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Chloride penetration and carbonation in concrete with rice husk ash and chemical activators

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Abstract

The use of industrial or agricultural by-product substitutions for cement has greatly contributed to sustainable development practices. The joint use of chemical activators has produced improvements in the mechanical properties of concrete but there are still few studies attempting to investigate the influence of activators on carbonation and chloride penetration. This study investigated the influence of chemical activators K_2SO_4, Na_2SO_4, Na_2SiO_3 on compressive strength, chloride penetration and carbonation of concrete mixtures with rice husk ash. Results indicate that the use of these activators has beneficial effects on initial strength and reduces chloride penetration. The mixture prepared with 20% rice husk ash and 1% K_2SO_4 as a chemical activator showed the lowest carbonation coefficients, which were in fact lower than the values found in the reference sample.

Keywords: Rice husk ash; Chemical activators; Durability

1. Introduction

The pressing need for the preservation of natural resources and reductions in CO_2 emissions, combined with the ever-rising concrete production volumes that are required to meet the needs of the developing world, have fueled the search for alternative solutions. Several industrial and agricultural by-products such as blast furnace slag, fly ash and rice husk ash have found use as cement additions or substitutions, thus offering a useful final destination for these potential pollutants.

The partial substitution of these by-products for cement causes a reduction in the concrete alkalinity and the amount of free lime because of the formation of calcium silicate and calcium aluminate hydrates. While these substitutions can yield improvements in some aspects of concrete durability, they sometimes reduce the protection of steel rebars against corrosion because of pH reductions. Furthermore, the early mechanical strength may also be reduced.

The use of these materials on a wider scale could be increased if a method were found to increase the rate of pozzolanic reactions so that strength is increased without affecting other properties. Different methods have been tried to increase the early initial strength of concrete: finer grinding of the materials [1–3], accelerated curing [4], and thermal activation [5]. For pozzolans, chemical activation seems to be the most effective method as far as cost and improvements in mechanical strength are concerned [6].

Among the characteristics and properties of alkali-activated concrete discussed in several studies [7–10] are higher early strength, lower hydration heat and improved resistance to aggressive chemicals. Some of the problems discussed are faster hardening times, increased shrinkage and cracking.

Although there are many studies investigating the changes in concrete strength when chemical activators are used in combination with blast furnace slag and fly ash, very few of these investigate both the influence of activators

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on concrete with rice husk ash and the changes arising from the use of chemical activators in aspects related to durability, chloride penetration and carbonation.

The aim of this study is to investigate the influence of chemical activators on compressive strength, chloride penetration and carbonation of concrete mortars with rice husk ash.

2. Experimental program

2.1. Materials

The study used high initial strength portland cement (CP V – ARI, Brazilian standard NBR 5733) and rice husk ash, obtained by burning rice husk under controlled conditions in a thermoelectric power plant. The physical and chemical properties of the cement and the rice husk ash are shown in Table 1.

Table 1
Physical and chemical characteristics of portland cement and mineral additions

	Portland cement	RHA
Physical tests		
Specific gravity kg/dm^3	3.14	2.11
BET – specific surface (m^2/g)	1.48	40
Chemical composition %		
Loss on ignition (%)	2.09	4.49
SiO_2 (%)	19.59	96.26
Al_2O_3 (%)	4.79	0.41
Fe_2O_3 (%)	3.07	0.22
CaO (%)	64.35	0.76
MgO (%)	1.69	0.50
SO_3 (%)	2.75	0.04
Na_2O (%)	0.07	0.03
K_2O (%)	0.98	1.44

Natural quartz sand with maximum particle size 1.20 mm and fineness modulus 2.02 was used as fine aggregate. Crushed diabasic rock with maximum particle size 19.00 mm and fineness modulus 6.97 was used as coarse aggregate.

The desired consistency of the different compositions was obtained with the aid of a superplasticizer (modified carboxylic ether) according to ASTM C 494.

