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Influence of High Volume Fly Ash and Recycled Aggregates in Chloride and Carbonation Resistance of Concrete

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Abstract. *This paper deals with the evaluation of the influence of recycled concrete aggregate (RCA) and the employment of high volume of fly ash (FA) on the physical, mechanical and durability (chloride ion penetration and carbonation) properties of concretes. The obtained values of which, being compared to those of conventional concretes. Concrete was produced using 0%, 25% and 50% FA in replacement of Portland cement, and 0% and 50% of RCA in substitution of natural aggregates. All the concretes were produced employing an effective water-cement ratio of 0.50. The physical properties at 28 days and the compressive strength at 7, 28 and 90 days were determined in all the concretes produced as well as the assessment of durability (penetration of chlorides and depth of carbonation) on all concrete mixtures. The depth of the carbonation was determined after submitting every concrete sample to a series of accelerated tests at 20% of CO_2 concentration during 7, 14 and 28 days after the curing period in the humidity room and pre-condition in the laboratory. The chloride penetration was determined at 28 and 90 days of curing. It was concluded that the employment of 50% of un-carbonated RCA increased the early strength of concrete produced using FA, and at late ages, RCA concretes achieved similar strength when 25% of FA was employed. The concrete produced with 50% of FA achieved the highest resistance to chloride ion penetration also when RCA was employed. Although the use of FA increased the carbonation depth of the concrete samples, the employment of the un-carbonated RCA reduced that effect. The employment of RCA with CEM II or binder with 25% of FA caused the lowest carbonation depth.*

Keywords: *Fly Ash, Recycled Aggregates, Concrete, Carbonation, Chloride Resistance.*

1 Introduction

Concrete production has a high impact on our environment due to the abundant consumption of energy and a large amount of CO_2 emissions in cement production. In addition, the demolition of concrete structures causes a considerable volume of waste to end up in landfills. These problems may be reduced, achieving a green concrete, by employing fly ash (FA) as supplementary cementitious materials and recycled concrete aggregates (RCA) in replacement of cement and natural aggregates, respectively for concrete production (Marinković, Dragaš, Ignjatović, and Tošić, 2017).

It is known that the RCA is suitable for concrete production (Chen *et al.*, 2019), in addition the employment of recycled aggregate concrete (RAC) as structural material has been widely analysed and validated for many applications (Pedro, De Brito, and Evangelista, 2014). However, the durability of concrete produced with RCA is actively being studied in order to improve its qualities (Guo *et al.*, 2018). According to Guo *et al.* (Guo *et al.*, 2018) RAC has lower chloride ion diffusion resistance than conventional concretes due to the RCA's high porosity. According to the results of a carbonation resistance test, when the RAC were produced employing at least 70% of RCA, the resistance was found to be higher due to the larger amount of mortar in recycled concrete. In contrast, the results of studies by Silva *et al.* (Silva *et al.*,

2015) determined that the carbonation of concrete produced with 100% of RCA was 2.5 times higher than that produced with natural aggregates.

On the other hand, today the use of FA up to 15-20% (Chandra and Bendapudi, 2015) or up to 15-30% (Xu and Shi, 2018) in concrete production is considered usual and it has been determined that the employment of high amount of FA controlled the temperature of concrete and achieved adequate mechanical and durability properties. It is known that the concretes produced with FA have low strength at initial ages, this effect being more evident when higher percentages of FA are employed in concrete production and less evident when concrete are produced with a low water/cement ratio. However at later ages, the strength of concrete increases due to the reaction of its FA with Portlandite (Kocak and Nas, 2014; Xu and Shi, 2018). According to Lam *et al.* (L. Lam, Y.L. Wong, 1998) the chloride ion penetration resistance of concrete is higher when FA is employed. Dinakar *et al.* (Dinakar, Kartik Reddy, and Sharma, 2013) described that concretes achieve their highest strength and chloride ion resistance when up to 30% of FA is employed for concrete production. However, several other researchers (Kurda, De Brito, and Silvestre, 2019) determined that concrete produced with FA achieves lower carbonation resistance than the concrete produced employing 100% of Portland cement.

