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Electrochemical Characterization of Modified Concretes with Sugar Cane Bagasse Ash

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Corrosion is one of the most serious causes that reduce service life of Reinforced Concrete Structures (RCS). This is why it is necessary to create concrete mixtures that add durability for steel and that reduce impact on the environment. The use of agro-industrial waste materials rich in SiO_2, Al_2O_3 and Fe_2O_3, added to concrete, has been the subject of research in recent years, because these pozzolanic materials improves o mecharacteristics of concrete, as mechanical strength, sulfate resistance and lower permeability. Binary Concretes were made and evaluated in the impact of Sugar Cane Bagasse Ash (SCBA) as a partial substitute for Portland cement, with the aim of reducing gtherate of corrosion induced by chloride ions and sulfate. The behavior of corrosion was monitored for 14 months in two aqueous solutions of NaCl and Na_2SO_4 both at 3.5%, using electrochemical techniques of corrosion potential (E_{corr}) and linear polarization resistance (R_p). Under the conditions of study, the binary mixture that showed a better corrosion protection was the one that contained 80% from sugar Cane bagasse ash and 20% Portland cement.

Keywords: Reinforced concrete structures, corrosion, corrosion potential, linear polarization resistance, sugar cane bagasse ash, Portland cement.

1. INTRODUCTION

The application of pozzolanic materials has been extended to the development of high performance concretes used for constructions of high specifications. The use of pozzolans in concrete production brings positive effects to the environment, since by substituting large quantities of cement in concrete production, reduces the problem associated with their disposal [1], and the decrease in the emission of greenhouse gases (CH_4 and CO_2) the main cause of global warming. Each ton of cement produces about one tonne of CO_2 [2,3] and the cement industry is responsible for 5% of CO_2 emissions worldwide [4,5].

Some of the most commonly used pozzolanic materials in concrete, such as fly ash and silica fume are subproducts of industrial processes [6]. Sin embargo también existen otras puzolanas que se han empleado aunque a menor escala, como las puzolanas naturales, metacaolin y cenizas agroindustriales como la cascarilla de arroz y las cenizas del bagazo de caña de azúcar [5,7,8]. However there are other pozzolans that have been used on a smaller scale, such as natural pozzolans, metakaolin and agribusiness ashes such as rice husks and sugar cane bagasse ashes [5,7,8].

An option to promote the use of pozzolanic materials in developing countries is by studying waste materials that are generated in abundance in the region, and do not require too excessive treatments that make more expensive the final products [9]. One of these materials is the sugar cane bagasse ash (SCBA).

Mexico ranks as fourth largest producer of sugar cane, surpassing the United States and South Africa (it’s first in Latin America).

In the period 2008-2009 only in the Mexican sugar industry almost 10 million tons of cane bagasse were burned and generated a significant amount of SCBA, which is mainly deposited in open dumps [10]. It has been demonstrated that this ash shows adequate chemical composition for its use as pozzolana, as it is mainly composed of SiO_2, Al_2O_3 and Fe_2O_3 [11-14].

There have been few studies to evaluate the behavior of the SCBA in concrete, but has been observed that over 20% of ordinary Portland cement can be replaced optimally with it, without any adverse effect on the desirable properties of hardened concrete. The specific benefits of such replacement were the development of high strength at early ages, a reduction in water permeability, significant resistance to penetration and diffusion of chlorides [15]. It has also been shown that a low ash pozzolanic activity below 50%, can reach values above 100% after a prolonged milling time. In partial replacement of Portland cement in 10, 15 and 20% in cement weight give no significant changes in the mechanical behavior (compressive strength and modulus of elasticity) using up to 20% ash [16].

However, there is still a large gap in knowledge about the study of electrochemical corrosion of reinforcement embedded in concrete modified with SCBA. It is for this reason that in this work presents the electrochemical characterization of modified concrete in which Portland cement replaced by up to 20% by weight, with SCBA.

Since reinforcement steel corrosion is the main cause of failure of reinforced concrete structures (RCS), the capability of pozzolans in mortars and concrete reinforcing steel passivation is a very important property to ensure the durability of RCS built using these materials. The passivating capacity and the permanence of the passive state once reached may depend on the nature and dosage of binder, as well as environmental conditions.

