Assessment of high performance concrete containing fly ash and calcium nitrite based corrosion inhibitor as a mean to prevent the corrosion of reinforcing steel

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Abstract. This research analyses the effectiveness of the water-to-cement ratio (w/c), fly ash and a calcium nitrite based corrosion inhibitor to prevent the corrosion of reinforcing steel embedded in high performance concrete. The interactive effect between the inhibitor and fly ash was evaluated because the occurrence of a negative effect when both ingredients are added together in a concrete mixture has been reported. All the concrete mixtures studied in this investigation had 8.2% of silica fume. Twenty seven prismatic concrete specimens were fabricated with dimensions of 55 x 230 x 300 mm each containing two steel rods embedded for the purpose of corrosion monitoring. The specimens were exposed to a simulated marine environment with two daily cycles of wetting and drying for one year. To evaluate the deterioration of the specimens corrosion potentials and linear polarization resistance tests were carried out. The results indicate that the use of a low w/c, the addition of fly ash and the addition of the corrosion inhibitor contributed to the reduction of the corrosion of steel in the concrete specimens. The results further suggest that the combination of fly ash and corrosion inhibitor does not promote the deterioration of the concrete matrix.

1. Introduction

High performance concrete (HPC) can be made with cement alone or any combination of cement and mineral components, such as, ground granulated glass blast-furnace slag (GGBS), fly ash (FA), silica fume (SF), metakaolin, and fillers, such as limestone powder. Ternary systems are increasingly used to take advantage of the synergy of some mineral components to improve concrete properties in the fresh and hardened states, and to make high performance concrete more economical and ecological [1-2]. Corrosion of reinforcing steel in ordinary and high performance concrete has become a major problem world-wide, especially in buildings, bridges, parking decks, tunnels and other buildings exposed to a seawater or de-icing salts. As a result of this deterioration process, the repair costs nowadays constitute a major part of the current spending on infrastructure [3].

The results reported in the literature on the use of the combination of Calcium Nitrite based corrosion inhibitor (CNI) and fly ash (FA) in high performance concrete, when used to prevent corrosion, differ considerably. According to Li et al., [4] the addition of CNI into the mix resulted in the deterioration of the resistance to chloride diffusion which had been previously enhanced by the incorporation of fly ash. Through the mercury intrusion porosimetry test, the influence of CNI on chloride diffusion was studied further. The results showed that the addition
of CNI leads to the increase of micropore diameter. In another research, the test results demonstrate that the incorporation of CNI accelerates the formation of calcium hydroxide and ettringite crystals, and weakens the pore refinement effect caused by the secondary hydration reaction of fly ash and microsilica [5]. Montes [6] mentioned that the inhibitor and fly ash alone do not provide sufficient protection against corrosion, but apparently the combination of the two provides a significant benefit in high performance concrete, increasing the resistance to chloride diffusion.

Because of the contrasting results more research is needed, especially on the interactive effects of fly ash and calcium nitrite based corrosion inhibitor when they are used as corrosion prevention methods.

In view of this, this paper presents the results of research aimed to investigate the effects of fly ash and CNI on the corrosion potentials and corrosion densities of reinforcing bars embedded in three different water-to-cement ratio concretes.

1. Experimental program

1.1. Materials and Methods

Maximum size of the coarse aggregate was 12.5 mm and its relative density was 2.69. Natural river sand was used as fine aggregate, which has a fineness modulus of 2.65 and a relative density of 2.62. CSA Type 10 Portland cement, which already has 8.2% silica fume as cement replacement, was used for all the concrete mixtures. The fly ash used belongs to Type F, according to the ASTM classification. The commercial Calcium Nitrite based corrosion inhibitor used in this study contains a minimum of 30% of Nitrite ions. The solution (simulated salt water) was prepared as recommended by the ASTM D 1141-80 Standards.

For the development of this project, a 33 factorial design was performed. Twenty seven concretes considering three water-to-cement ratios (0.29, 0.37 and 0.45), three fly ash replacement levels (0%, 20% and 40%) and three dosages of Calcium Nitrite based corrosion inhibitor (0, 12.5 and 25 l/m3) were prepared. To evaluate the effect of artificial seawater on the corrosion process of the reinforcing bars, twenty seven small-scale slabs were cast. Each slab had embedded two black steel bars. A marine environment simulation setup was utilized to test the specimens made from each mixture. The setup for accelerated corrosion testing consists of two chambers where it is possible to simulate wetting and drying cycles in concrete specimens in marine exposure conditions. Two complete cycles are performed within a 24-h period as compared with two tidal cycle in a natural marine environment. Also, the effect of temperature ranging from 26 ± 2°C in the wet cycle to 55 ± 2°C in the dry cycle is considered.

When there is active corrosion, current flow through the concrete between anodic and cathodic sites, the current is accompanied by an electric potential field surrounding the corroding bar. The equipotential lines intersect the surface of the concrete and the potential at any point can be measured using the half-cell potential method [7]. The polarization resistance can be measured by direct current measurements, impedance spectra, and transient techniques [8].