In this paper, the influence of RCA and the employment of high volumes of FA on the physical, mechanical and durability (chloride ion penetration and carbonation) properties of concretes have been evaluated, and those values were compared to those of conventional concretes. Concretes were produced using 0%, 25% and 50% FA in replacement of Portland cement, and 0% and 50% of RCA in substitution on natural aggregates

2 Materials

2.1 Binder

The cement types of CEM II A-L 42.5R (with 12% limestone, named CEMII) and CEM I 52.5R (high strength-rapid hardened, named CEMI) with the densities of 3.1 kg/dm^3 were employed. Class F fly ash (FA) with a density of 2.16 kg/dm^3 was also employed.

2.2 Aggregates

Three fractions of natural limestone aggregates were used for concrete production: fine (NS of 0/4mm,) and coarse aggregates (CA1 of 5/10mm and CA2 of 8/20 mm). The dry density of NS, CA1 and CA2 were 2.58kg/dm^3, 2.67kg/dm^3 and 2.67kg/dm^3, respectively. The absorption capacity was of 1.79%, 0.75% and 0.57%, respectively.

The recycled concrete aggregate (RCA) was produced via the crushing of a parent concrete, namely one-year-old waste, 30 MPa concrete specimens from a concrete company. The component of the parent concrete being CEM II A-L 42.5R cement and limestone aggregates. The RCA was used for concrete production immediately after the parent concrete was crushed, and the RCA aggregates were un-carbonated. The grading distribution was defined by the fraction 5/20mm. Its density was of 2.33 kg/dm^3 and an absorption capacity of 5.35%.

3 Mix Design and Production Process

Two stages of concrete productions were carried out. In stage 1, all the concretes were produced employing 100% of natural aggregates. Four different concretes were produced in which different binders were employed. CC, 100% of CEMII; CFA25, 25% (in weight) of CEMII was replaced by FA; CFA50: 50% of CEMII was replaced by FA and CFA50.2: 50% of binder was CEMI and 50% of FA (see Table 1). In stage 2, all the mixtures were produced employing 50% of the aggregates volume defined in the CC mixtures replaced by RCA. Four different concrete mixtures were produced: CRA, 100% of CEMII; CRAFA25, 25% (in weight) of CEMII was replaced by FA; CRAFA50, 50% of CEMII was replaced by FA and CRAFA50.2, 50% of binder was CEMI and 50% of FA (see table 1).

The effective w/c ratio of 0.50 was maintained constant in all concretes. In stage 1, in order to determine the effective w/c ratio, the effective absorption capacity of 90%, 50% and 50% of the total absorption capacity of NS, CA1 and CA2, respectively were determined. In addition, in stage 2, the effective absorption capacity of RCA was determined as being 80% of its total absorption capacity. The RCA was used with high humidity, having 75-80% of water absorption capacity, and their moisture content was measured prior to their use.

The concrete specimens were produced and cured following UNE EN 12390-2:2001 regulations and were manually compacted using a steel rod. The concrete specimens were then covered with a plastic sheet and air-cured for the first 24 h. After 24 h of casting, the specimens were demoulded and then stored in a humidity room and kept at 21ªC and 95% of humidity until the test ages were reached for the physical, mechanical and chloride ion penetration test. The specimens taken from the humidity room after 28 days for carbonation resistance testing were sent to the laboratory to undergo pre-conditioning for 14 days at 400ppm, 24ºC and 55% humidity before being placed in the CO_2 chamber.

A superplasticizer based on modified polycarboxylates was employed in all mixtures. A 0.50% with respect to cement weight was needed in all the concrete mixtures in order to achieve a slump test of 17-19cm. The density at fresh state of all the concrete mixtures was also determined. Table 1 shows that the employment of FA increased the density of concrete due to its capacity to densify the cement paste, in contrast the employment of RCA decreased the density of concrete (Etxeberria *et al.*, 2007).

Table 1. Mix proportions of Stage 1 and Stage 2 concrete mixtures. The values are given of kg of component/m^3 of concrete production (W: water, Ad: admixture, Effect: Effective).