No information in the literature on studies of the problem of deterioration caused by corrosion of steel embedded in concrete modified with Sugar Cane Bagasse Ash. So that in this paper we study the electrochemical behavior of modified concrete with CBCA, exposed for 14 months in environments with chlorides and sulfates to 3.5%. The electrochemical techniques were Corrosion potential (E_{corr}) and Linear polarization resistance (LPR). Used to determine the corrosion rate and durability of these materials

2. EXPERIMENTATION

2.1. Materials

For the development of this study commercial Portland cement Type I was used according to ASTM C 150-02 Standard [17]; sugar cane bagasse ash according toASTM C 618-03 Standard [18], obtained from Cane Factory “Mahuixtlán” in the state of Veracruz, Mexico during the 2008-2009 harvest.

The chemical composition of these materials is shown in Table 1.

Table 1. Chemical composition (%) of the materials.

Chemical compositions (%)	Type I cement	CBCA
Silicon dioxide, SiO_2	21.0	70.5
Aluminum oxide, Al_2O_3	5.9	5.23
Ferric, Fe_2O_3	3.2	3.24
Calcium oxide, CaO	62.25	4.19
Magnesium oxide, MgO	3.02	2.28
Sodium oxide, Na_2O	0.12	0.93
Potassium oxide, K_2O	0.78	8.41
Sulfur trioxide, SO_3	2.1	0.07
Sulfur dioxide, SO_2	--	--
Sulfur, S	--	--
Titanium dioxide, TiO_2	--	0.42
Chlorine, Cl	--	0.02
Loss on ignition	1.61	1.78

2.2. Measurement Methods

Experiments were performed on small prismatic specimens measuring 9×15×15 cm, see Figure 1, and 4. Were designed 4 binary mixtures and 1 for control, with two embedded steel bars that were used as working electrode (WE) and counter electrode (CE), a copper-copper sulfate ($Cu/CuSO_4$) electrode was used as reference for electrochemical measurements, with the proportions shown in Table 2. It made a replacement of Portland cement of 5, 10, 15 and 20% of its weight for SCBA with particle sizes lower than 75µm. The specimens were made in duplicate and exposed in aqueous solutions of NaCl and Na_2SO_4, both at 3.5% for 14 months.

