with silica fume at 20% (4BN) and fly ash at 20% (4CN). The only variation is the reinforment metal, in this case the reinforcement metal was AISI 1018 steel. In general, The corrosio rate during the total exposure time and in all conditions, are high with values between 1-10 μA/cm^2. According to this corrosion rate is possible to point out that the concrete structures with this corrosion rate need interventions, almost immediately, in order to preserve the structural integrity [45]. The concrete structures with prestressed concrete exposed to chlorides ions must need too the corrosion monitoring and control [46].

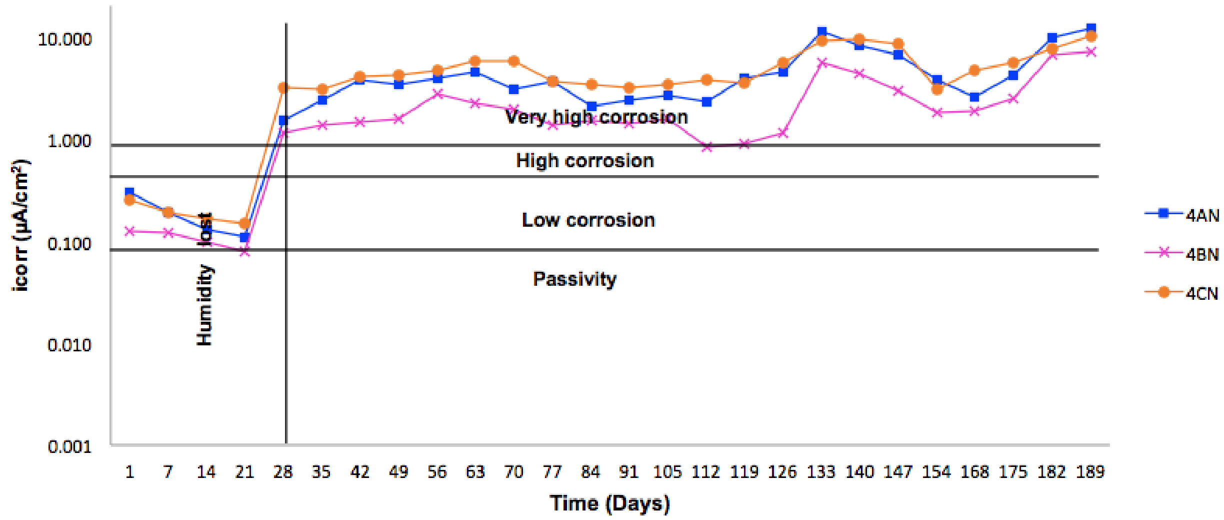

Figure 7. i_{corr} of the concrete specimens reinforced with AISI 1018 steel immersed in 3.5 % NaCl solution

Figure 8 shows the comparison of the corrosion rate of the concrete specimen reinforcement with SS 304 and AISI 1018 steel. It can be seen the great benefit of using stainless steel 304 as reinforcement in sustainable concrete exposed to an aggressive environment, also being observed positive influence of the use of industrial wastes such as silica fume and fly ash for preparation of durable concrete.

