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Influence of curing time on the chloride penetration resistance of concrete containing rice husk ash: A technical and economical feasibility study

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ABSTRACT

This study investigates the influence of the curing time on the chloride penetration behavior of concrete produced with different concentrations of rice husk ash. Compressive strength and chloride penetration at 91 days were assessed according to ASTM C1202. Concentrations of 10%, 20% and 30% of rice husk ash were used and the results were compared with a reference mix with 100% Portland cement and with two other binary mixes with 35% fly ash and 50% ground blast furnace slag. Increases in rice husk ash content produced lower Coulomb charge values. Longer curing times reduced Coulomb charges values for all mixes investigated. However, the extent of the effect of curing times on compressive strength and chloride penetration in concrete is related to the type of mineral addition, the concentration of the substitutions used, the *w*/*b* ratio and the curing time used. This behavior points at an optimal curing period for each type of binder to meet specific technical and economical criteria, namely durability and compressive strength specifications for the structure.

1. Introduction

The partial substitution of mineral additions such as rice husk ash, blast furnace slag and fly ash for cement helps lower CO_2 emissions [1] and reduces the need for fresh materials. This can also lower the cost of final products and provide an end-use for industrial waste, thus contributing towards sustainable development practices [2].

The physical benefits resulting from the addition of these materials to concrete make their use mandatory in many cases [3], regardless of any economical and environmental considerations, given the fact that concrete is a structural material and as such should provide safety and meet its projected working life [4]. When structures are designed and built to last, the need for maintenance or replacement is reduced, which means the use of natural resources and the production of waste are also reduced.

It follows that the design of a concrete structure should start by establishing the environmental conditions to which the concrete will be exposed and in this way determine the concrete composition and the building techniques that should be used to achieve the intended service life for a given structure. When concrete is subjected to external chemical attack, concrete porosity and permeability should be reduced to decrease the rate of penetration of aggressive agents and mitigate the effects of this aggression [5].

The penetration of aggressive agents, which is processed through different mechanisms, can be managed by the use of a suitably thick concrete layer made with a suitable composition. To ensure good chloride resistance, concrete with low ion diffusivity should be used [4] and the pore structure of the concrete should hinder chloride penetration. The pore structure, in turn, is affected by the type of the cement, the water/binder ratio, the degree of hydration and the presence of mineral additions and chemical activators, which can change the microstructure of the paste and the paste-aggregate transition zone [6] and affect durability [7,8].

It is a well-known fact that the curing process contributes to improve cement hydration and pozzolanic reactions while preventing the early water release from the pore interior [4]. This process creates a denser microstructure, with a smaller volume of capillary pores and results in concrete with lower permeability [5]. However, researchers do not yet agree on how long the curing process in concretes mixes with mineral additions should last [9]. This period will depend on factors such as the curing type and temperature but also the type of addition used, the concentrations of the substitution for Portland cement, *w*/*b* ratios, weather conditions, building techniques and the desired properties (carbonation, chloride and sulfate resistance, mechanical strength).

The changes to chloride penetration promoted by the use of mineral additions in concrete are related to factors such as the type, content, thickness and curing conditions [10–18], on changes in pore solution composition and, therefore, in electrical conductivity [19–22], in pore size [12,23,24] and capacity of combination, resulting in lower free chloride content [25–27].

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In addition to the technical benefits, the use of partial substitutions of mineral additions for cement also affects production costs because of their lower cost when compared with cement. In some cases, larger amounts of an admixture are required to achieve the same consistency of a concrete without mineral addition.

The choice of a specific type of cementitious material such as rice husk ash, slag, fly ash, silica fume is guided chiefly by concerns of availability and the performance features specified for the concrete at a given age, as well as production costs. The performance of concrete with rice husk ash has been studied by several authors. However, only a few studies discuss the effects of curing time on compressive strength, chloride penetration and cost of concrete. There are no comparative performance studies using mixtures with the same compressive strength and concrete with fly ash and slag, which are which are often used in concrete.

The chloride penetration resistance of concrete mixtures with different contents of rice husk ash submitted to different curing times was investigated according to ASTM C1202, [28]. Results were compared with a reference concrete (100% Portland cement) and with mixtures with substitutions of 35% fly ash or 50% slag for cement. These concentrations represent standard values of these additions in pozzolanic Portland cement and blast furnace Portland cement manufactured in Brazil. According to Bryant et al. [29] specifications based on ASTM C1202 are common in the US concrete construction industry. He states that the Virginia Department of Transportation is presently conducting a pilot program using ASTM C1202 as an end-use performance specification, whereas the Port Authority of New York and New Jersey also uses ASTM C1202 in their concrete performance specifications.

This study also presents a comparative analysis of durability, resistance to chloride penetration and concrete costs with and without mineral additions, rice husk ash, fly ash and blast furnace slag. This analysis was based on each mixture's compressive strength values, which is often used as a reference for designers when planning concrete structures. Therefore, mixtures with the same compressive strength values (40 MPa, 50 MPa and 60 MPa) were analyzed.

2. Experimental program

2.1. Materials

The cementitious materials used in this paper were high-early strength Portland cement, rice husk ash produced in a thermal power plant under controlled burning conditions, blast furnace slag produced in a local steel mill plant and cooled using a wet process, and untreated fly ash from coal burned in a thermal power plant. Their chemical compositions and physical properties of these materials are shown in Table 1.

The fine aggregate was natural sand with maximum characteristic size 2.36, fineness modulus of 2.06 and specific gravity of 2.60. The coarse aggregate was crushed basaltic rock with a maximum characteristic size of 19 mm, fineness modulus 6.67 and specific gravity of 2.50.

2.2. Mixture proportions

Six binder mixtures were investigated. The first with 100% Portland cement (labeled reference mixture – REF), and the others with rice husk ash in concentrations of 10%, 20% and 30% (labeled 10RHA, 20RHA, 30RHA, respectively), 35% fly ash (35FA) and 50% ground-granulated blast furnace slag (50S) by weight of cement. The substitution concentrations of the last two mixtures were

Table 1
Properties of cementitious materials.

Constituent/property	Portland cement	Rice husk ash	Fly ash	Slag
Loss on ignition (%)	2.09	5.0	1.16	0.71
SiO_2 (%)	19.59	90	64.57	34.98
Al_2O_3 (%)	4.79	0.28	27.27	13.06
Fe_2O_3 (%)	3.07	0.14	2.21	1.11
CaO (%)	64.35	0.45	1.51	42.28
MgO (%)	1.69	0.28	0.76	6.01
SO_3 (%)	2.75	0.02	0.06	0.11
Na_2O (%)	0.07	0.08	0.15	0.17
K_2O (%)	0.98	1.55	1.50	0.40
Specific gravity (kg/dm^3)	3.11	2.17	2.19	2.89
BET – specific surface (m^2/g)	1.48	4.0	2.32	1.07
Compressive strength (MPa)		–	–	–
1 day	22.5	–	–	–
3 days	35.1	–	–	–
7 days	41.2	–	–	–
28 days	49.6			

Table 2
Composition of the concrete mixtures.