Potassium sulfate (K_2SO_4), sodium sulfate (Na_2SO_4) and sodium silicate (Na_2SiO_3) were used as chemical activators in concentrations of 1% by weight of cement. To keep costs at a minimum, all activators used were commercial grade. Table 2 lists the composition of the concrete mixtures (kg/m^3) and their cost (US\$/m^3).

2.2. Methods

Water/binder ratios used were 0.35, 0.50 and 0.65 and binder/aggregate ratios were 1:3.75, 1:5.25 and 1:6.9. Rice husk ash used was used as a substitution of 20% of the weight of cement.

The percentage of mortar by volume was set at 51% and the amount of sand added changed to compensate for the increase in mortar volume because of the lower specific mass of RHA. This way, the mortar volume did not change and the water requirement remained constant.

The molding temperature was set at 18 °C because the molding took place in a period of low temperatures. These lower temperatures could result in changes in hardening times and lower early strength. To control the temperature of concrete, the mixing water was heated as proposed [11].

The tests of axial compressive strength were performed in test specimens measuring 10×20 cm, which were stored in a wet chamber at 23 ± 2 °C and RH > 95% until the date of the test, 7, 28 and 91 days, as specified by Brazilian Standards NBR 5738 and NBR 5739.

Table 2
Composition of the concrete mixtures, kg/m^3 and their cost (US\$/m^3)

Mixture	*w*/*b*	Portland cement, kg/m^3	Rice husk ash, kg/m^3	Water	Fine Agg., kg/m^3	Coarse Agg., kg/m^3	S.P. dm^3/m^3	Cost/m^3 US\$
REF	0.35	464	–	161	659	1082	1.16	111.58
	0.50	346	–	173	757	1058	–	81.61
	0.65	271	–	176	821	1048	–	67.21
20RHA	0.35	372	93	158	627	1082	4.88	139.65
	0.50	277	69	171	733	1058	2.07	98.00
	0.65	217	54	175	802	1048	0.81	75.00
20RHA$_1$ 1% Na_2SO_4	0.35	372	93	153	627	1082	9.29	171.90
	0.50	277	69	168	733	1058	4.49	116.65
	0.65	217	54	173	802	1048	3.25	92.99
20RHA$_2$1% K_2SO_4	0.35	372	93	156	627	1082	6.73	161.65
	0.50	277	69	170	733	1058	3.11	112.28
	0.65	217	54	174	802	1048	2.17	89.58
20RHA$_3$ 1% Na_2SiO_3	0.35	372	93	154	627	1082	8.82	168.44
	0.50	277	69	169	733	1058	3.46	109.84
	0.65	217	54	173	802	1048	2.71	89.32

Note: S.P. = superplastizer. Slump of the concrete 70 ± 10 mm.

For the carbonation tests, test specimens measuring 10 × 10 cm were cured for 28 days. Their top surface was sealed and they underwent a preconditioning cycle as required by RILEM TC 116-PCD [12]. They were then placed in a controlled atmosphere chamber with 5% CO_2, at 23 ± 1 °C and RH 65 ± 1%. The carbon dioxide penetration depth was measured at different exposure times, 4, 8 and 12 weeks by means of the phenolphthalein test carried out on the transversely split section of the cylinders specimens using the RILEM CPC-18 [13] method.

Chloride-ion penetration was measured according to ASTM C 1202 [14] using cylindrical concrete test specimens measuring 95 mm × 150 mm, which were cast and cut to standard sizes (95 mm × 51 mm) using a diamond saw.

3. Results

3.1. Compressive strength

Compressive strength results are shown in Table 3. The reference sample (labeled REF) was prepared with 100% portland cement and was used for comparison with the mixtures with mineral admixtures and chemical activators.

The mixture with 20% rice husk ash (20RHA) and *w*/*b* ratio = 0.50 showed compressive strength values equal to the reference mixture (REF) at 7 days. The same mixture with different *w*/*b* ratios (0.35 and 0.65) showed lower strength when compared with the reference mixture. At 28 and 91 days, compressive strength values were higher than those of the reference samples for all *w*/*b* ratios. A strength value of 75.2 MPa at 28 days was found for the sample with the same substitution (20% RHA) and *w*/*b* ratio = 0.35 using RHA burned under controlled conditions [15]. In this study, a similar value was only reached with the use of chemical activators.