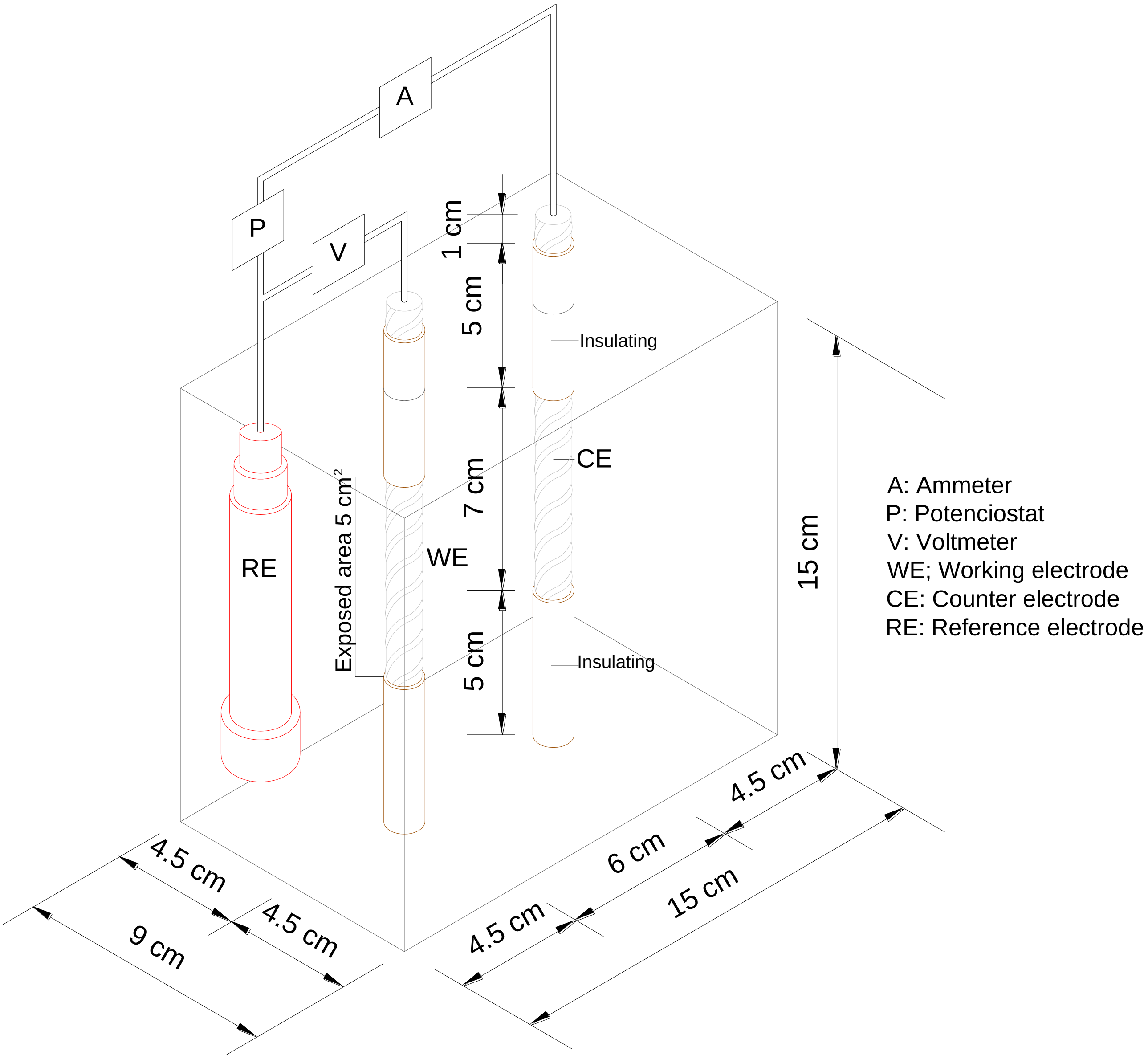

Figure 1. Scheme of the prismatic specimen used.

The electrochemical behavior was evaluated using the following techniques:

Corrosion potential (E_{corr}) values. The E_{corr} parameter may be used to determine the probability of corrosion. According to ASTM C876-99 Standard, for E_{corr} <– 350 mV vs. $Cu/CuSO_4$ high corrosion probability (~ 90%), for –350 mV < E_{corr} <– 200 mV vs. $Cu/CuSO_4$ uncertainty of corrosion, and for E_{corr} <– 200 mV vs. $Cu/CuSO_4$ 10% probability of corrosion[19].

Linear polarization resistance (LPR). According to the Stern-Geary equation [20] $i_{corr} = \frac{B}{R_p}$, applying $\Delta E \pm 20$ mV with a scan rate of 16 mV s^{-1}, the constant B was 26 mV. Corrosion levels were defined according to the Durar Network Specifications [21]. For i_{corr}<0.1 µA cm^{-2} passivity, for 0.1

μA cm^{-2}<i_{corr}<0.5 μA cm^{-2}low corrosion, for 0.5 μA cm^{-2}<i_{corr}<1.0 μA cm^{-2} high corrosion, and i_{corr}>1.0 μA cm^{-2} very high corrosion.

Table 2. Mixproportions of concrete.

Materials	**CTRL**	**CP-CBCA**			
	100-0	95-15 >75	90-10 >75	85-15 >75	80-20 >75
Type I Cement kg/m^3 (CP)	27.18	25.821	24.462	23.103	21.744
Sand aggregate kg/m^3	52.4	52.4	52.4	52.4	52.4
Coarse aggregate kg/m^3	50.43	50.43	50.43	50.43	50.43
CBCA < 75μm kg/m^3	--	1.359	2.718	4.077	5.436
Water kg/m^3	12.2	12.2	12.2	12.2	12.2
Superplasticizer kg/m^3	--	--	--	--	--
Relation w/c	0.45	--	--	--	--
Relation w/(c+CBCA)		0.45	0.45	0.45	0.45

3. RESULTS

Tests of mechanical strength were performed at 14, 28 and 90 days according to ASTM C 39-99 Standard [22], to assess the evolution of hardening concrete mixtures.

