

CORROSION OF REINFORCEMENT OF THE SELF-COMPACTING CONCRETE OBTAINED FROM RICE HUSK ASH AND GRANULATED BLAST FURNACE SLAG

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ABSTRACT

Electrochemical evaluations of self-compacting concrete were performed using the following criteria: cost of materials and construction, durability, and good environmental behavior and therefore, substantial amounts of additives were used, such as minerals obtained from rice husk ash (RHA) and ground granulated blast furnace slag (GBFS). In the first stage, it is necessary to make a design of self-compacting concrete using the materials described above to fulfill this purpose, which will assess the effect of the incorporation of such industrial wastes in the mechanical properties and durability against corrosive phenomena such as the inclusion of carbon dioxide and chloride ion in concrete. Using techniques Corrosion potential and linear polarization resistance were evaluated additionally corrosion products by Mossbauer spectroscopy technique. It was found that the addition of silica mixture derived from the burning of rice husk ash has a protective effect against corrosion phenomena, when incorporated up to 15% in the steel slag.

Key words: Cement, concrete, Mechanical response, Environmental performance, Corrosion, Products of corrosion.

INTRODUCTION

Portland cement concrete has clearly emerged as the material of choice for the construction of a large number and variety of structures in the world today^{1,2}. This is mainly attributed to the low cost of materials and construction of concrete structures, as well as the low cost of maintenance³. Therefore, it is not surprising that many advancements in concrete technology have occurred as a result of two driving forces, specifically the speed of construction and durability of concrete^{4,5}. During the 1940-1970 period, the availability of portland cements with high early strength, allowed the use of high water content in concrete

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mixtures that were easy to handle⁶. This approach, however, led to serious problems in the durability of structures, especially those subject to severe environmental exposures⁷.

Among recent developments, most notably is the development of concrete mixes super-fluidized; they give very high fluidity with relatively low water content. Because of its low porosity, hardened concrete is generally characterized by high strength and durability. Cements without macro-defect and chemically bonded ceramics are examples of alternative technological methods to obtain low porosity and high strength⁸. In addition to the speed of construction and durability, there is now a third driving force, namely, the favorable environmental performance of industrial materials, which is becoming increasingly more important in technology assessment for the future⁹.

The shortage of labor and savings in construction time are the main reasons behind the development and increased use of self-compacting concrete¹⁰. In some countries, readymix concrete industry is using self-compacting concrete as a noise-free product that can be used 24 hrs in urban areas¹¹. The savings in labor and longest steel molds life, industry precast concrete products is also investigating the use of the material¹². The successful development of self-compacting concrete mixtures is basically due to the high fluidity and resistance to segregation obtained by simultaneous use of a superplasticizer additive and an additive, which increased viscosity¹³. The viscosity of self-compacting concrete mixtures is greatly influenced by the dust content. A high content of cement can cause thermal cracking in some structures¹⁴. Therefore, one could use substantial amounts of mineral additives such as obtained from rice husk ash, ground granulated blast furnace slag or limestone powder.

Currently, the annual output of ash in the world is around 450 million tons. Only about 25 million tonnes, i. e. 6 percent of total ash available, is being used as a pozzolan in portland cement or concrete mixes¹⁵. The favorable environmental behavior of concrete can be made considerable, if the rate of utilization of ash from the concrete industry is accelerated in ash-producing countries¹⁶. Countries, where large quantities of blast-furnace slag as a byproduct are available, they can also benefit from the use of large volumes of granulated slag; either as an additive or as a concrete additive in the manufacture of portland cement with slag¹⁷. Every year, about 100 million tons of blast furnace slag in the world are produced. Its utilization rate as cementing material is quite low because in many countries, only a small portion of the slag is available in granular form, which it is cementitious¹⁸. Although combined portland cements containing up to 65 percent of slag is allowed according to the standard ASTM specifications, generally the slag content of commercial cements does not exceed 50 percent.