Mixture	w/b	Rice husk ash (kg/m^3)	Portland cement (kg/m^3)	Slag (kg/m^3)	Fly ash (kg/m^3)	Water	Fine agg. (kg/m^3)	Coarse agg (kg/m^3)	SP (%)
10RHA	0.35	439	49	–	–	171	614	1076	0.50
	0.50	323	36	–	–	179	726	1055	0.20
REF	0.35	488	–	–	–	171	632	1076	0.20
	0.50	359	–	–	–	179	739	1055	–
	0.65	284	–	–	–	184	802	1043	–
10RHA	0.35	439	49	–	–	171	614	1076	0.50
	0.65	255	28	–	–	184	791	1043	–
20RHA	0.35	390	98	–	–	171	596	1076	0.95
	0.50	287	72	–	–	179	713	1055	0.50
	0.65	227	57	–	–	184	781	1043	0.30
30RHA	0.35	342	146	–	–	171	579	1076	1.95
	0.50	251	108	–	–	179	700	1055	1.05
	0.65	199	85	–	–	184	771	1043	0.70
35FA	0.35	317	–	–	171	171	572	1076	0.25
	0.50	233	–	–	126	179	695	1055	0.10
	0.65	184	–	–	99	184	767	1043	–
50S	0.35	244	–	244	–	171	616	1076	0.17
	0.50	179	–	179	–	179	728	1055	–
	0.65	142	–	142	–	184	793	1043	–

Note: SP = superplastizer, slump of the concrete = 80 ± 10 mm.

chosen from the mean values used in the industrial production of pozzolanic Portland cement and blast furnace Portland cement. Water/binder ratios were set at 0.35; 0.50 and 0.65 with ratios of binder: fine aggregate: coarse aggregate set at 1:3.5; 1:5.0 e 1:6.5, respectively.

Table 2 presents the mass of materials used (kg/m^3) in each of the binder mixtures tested. The amount of fine aggregate was adjusted to compensate for the substitutions of Portland cement by mineral additions and to keep mortar content constant at 51%. The desired slump (80 ± 10 mm) of the different compositions was obtained with the aid of a superplasticizer (modified carboxylic ether). RHA, because of its irregularly shaped particles and porous cellular surface, called for the use of larger amounts of SP.

The test specimens were prepared in a period of low temperature and therefore the casting temperature was set at 18 °C. To control the temperature of the concrete, the mix water was heated to match the temperature of the other materials [30].

2.3. Test details

Compressive strength values were determined in cylindrical test specimens (100 × 200 mm) molded in a vibration table and tested according to the procedures listed in Brazilian standards ABNT NBR 5738 and 5739. The test specimens were stored in a wet chamber, with temperature set at 23 ± 2 °C and relative humidity greater than 95% for the curing times of the test (3, 7 and 28 days). They were then stored in the laboratory until the test period of 91 days was reached. Four specimens from each mixture were tested at each testing age.

Chloride-ion penetration was measured according to ASTM C1202 [28] using cylindrical concrete test specimens measuring 95 mm × 150 mm, which were cast and cut to standard sizes (95mm × 51 mm) using a diamond saw. For each of the six binder mixtures, water/binder ratios (0.35, 0.5, 0.60) and curing times, two specimens at the age of 91 days were tested, and their mean was used as a representative value as long as the standards concerning the difference in those results were met.

3. Results and discussion

3.1. Compressive strength

Table 3 shows the results of compressive strength for different curing times, and the equations Cs = $A/B^{w/b}$, which were obtained from the correlations between the compressive strength values and w/b ratios and their corresponding coefficients of determination R^2 at the age of 28 and 91 days.

The results confirm the observations of other researchers [17,31,32]. Rice husk ash is considered a highly reactive pozzolan, since all the mixtures in which the cement was replaced with this mineral addition showed better performance than the reference mixture in the three substitutions used and in the three w/b ratios, at 28 and 91 days. Other researchers have found higher values at 7 days [33,34] and at 3 days [31], when compared with the reference mixture. The higher compressive strength of RHA concrete when compared with the reference sample can be attributed to a reduction in porosity, lower CH and reduced width of the interface between the paste and the aggregate [35].

When compared with the mixture with 30% FA, compressive strength values for the mixture with 35% RHA are 7–79% higher at 28 days and 11–55% higher at 91 days. This can be explained by the greater fineness and the larger amounts of amorphous silica found in RHA when compared with fly ash.

An increase in compressive strength from 28 to 91 days is observed. However, the rate of increase is related to several factors, such as the reactivity of each addition, the concentration of the substitution, the w/b ratio and the curing time used in the concrete, as other researchers also observed [36–38].

Table 3
Compressive strength at 28 and 91 days for different curing times in wet chamber and cost/m^3 for w/b ratios equal to 0.35, 0.50 and 0.65.

Mixture	Curing time (days)	Compressive strength (MPa)			Cost/m^3 US($)			Compressive strength (MPa)					
		28 days						91 days					
		w/b			w/b			w/b			Coefficients[A]		
		0.35	0.50	0.65	0.35	0.50	0.065	0.35	0.50	0.65	A	B	r^2
REF	3	40.2	32.8	20.4	126.12	94.98	80.41	59.2	40.3	30.3	127.20	9.32	0.9845
	7	45.8	40.7	24.1		$C = \frac{209.10539}{4.483113^{w/b}}$		64.3	48.9	33.9	137.80	8.45	0.9999
	28	53.7	47.3	27.6				67.9	51.4	35.0	149.73	9.11	0.9957
						R^2 = 0.9787							
10RHA	3	49.9	34.2	19.6	136.31	100.23	81.02	60.5	44.0	31.7	128.80	8.62	0.9964
	7	60.1	43.2	26.0		$C = \frac{246.18694}{5.663935^{w/b}}$		71.5	54.2	32.9	183.52	13.30	0.9982
	28	68.1	46.9	31.7				76.4	62.1	38.6	177.19	9.73	0.9903
						R^2 = 0.9848							
20RHA	3	62.0	42.3	20.1	151.08	107.73	86.95	71.8	49.3	29.9	203.69	18.54	0.9991
	7	68.2	47.7	24.5		$C = \frac{281.946510}{6.306542^{w/b}}$		81.4	55.4	35.6	215.68	15.75	0.9969
	28	72.0	52.3	33.2				85.6	62.9	41.7	201.52	10.99	0.9998
						R^2 = 0.9799							
30RHA	3	58.7	41.2	21.9	182.61	120.83	94.65	63.0	48.4	29.0	162.34	13.28	0.9967
	7	61.3	44.9	23.2		$C = \frac{382.19049}{8.940184^{w/b}}$		66.7	55.1	31.7	168.74	11.94	0.9815
	28	67.4	50.1	29.9				78.9	65.1	37.3	200.94	12.15	0.9816
						R^2 = 0.9738							
35FA	3	54.9	23.8	13.8	99.73	76.69	64.17	57.0	31.6	20.8	179.57	28.80	0.9739
	7	55.1	28.5	14.2		$C = \frac{164.48330}{4.348230^{w/b}}$		60.0	43.7	22.8	196.13	25.16	0.9974
	28	58.2	36.6	16.7				66.8	44.6	24.1	227.32	29.91	0.9997
						R^2 = 0.9857							
50S	3	46.3	30.8	20.2	97.00	74.24	64.02	54.7	40.6	25.7	135.59	12.40	0.9998
	7	49.3	32.8	21.8		$C = \frac{154.407561}{3.995031^{w/b}}$		58.0	44.2	27.0	146.84	12.79	0.9980
	28	52.8	35.2	23.2				61.8	46.1	29.0	153.70	12.45	0.9996
						R^2 = 0.9767							

$A = A$ and B are coefficients of equations compressive strength = $A/B^{w/b}$. r^2 = coefficients of determination.