	CEM	**FA**	**W Total**	**NS**	**CA1**	**CA2**	**RCA**	**Ad. (%)**	**Effect. w/c**	**Density (kg/dm^3)**
					STAGE 1					
CC	350		192.5	900	275.2	647	0	0.50	0.5	2.24
CFA25	262.5	87.5	192.5	867.9	275.2	647	0	0.50	0.5	2.34
CFA50	175	175	192.5	835.9	275.2	647	0	0.50	0.5	2.36
CFA50.2	175	175	192.5	835.9	275.2	647	0	0.50	0.5	2.36
					STAGE 2					
CRA	350		213.4	900	137.6	323.5	400	0.50	0.5	2.31
CRAFA25	262.5	87.5	213.4	867.9	137.6	323.5	400	0.50	0.5	2.30
CRAFA50	175	175	213.5	835.9	137.6	323.5	400	0.50	0.5	2.31
CRAFA50.2	175	175	213.5	835.9	137.6	323.5	400	0.50	0.5	2.33

4 Test Procedure

4.1 Physical and Compressive Strength

Physical properties were measured according to ASTM C 642 ‘‘Standard Test Method for Density, Absorption and Voids in Hardened Concrete” at 28 days after casting. Three cubic specimens were used in this test for each concrete mixture produced.

The compressive strength of concretes at 7, 28 and 90 days were determined following UNE-EN 12390-3:2009 specifications. Three cylindrical specimens were used for each concrete mixtures.

4.2 Carbonation and Chloride Resistance

The concretes were submitted to accelerated carbonation test, following GB T50082-2009 standards, in order to assess the carbonation penetration resistance of each concrete produced employing different types of binders as well as the RCA. The concrete specimens were placed in a CO_2 chamber at 20% CO_2, 20ºC and 60% of RH for 7, 14 and 28 days after their curing process of 28 days and pre-conditioning period of 2 weeks. The concentration of the CO_2 employed was very high. It is known that the carbonation coefficient increases with an increase in carbon dioxide concentration (Shah and Bishnoi, 2018). In addition, at long test periods, the high concentrations of CO_2 cause a change of the cement paste microstructure compared to that of samples placed in natural exposure (Castellote *et al.*, 2009). However, the high concentration of CO_2 conditions, in short periods of testing, allow the concrete's resistance to carbonation to be characterized (Hyvert *et al.,* 2010). Two specimens of each concrete were employed for carbonation depth measurement. The compressive strength of each concrete was also determined.

The chloride penetrability of concrete was determined following the ASTM C1202 (1997) standard. The chloride ion penetration resistance of concrete is represented by the total charge passed in Coulombs during a test period of 6 h. In this study, the chloride ion penetrability test was carried out on the concrete specimens at the ages of 28 and 90 days and each result was the average of two measurements.

5 Results

5.1 Physical and Compressive Strength

Table 2 shows the physical properties obtained by all the concretes analysed. The employment of FA increased the density and decreased the absorption capacity of concrete due to its reaction with $Ca(OH)_2$ (Deschner *et al.,* 2012). The CFA50.2 produced with 50% of FA in substitution of CEMI achieved the lowest absorption capacity. The employment of RCA, in stage 2, decreased the density of its Stage 1 corresponding concrete. The CRA achieved 18% higher absorption capacity than that of CC concrete. Similar results were obtained by Kurda *et al.* (Kurda, de Brito, and Silvestre, 2019). The absorption capacity of recycled aggregate concrete was lower when FA was employed in its production. The CRAFA50.2, produced with CEMI, achieved the lowest absorption capacity. CRAFA50 and CRAFA50.2 achieved a higher density, lower absorption and porosity than that of the CC concrete.

Table 2 also shows the compressive strength at 7 days, 28 days and 90 days of all the concretes produced. The CC mixture achieved the highest compressive strength at 7, 28 and 90 days. In addition, the concretes produced employing 25% of FA achieved the strength of CC concrete. Similar results were obtained by Nath and Sarker (2011) at 28 and 90 days. The concretes produced with 50% of FA achieved lower strength than the CC concrete in all the tested ages. Although the employment of CEMI improved the properties achieved by concrete produced using CEMII, the CFA50.2 proved to have 14.8% lower strength than that of CC after 90 days (see figure 1). This in all probability was due to a none reaction in some of its high volume of FA (Hemalatha and Ramaswamy, 2017; Xu and Shi, 2018). In stage 2, the concrete CRA achieved the highest strength at 7 and 28 days, and the CRAFA25 concrete after 90 days.