The greatest problem that occurs in structures made with concrete base is suffering corrosion of reinforcing steel¹⁹. This problem has a great dimension due to the high costs involved in repairing structures. Many times, these costs exceed the values of the initial construction and in extreme cases structure is to be destroyed²⁰. The most important causes of corrosion of reinforcing steel is: (i) Located depassivation of reinforcing steel due to chloride ion ingress and (ii) The complete depassivation of reinforcing steel due to the inclusion of carbon dioxide present in the atmosphere²¹. Harmful chloride ions may be present in the concrete, as the result of using contaminated in the manufacture of the mixture ingredients, or external contamination prior to construction.

In this article, the evaluation was done by electrochemical half-cell potential and linear polarization resistance for corrosion of steel reinforcement embedded in concrete structures having increased self-compacting concrete structures strength and decrease void spaces within the own material.

EXPERIMENTAL

Three different cement concrete mixtures were obtained: Mixture pattern (steel slag without addition), and the remaining two with different proportions of adding rice hull ash obtained from husk at combustion temperatures 700°C in percentages of 0, 10% and 15% relative to the amount of steel slag cementitious. Subsequently, cylinders $3" \times 6"$ were developed and the compressive strength at ages curing 28 and 90 days was evaluate. Similarly, cylinders were produced with the same characteristics and a corrugated steel rod with which the durability properties of the concrete was determined.

In the cementitious mixtures, it was activated with sodium silicate at a concentration of 5% expressed as weight percent of the cementitious material. The manufacture of concrete mixtures in both cases containing a dosage of cementitious material of 450 Kg/m³ was done. It was assumed that the water/cement + activating solution and water/binder is equivalent in both cases (with and without addition). This ratio was 0.45 in order to obtain proper seating (70 to 100 mm). Structural steel AISI 1020 reference commercial ASTM A706 is commonly used in earthquake-resistant construction, with a diameter of 1/8" and without any pretreatment. During corrosion tests, this served as the working electrode. For the development of electrochemical testing, it was 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 carbonation system in particular steel, they were applied to the specimens of each pretreatment. After completing the setting of the three types of material specimens, without moisture, were introduced and water from the pores in a chamber at controlled

conditions. Selected samples to simulate harsh environments were carbonated in a chamber with 65% relative humidity and 20°C, in contact with a stream of CO_2 to 3% by volume. This has done in order to ensure full carbonation of the concrete mass.

Another purpose of the study was to analyze the effect of chloride ions on the corrosion of reinforcing steel. Overexposure to chlorides was made onto specimens. Armed specimens were placed in immersion in a saturated solution of analytical 3.5% sodium chloride (NaCl PA131655.1211 Panreac 99.0%) for nine months.

The mechanical tests were performed according to the points made in ASTM C39: 2005: Test for resistance to compression of normal concrete cylinders. To evaluate the performance of mortars containing rice husk ash to the penetration of chloride ions; was performed, the permeability test, rapid chlorides based on the ASTM C1202 standard. These tests were performed after 28 days of curing.

Steel behavior was monitored using electrochemical techniques, obtaining the values of corrosion potential and polarization resistance. Except in the first, the other procedures provide quantitative measurements of corrosion rates as a parameter of the activity or passivity of steel embedded in concrete. Once the specimens electrochemical studies were completed open longitudinally by a cutter with a diamond blade, to visually study the steel-concrete interface. Corrosion products formed were established with Mössbauer spectroscopy technique.

RESULTS AND DISCUSSION

Properties of normal strength concrete

The evaluation is shown in Fig. 1. The addition of rice husk ash to obtain a concrete with a mechanical strength greater than 70 MPa, in ash mixtures, they were introduced with a particle size of 0.037 mm and addition percentages 0%, 10% and 15%. In this case the strength to addiction systems was higher than any age that slag cement (GBFS). The best results in resistance were obtained using cement with a percentage of 15%. This is due to the morphological characteristic such as high porosity and high surface area²². The increase is also due to the crystallinity that registers best behaviour in specific pattern, because the GBFS has more amorphicity. This phenomenon is due to the high fineness that enables the ash pozzolanic activity and improves the interface between the aggregates and cement paste, that is justified by the pozzolanic effect.