The same mixture (20RHA) was then prepared using 1% Na_2SO_4, K_2SO_4 or Na_2SiO_3 by weight of cement. It was observed that the three activators yielded a huge increase in strength at 7 days, which was the desired goal. The mixture activated with K_2SO_4 showed the highest increase when compared with the sample without activator. The percentage increases were 21%, 30% and 63% at 7 days, 11%, 13% and 44% at 28 days and 9%, 33% and 44% at 91 days for the mixtures with *w*/*b* ratio = 0.35, 0.50 and 0.65, respectively. When compared with the reference sample, the increases for the same *w*/*b* ratios and ages ranged from 13% to 52%. The use of K_2SO_4 as an activator yielded good results in studies with fly ash [16].

The fact that the growth was more evident in the samples with *w*/*b* = 0.65, mainly in the sample activated with K_2SO_4, can be attributed to the increase in pH and the changes in the RHA structure caused by the activator, which improves hydration. In addition, more space is available for the deposition of hydration products when compared with lower *w*/*b* ratios. This composition shows higher strength at 7 days (28.9 MPa) when compared with the sample without activator (17.7 MPa) and the reference sample (24.6 MPa), which illustrates the benefits of the activator.

Table 2 shows the cost/m^3 for each *w*/*b* ratio and binder composition in the study. For the composition with RHA without activator, by applying a regression between the value of cost/m^3 (US$ 139.65; US$ 98.00 and US$ 75.00 for *w*/*b* ratio = 0.35; 0.50 and 0.65 respectively) and the respective compressive strength values for 7 days (54.2 MPa; 36.4 MPa and 17.7 MPa) the following equation is obtained: $\text{cost/m}^3 = 54.59/0.983^x$, $R^2 = 0.98$. By substituting x for the 7-day strength values of the sample with 1% K_2SO_4, (65.9 MPa, 47.2 MPa and 28.9 MPa), the cost/m^3 of the composition can be calculated to reach the same strength level as in the sample without activator.

Table 3
Compressive strength, total charge passed (C), carbonation coefficient (K_c)

Mixture	*w*/*b*	Compressive strength, MPa			Total charge passed – C		K_c (mm/week$^{0.5}$)
		7 day	28 day	91 day	28 day	91 day	
REF	0.35	58.3	64.2	76.1	1727	1288	0.10
	0.50	36.4	47.7	53.5	3166	2136	5.47
	0.65	24.6	28.0	31.9	3681	2866	16.01
20RHA	0.35	54.2	69.7	83.4	999	452	0.10
	0.50	36.4	48.1	53.9	1557	692	7.50
	0.65	17.7	27.0	33.6	2677	1176	14.14
20RHA$_1$ 1% Na_2SO_4	0.35	59.2	73.3	82.8	933	515	4.26
	0.50	39.5	50.7	56.5	1393	630	7.42
	0.65	25.3	36.8	42.5	2004	760	10.73
20RHA$_2$1% K_2SO_4	0.35	65.9	77.4	91.0	820	326	0.10
	0.50	47.2	54.3	71.8	1312	552	4.69
	0.65	28.9	38.9	48.3	2242	818	10.68
20RHA$_3$ 1% Na_2SiO_3	0.35	54.2	74.4	77.5	704	342	0.10
	0.50	37.4	48.7	53.8	914	578	7.39
	0.65	29.1	40.3	45.1	1470	732	15.61

The calculated costs were US$ 166.39, US$ 122.62 and US$ 80.6, respectively, i.e., an excess of US$ 5.04 and US$ 9.64 for strength levels of 65.9 MPa and 47.2 MPa but a similar cost for a strength of 28.9 MPa.

