

Sulfate Attack and Reinforcement Corrosion in Concrete with Recycled Concrete Aggregates and Supplementary Cementing Materials

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As strategies to contribute to the concrete industry sustainability, reinforced concrete was fabricated using recycled concrete coarse aggregate and replacing partially portland cement with supplementary cementing materials as fly ash and silica fume. On test specimens, partially immersed in 3.5% Na₂SO₄ aqueous solution, the effect of the recycled and supplementary materials against sulfate attack and reinforcement corrosion was evaluated. For such aim, weight loss of concrete and corrosion potentials, corrosion current density of reinforcement were determined by means of electrochemical techniques as open circuit potential and linear polarization resistance, respectively.

Keywords: Recycled aggregate concrete, Sulfate attack, Supplementary cementing materials, Corrosion

1. INTRODUCTION

Concrete exposed to sulfate solutions can be attacked and suffer deterioration by expansion. The deterioration of reinforced concrete by sulfate attack causes the reinforcing steel to be exposed to the action of aggressive agents starting the corrosion of the reinforcement [1]. It is known that the concrete resistance to sulfates can be significantly improved producing a dense waterproof concrete. However, with the urgent need of using recycled materials to contribute in sustainability, from the year

2000 the number of studies of Recycled Aggregate Concrete (RAC) has significantly increased [2-11], with the purpose of using it in the construction of structures of plain concrete and reinforced concrete. By the nature of the recycled concrete aggregates, RAC is more permeable and has a lower density than conventional concrete and therefore, sulfates attack on RAC could be more aggressive than on conventional concrete. It is necessary to know the characteristics of RAC exposed to sulfates, so that necessary precautions can be taken to minimize the deterioration to insignificant levels. Unlike conventional concrete, there is little research [12-16] about the performance of RAC with Supplementary Cementing Materials (SCM) but no of these investigations approaches the subject of external sulfate attack. This phenomena is well known and is described in other works [17,18].

The objective of this work was to evaluate the behavior of RAC with SCM exposed to sulfate solution. The deterioration of concrete (weight loss) and corrosion rate of reinforcement by means of electrochemical techniques were evaluated.

2. EXPERIMENTAL PART

It was produced three sets of specimens with water-cementing material ratio of 0.48: one series made with 100% recycled coarse concrete aggregate (RCA) and 100 % Compound Portland Cement (CPC) [19], series made with 100% RCA and 30% FA as a partial replacement of the CPC, and finally, series made with 100% RCA and 10% SF as a partial replacement of the CPC. These specimens were cured for 28 days in a chamber with temperature of 23 ± 2 °C and 98 ± 1 % of RH. Characteristics and proportions of mixtures are presented in Table 1.

Table 1. Characteristics and proportion of the test mixtures (by 1m^3 of concrete).

Materials (Kg)	Mixtures identification		
	RA 100% CPC	RA 30% FA	RA 10% SF
Water	213.31	213.31	213.31
RCA	870.58	870.58	870.58
Sand	915.35	915.35	915.35
Cement	444.44	311.11	400.00
SCM	0.000	133.33	44.44

2.1. Materials

RCA comes from the crushing of concrete specimens made with natural aggregates, CPC with a water-cement ratio of 0.50 and curing for a 28-day period with controlled temperature and relative humidity (RH) of 23 ± 2 °C and 98 ± 1 %. Natural aggregates come from quarry crushed rock (coarse) and river sand (fine). Table 2 shows some of the physical properties of these aggregates.

Table 2. Physical properties of the aggregates used in concrete mixtures

Type of aggregate	Relative density (g/cm ³)	Absorption (%)	Humidity (%)	Fineness module (%)	Maximum size (mm)
Recycled coarse	2.19	6.55	2.14	-	19
Natural coarse	2.50	0.44	0.28	-	19
Natural fine	2.43	4.08	6.66	2.73	4.76

As SCM, Mexican Class F FA according to ASTM C618 [20] and SF North-American with the requirements of ASTM C1240 [21] were used. Table 3 shows the physical and chemical properties of these materials.

Table 3. Physico-chemical properties of cementing materials.