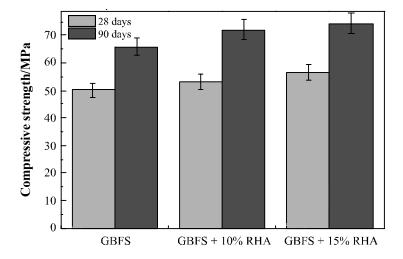


Fig. 1: Mechanical performance of GBFS reference concrete and the additions of rice husk ash 10 to 15%, showing their performance at 28 and 90 days

Chloride ion penetration resistance

The study of the effect of RHA with different percentages of addiction found by testing rapid penetration of chloride ion (ASTM1202) is reported (In Table 1). The penetration of chloride ion change is moderate (reference mixture GBFS) as low as proposed by the standard scale. 15% addition showed the best results in terms of penetration of the ion; in both cases the behaviour of the rice husk ash was the best, as it showed a reduction in the total charge passed through the concrete. It is attributed to this effect, where lower is porosity in the concrete, because their porosity decreased with increasing the built RHA. Similar test performance of the rapid penetration of chloride ion is due to increasing the resistance to chlorides with increasing admixture rate, passing from moderate to the standard sample very low in the samples spiked with RHA, achieving values below 1000 columbs²³.

	Coulombs passed	Chloride permeability	Initial current [A]
GBFS	1095.21	Low	0.0252
GBFS + 10% RHA	621.36	Very low	0.0176
GBFS + 15% RHA	521.21	Very low	0.0125

Table 1: Chloride	permeability	of concrete,	, with additions	of rice husk ash

Corrosion potential and linear polarization resistance subject to carbonation

The procedure for evaluating the potential for corrosion of steel reinforcement concrete was conducted under the ASTM C876 standard; which sets criteria relating to the potential for corrosion and corrosion condition. To carry out the technique of resistance to linear polarization (LPR), records of current is located relative to potential, where its slope is the value of the polarization resistance (Rp) and through this, one can find the corrosion current (I_{corr}), according to equation (1). This technique also provides information about LPR corrosion potential (E_{corr}) and has the advantage of being the simplest and most user-friendliness in addition to being non-destructive character²³.

$$I_{corr} = \beta/Rp \qquad (\mu A/cm^2) \qquad \dots (1)$$

Where: β = Constant, typically the value is 26 mV for steel in process of corrosion.

Rp = Polarization resistance (Ohm-cm²)

 $I_{corr} = Corrosion current (\mu A cm^{-2})$

The behavior of reinforced concrete is shown with and without the addition of rice husk ash to accelerated carbonation in Fig. 2. One can see that even an exposure time of 50 days, all reinforced concrete have good behavior, since they are potential positive ranking in the passivity denominated zone. When one reaches 60 days of exposure, it evidenced a slight decrease in the potential of the system containing activated slag, as opposed to the 10 and 15% addition, in which a slight increase in potential is observed.

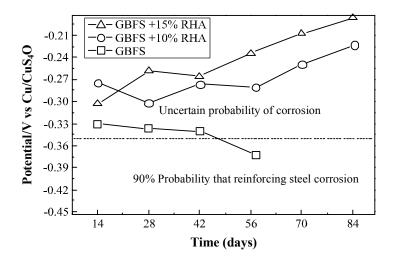


Fig. 2: Potential corrosion cementitious mixtures; evaluated at different time depending on the income of CO₂

The concretes with 15% ash; are mixtures that present a better performance up to 60 days of exposure in this medium, presenting positive corrosion potential. The steel slag concrete, has carbonatation in its entirety after 60 days, however with RHA mixtures, have adequate carbonation. Therefore it was continued 105 days, demonstrating that the addition of fly ash in concrete carbonation decreases GBFS; thereof regarding not added, indicating the use of this type of pozzolan, it requires more time reactivity to achieve their full pozzolanic activity.