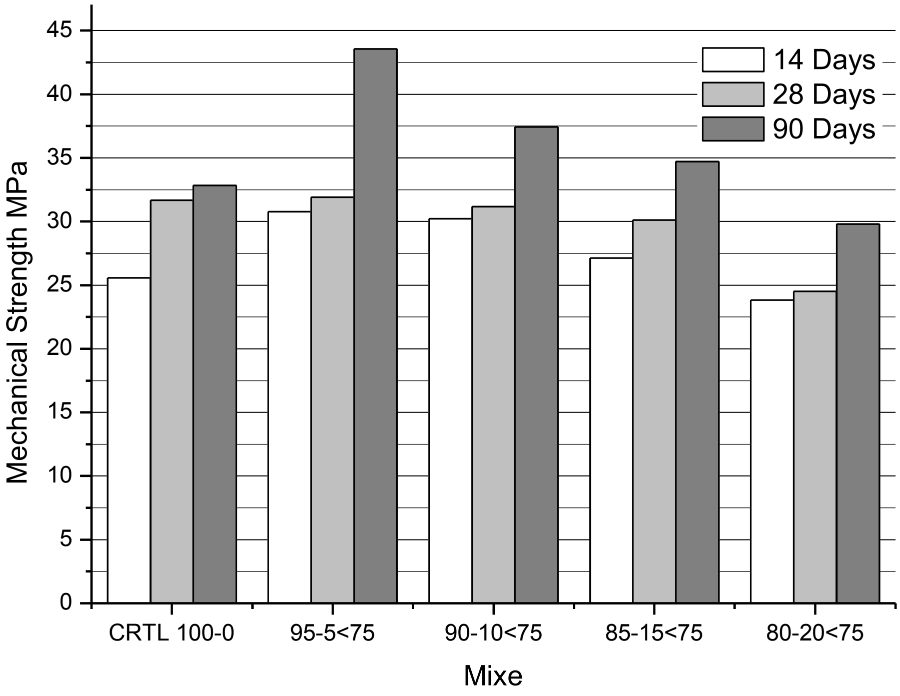

Figure 2. Mechanical strength for specimens (CTRL 100-0) (95-5 <75), (90-10 <75), (85-15 <75) and (80-20 <75) after 14, 28 and 90 days.

Figure 2 shows the results of mechanical strength of the specimens (CTRL 100-0) (95-5 <75), (90-10 <75), (85-15 <75) and (80-20 < 75) at 14, 28 and 90 days. It is observed the quantity of SCBA in mixtures of concrete is inversely proportional to the mechanical performance in this type of test. The mixture with 100% Portland cement (CTRL 100-0) obtained strength of 25.5MPa at 14 days, 32 and 33MPa at 28 and 90 days respectively. However, the mixture (95-5 <75) at 90 days developed a strength of 43MPa almost 25% more than the mixture (CTRL 100-0). The mixture that did not provide adequate performance to mechanical testing was (80-20 <75) because the resistances obtained were much lower than the (CTRL 100-0). It is important to note that concrete made with SCBA particles with size lower than 75μm develop strength more slowly than the CTRL mixture, this indicates that the amount of pozzolan of SCBA is directly related to the evolution and increased mechanical strength. The amorphous silica of the SCBA reacts slower with calcium silicates hydrated (CSH) of Portland cement, causing that at 90 days age they presented higher mechanical resistance compared with a conventional concrete.

3.1. Corrosion potentials

Figures 3 and 4 show the E_{corr} results of the specimens exposed in solutions of NaCl and Na_2SO_4, respectively. The horizontal lines indicate the limits for the ranges of probability of corrosion according to ASTM C876-99 Standard [19].