Chemical composition (% of weight)								
Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	K ₂ O	Na ₂ O	MgO
CPC	19.94	4.40	2.97	63.50	3.08	0.42	0.12	-
FA	58.84	16.72	3.52	7.35	0.13	0.79	0.94	1.76
SF	95.22	0.08	2.37	0.26	0.11	0.56	0.30	0.24
Physical properties								
	Density (g/cm ³)	Specific surface, BET (m ² /kg)			Average size (μm)			
CPC	3.15	1400			15-25			
FA	2.35	1200			5-15			
SF	2.27	19600			0.1-0.2			

2.2 Methods

Concrete cylinders, 15 cm in diameter and 30 cm in height, with two centrally-embedded reinforcing bars, were used to study the effect of sulfate environment on the weight loss of concrete and rebar corrosion of reinforcing steel. The test specimens were exposed in a 3.5% of Na₂SO₄ aqueous solution and the reduction/increase in weight of the reinforced concrete specimens was evaluated periodically, whereby the specimens were retrieved, air-dried for one day in a laboratory environment (21 ± 2°C) and weighed. The weight loss (WL) was determined using the following relationship:

$$WL(\%) = \left[\frac{W_i - W_f}{W_i} \right] \times 100$$

Where W_i = average initial weight of triplicate specimens (g); and W_t = average weight of triplicate specimens after a prescribed exposure period (g).

Reinforcement corrosion of the embedded steel was monitored by measuring the corrosion potentials and polarization resistance at regular intervals. The corrosion potentials (E_{corr}) were measured using a high impedance voltmeter and recording the potentials with respect to a copper/copper sulfate (Cu/CuSO₄) reference electrode. The linear polarization resistance (LPR) technique was used to measure the polarization resistance (R_p) in a Potentiostat/Galvanostat of ACM Instruments. Details of the electrochemical techniques can be found in another work [22]. The test parameters were a potential scan of ± 20 mV to a scan speed of 10 mV/min. The basics principles of electrochemical corrosion of reinforced concrete is well known [23,24] and the experimental testing is shown in Figure 1.

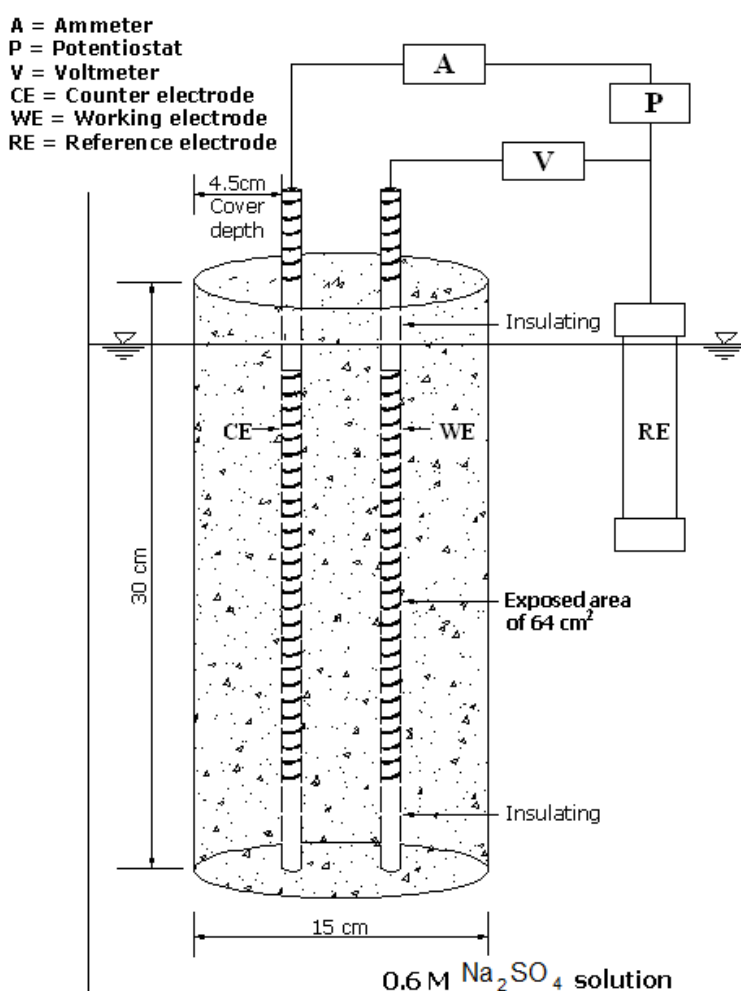


Figure 1. Experimental scheme for testing LPR.

From the curves potential against current density the R_p of the systems in study was obtained, same that was used to calculate the corrosion current density (i_{corr}) of the systems through Equation 1

[25], where B is a Tafel constant with recommended value [26-29] of 0.052 V for the passive corrosion of steel in concrete.

$$i_{corr} = \frac{B}{R_p} \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. Concrete weight loss

The data on the weight loss of reinforced concrete specimens exposed to sulfate solution are schematically presented as a function of the exposure time in Figure 2. These data indicate that the weight loss of concretes initially decreased due to an increase in the weight of specimens upon exposure to the test solution compared with their initial weights. Thereafter, the weight loss increased considerably after four months in the RA 100% CPC concrete. For the specimens with SCM the increase of weight loss is not considerable and it appears after four months. This behavior obeys to that at the beginning the capillary pore system is filled by little expansive reaction products compacting the cementing matrix and increasing the weight. Immediately, the expansion of these products is increased to a great extent generating fractures in the cementing matrix, loosening of material and therefore the weight of specimen decreases.