For a better understanding of the influence of curing conditions on the mechanical strength of concrete, a variable called Cure Performance Rate – CPR was introduced. This variable makes it possible to make relative comparisons of compressive strength values in each mixture with the reference mixture when the wet curing time is changed and water/binder ratios and the age of the mixtures are kept constant.

To calculate the CPR, the mixtures without addition (REF with $w/b = 0.35$, 0.50 and 0.65) are cured for 3 days and are then used as a standard for each set of mixtures and are assigned a value of 100%. The CPR_{AD} of each mixture was then obtained by calculating the ratio between the compressive strength of each sample and that of the reference mixture, and the result was multiplied by 100, as shown in:

$$CPR_{AD(i,x;tc)}(\%) = [fc_{M(i,x,tc)}/fc_{REF(i,x,tc=3d)}] \cdot 100 \quad (1)$$

where CPR_{AD}: Cure Performance Rate, for the mixture with addition AD, at age (i), with w/b ratio (x) and curing time (tc), in%; fc_M: compressive strength of the mixture with addition AD, at age (i), with w/b ratio (x) and curing period (tc), in MPa; fc_{REF}: compressive strength of the reference mixture (without addition), at age (i), with w/b ratio (x) and cure period (tc) equal to 3 days, in MPa.

Fig. 1 shows the values of CPR_{AD} calculated for all the mixtures at the age of 28 days. These results show the positive effects of longer curing periods, such as improved mechanical strength, as shown in Fig. 1. To illustrate, strength increments of 32% were observed when the curing time is extended from 3 to 7 days (mixture 10RHA; $w/b = 0.65$; at 28 days) and 66% with wet curing extended from 3 to 28 days. Also, a study of the samples at 28 days revealed that from all the mixtures in which different amounts of rice husk ash were substituted for cement, mixture 10RHA showed the greatest improvement when the curing time was increased from 3 to 7 days, with increases in strength from 20% to 32%, for $w/b = 0.35$ and 0.65, respectively. In fact, mixture 10RHA ($w/b = 0.65$), when cured for 3 days showed the lowest strength of all mixtures with the exception of 35FA. When cured for 7 days, mixture 35FA showed the highest strength of all, exceeding that of mixture 50S by 19%.

Similarly, for $w/b = 0.35$, mixture 10RHA cured for 3 days showed compressive strength values of 49.9 MPa at 28 days versus

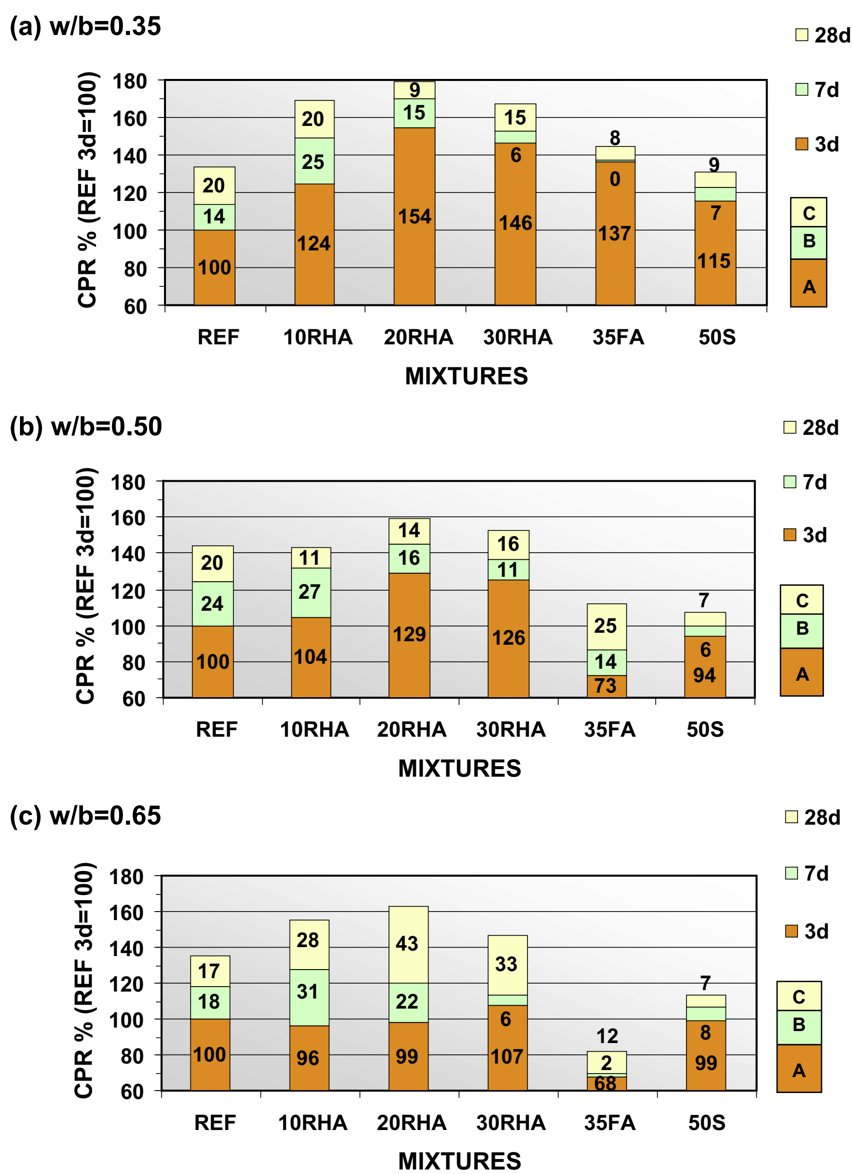

Fig. 1. Influence of the wet curing time (3, 7 and 28 days) on axial compressive strength at 28 days, based on water/binder ratio, for all mixtures, measured using Curing Performance Rate – CPR_{AD} (%). $A = CPR_{3d}$; $B = (CPR_{7d} - CPR_{3d})$; $C = (CPR_{28d} - CPR_{7d})$.

58.7 MPa for mixture 30RHA. However, these mixtures showed similar strength when cured for 7 days (60.1 MPa for 10RHA and 61.3 MPa for 30RHA). A similar behavior is observed for $w/b = 0.50$.

When the concrete is cured for a longer time (28 days), the strength of mixture 10RHA shows again the greatest increases for $w/b = 0.35$ and 0.50. However, for $w/b = 0.65$, mixture 20RHA was the one with the greatest increase after the extended curing time, with a rise of 66% in strength. For the same w/b ratio, sample 10RHA also presents a large increase in strength (approximately 61%), and this was also observed in samples 30RHA, with an increase of 36% when the curing period was extended from 3 to 28 days.