Table 2. Physical properties of concretes produced in Stage 1 and 2, Compressive strength of concretes at 7, 28 and 90 days.

	Physical properties			Compressive strength (MPa)		
	Absorption (%)	**Dry Density (kg/dm3)**	**Vol. of accesible porous (%)**	**7 days**	**28 days**	**90 days**
			STAGE 1			
CC	4.70	2.19	10.29	36.7	42.0	49.6
CFA25	3.98	2.28	9.09	29.0	39.3	49.4
CFA50	3.95	2.29	9.04	17.5	29.1	39.5
CFA50.2	3.70	2.32	8.38	22.1	32.7	42.2
			STAGE 2			
CRA	5.56	2.16	12.04	34.5	41.3	47.5
CRAFA25	4.52	2.24	10.11	31.5	38.7	48.1
CRAFA50	4.16	2.24	9.32	19.2	26.9	37.8
CRAFA50.2	4.06	2.23	9.06	23.7	30.5	41.8

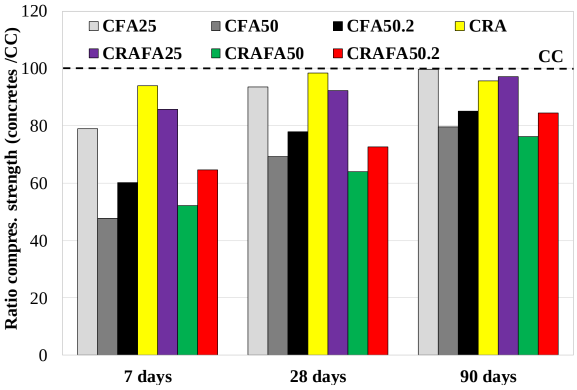

Figure 1. Ratio of the compressive strength of all the concrete with respect to that of CC concrete.

At 7 days of curing, the concretes produced employing RCA and FA achieved a higher strength than that of the concretes produced employing FA and NA (see Figure 1). The rough surface and attached un-carbonated mortar of the RCA caused adequate ITZ in CRA (Etxeberria *et al.*, 2007).

At 28 days and 90 days, the concrete produced with RCA achieved a slightly lower strength to the concretes produced employing natural aggregates. In stage 2, the CRAFA25 achieved the highest strength at 90 days due to the pozzolanic effect of FA and its reaction with Ca(OH)2, similar behaviour was determined by Kou and Poon (2013).

In addition, the two concretes produced employing 25% of FA achieved the strength of the CC concrete. Cement type I 52.5R (CEMI) was required for concrete employing 50% of FA in order to avoid a high strength reduction at 90 days.

5.2 Carbonation and Chloride Resistance

Figure 2a shows the chloride penetration resistance of each concrete at 28 and 90 days, in accordance with the total charge passed value obtained, which are categorized as low, moderate and high corrosion risk.

At 28 days, almost all of the concretes were classified with moderate risk for corrosion, except the CC and CRA concretes, which were classified as high risk of corrosion. The employment of a higher percentage of FA reduced the corrosion risk. The concretes produced employing 50% of FA and RCA (CRAFA50 and CRAFA50.2) achieved the lowest value of the total charge passed. At 90 days, the concretes produced with 50% of FA, CFA50.2 and CRAFA50.2, achieved the lowest value. The CRA concrete was found to still have a high risk of corrosion after 90 days of curing.

In stage 1, the concretes produced with 50% FA and natural aggregates achieved the highest decrease of the total charge passed value from 28 days to 90 days. The reduction of the total charge passed of the CFA50.2, CFA50, CFA25 and CC concretes were 53%, 40%, 25% and 19% respectively. In stage 2, the reduction rate of CRAFA50.2, CRAFA50, CRAFA25 and CRA were 27%, 10%, 41% and 9%, respectively. The RCA was also found to have an influence on the chloride resistance.