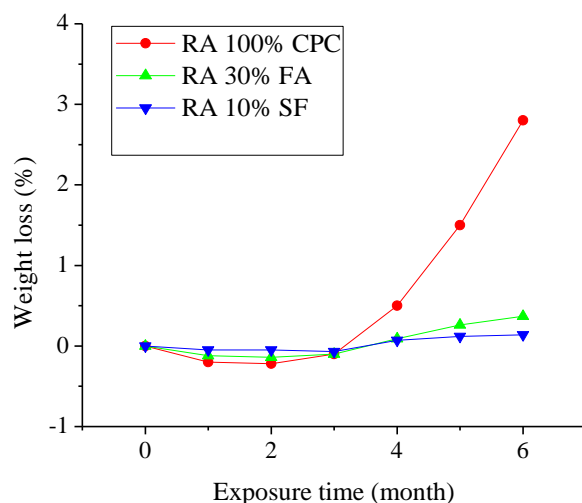


Figure 2. Weight loss of concrete in sulfate environment.

The maximum weight loss was 2.8% after six months of exposure in the RA 100% CPC concrete specimens followed by a weight loss of 0.37% in the RA 30% FA concrete, and the minimum weight loss (0.14%) was in RA 10% SF concrete. From these results is evident the contribution of SCM in pore refinement of cementing matrix, which prevents the easy penetration of sulfate ions

towards and within concrete. Another probable cause of the effectiveness of the SCM in decrease the deterioration by sulfate attack is the calcium hydroxide $[Ca(OH)_2]$ or $[CH]$ consumption during the pozzolanic reaction, which means that the amount of formed gypsum can be smaller in the mixtures with SCM with respect to mixtures with 100% CPC.

3.2. Corrosion potentials

In Figure 3 the results of corrosion potentials of evaluated test specimens are shown. The horizontal broken lines show the limits corresponding to the corrosion probability criterion suggested in the norm ASTM C876 [30].

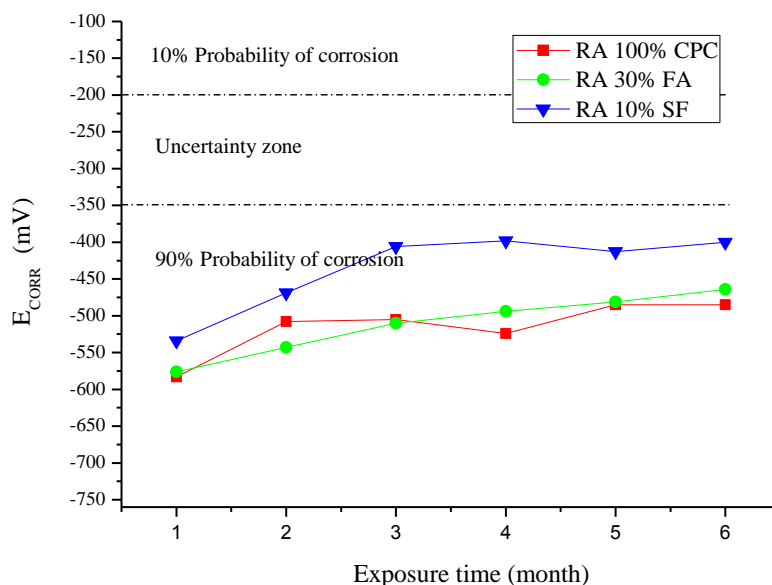


Figure 3. Variation of E_{corr} of the reinforcement steel as a function of the exposure time.

In Figure 3 it can be observed that in the six months of exposure the corrosion potentials, of all the reinforced concrete systems, show fluctuation ranging from -550 to -400 mV / Cu-CuSO₄ with a slight decrease during the months, towards more noble values; according ASTM C 876 these E_{corr} values indicate that exists a 90% probability of active corrosion during all the exposure period; however, the criterion is based on partially saturated specimens and in this study the specimens were totally saturated, indicating that the ASTM C 876 criterion is not applicable to evaluate the corrosion of reinforcement in these concrete specimens. Therefore, it can be concluded that all steel bars were in a passive state during the six months of immersion in the sulfate solution.

