Evaluation of electrochemical phenomena of fly ash and blast furnace slag in commercial cement mixtures

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Abstract. Steel reinforced concrete is the most commonly used composite material in construction; however, large amounts of energy, natural resources are required for its manufacture and is susceptible to corrosion in the presence of aggressive environments. However, there are alternatives aimed at sustainable development, through the gradual replacement of ordinary cement with other Supplementary cementitious materials. Consequently, the present investigation evaluates the effect of fly ash and granulated blast furnace slag on the electrochemical phenomena of steel bars, embedded in a cement paste matrix, characterized by scanning electron microscopy, X-ray fluorescence and area surface to establish variations in electrochemical phenomena evaluated by Tafel extrapolation curves, half-cell potential, resistance to linear polarization and electrochemical impedance spectroscopy. The electrochemical conditions show that the surface areas and composition affect the passivation degree; therefore, mixtures with FA generate passive protection and on the contrary, the mixture with GBFS does not present any type of corrosion protection.

1. Introduction
Reinforced concrete (RC), thanks to its versatility, low cost, ease of production, high mechanical strength and durability is the most used construction material in the world [1]. However, several problems affect its integrity in terms of durability, mainly related to corrosion of the reinforcement in aggressive environments; although, the pH of the ordinary Portland cement (OPC) is highly alkaline (pH > 12.5), which helps the formation of a passive film that can prevent corrosion [2-3]. Nevertheless, the reduction of the pH of the electrolyte in the pores undermines the stability of the passivation film, corrodes the surface of the reinforcing steel, reducing the load capacity, seismic resistance and the useful life of the structure [3-4]. The binder plays a fundamental role in the prevention or acceleration of the corrosion phenomenon due to the porous microstructure facilitates or hinders the penetration of dissolved gases and contaminants in the concrete formed in the hydration processes; consequently, the protection of reinforcing steel against corrosion is directly influenced by the cement, which will provide the only barrier between steel and the external environment [5-6]. Likewise, the use of industrial by-products has become a new field for the development of supplementary cementation materials (SCM), which have contributed to the fight against the depletion of natural resources, the reduction of greenhouse gases and the elimination of waste solids [1-8]. Therefore, it's possible to add fly ash (FA) and granulated blast furnace slag (GBFS), according to ACI 232 and ACI 233 standards [9-10], for the reaction process with these SCMs is similar to that produced by the hydration of the CPC, therefore, are routinely specified in the manufacture of cements and have significant influence on the hydration...
behavior and refinement of the pore structure [5-7]. Consequently, the present investigation evaluates the electrochemical potential and corrosion rates using steel bars, embedded in CPC paste added with FA and GBFS, in order to establish the relationship of these SCMs in the electrochemical activity of the mixtures and their corrosion protection capacity due the effects of these SCMs in conventional cements are not entirely clear, especially the electrochemical potential, directly related to the formation of the passivating film in the steel reinforcement which protects against corrosion in the time [5-11].

2. Materials
The CPC of general use (UG) and SCM used occurs in the region of Boyacá, Colombia; The CPC for general use is produced by Colombian cement companies [12]. FA and GBFS are produced and supplied by the thermoelectric power plant "Termopaipa" and by the steel company "Acerías Paz del Río" respectively. The reinforcement used were low alloy corrugated bars for concrete reinforcement, grade 60 mm and 6.35 mm (1/4”) diameter according to the ASTM A-706 standard [13].