Response to the variation of the potential subsequent corrosion potential measurement and response depending on the corrosion current (Icorr) is presented in Fig. 3. The measurements suggest that the concrete evaluated before 50 days, indicates a lower corrosion current $0.1 \,\mu\text{A cm}^{-2}$, which places them at a minimum level of corrosion, Posterior at 50 days GBFS concrete, leads to increased corrosion current density, moving to an area of active corrosion. For concrete best performed is with 15% addition as they have a corrosion current, which is placed in the region of low corrosion. Since the mixtures added with 10 and 15% fly ash have not been carbonated, its steel reinforcement does not show signs of corrosion, for up to 60 days of exposure, these are located in low area corrosion.

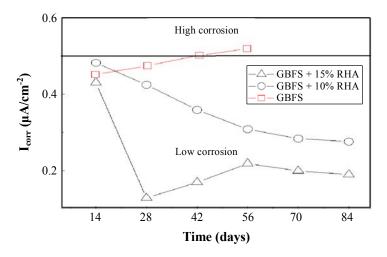


Fig. 3: Current density steel corrosion embedded in the concrete with and without addition of rice husk ash

Therefore, it is established that the reduction of the corrosion resistance of steel reinforcement caused by carbonation of steel slag concrete increases the corrosion rate. This is attributed to the activation of gehlenite in concrete reacts with the CO_2 and this in turn, reacts with the sodium hydroxide present, leading to a slight depassivation of steel reinforcement.

Corrosion potential and polarization resistance subject to environments containing chloride ions

Fig. 4 shows the behavior of the potential of corrosion of reinforced mixtures with and without addition of ash immersed in electrolyte containing chloride ion, after exposure to the CO₂ chamber and having achieved the carbonation. It is observed that the corrosion potential (E corr) of the samples with additions of ash up to 90 days of immersion, is located above those -350 mV vs Cu/CuSO₄, which places them in a corrosion uncertainty zone. After 100 days of immersion, a decrease is observed potential values, by moving to an area of 90% probability of corrosion process to occurs. This behavior can be attributed to that this time, pozzolanic reactions have not developed significantly. However, the 125 days of immersion, one starts looking at differences in performance of reinforced concrete. Samples with best performance are those containing 15% RHA of addition, as they have the tendency toward corrosion uncertainty zone, whereas the concrete without adding more negative potentials continue to show that obtained after carbonation process as always in a zone of 90% probability of occurring corrosion.

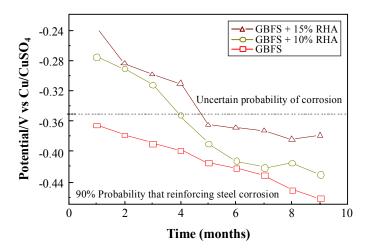


Fig. 4: Diagram corrosion probability of concrete with and without addition of rice husk ash, after having undergone subsequent carbonation and chloride ion

In Fig. 5, It is found that after 90 days of immersion, GBFS concrete mixtures with rice husk ash generate corrosion currents above those $0.5 \ \mu A \ cm^{-2}$. This behavior indicates a high level of corrosion. In the graph, it is observed that after 120 days immersion, concretes without content of ash, set up the corrosion current increased in the range of 1 $\ \mu A \ cm^{-2}$, placing the samples in a very high level of corrosion.

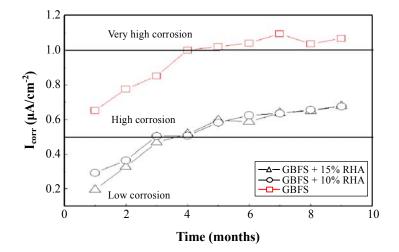


Fig. 5: Corrosion current density of concrete, which they are subject to incoming chloride ions after exposure to carbonation processes

Thus, reinforced concrete containing no addition of rice husk ash showed the worst performance, always working with more negative potentials than other mixtures tested. This is attributed to the low pozzolanic activity of the steel slag due to the high particle size with which work was done. Nevertheless it may also be attributed to the high percentage of inert material having GBFS mixture. Thus, when placing ash RHA in the mixture, greater pozzolanic activity was achieved. It is found that the higher is the percentage of fly ash, the lower is the amount of inert material added; thus, affecting the reactivity of the ash in the mixture. With the results obtained; it was found that the optimum percentage of fly ash added under circumstances is oversized 15% addition²⁴.