However, it can be observed that the SCM that could have a greater efficiency against corrosion is SF since the system with this material presented the most noble corrosion potentials during the exposure period. The RA 30% FA system presented corrosion potentials similar to the RA 100% CPC system, which could indicate that FA does not contribute significantly to inhibit the corrosion of the reinforcement. It is necessary to clarify that the corrosion potential technique provides qualitative information on reinforcement corrosion. Therefore, quantitative information on reinforcement

corrosion was developed by determining the polarization resistance using the linear polarization resistance technique.

3.3. Polarization resistance

From the curves potential against current density R_p was obtained for all the systems in study and i_{corr} was calculated representing the results in Figure 4; the horizontal broken line point out the threshold of active to passive corrosion [31].

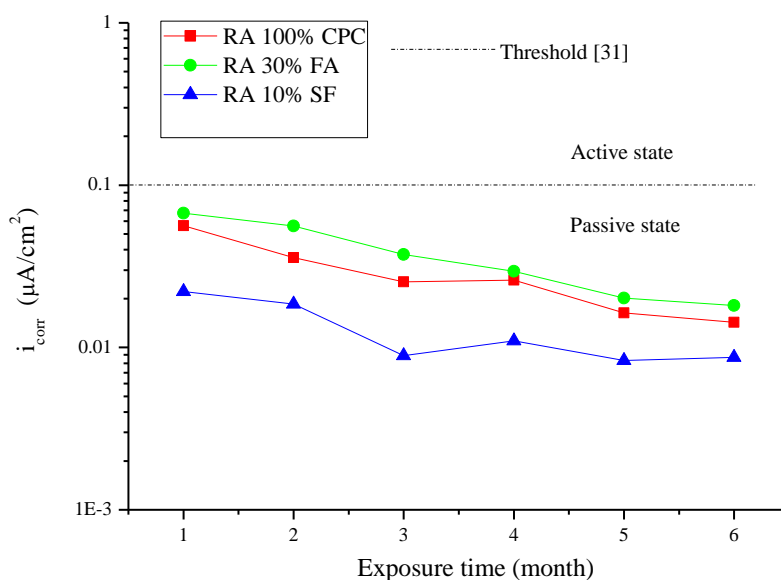


Figure 4. Variation of i_{corr} of the reinforcement steel as a function of the exposure time

In Figure 4 it can be observed that the system steel-concrete that presents a highest corrosion resistance induced by sulfates is RA 10% SF, because its corrosive activity was the lowest in the exposure time and decreased significantly until it reached a low level of corrosion ($0.008 \mu A/cm^2$) at the end of the period. The RA 30% FA system showed levels of corrosion between 0.06 and $0.02 \mu A/cm^2$, slightly superiors to the system RA 100% CPC, which means that FA does not contribute significantly to inhibit the corrosion of the reinforcement in the initial six months.

The negligible effect of FA on corrosion current density at initial months is mainly attributed to the delay of the kinetics of texturing of the cementing paste due to the slowness of the pozzolanic reaction of the FA with CH by the curing conditions which the test specimens were exposed. As to the RA 10% SF system, its significantly effect on corrosion is due to the SF accelerating effect during the hydration process of the cementing paste, as well as the possible dense structure of pores formed. Previous researches [32-35] reported that FA hydration produces a compact texture of calcium-silicate-hydrated glass (CSH) result of the reaction of the silica of the pozzolan with the hydrated phases contained in the mixture interstitial solution. This pozzolanic reaction delays the cement hydration speed because of the difficulty to dissolve the crystalline phase, which could be achieved at early ages

increasing considerably the cure temperature. Other researchers [36-39] define SF as a high reactivity pozzolan that has an accelerating effect in the hydration of the cement paste, besides that for the fineness of its particles, creates very dense pore structures. Table 3 shows that the SF is approximately 100 times finer than cement and FA, providing much SiO₂. Because hydration and pozzolanic reactions are surface phenomena, it is deduced that the microstructure of concrete with SF becomes denser than the rest of the systems due to the production of more CSH which replaces CH and generates pore refinement, and therefore, it reports a decrease in both, sulfate ion penetrability and corrosion current density.

4. CONCLUSIONS

With the results obtained in the concrete test specimens made with 100% recycled coarse aggregate, the following can be concluded: fly ash and silica fume contribute in increase the resistance of recycled aggregate concrete to sulfate attack. The addition of 10% of SF as a partial replacement of cement, reduces around 20 times the weight loss, whereas the addition of 30% of FA as a partial replacement of cement, reduces around 8 times the weight loss by sulfate attack; with respect to the concrete without supplementary cementing materials. Silica fume contribute significantly in increase the steel corrosion resistance, due to cementing matrix densification and pore refinement. Therefore, the durability of the reinforced recycled aggregate concrete structures exposed to underground water or filtrations with high sulfate content can increase significantly using supplementary cementing materials, as a partial replacement of cement, contributing to the concrete industry sustainability.

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