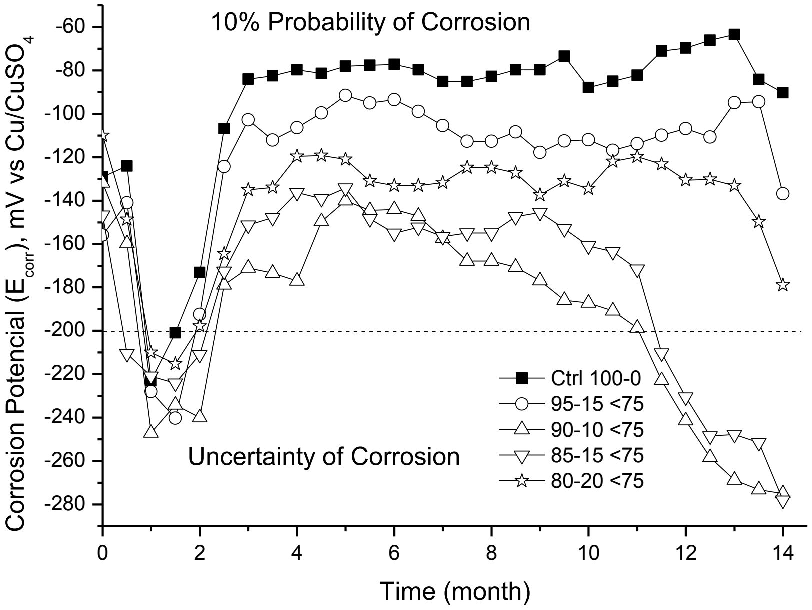

Figure 3. Corrosion potential (E_{corr}) versus time for steel bars embedded in concrete (CTRL 100-0) (95-5 <75), (90-10 <75), (85-15 <75), and (80-20 <75) the specimens were immersed in a 3.5% NaCl solution at room temperature.

Figure 3 shows the E_{corr} values of the specimens tested during the 14 months of exposure in NaCl. It is seen that all specimens studied had values of 10% probability of corrosion at the beginning of the experiment, but between months 1 and 2, the values were more negative; between -220 and -250 mV vs. Cu/CuSO4, reaching in the range of incertitude. After 3 months, most of the mixtures with values of E_{corr} greater than -200mV vs. Cu/$CuSO_4$, except the rods embedded in concrete (90-10 <75) and (85-15 <75).

The results of the evaluation of E_{corr} of the specimens exposed to Na_2SO_4 is presented in Figure 4, which shows that the generality of the specimens show a similar behavior, between months 1 and 2 develop more negative potentials. However, specimens (CTRL 100-0) and (90-10 <75) reach potential uncertainty of corrosion, but after 3 months, again showing potential 10% probability of corrosion or state of passivity.

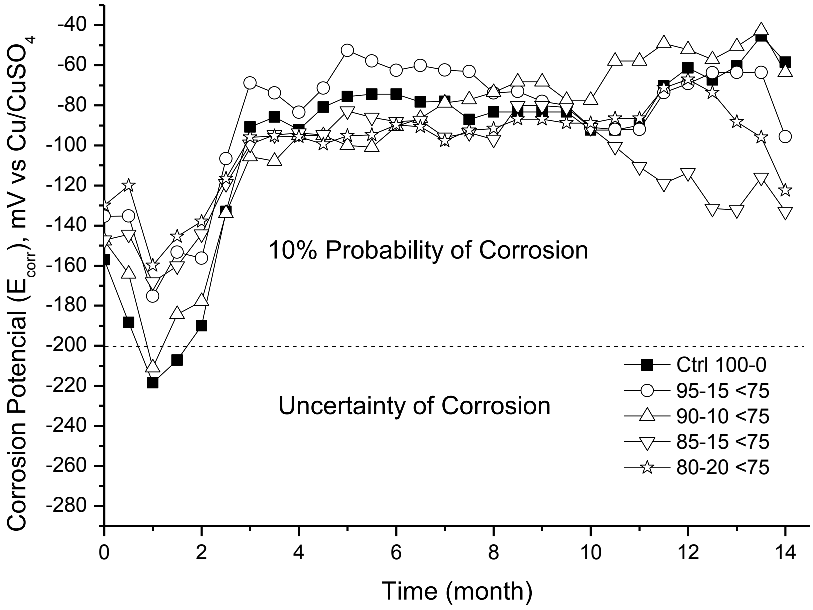

Figure 4. Corrosion potential (E_{corr}) versus time of the bars embedded in concrete (CTRL 100-0) (95-5 <75), (90-10 <75), (85-15 <75), and (80-20 <75) the specimens were immersed in a 3.5% Na_2SO_4 solution at room temperature.

3.2. Linear polarization resistance.

Figure 5 and 6 show the corrosion rate (i_{corr}) results of the specimens exposed in solutions of NaCl and Na_2SO_4, respectively. Horizontal lines indicate the limits corresponding for a range of passivity and low corrosion as defined in the DURAR Network [21].