3. Preparation of specimens
The mechanical mixing of cement paste was performed in accordance with ASTM C-305 [14]; for the sample preparation, water/cement ratio (a/c) was used according to the amount of water required for normal consistency followed ASTM C-187 standard [15]. The preparation of 50 mm cubic samples was performed following the ASTM C-109 standard [16], molding three samples for each type of mixture as shown in Table 1.

| Table 1. Proportions and quantity of cement paste cubes. |
|----------------|----------------|------|
| Quantity Paste composed  | w/c  |
| 3  | 100% CPC | 0.33 |
| 3  | 60% CPC + 40% FA | 0.47 |
| 3  | 60% CPC + 40% GBFS | 0.33 |

In addition, the cubes were made using a classical configuration of a three-electrode cell observed in Figure 1. A polished steel rod with 5 mm of diameter was used as a work electrode (WE), covered with anticorrosive epoxy at each end to isolate the study area; the reference electrode (RE) used was Copper/Copper Sulphate - saturated calomel electrode (Cu/CuSO₄ – SCE) and stainless steel bars were used like counter electrode (CE). Subsequently, the preparation, cleaning and evaluation of samples for corrosion tests was performed according to ASTM G1 standard [17].

![Figure 1](image_url)  
(a) Specimen and experimental arrangement. (a) Experimental arrangement; (b) Sample preparation and curing.
4. Raw materials characterization

Micrographs by scanning electron microscopy (SEM) are shown in Figure 2.

![SEM micrographs of cements at 5000x. (a) CPC; (b) FA; (c) GBFS.](image)

Figure 2, the SEM analysis allowed to establish typical microstructural characteristics of AF under study, such as its spherical shape, smooth surfaces and high surface area [18-19] and morphological characteristics of GBFS such as the larger particle size between cementants, angular shapes and sharp edges, presumably due to grinding [20]; therefore, the decrease the surface area in GBFS generates reduction in reactivity, which depends the chemical composition, mineralogy and fineness, affecting the degree of hydration, microstructure and porosity [21-22], which is consistent with the specific surface results according to the ASTM C-204 standard [23], together with the physisorption analysis using the mathematical treatment proposed by Brunauer Emmett and Teller (BET); The results obtained are indicated in Table 2.

| Material | Surface area (m$^2$/g) | Pore volume (cm$^3$/g) | Pore size (nm) |
|----------|------------------------|------------------------|----------------|
| CPC      | 4230                   | 2.0                    | 0.002          | 16.9 |
| FA       | 4640                   | 5.0                    | 0.010          | 7.9  |
| GBFS     | 1240                   | 0.5                    | 0.003          | 25.5 |

Specific surface analysis, together with SEM, determined that FA has low density and high porosity, which is consistent with its high surface area and high pore volume, therefore, was necessary add more water for optimum consistency as shown in Table 1; nevertheless, GBFS has the lowest surface area, which offers the most unfavorable conditions for hydraulic reactions from the point of view of the fineness of the material; likewise, the cementitious materials evaluated by X-ray fluorescence (XRF) exposed in Table 3, in order to establish the compositions that may affect its reactivity.

| Component | CPC         | FA          | GBFS        |
|-----------|-------------|-------------|-------------|
| SiO$_2$   | 16.86± 0.88 | 61.86± 3.71 | 32.05± 3.79 |
| CaO       | 60.01± 2.70 | 0.71± 0.04  | 21.33± 2.67 |
| Al$_2$O$_3$| 3.73± 0.29  | 22.61± 4.14 | 9.35± 2.17  |
| MgO       | 0.93± 0.13  | 0.53± 0.06  | -           |
| Fe$_2$O$_3$| 1.90± 0.61  | 4.83± 0.14  | 31.07± 7.59 |
| SO$_3$    | 2.57± 1.03  | -           | 1.00± 0.25  |
| MnO       | 0.03± 0.01  | -           | 1.19± 0.63  |
| K$_2$O    | 0.28± 0.04  | 1.60± 0.23  | 0.33± 0.09  |
| TiO$_2$   | 0.14± 0.02  | 1.09± 0.01  | 2.30± 7.97  |

Five samples of each material were used, using the t-test and a confidence of 95% (p≤ 0.05).
Based in Table 3, the CPC has CaO and SiO$_2$ content greater than 80%, which are the main compounds for the development of calcium silicate hydrates and consequently favorable mechanical strengths [24-25]. The composition of AF is similar to other studies, with majority contents of SiO$_2$ and Al$_2$O$_3$ [24], and Slag contains Fe$_2$O$_3$; component considered as an impurity because of its insufficient cementing capacity [26].