Characterization of corrosion products interface in concrete-steel through Mossbauer spectroscopy

The nuclear technique Mössbauer spectroscopy was used to characterize the corrosion products formed on the surface of steel ASTM A706. They are immersed in the activated slag concrete to which rice husk ash were added, with a percentage of 10 to 15%. Corrosion products were analyzed formed in two ways, exposed to different means (accelerated carbonation and then immersed in a solution containing 3.5% NaCl); thereby generating corrosion products on the steel surface. The formation of these products depends on the composition and characteristics of cementitious and the conditions to which it was exposed.

The Mössbauer source was used with bar ⁵⁷Co rhodium in a matrix, which decays

radioactively to ⁵⁷Fe, since the radioactive source process ⁵⁷Co different types of radiation emitted, Transmission Mossbauer spectroscopy (TMS) was used. The information yielded by the TMS, it is supplemented with the corrosion potential and polarization resistance. All this allowed us to detect qualitative and morphological differences in the corrosion products.

Mössbauer spectrum at room temperature of steel sample activated slag (6a), with addition of 10% of rice husk ash (6b) and an ash percentage of 15% (6c) shown in Figs. 6 (a, b and c)

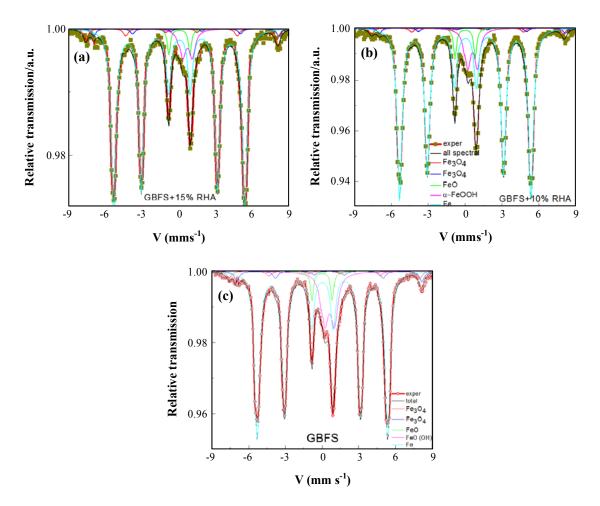


Fig. 6: Mössbauer spectra as a result of steels embedded within the matrix of the steel slag cement and additions of 10 and 15% of rice husk ash

For a curve that contains a number of points that may meet a number of additional restrictions, Mössbauer spectrum a number of Lorentzian and two doublets were used. They involved points of the experimental curve with hyperfine parameters measured giving a value of (Bf) 45.2 and 44.1 T, quadrupole splitting factor (Δ); zero to two, and isomeric deviation (δ) of 0.14 to 0.63 mm/s, They are attributed to a non-stoichiometric spinel phase magnetite (Fe_{3-x}O₄). The other singlet adjusted parameters, Bf = 32.9 T, Δ = 0.00 mm/s and $\delta = 0.55$ (1) mm/s, It is attributed to a phase of iron. For one of the doublet Δ was found 1.58 mm/s and $\delta = -0.03$ mm/s, corresponding to the presence of Wuestite; as for the other doublet Δ was found 0.78 mm/s and $\delta = 0.55$ mm/s, corresponding to the presence of goethite. For concrete with addition of 10% rice husk ash, it was found parameters of singlets. They are similar to those found for the mixture, which has no RHA, the difference is that one of the Lorentzian adjusted with parameters, Bf = 34.2 T, Δ = -0.022 mm/s and δ = 0.01 mm/s, which was attributed to a phase of iron. Regarding doublets, the following values were found $\Delta = 1.68$ mm/s and $\delta = 0.02$ mm/s, corresponding to the presence of Wuestite; in the presence in the spectrum of another doublet with values; to $\Delta = 0.71$ mm/s and $\delta = 0.52$ mm/s, is appropriate to the presence of goethite. For concrete with 15% ash was laid out the Lorentzian, which was adjusted corresponding to the parameters Bf = 31.8 T, Δ = -0.015 mm/s and $\delta = -0.00$ mm/s and is attributed to a phase of iron. In parallel, the value of one of the doublet is found $\Delta = 1.59$ mm/s and $\delta = 0.09$ mm/s; as a result of the presence of Wuestite. Meanwhile, another doublet with values of $\Delta = 0.72$ mm/s and $\delta = 0.62$ mm/s distinguished gives the representation of goethite.