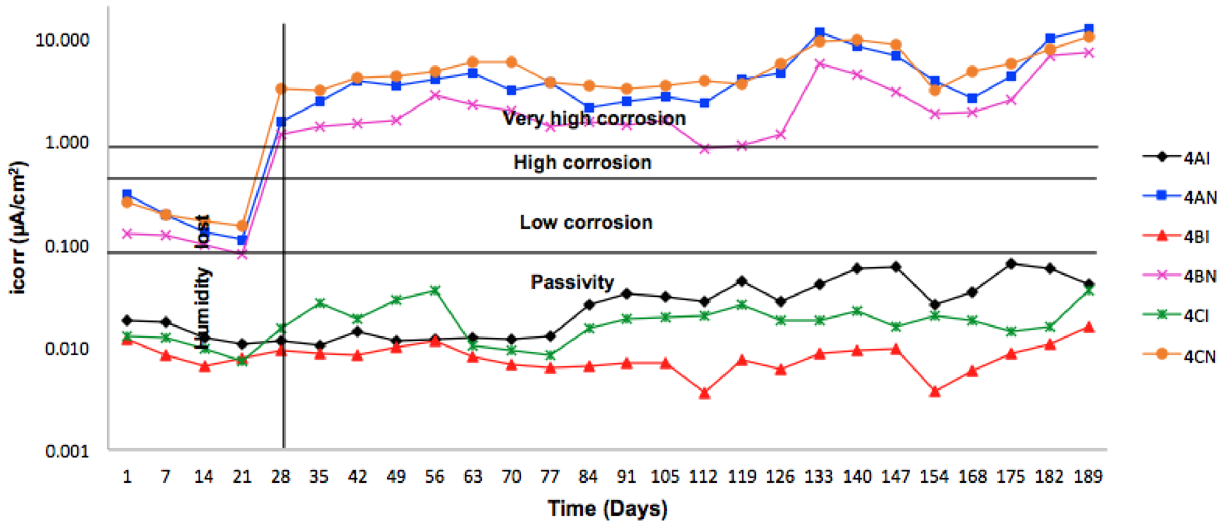

Figure 8. i_{corr} of the concrete specimens reinforced with SS 304 and AISI 1018 steel immersed in 3.5 % NaCl solution

4. CONCLUSIONS

According the norm ASTM C-876 and the results obtained in the electrochemical evaluation of the SS 304 embedded in concrete sustainable is possible to conclude that the SS 304 immersed in aggressive medium (3.5% NaCl solution) and after 180 days of the exposure time, the corrosion probability is a 10% with values lower than -200 mV.

On the other hand, with respect to the corrosion rate (i_{corr}) and according to the norm ASTM G59, the SS 304 after 180 days of the exposure in the aggressive medium, the values was 0.1 $\mu A/cm^2$ approximately in the three evaluated concretes. In this case, the best steel performance was observed in the concrete with silica fume at 20%, followed by the steel embedded in concrete with fly ash at 20%, finally, the concrete without added. According to the i_{corr} behaviour is possible to point out that the mix of the concrete with silica fume and fly ash (sustainable concrete) generated a high corrosion resistance in the SS 304, but in the AISI 1018 steel do not happened this behaviour. The i_{corr} values obtained in concrete specimen reinforced with AISI 1018 steel indicate a severe corrosion process independently to the silica fume or fly ash added.

The SS 304 used as reinforcement in sustainable concrete (concrete plus silica fume or concrete plus fly ash) after 180 days of the exposure time in aggressive medium (solution with chlorides ions) is up to 100 times more resistance than AISI 1018. The use of some solid or industrial wastes such as silica fume or fly ash in the concrete can increase the corrosion resistance of the SS 304 provoking with this fact the increment of the concrete durability.

With the presented results, it can recommendable used AISI 304 stainless steel as reinforcement in concrete structures built in marine environments and also use of silica fume as a partial replacement for Portland Cement for the production of mix concrete, to increase resistance against corrosion and durability of the structure.

The use of AISI 304 stainless steel in combination of concrete made with industrial wastes is a steel-concrete system that in this research is called Sustainable Concrete, because it is to replace part of Portland Cement by industrial waste, implies, if will take place in the lig reinforced concrete builds such as bridges, pavements, dams, docks, a decrease in demand Portland Cement and user friendly to the environment of such wastes, also that the demand for raw materials is reduced, energy consumption required Cement manufacturing, addition to the above, this type of Sustainable Concrete also increases the durability of structures, increasing the life of these, thus saving everything that is used in the construction of civil infrastructure, as materials, energy, natural resources, pollution.

In summary to build structures with Sustainable Concrete, contribute significantly to sustainable development of our societies.

ACKNOWLEDGEMENTS
G. Santiago-Hurtado grateful to CONACYT of Mexico by the Doctoral Scholarship. Also thanks for the technical support from Asphaltpave S.A. de C.V.

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