For mixtures 35FA and 50S the increase in strength at 28 days is not as great due to the specimens being stored longer in saturated environments. The sole exception is mixture 35FA with $w/b = 0.50$, whose compressive strength values showed increases of 19% and 29% when the curing time was extended from 3 to 7 days and from 7 to 28 days, respectively. From 3 to 28 days, the compressive strength in this mixture increased by 53%.

These observations show that these improvements in both the initial and final mechanical strength of concrete are a result of the substitution of rice husk ash for some of the cement content, thus attesting the great reactivity of this pozzolan. This effect becomes more noticeable as the concrete is cured for longer periods. Some comparisons must be highlighted: at 28 days, mixture 10RHA ($w/b = 0.35$) showed compressive strength values of 49.9 MPa at 3 days versus 54.9 MPa of mixture 35FA ($w/b = 0.35$). When the cure is extended to 7 days, the compressive strength in this mixture increases to 60.1 MPa, a value that is higher than that found in the mixture 35FA at 28 days. Also at 28 days, mixtures 10RHA, 20RHA, 30RHA and 50S, all with $w/b = 0.65$, show similar strength levels when cured for 3 days. However, when cured for

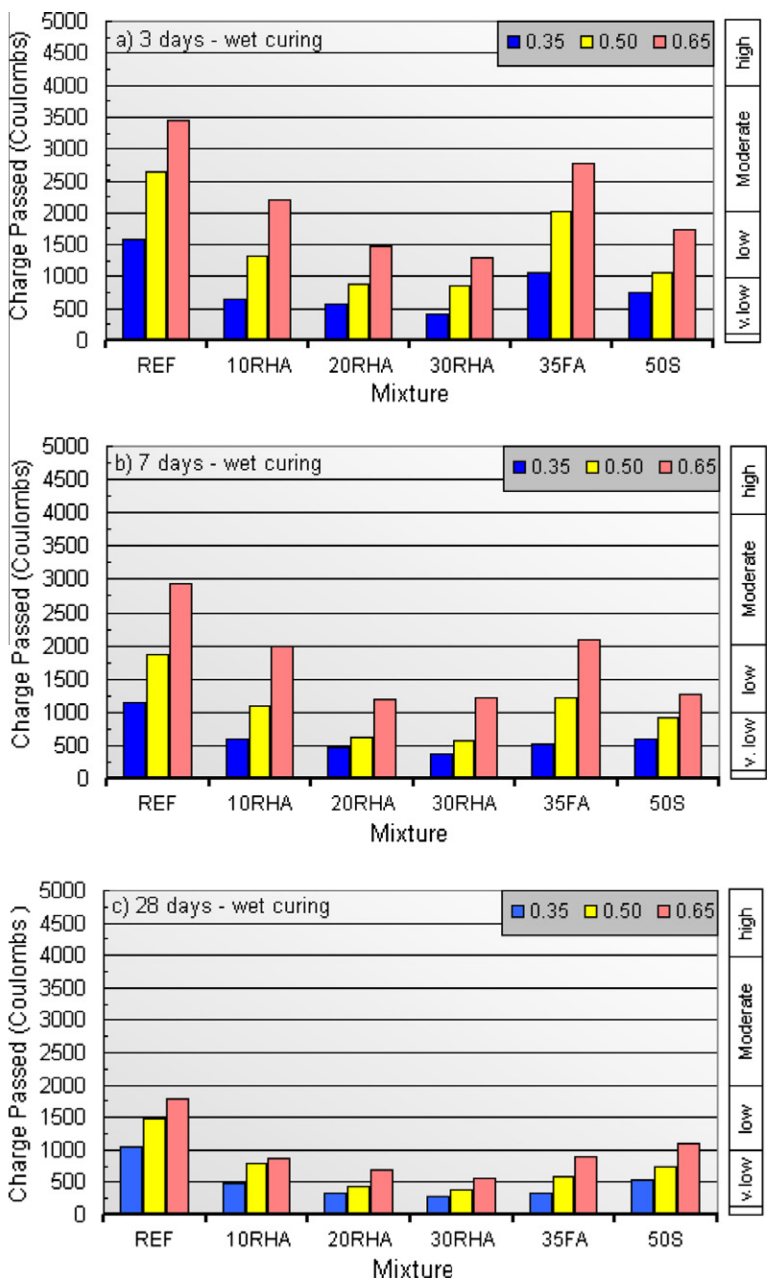

Fig. 2. Total Coulomb charge at 91 days for all mixtures in the study according to w/b ratio and curing time. Each chart shows the ASTM C1202 classification of the mixtures according to chloride penetration.

7 days, mixture 10RHA shows strength values of 8% to 19% higher than the other mixtures. When the curing time is extended to 28 days, mixture 20RHA shows the best performance, with strength values now 5% higher than those of mixture 10RHA and 33% higher than mixture 50S.

The results of these studies are not exhaustive in relation to the effects of wet cure in the compressive strength of concrete mixtures containing mineral additions. Concrete samples with fly ash (25% and 58%) and blast furnace slag (25% and 50%) seem to be more sensitive to the absence of a wet cure than the concrete without additions, and the sensitivity of the concrete with mineral additions to the elimination of a curing process is greater for higher substitution contents [12]. However, experiments with concrete with 10% silica fume showed that the compressive strength of concrete made with this pozzolan is not readily affected by a poor cure [39]. Other studies indicate that when a wet cure is used instead of a dry cure, strength increases are higher in concrete mixtures with fly ash and blast furnace slag than in those with plain cement.

An overall view of the results of compressive strength in the mixtures investigated shows that the reference mixtures and those with RHA are more sensitive to changes in wet curing conditions. However, the mechanical strength of mixtures 35FA and 50S shows small variations when the period of cure is extended, with the exception of mixture 35FA with $w/b = 0.50$.

It should be pointed out that while increases in the wet curing time resulted in higher values of axial compressive strength in all mixtures in the study, the changes in the curing periods affect each mixture differently. The increase in strength as a result of an extended curing time is more visible in concretes with higher w/b ratios at 28 days.

Such behavior suggests the existence of an optimal curing time for each type of addition. This should take into account technical and economical criteria and will depend on the amount of substitution, the w/b ratio used and the specific age at which the concrete mixture is to reach the desired strength threshold.

3.2. Chloride penetration resistance

Fig. 2 presents the results of resistance to chloride penetration and Table 4 the coefficients C and D of equations $Q = C/D^{w/b}$ and the coefficient of determination (r^2) calculated according to the correlation between the total Coulomb charge (Q) and the w/b ratio of each mixture investigated.

Overall, the total Coulomb charge values show wide variability between the concretes with different compositions, w/b ratios and curing times in the wet chamber. However, these results are in line with the finding of other researchers about the reduction in Coulomb charge observed when mineral additions are substituted for cement [15,22,40].

The mixtures with RHA usually displayed Coulomb charge values lower than those of the other mixtures in this study, and values tended to decrease as the cement content decreases (i.e. with higher substitution contents). The improved performance of RHA mixtures was also observed by other researchers [17,41,42].