For the sample activated with 1% K_2SO_4 the equation that relates the cost/m^3 with compressive strength is: cost/m$^3 = 55.225/0.984^x$, $R^2 = 0.98$. By substituting x for the 7-day strength values of the sample with 1% Na_2SO_4 (54.9 MPa, 39.5 MPa and 25.3 MPa), the following values were found: US$ 143.49, US$ 104.43 and US$ 83.05. These values are lower than the actual cost of this composition (US$ 171.90, US$ 116.65 and US$ 92.99). If the same calculation is applied to the 7-day strength values of the samples activated with 1% Na_2SiO_3 (54.2 MPa, 37.4 MPa and 29.1 MPa), the following values are obtained: US$ 132.37, US$ 100.95 and US$ 88.3, which are lower than the actual cost of this composition (US$ 168.44, US$ 109.84 and US$ 89.32). This attests that K_2SO_4 has a better performance when compared with the other activators in this study.

3.2. Chloride-ion penetration

The test results for the test of resistance to penetration of chloride ions into concrete, measured by means of the electric charge passed through the specimens (coulomb) at 28 and 91 days, are given in Table 3. At 28 and 91 days, the reference mixture showed the highest value.

The 20% substitution of rice husk ash for cement (mixture 20RHA) yields a significant reduction in the total charge passed at 28 days. This reduction amounts to 42%, 51% and 27% for w/b = 0.35, 0.50 and 0.65, respectively. At 91 days, the same w/b ratios showed reductions of 65%, 68% and 59%.

The activated mixture, 20RHA$_1$, 20RHA$_2$, 20RHA$_3$, showed lower total charge passed values when compared with the mixture without activator, 20RHA. At 28 days, the best results were seen in the mixture activated with Na_2SiO_3 (20RHA$_3$), with reductions in total charged passed values of 30%, 41% and 45% for $w/b = 0.35$, 0.50 and 0.65, respectively. When compared with the reference mixture at the same age and w/b ratio, the reductions in total charge passed corresponded to 59%, 71% and 60%.

At 91 days, the best results were seen in the mixture activated with K_2SO_4 (20RHA$_2$) for $w/b = 0.35$ and 0.50, where reductions of 28% and 20% in charge passed values were observed when compared with the corresponding mixtures with no activator. For $w/b = 0.65$, the lowest charge passed value was seen in the mixture with Na_2SiO_3 (20RHA$_3$), with a reduction of 48% in charge passed.

All activated mixtures, including those with $w/b = 0.65$ (a high value as far as durability is concerned), showed charge passed values at 91 days that can be rated as very low (100–1000 C) according to the table in ASTM C1202. The same results are obtained at 28 days for mixtures with $w/b = 0.35$.

3.3. Carbonation

Table 3 shows the carbonation coefficients of the different mixtures and Fig. 1 shows the changes in these coefficients for the w/b ratios used. For all mixtures investigated, K_c increases as the w/b ratio is increased because of the increase in concrete porosity and the lower concentration of cement.

Mixture 20RHA$_2$ with 1% K_2SO_4 showed the lowest carbonation coefficient of all mixtures investigated. The carbonation coefficient of this mixture was considered negligible for $w/b = 0.35$ and was lower than the coefficient of the reference mixture for $w/b = 0.50$ and 0.65. When compared with the mixture with no activator, 20RHA, the carbonation coefficients of the mixture with 1% K_2SO_4 (20RHA$_2$) dropped from 7.50 to 4.69 mm/week$^{0.50}$ for $w/b = 0.50$ and from 14.14 to 10.68 mm/week$^{0.50}$ for $w/b = 0.65$. When compared with the mixture with 20% RHA, the one with 1% Na_2SO_4 (20RHA$_1$) showed a carbonation coefficient lower than the reference sample but only for $w/b = 0.65$, where the coefficient found was 10.73 mm/week$^{0.50}$.