CONCLUSION

In general, the inclusion of rice husk ash in concrete has had a significant effect in terms of mechanical performance, since it has been possible to obtain high strength concrete, where factors such as admixture percentage, particle size, crystal structure and temperature of burning husks perform an important task, when obtaining a silica product suitable for such applications.

The electrochemical techniques indicate adequate performance corresponding to the addition of rice husk ash in the two media analyzed; as it lowers the corrosion rate with respect to the mixture corresponding to reference GBFS, additions provide improved yield.

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REFERENCES

- 1. C. R. Gagg, Engg. Failure Anal., 40, 114 (2014).
- 2. B. Suhendro and T. Green, Procedia Engg., 95, 305 (2014).
- 3. E. Axinte, Mater. Design, **32**, 1717 (2011).
- 4. L. Czarnecki, I. Hager and T. Tracz, Procedia Engg., 108, 3 (2015).
- 5. J. W. Bullard, G. W. Scherer and J. J. Thomas, Cement Concrete Res., 74, 26 (2015).
- 6. J. E. Gillott, Engg. Geol., 9, 303 (1975).
- 7. A. Müller, V. Aragonés, Res. Transport. Business Manage., 6, 51 (2013).
- 8. M. Drábik, L. Gáliková, S. Balkovic and R. C. T. Slade, J. Phys. Chem. Solids, 68, 1057 (2007).
- 9. J. Haisma and G. A. C. M. Spierings, Mater. Sci. Engg., 37, 1 (2002).
- 10. M. F. Granata, Constr. Build. Mater., 96, 581 (2015).
- D. Carro-López, B. González-Fonteboa, J. de Brito, F. Martínez-Abella, I. González-Taboada and P. Silva, Constr. Build. Mater., 96, 491 (2015).
- R. Madandoust, M. Mohammad, R. Ghavidel and S. Fatemeh, Mater. Design., 83, 284 (2015).
- 13. Y. Hao, H. Hao, Constr. Building Mater., 48, 521 (2013).
- 14. F. Mahmoodzadeh and S. E. Chidiac, Cement Concrete Res., 49, 1 (2013).
- 15. H. T. Le, M. Kraus, K. Siewert and H. M. Ludwig, Constr. Build. Mater., **80**, 225 (2015).
- 16. D. Chopra and R. Siddique, Biosystems Engg., 130, 72 (2015).
- 17. M. E. Rahman, A. S. Muntohar, V. Pakrashi, B. H. Nagaratnam and D. Sujan, Mater. Design, **55**, 410 (2014).
- 18. V. Kannan and K. Ganesan, Constr. Build. Mater., 51, 225 (2014).
- 19. M. M. Kashani, A. J. Crewe and N. A. Alexander, Constr. Build. Mater., 41, 388 (2013).
- M. E. Mitzithra, F. Deby, J. P. Balayssac and J. Salin, Nucl. Engg. Design, 288, 42 (2015).

- 21. P. Garcés, P. Saura, E. Zornoza and C. Andrade, Corrosion Sci., 53, 3991 (2011).
- 22. N. K. Brown, M. J. Kowalsky and J. M. Nau, J. Constr. Steel Res., 107, 111 (2015).
- 23. P. Gaydecki, I. Silva, B. T. Fernandes and Z. Z. Yu, Sensors and Actuators A: Phys., 84, 25 (2000).
- 24. A. Bautista, S. M. Alvarez, E. C. Paredes, F. Velasco and S. Guzman, Constr. Build. Mater., **95**, 186 (2015).

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