Longer curing times improved the quality of the concretes in this study, according to the ratings proposed by ASTM C1202. Fig. 2 shows that the REF mixture ($w/b = 0.50$) falls within the moderate chloride penetration rating when cured for 3 days. When the cure is extended to 7 days, the same mixture is classified as "low chloride penetration concrete". Another good example is mixture 10RHA, with $w/b = 0.65$. With a cure of 3 days, chloride penetration is moderate but when the cure is 7 days, chloride penetration is classified as low. When the cure is extended to 28 days, this mixture displays features of concretes with very low chloride penetration. An identical case is mixture 35FA, with $w/b = 0.50$. For mixtures 20RHA and 30RHA and $w/b = 0.65$, the resistance to chloride penetration also increased when the curing time was extended from 7 to 28 days, with their chloride penetration rating changing from low to very low.

Table 4
Coefficients C and D of equations $Q = C/D^{w/b}$ and the coefficient of determination (r^2) calculated according to the correlation between the total Coulomb charge (Q) and the w/b ratio of each mixture investigated and curing time in wet chamber.

Mixture	Curing time (days)	Total charge passed (Coulombs)		
		Coefficients[A]		
		C	D	r^2
REF	3	668.35	0.075	0.9978
	7	387.09	0.044	0.9940
	28	571.14	0.167	0.9939
10RHA	3	155.19	0.016	0.9969
	7	142.08	0.017	0.9864
	28	246.53	0.127	0.9425
20RHA	3	177.55	0.039	0.9879
	7	142.33	0.041	0.9520
	28	127.15	0.075	0.9816
30RHA	3	117.51	0.023	0.99
	7	88.72	0.019	0.9510
	28	113.28	0.085	0.9895
35FA	3	365.10	0.041	0.9976
	7	109.23	0.010	0.9980
	28	114.45	0.041	0.9980
50S	3	272.17	0.059	0.9802
	7	258.24	0.085	0.9993
	28	236.64	0.096	0.9859

$A = C$ and D are coefficients of equations $Q = C/D^{w/b}$, r^2 = coefficients of determination.

Fig. 3 shows the curves that correlate the total Coulomb charge (Q) versus the curing time adopted for all mixtures in this study. The displacement of the curves towards the smaller values of Q as the curing time is extended from 3 to 7 or 28 days can be clearly seen. It can also be noted that this displacement follows the increase in water content in the mixture (as shown by the w/b ratio). A similar behavior was observed by other researchers [9].

To better assess the influence of the wet curing time in the chloride penetration resistance of concrete mixtures containing mineral additions, the performance of each mixture is compared with the reference or control concrete. The variable Cure Performance Rate, related to the decrease in Coulomb charge (Q) and measured according to ASTM C 1202, offers a quantitative measure of the percent changes in the Coulomb charge as curing times are extended for each mixture at 91 days. Eq. (2) defines this variable as follows.

$$\mathrm{CPR}^{Q}_{\mathrm{AD}(i,x;tc)}(\%) = \{-[(Q_{\mathrm{AD}(i,x,tc)}/Q_{\mathrm{REF}(i,x,tc=3d)}) - 1] \cdot 100\} + 100 \qquad (2)$$

where $\mathrm{CPR}^{Q}_{\mathrm{AD}}$: Cure Performance Rate, related to the decrease in the total Coulomb charge of the concrete with addition AD, at age (i), with w/b ratio (x) and curing time (tc), in%; Q_{AD}: Cure Performance Rate of the concrete with addition AD, at age (i), with w/b ratio (x) and curing time (tc), in Coulombs; Q_{REF}: Total Coulomb charge of the reference concrete (without addition) at age (i), with w/b ratio (x) and curing time (tc) equal to 3 days. The negative sign at the beginning of the equation means that the nominal value of the performance rate can better represent its technical meaning, i.e., the Coulomb charge values (Q_{AD}) below Q_{REF} indicate a good performance by the mixture with mineral addition AD in relation to the REF mixture, and $\mathrm{CPR}^{Q}_{\mathrm{AD}}$ should therefore be positive.

Fig. 4 shows the cure performance rates calculated for each mixture, according to their w/b ratio. It should be noted that in the concrete mixtures with $w/b = 0.35$, mixture 35FA showed the greatest improvement with the increase in curing time from 3 to

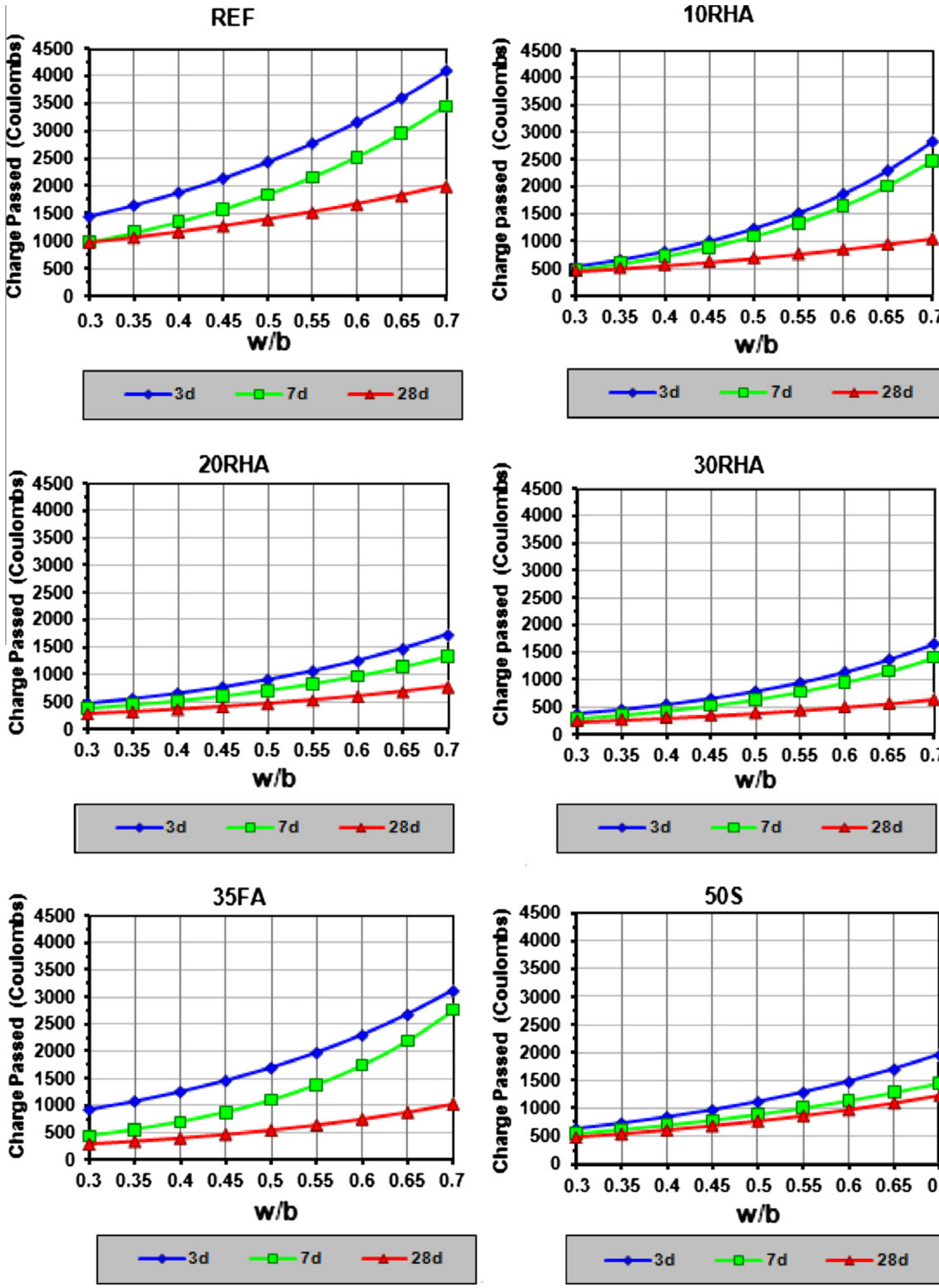

Fig. 3. Variation of total charge passed of each mixture investigated at 91 days based on *w*/*b* ratio and wet curing time.