Table 4 presents the w/b ratios of the compositions in the study to obtain a carbonation depth of 40 mm in 100 years (for the equality base of 1 mm/week$^{0.50}$ = 1 mm/year$^{0.50}$ i.e., one week in the carbonation chamber is equivalent to 12 months in the natural environment) [17], as well as compressive strength at 28 days strength and the cost/m^3 of concrete. The reference composition reaches this value when $w/b = 0.47$ with the lowest cost/m^3 (US$ 87.30). The activated composition with the lowest cost /m^3 was the one with 1% K_2SO_4.

The mixtures with RHA (with and without the chemical activator 1% de K_2SO_4) meet this requirement and show

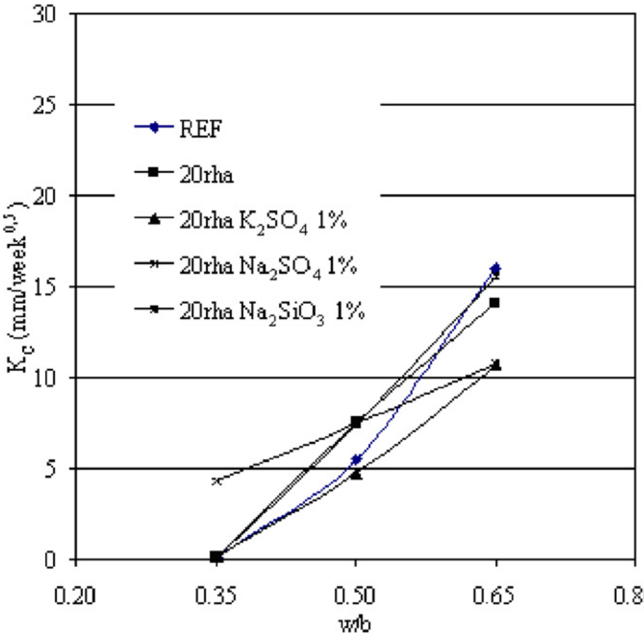

Fig. 1. Carbonation coefficients with reference to the w/b ratios.

Table 4
w/*b* ratios, compressive strength at 28 day and cost/m^3 for a carbonation depth of 40 mm in 100 years

Mixture	*w*/*b*	Compressive strength, MPa	Cost/m^3 US$
REF	0.47	47.9	87.3
20RHA	0.43	56.0	116.4
20RHA$_1$ 1% Na_2SO_4	0.34	74.4	178.5
20RHA$_2$ 1% K_2SO_4	0.48	57.2	116.4
20RHA$_3$ 1% Na_2SiO_3	0.43	60.7	132.6

similar compressive strength and cost/m^3. However, in the mixture without activator the *w*/*b* ratio is 0.43 and with the activator the ratio is 0.48. It is know that the use of lower *w*/*b* ratios is beneficial to the concrete therefore it is better to use the mixture without chemical activator.

4. Conclusions

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

- The samples with chemical activators showed higher compressive strength values when compared with their equivalent mixture with no activator. This effect was more dramatic in the initial ages and the mixture activated with K_2SO_4 showed higher compressive strength values at all ages and *w*/*b* ratios when compared with the reference concrete.
- The mixtures with rice husk ash with or without the addition of activators showed a sharp drop in total charge passed values when compared with the reference mixture. The mixtures activated with K_2SO_4 showed the best results. At 28 days, the mixture activated with Na_2SiO_3 showed the lowest charge passed values. Overall, the best results at 91 days were seen in the sample activated with K_2SO_4.
- All mixtures with chemical activators showed very low charge passed values (100–1000 C), even for *w*/*b* ratios as high as 0.65.
- For the same *w*/*b* ratio (0.35, 0.50 and 0.65), the lowest carbonation coefficients were seen in the mixture with RHA and 1% K_2SO_4 showed. The values obtained were lower than those in the reference concrete.
- For a carbonation depth of 40 mm in 100 years, the reference mixture provides the lowest cost. In the samples with chemical activators, the lowest cost is that of the sample with 1% K_2SO_4. However, it is best to use this mixture without the activator because it provides the same cost/m^3 with a lower *w*/*b* ratio.

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