The average carbonation depth of each concrete specimen after their exposure to 20% of CO_2 during 7 days, 14 days and 28 days is shown in Figure 2b. After 7 days of exposure, the concretes produced with 50% of FA and NA suffered the highest carbonation depth, the use of 50% of RCA reduced the CO_2 penetration.

It is clear that the employment of FA increased the depth of carbonation within the concrete samples. Several researchers have also determined this (Khunthongkeaw, Tangtermsirikul, and Leelawat 2006; Kurda, De Brito, *et al.*, 2019). The concretes produced with 100% of CEMII as well as employing 25% of FA achieved the highest resistance to carbonation at any time, being higher when RCA was employed for concrete production. In this research work un-carbonated RCA aggregate was employed, which was carbonated during their contact with CO_2, increasing the concretes carbonation resistance. Similar results were obtained by Thomas et al. (Thomas *et al.*, 2013). Most of the research work carried out up to date define that concrete produced employing RCA achieved lower carbonation resistance due to its high porosity of RCA (Kurda, De Brito, *et al.*, 2019; Leemann and Loser 2019), however the carbonated or un-carbonated state of RCA could modify this behaviour. After 28 days of CO_2 exposure, the concretes produced with 50% of RCA and 50% of FA suffered a greater carbonation process. In all probability, the result was due to a higher presence of cement paste which became modified as a result of a high CO_2 concentration (Castellote *et al.*, 2009). However, this effect will be lower at natural exposure.

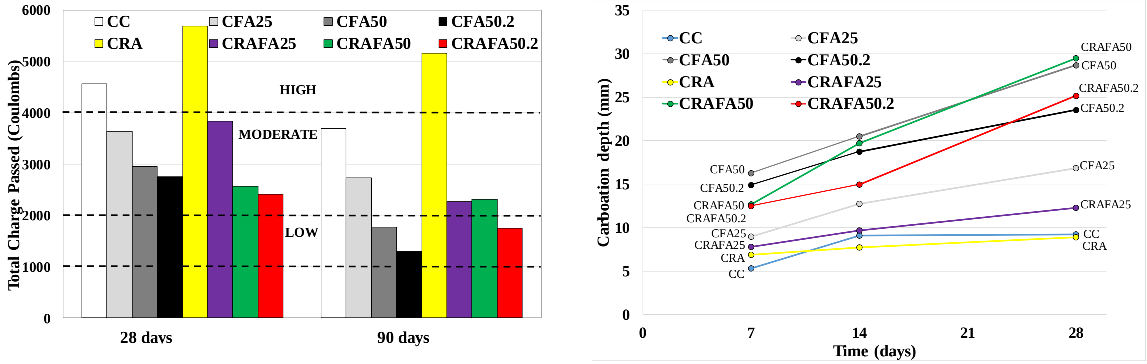

Figure 2 a) Chloride-ion penetration of concrete mixtures and ASTM corrosion ranges. b) carbonation depth of concrete mixtures.

6 Conclusions

The following conclusions can be drawn based on the results presented above:

- The effect of RCA in decreasing and increasing the density and absorption capacity, respectively, of concretes was lessened by employing FA. The CRAFA50 and CRAFA50.2 achieved a higher density, lower density and porosity than that of the CC concrete.
- The results of compressive strength test at 7 days determined that the concretes produced employing FA achieved higher strength when RCA was used than the concretes produced with NA. At 28 and 90 days. The concrete produced with 50% of RCA with or without employing 25% of FA achieved similar strength to that of the CC concrete. At 90 days, the concretes produced with CEM I and 50% FA achieved 14% lower strength than the CC concrete
- Chloride ion penetration was more influenced by the type of binder employed than the type of aggregates used. The concrete produced with 50% of FA achieved the highest resistance to chloride ion penetration. The concrete produced with 50% of RCA achieved high resistance to corrosion when 25% or 50% of FA was employed for concrete production. CRA (the concrete without FA) proved to achieve the lowest resistance to chloride ion penetration.
- The employment of FA increased the depth of the carbonation of the concrete samples. After 7 days of 20% CO_2 exposure, the use of RCA was shown to reduce the carbonation depth of the concretes produced with 50% FA and NA. The employment of RCA in concrete production with CEM II or employing 25% of FA caused the lowest carbonation depth.

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