7 days, with a decrease of 51% in Coulomb charge. Nevertheless, for a cure of 28 days and the same *w*/*b* ratio, mixtures 20RHA and 30RHA showed the greatest increase (approximately 14% when compared with a curing time of 7 days).

For *w*/*b* = 0.50, when the curing time was extended from 3 to 7 days, mixture 35FA again showed the greatest decrease in Coulomb charge (40%), followed by mixtures REF (29%), 30RHA (35%) and 20RHA (30%). When the curing time was extended from 7 to 28 days, mixture 35FA showed a decrease of 51% in the Coulomb charge and the mixtures with RHA in the three concentrations in the test showed a mean decrease of 29%.

Of all mixtures with *w*/*b* ratio = 0.65, mixture 50S showed the greatest decrease in Coulomb charge (approximately 27%) when the curing time was increased from 3 to 7 days. However, when the curing time was extended from 7 to 28 days, more significant decreases were observed in mixture 35FA (57%), followed by mixtures 10RHA (56%), 30RHA (54%), 20RHA (42%) and REF (39%).

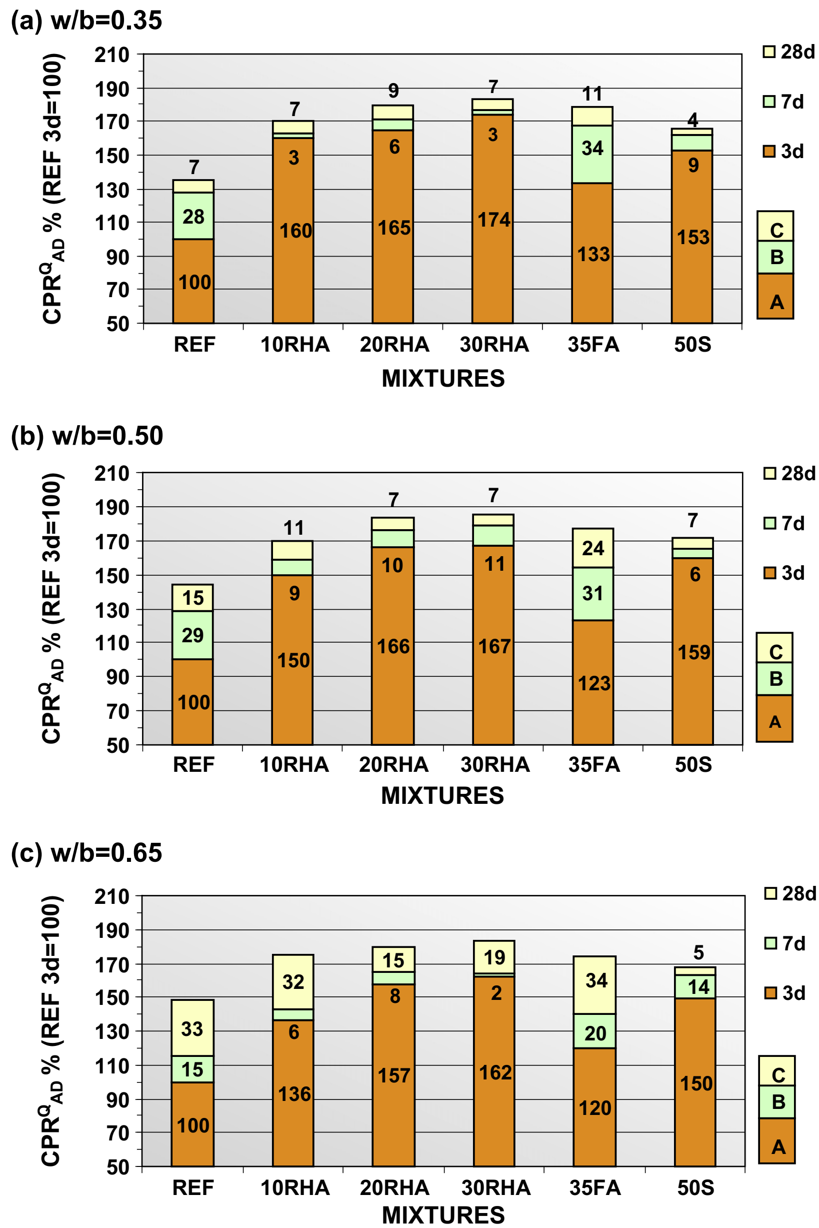

Fig. 4. Curing Performance Rate with reference to the reduction of the total Coulomb charge of several mixtures investigated, according to *w*/*b* ratio and curing time. $A = CPR^Q_{3d}$; $B = (CPR^Q_{7d} - CPR^Q_{3d})$; $C = (CPR^Q_{28d} - CPR^Q_{7d})$.

When the differences in CPR^Q_{AD} between 3-day and 28-day curing times are calculated $[1 - (Q28d/Q3d)]^*100$, we see that its range of values becomes wider as *w*/*b* ratio is increased. Mixture 35FA showed the greatest variations in CPR^Q_{AD} for all *w*/*b* ratios (approximately 68–71%) while mixture 50S showed the smallest variations, from 27% to 37%.

For the mixtures with RHA, the decreases in the Coulomb charge when the curing time is extended from 3 to 28 days depend on the concentration of the substitution and the *w*/*b* ratio, since the greatest reductions in *w*/*b* = 0.35, 0.50 and 0.65 were found in mixtures 20RHA (42%), 30RHA (56%) and 10RHA (60%), respectively. Thus, it can be stated that the curing process has great influence on the resistance of concrete to the penetration of aggressive agents such as chloride ions.

Fig. 5 shows the correlation between the values of total Coulomb charge (*Q*) and axial compressive strength (Cs) for samples with the same *w*/*b* ratio at 91 days in all mixtures in this study. This figure shows a great dispersion of these values, which indicates that a clearly defined behavior for this set of values cannot be identified. Different values of Coulomb passed are matched to identical values of compressive strength, i.e. mixtures with similar compressive strength present very different values of total Coulomb charge. In addition, as noted earlier, *Q* values in a mixture with the same composition and *w*/*b* ratio can be different if these mixtures are submitted to different curing times in a wet chamber.

This demonstrates that all these factors – type of addition (chemical composition, fineness and reactivity), substitution content and curing time – will affect the compressive strength and total Coulomb charge of a concrete mixture to different degrees.