In this research, the corrosion current density (Icorr) was estimated from results of Linear Polarization Resistance (LPR) using a CMS 105 equipment (Gamry instruments Inc.) was used. The parameters to carry out this test were: scan rate of -20 to 20 mV. For the corrosion potentials test (Ecorr) [9] a calomel/mercuric chloride reference electrode and a high impedance voltmeter were used. Measurements for both corrosion potentials and corrosion current density were taken every other month during one year.
2. Test results and discussions

Figure 1 shows results of the corrosion potentials. For their analysis and interpretation the threshold values proposed by the ASTM 876 standard [10] can be used. The standard divides the corrosion condition in low risk, intermediate risk, high risk and severe corrosion. In this research, the measurements indicate that the water-to-cement ratio has a significant effect on the probability of corrosion. Results also show that the lower the water-to-cement ratio the lower the probability of corrosion. However, the 0.45 water-to-cement ratio concrete was not able to protect the steel reinforcement because at the end of the experiment had severe corrosion. Results are consistent with findings related to the use of a w/c lower than 0.4 when durable reinforced concrete is required [11]. The addition of 20% fly ash decreased the probability of corrosion and this effect was more evident for 0.29 w/c concrete. For higher w/c ratios seems that 20% fly ash is not good enough to prevent severe corrosion. Nevertheless, 40% fly ash was able to prevent severe corrosion, especially for 0.29 and 0.37 w/c concretes. Similar effect than that observed for fly ash can be observed when 12.5 L/m$^3$ of CNI was added to the concrete, this is, it was more effective in lower w/c concretes. In this case, even the addition of 25 L/m$^3$ of CNI was not enough to prevent the corrosion of 0.45 w/c concrete. The combination 1, consisting of 20% fly ash and 12.5 L/m$^3$ of CNI, was effective to decrease the corrosion potential of 0.29 and 0.37 w/c concretes to a low risk; however, the 0.45 w/c concrete showed severe corrosion at the end of the experiment.

The combination 2, consisting of 40% fly ash and 12.5 L/m$^3$ of CNI, did show only a slight difference reducing the corrosion risk of the steel reinforcement when compared to the combination of 20% fly ash and 12.5 L/m$^3$ of CNI. Nevertheless, the corrosion risk of the 0.45 w/c concrete containing this combination was less than for combination 1. The combination 3, consisting of 20% fly ash and 25 L/m$^3$ of CNI, had similar effect than combination 1 showing a reduction of the corrosion risk of the steel bars for 0.29 and 0.37 w/c concretes and not significant reduction for the 0.45 w/c concrete. Finally, the combination 4, consisting of 40% fly ash and 25 L/m$^3$ of CNI, was the most effective of all maintaining a intermediate corrosion risk for all the w/c ratio concretes studied.

Figure 2 shows the corrosion current densities recorded for all the specimens tested. In this case, the criterion proposed by Broomfield [12] was used for the classification of the corrosion condition. In such a work, similarly to the corrosion potentials technique, Broomfield proposes that the corrosion condition can be passive, low, intermediate and severe. The tendencies of the corrosion current densities agree in a great deal with those from the potentials. This corroborate the positive observed effects of the different combinations of fly ash and Calcium Nitrite Inhibitor on the reduction of corrosion of the steel reinforcement embedded in high performance concrete of inhibitor and the addition of 40% fly ash values of 50% probability of corrosion were presented. To the water/cement ratio of 0.45 is observed that, at higher amounts of fly ash and corrosion inhibitor, values lower risk probability corrosion are obtained. Severe corrosion values (greater than 90% risk) was reduced to values of 10% risk of corrosion using a combination of 40% ash and 25 L/m$^3$. Is also observed in the graph h) the water/cement ratio of 0.29 and 0.37, in combination with 20% fly ash and 25 L/m$^3$ inhibitor, values lower risk of corrosion were obtained. Based on the criteria established by Broomfield [10] and the analysis of the graphs of Figure 2 in which it is observed that the combination of fly ash and corrosion inhibitor decreases the corrosion rate for the water/cement ratios studied, and that higher amounts of fly ash and corrosion inhibitor generate lower rates corrosion of the reinforcing steel, it is concluded that the combination of fly ash and corrosion inhibitor decreases the reinforced concrete corrosion when subjected to a chloride contaminated environment.
Figure 1 - Corrosion potentials vs Reference electrode
Fly Ash Content

0%  20%  40%

Figure 2 - Corrosion density
3. Conclusions
Based on the analysis of the results the following conclusions can be drawn:
1.-It was demonstrated that the incorporation of fly ash or CNI into concrete alone is useful to
decrease the level of corrosion; however, this is a temporary effect as they do not provide full
protection to the steel reinforcement because only a delay the corrosion process is experienced.
Also, it was corroborated that reinforced concrete exposed to a chloride contaminated environment
should be prepared with a w/c lower than 0.4.
2.-The addition of 20%fly ash and 12.5 L/m$^3$ of CNI is effective decreasing the corrosion of steel
reinforcing embedded in low w/c concretes.
3.-The addition of 40%fly ash and 12.5 L/m$^3$ of CNI is also effective decreasing the corrosion of
steel reinforcing embedded in low w/c concretes; however, the increase from 20 to 40%fly ash
shows only a marginal effect decreasing corrosion.
4.-The addition of 20%fly ash and 25 L/m$^3$ of CNI is effective decreasing the corrosion of steel
reinforcing embedded in low w/c concretes.
5.-The addition of 40%fly ash and 25 L/m$^3$ of CNI is effective decreasing corrosion of the concretes
evaluated in this research maintaining an intermediate level of corrosion during the testing period.

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