5. Analysis of electrochemical phenomena

The evaluation of the kinetic electrochemistry was carried out using the Gamry® equipment, reference 750, averaging the results generated in all analyzed.

5.1. Electrochemical potential measurements monitoring

The open circuit potential measurement (OCP) technique was performed on the interface, evaluating the potential difference between the steel surface and the RE, following the guidelines established in the ASTM C-876 standard [27], which establishes that potentials less than $-0.35$ V CSE generate corrosion in reinforcing steel at the time of measurement with a probability greater than 90%; The results of the OCP are observed in Figure 3.

![Figure 3. Electrochemical potential of cementitious materials.](image)

Analysis of Figure 3 indicates stabilization of the electrochemical potentials occurred after fourth day of the test, showing corrosion activity of CPC+FA, which is 74% lower than CPC, therefore, FA doesn't affect the potential electrochemical behavior in the CPC mixtures. However, CPC + GBFS has 57.4% more negative corrosion potentials, which indicates greater electrochemical activity and consequently greater possibility of corrosion, associated with presence of passivation in reinforcing steel, product of less consolidation in pore network of cement mixture in hardened state, due to low fineness and the high electrical conductors like iron.

5.2. Tafel extrapolation technique

Tafel extrapolation polarization curves (TP) of Figure 4 describe the relationship between the current density and the electrical potential of the submerged mixtures for 28 days.

The Tafel extrapolation technique (TP) showed in Figure 4, is an electrochemical method to calculate the corrosion rate according to the intensity of the corrosion current (Icorr) and the Tafel slopes [28]. Therefore, the polarization curves show the steel passivity state and the oxygen intrusion in the submerged. In addition, great slopes of the anodic reaction denote stabilization of the current with respect to the change of potential, which leads to a state of protection by a passive film. On the contrary, Low (or intermediate) slopes, implies absence of this protection [29]. The CPC + GBFS specimen presents a higher anode current (Icorr) and a lower passivation degree than the other two mixtures; therefore, it exhibits a higher corrosion rate. The most passivated steel is found in the CPC paste. The three mixtures present similar oxygen diffusion rates, demonstrated in the linearity of the cathodic
curves [30]. Additionally, the diagrams provide the corrosion potential (Ecorr); which coincides with the proportions found in the previous section.

![Tafel polarization curves of cementitious materials.](image)

**Figure 4.** Tafel polarization curves of cementitious materials.

### 5.3. Linear polarization resistance results analysis

The linear polarization resistance (LPR) technique is a procedure used to measure the corrosion rate based on the linear relationship of the current with its corrosion potential [31]. In the LPR tests the potential was varied between ± 30 mV with respect to the Ecorr and the sweep speed was 0.17 mV/s, in accordance with that recommended by the ASTM G59 standard [32]. Table 4, shows the results of the LPR technique.

| Time (days) | Parameter | CPC | CPC+FA | CPC+GBFS |
|-------------|-----------|-----|--------|----------|
| 28          | Ecorr (mV) | -639.10 | -566.60 | -79380 |
|             | Rp (kohms) | 10.79 | 5.20 | 2.19 |
|             | Icorr (μA/cm²) | 0.57 | 0.62 | 2.40 |
|             | CR (mmy) | 0.0066 | 0.0072 | 0.0278 |
| 32          | Ecorr (mV) | -773.60 | -576.20 | -760.70 |
|             | Rp (kohms) | 2.53 | 5.03 | 2.36 |
|             | Icorr (μA/cm²) | 1.01 | 0.63 | 2.22 |
|             | CR (mmy) | 0.0117 | 0.0073 | 0.0258 |
| 41          | Ecorr (mV) | -648.30 | -567.80 | -746.50 |
|             | Rp (kohms) | 3.20 | 4.80 | 2.03 |
|             | Icorr (μA/cm²) | 0.89 | 0.66 | 2.87 |
|             | CR (mmy) | 0.0103 | 0.0077 | 0.0333 |