3.3. Assessment of production cost and index binder intensity

This section presents an assessment of the concrete production costs (m^3) for the mixtures in this study to determine the influence

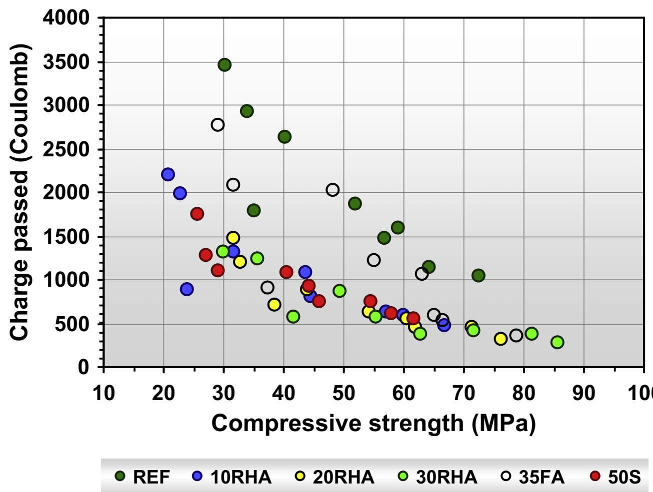

Fig. 5. Total Coulomb charge versus compressive strength at 91 days for the same w/b ratio, for all mixtures and curing times in the study.

of RHA content and curing time on compressive strength for strength levels of 40 MPa, 50 MPa and 60 MPa, and chloride-ion penetration resistance for use in civil construction. This behavior is compared with the reference mixture (100% Portland cement) and mixtures with fly ash and blast furnace slag. Compressive strength is used as a standard by engineers and architects when designing concrete structures.

The total cost of one cubic meter of concrete as shown in Table 3 was calculated using the cost for 1 metric ton of each component. The compressive strength and age of the concrete mixtures were set at a fixed value and w/b ratios were calculated from equations $CS = A/B^{w/b}$, whose coefficients for each mixture and curing time are given in Table 3. Using the w/b ratios, the values of the Coulomb charge were calculated using equations $B = C/D^{w/b}$ presented in Table 4 and the cost/m^3 was calculated using equations $C = G/F^{w/b}$ presented in Table 3.

When compared with the reference mixture (100% Portland cement), the cost/m^3 increases in mixtures 10RHA, 20RHA and 30RHA and 3-day curing time for strength levels 40 MPa, 50 MPa and 60 MPa ranged from 1% to 22% (10RHA), 3% to 28% (20RHA) and 3.5% to 30% (30RHA), as shown in Table 5.

For the 7-day cure and the same levels of compressive strength, the increase in cost in relation to the reference mixture (100% Portland cement) ranged from 0% to 1% (10RHA), 2.8% to 4.7% (20RHA) and 22.5% to 30.7% (30RHA). For the 28-day cure, only mixture 30RHA showed cost increases ranging from 8.2% to 18%. Mixtures 10RHA and 20RHA showed cost decreases from 4% to 6.2% and 0.7% to 4.5% respectively.

Mixture 50S for the same strength levels (40, 50 and 60 MPa) and curing times (3, 7 and 28 days) showed cost decreases ranging from 17% to 22% for a 3-day cure and from 13% to 18% for the 7- and 28-day cure. For these same conditions mixture 35FA shows cost reductions ranging from 10% to 22% (3-day cure), 8.6% to 16.8% (7-day cure) and 8.6% to 18% (28-day cure). The increases in cost observed in RHA mixtures can be explained by the cost of this ash and the need for larger amounts of superplasticizer additive to achieve the required slump values, 80 ± 10 mm.

If the cost/m^3 of the RHA mixture for a given strength level of a mixture cured for 3 days is used as a standard and comparing the cost/m^3 of the same mixture for the same compressive strength levels when the curing time is extended to 7 days, a reduction of 8% is observed in the three concentrations of this substitution (10%, 20% and 30%). When the cure is extended from 7 to 28 days, there is a decrease in cost ranging from 7% to 10% in mixtures 10RHA and 20RHA for the three levels of mechanical strength investigated and from 12% to 14% for mixture 30RHA.

For the reference and 35FA mixtures, the reduction ranged from 3% to 4% and for mixture 50S it was 2.7% for the three levels of compressive strength in the study. Thus, the cost reduction by m^3 when the curing time is extended from 7 to 28 days for the reference, fly ash or slag mixtures does not make up for the additional amount that would be required for extending the curing time.

Mixture 50S presented Coulomb charge values similar to mixture 20RHA but at a lower cost/m^3 for strength levels of 40 MPa, 50 MPa and 60 MPa and curing times of 3, 7 and 28 days. The reduction averaged 23% for a 3-day cure, 19% for a 7-day cure and 13% for the 28-day cure.

ACI 318 [43] states that for concrete exposed to freezing and thawing, the maximum w/b ratio is 0.45 and minimum $f'_c \geqslant$ 31 MPa. In contact with water requiring low permeability concrete (max $w/b = 0.50$ and min $f'_c = 35.0$ MPa) for sulfate exposure (max $w/b = 0.45$–0.50 and min $f'_c = 27.6 - 31.0$ MPa); conditions requiring corrosion protection of reinforcement (max $w/cm = 0.40$ and min $f'_c = 35.0$ MPa). Thus, mixture 50S (US$ = 88.73/m^3) with a

Table 5
w/b ratio, total charge passed (C) and cost/m^3 for levels of compressive strength of 40 MPa, 50 MPa and 60 MPa, and wet cure of 3, 7 and 28 days.

Compressive strength	Curing time 3 days			Cost (m^3)	Curing time 7 days			Cost (m^3)	Curing time 28 days			Cost (m^3)
	Mixture	w/b	Charge passed (C)		Mixture	w/b	Charge passed (C)		Mixture	w/b	Charge passed (C)	
40 MPa	REF	0.52	2567	95.84	REF	0.58	2366	87.59	REF	0.60	1668	85.0
	10RHA	0.54	1446	96.51	10RHA	0.59	1557	88.50	10RHA	0.65	950	79.75
	20RHA	0.56	1096	100.53	20RHA	0.61	997	91.68	20RHA	0.67	729	82.09
	30RHA	0.54	906	117.10	30RHA	0.58	874	107.28	30RHA	0.65	558	92.02
	35FA	0.44	1493	86.15	35FA	0.49	1046	80.05	35FA	0.51	564	77.73
	50S	0.48	1056	79.42	50S	0.51	910	76.19	50S	0.53	829	74.11
50 MPa	REF	0.42	1982	111.35	REF	0.47	1679	103.30	REF	0.50	1391	98.76
	10RHA	0.44	956	114.79	10RHA	0.50	1081	103.44	10RHA	0.55	776	94.85
	20RHA	0.48	845	116.48	20RHA	0.53	773	106.24	20RHA	0.58	573	96.89
	30RHA	0.45	644	142.62	30RHA	0.49	613	130.65	30RHA	0.56	447	112.08
	35FA	0.38	1232	94.09	35FA	0.42	758	88.72	35FA	0.45	460	84.89
	50S	0.40	842	88.73	50S	0.42	728	86.30	50S	0.44	673	83.95
60 MPa	REF	0.33	1570	127.45	REF	0.39	1308	116.48	REF	0.41	1200	113.04
	10RHA	0.36	687	131.87	10RHA	0.43	813	116.79	10RHA	0.48	658	107.09
	20RHA	0.42	695	130.10	20RHA	0.46	618	120.85	20RHA	0.50	470	112.27
	30RHA	0.38	495	166.25	30RHA	0.42	465	152.30	30RHA	0.48	374	133.55
	35FA	0.32	1017	102.77	35FA	0.36	574	96.90	35FA	0.39	389	92.72
	50S	0.32	672	99.12	50S	0.35	613	95.09	50S	0.37	568	92.49

Table 6
Consumption of binder materials and index binder intensity for levels of compressive strength 40 MPa, 50 MPa e 60 MPa and wet cure of 3, 7 and 28 days.