Figure 5 shows that the specimen made of conventional concrete (CTRL 100-0) presents a lower resistance to corrosion in NaCl solution, then throughout the experiment was established within the limits of passivity and corrosion moderate (0.09 $\mu A/cm^2$). Además se aprecia claramente que todos los especímenes fabricados con CBCA manifiestan corrosión pasiva, pues en promedio presentan valores de 0.015 $\mu A/cm^2$. Furthermore it is clear that all specimens made with SCBA manifest passive corrosion, (on average present values of 0.015 $\mu A/cm^2$) Concrete that has the best performance (80-20 <75), as its i_{corr} values during the 14 months of exposure are less than 0.010$\mu A/cm^2$.

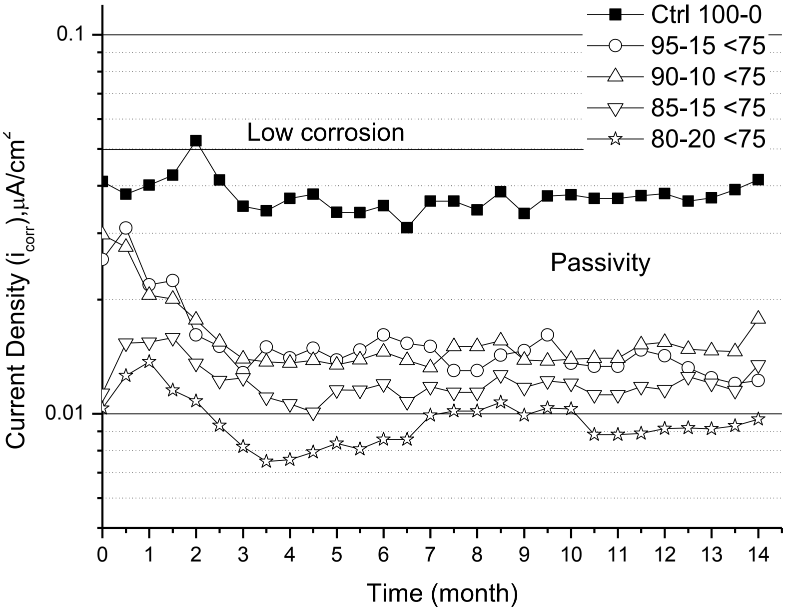

Figure 5. Corrosion rate (i_{corr}) of the specimens (CTRL 100-0) (95-5 <75), (90-10 <75), (85-15 <75) and (80-20 <75) exposed in NaCl 3.5%

Figure 6 shows the results of i_{corr} of the specimens exposed to Na_2SO_4. In this medium, the values of all specimens are similar, since they are in passivity state. However specimens (CTRL 100-0) and (95-5 <75) have less corrosion protection (0.05 and 0.07) µA/cm^2. Specimens (85-15 <75) and (80-20 <75) developed low values of corrosion between 0.1 and 0.008 µA/cm^2 during 14 months of exposure in this medium.