Table 4 shows the corrosion indicators evaluated by LPR are consistent with the corrosion results by Tafel and OCP technique, where the CPC + FA mixture reduced the corrosion rate (CR) up to 25% compared to the single CPC mixture; on the contrary, CPC + GBFS has the lowest value of polarization resistance (Rp); therefore, the highest rates of Icorr and CR, the latter with an increase of mmy (millimeters per year) up to 320%, which reveals a low resistance to the polarization of the samples that simulates the reinforcing steel in CPC + GFBF; therefore it is inferred that the electrochemical activity on the surface of the reinforcing steel embedded in mixtures with GBFS prevents its passivation.

### 5.4. Electrochemical impedance spectroscopy

Is a technique used to determine the contribution of electrodes or electrolytic processes, through the measurement of opposition to the electrical signal or the impedance of the electrical circuit when combining passive elements of an electrical circuit: resistance, capacitance and inductance, when an alternating current is applied to these elements, the resulting current is obtained using Ohm’s law [33].
At low frequencies, the total impedance, $R_p + R_c$, is defined; (electrical resistance of the medium) in high frequency, in order to evaluate $I_{corr}$ and $CR$; these parameters are shown in Table 5.

**Table 5. EIS technique parameters evaluation.**

| Time (days) | Parameter | CPC | CPC+FA | CPC+GBFS |
|-------------|-----------|-----|--------|----------|
| Day 28      | $R_c$ (kohms) | 0.17 | 0.06  | 0.19     |
|             | $R_p$ (ohm)   | 3.48 | 8.93  | 3.60     |
|             | $I_{corr}$ ($\mu$A/cm$^2$) | 0.73 | 0.34  | 1.43     |
|             | $CR$ (mmy)    | 0.0085 | 0.0040  | 0.0166 |
| Day 32      | $R_c$ (kohms) | 0.11 | 0.09  | 0.11     |
|             | $R_p$ (ohm)   | 3.46 | 9.1   | 3.55     |
|             | $I_{corr}$ ($\mu$A/cm$^2$) | 0.73 | 0.34  | 1.46     |
|             | $CR$ (mmy)    | 0.0085 | 0.0039  | 0.0169 |
| Day 41      | $R_c$ (kohms) | 0.30 | 0.07  | 0.12     |
|             | $R_p$ (ohm)   | 3.65 | 8.90  | 3.43     |
|             | $I_{corr}$ ($\mu$A/cm$^2$) | 0.71 | 0.34  | 1.51     |
|             | $CR$ (mmy)    | 0.0082 | 0.0040  | 0.0175 |

Table 5 shows the evaluation the effect of the resistance of the $R_c$ medium (ohmic fall of the cementitious paste), which generated lower values for the CPC + FA mixture. The $R_p$ (polarization resistance) values show that the CPC + FA samples have the highest $R_p$ values. The size of the area exposed to corrosion allows the CPC and CPC + GBFS samples to produce similar $R_p$ values; however, the CPC + GBFS sample has values of $I_{corr}$ and $CR$ 210% higher than CPC while CPC + FA shows values up to 47% lower than CPC.

**6. Conclusions**

The measurement of electrochemical phenomena through different techniques, together with the influence of the surface area and the composition allowed to establish the influence of FA and GBFS in the passivation of the reinforcement steel embedded in cement mixtures, where the highest degree of electrochemical activity corresponds to The CPC + GBFS mixture caused by the high concentration of iron oxides that make up this material, its low surface area and its high porosity, which generates a reinforcing steel surface free of passivation and consequently, greater susceptibility to corrosion. In contrast, CPC and CPC + FA have a typical degree of passivation in alkaline systems; therefore, the use of ashes is favorable as an addition in CPC to protect the current attack reinforcements and at the same time reduce the environmental impact generated by its production.

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