Compressive strength	Curing time 3 days			Binder intensity	Curing time 7 days			Binder intensity	Curing time 28 days			Binder intensity
	Mixture	w/b	Binder (kg/m^3)		Mixture	w/b	Binder (kg/m^3)		Mixture	w/b	Binder (kg/m^3)	
40 MPa	REF	0.52	355	8.9	REF	0.58	318	8.0	REF	0.60	307	7.7
	10RHA	0.54	342	8.6	10RHA	0.59	313	7.8	10RHA	0.65	281	7.0
	20RHA	0.56	330	8.3	20RHA	0.61	302	7.6	20RHA	0.67	271	6.8
	30RHA	0.54	342	8.6	30RHA	0.58	318	8.0	30RHA	0.65	281	7.0
	35FA	0.44	410	10	35FA	0.49	375	9.4	35FA	0.51	361	9.0
	50S	0.48	381	9.5	50S	0.51	361	9.0	50S	0.53	348	8.7
50 MPa	REF	0.42	425	8.5	REF	0.47	388	7.8	REF	0.50	368	7.4
	10RHA	0.44	410	8.2	10RHA	0.50	368	7.4	10RHA	0.55	336	6.7
	20RHA	0.48	381	7.6	20RHA	0.53	348	7.0	20RHA	0.58	318	6.4
	30RHA	0.45	402	8.0	30RHA	0.49	375	7.5	30RHA	0.56	330	6.6
	35FA	0.38	457	9.1	35FA	0.42	425	8.5	35FA	0.45	402	8.0
	50S	0.40	441	8.8	50S	0.42	425	8.5	50S	0.44	410	8.2
60 MPa	REF	0.33	500	8.3	REF	0.39	449	7.5	REF	0.41	433	7.2
	10RHA	0.36	474	7.9	10RHA	0.43	417	7.0	10RHA	0.48	381	6.4
	20RHA	0.42	425	7.1	20RHA	0.46	395	6.6	20RHA	0.50	368	6.1
	30RHA	0.38	457	7.6	30RHA	0.42	425	7.1	30RHA	0.48	381	6.4
	35FA	0.32	509	8.5	35FA	0.36	474	7.9	35FA	0.39	449	7.5
	50S	0.32	509	8.5	50S	0.35	482	8.0	50S	0.37	465	7.8

3-day cure, 50 MPa strength and $w/b = 0.40$ meets all requirements for freezing and thawing exposure, including maximum percentage of total cementitious materials by weight. This mixture has a 20% lower cost/m^3 than the reference mixture, 100% Portland cement, and it is given a "very low probability of chloride penetration" rating by ASTM C 1202.

Table 6 shows the amount of cementitious materials and the binder intensity index (bi_{cs}) proposed by Damineli et al. [44] for compressive strength values of 40 MPa, 50 MPa and 60 MPa and curing times of 3, 7 and 28 days. The amount of cementitious materials was calculated using equation $CM = H/I^{w/b}$, where H and I were calculated from the correlation between the amounts of cementitious materials (488, 359 and 284) and w/b ratios (0.35, 0.50 and 0.65).

The binder intensity index (bi_{cs}) proposed by Damineli et al. [44] allows measuring the amount of binder necessary to deliver a unit of strength, and consequently the efficiency of the use of binders. It is calculated using equation $bi_{cs} = b/p$ where b is the total consumption of binder materials (kg m^{-3}) and p is the performance requirement, compressive strength in this case.

This table shows that increases in compressive strength and curing times resulted in lower bi_{cs} in all mixtures in the study. The mixtures with RHA showed lower bi_{cs} when compared with the reference mixture for the three curing periods and compressive strength values investigated, with the lowest bi_{cs} observed in the sample with 20% RHA. The opposite behavior was observed in mixtures 35FA and 50S, which showed higher bi_{cs} when compared with the reference mixture for the three curing periods and compressive strength values investigated.

4. Conclusions

For the concrete tested in this study it was found that:

In all the mixtures in which rice husk ash was substituted for cement, compressive strength values were either equal to or higher than those of the reference mixtures at both 28 and 91 days, attesting the great reactivity of this pozzolan. In slag and fly ash mixtures, only those with w/b ratio = 0.35 at 28 days presented equal or better performance than the REF mixture.

The use of longer curing times resulted in higher compressive strength values (28–91 days) for all the mixtures investigated. With the exception of mixtures with slag, all displayed significant strength improvements. In the RHA mixtures, the increases accompanied the increase in w/b ratios. At 28 days, mixture 20RHA, cured for 7 days, showed compressive strength values 32% higher than the mixture cured for 3 days. When the curing time of this mixture was extended from 3 to 28 days an increase of 61% in compressive strength followed.

Mixture 20RHA displayed the highest compressive strengths values, while mixture 35FA displayed the lowest, at both 28 and 91 days.

Longer curing times reduced Coulomb charge values for all mixtures in the study, and again the reduction increased as w/b ratios were increased. Mixtures REF and 35FA showed the highest reductions in Coulomb charge values when the curing period was extended from 3 to 28 days. In all RHA mixtures, the decreases in Coulomb charge values as the cure period was extended from 3 to 28 days were 20%, 30% and 38% on average for w/b equal to 0.35, 0.50 and 0.65, respectively.

The increase in the content of rice husk ash reduced Coulomb charge values, resulting in concrete with higher resistance to chloride penetration.

In the present study, both the mixtures with additions and those with Portland cement only were influenced by longer wet curing times. However, the magnitude of the curing effects upon mechanical strength and resistance to chloride penetration depended on the type of mineral addition, the amount of substitution, the w/b ratio and the curing time used. This behavior points at the existence of an optimal curing time for each type of binder (cement + addition) to meet technical and economic criteria, which depend on the designed durability and mechanical strength for a given structure.

For a given compressive strength level, longer curing times resulted in lower cost/m^3 and increased chloride penetration resistance in all mixtures in the study. The mixtures with RHA display better performance but depending on the curing time used and level of compressive strength desired, higher w/b ratios may be necessary, which would adversely affect durability. For a compressive strength value of 50 MPa, mixture 50S cured for 3 days showed lower cost/m^3 when compared with mixtures RHA and REF and meets all ACI 318 requirements for durable concrete.

The mixtures with 10%, 20% and 30% RHA showed lower binder intensity indexes when compared with the reference mixture. The mixture with 20% RHA showed the lowest binder intensity index of all mixtures.

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