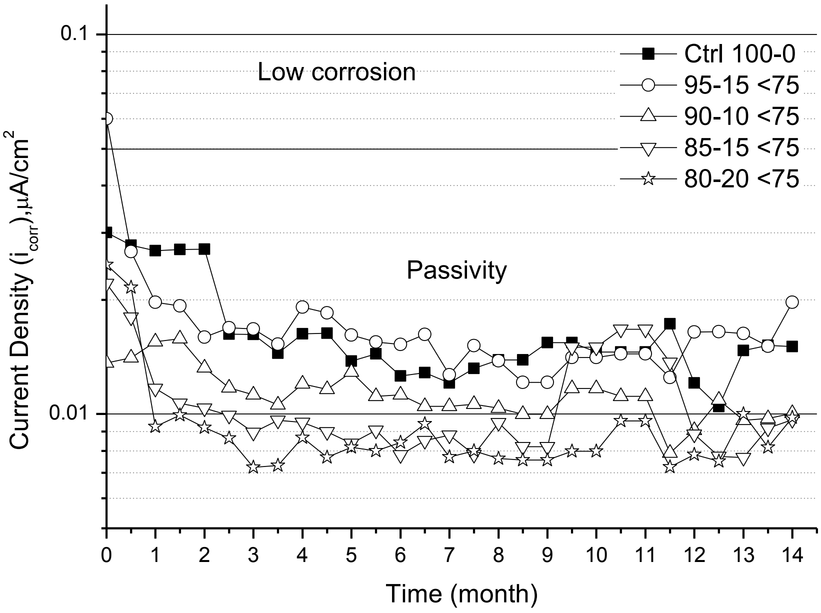

Figure 6. Corrosion rate (i_{corr}) of the specimens (CTRL 100-0) (95-5 <75), (90-10 <75), (85-15 <75) and (80-20 <75) exposed to Na_2SO_4 3.5%

The rate of corrosion in this medium is low, since the Na_2SO_4salts are neutral and direct affectation in steel reinforcement is minimal. The greater affectation may occur in this medium is for the concrete originating cracks and weight loss.

3.3. Discussion

One way to discuss the results, not used until today is the comparison of the accumulated corrosion instead of comparing the corrosion rate. Thus, in Figure 7 and Figure 8 shows the accumulated corrosion calculated by the integral of speed to the corresponding age. This form of representation has the advantage that the accumulated corrosion, calculated by integrating the speed until the proper age, always grows with time and allows a better comparison of the effects. Figures 7 and Figure 8, show an increase in the total corrosion as time passes, because of the arrival of aggressive agents to steel reinforcement. It is observed that corrosion is greater whit the lower amount of SCBA in the concrete.

Figure 7 shows in a clearer way how the specimen (CTRL 100-0) has a higher speed with respect to the specific modified CBCA. Specimens (95-5 <75) and (90-10 <75) develop cumulative rates of corrosion in the same range, and finally the concrete (85-15 <75) and (80-20 <75) present a best performance as corrosion protection in NaCl.

In Figure 8, there is a very high accumulated corrosion rate for the specimen (CTRL 100-0), and again modified concrete (80-20 <75) presents major advantages against corrosion.

These results may be caused by secondary reactions of portland cement hydration and the high percentage of SiO_2 of the SBA, resulting in a denser cement matrix with fewer pores that prevents the rapid entry of aggressive agents (NaCl and Na_2SO_4) and the same compact structure of calcium silicates hydrated (CSH) provide a greater advantage in terms of mechanical properties and corrosion of the reinforce steel bar.

The CSH is responsible for the hardness and compactness of the concrete, the SiO_2 of the SCBA the pozzolan reacts as follows:

First reaction of hydration (First production of CSH):

$$2(3CaO\cdot SiO_2) + 6H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + 3Ca(OH)_2$$

Second reaction of hydration after 14 days of conventional curing (second production CSH) [23.24].

$$3Ca(OH)_2+2SiO_2+H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O$$

The good corrosion resistance of concrete modified with SCBA, can also be due to the appropriate particle size (lower than 75µm) that the pozzolan in the study presented, because it makes denser concrete inhibiting the ingress of oxygen and moisture, which are essential for the cathodic reaction, and it results that corrosion rate is reduced.

Although the results show that concrete containing SCBA provides passivation of the steel reinforcement in a more efficient way than conventional Portland cement concrete, also show that the passivity of the steel bars depends on the amount of SCBA that replace cement. So, from the scientific, technological and economic point of view, there is a need for greater quantity of essays and testing, to avoid unnecessary risks related to the durability of structures made with these new materials.

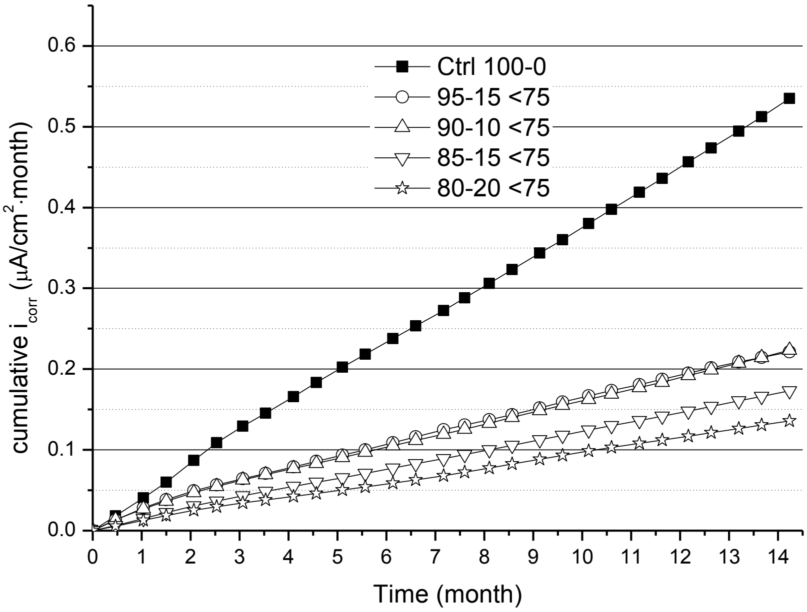

Figure 7. Evolution of the accumulated corrosion rate of specimens (CTRL 100-0) (95-5 <75), (90-10 <75), (85-15 <75) and (80-20 <75) exposed in NaCl 3.5% as a function of time.

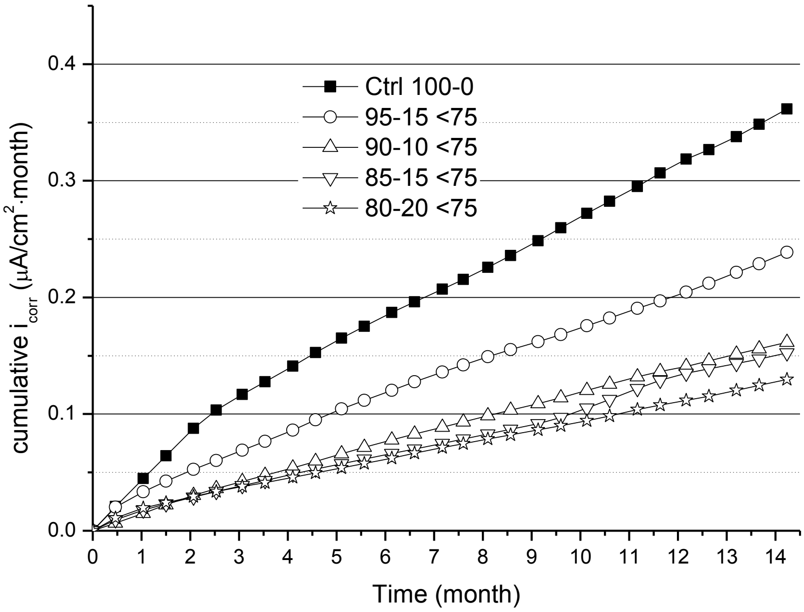

Figure 8. Evolution accumulated corrosion rate of specimens (CTRL 100-0) (95-5 <75), (90-10 <75), (85-15 <75) and (80-20 <75) exposed Na_2SO_4 to 3.5% depending on the time.

Recent research [24-29] have found that the pozzolanic reactivity of the CBCA does not affect the compressive strength, decreases porosity and capillary absorption coefficient of the concretes modified with this pozzolan. With the results of this study found that replacement of portland cement by the CBCA decreases corrosion rate and have more durable concretes

5. CONCLUSIONS

The mechanical strength measurements indicate that the best properties were obtained in the specimen with 95% Portland cement (PC) and 5% Sugar Cane Bagasse Ash (SCBA), which at 90 days developed a resistance of 43MPa, almost 25% more than the concrete with 100% Portland cement (conventional concrete). Moreover, by substituting a 20% ash from sugarcane bagasse, the mechanical strength was disadvantaged, because this decreased to 90 days approximately 7% compared to the control concrete.

The concretes that were modified with sugarcane bagasse ash showed lower values than those of concrete with 100% of portland cement. In particular, concrete with 80% of sugar cane bagasse Ash shows more technological benefits to protect against corrosion, as i_{corr} values decreased considerably compared to conventional concrete. SCBA also contributes to the densification of the cementitious matrix of concrete, which prevents the entry of passivating agents.

The durability of structures exposed to NaCl environment (shoreline) and Na_2SO_4 (groundwater or wastewater), can significantly increase the use of SCBA pozzolans as partial replacement for portland cement. This contributes to the generation of environmentally sustainable concrete.

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