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# Effect of rice-husk ash on durability of cementitious materials

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ABSTRACT

In this paper the effects of partial replacements of Portland cement by rice-husk ash (RHA) on the durability of conventional and high performance cementitious materials are investigated. Different percentages of RHA replacement levels, two RHAs (amorphous and partially crystalline optimized by dry-milling) and several water–cementitious materials ratio are studied. The following durability aspects were tested: air permeability, chloride ion penetration, alkali-silica expansion, sulfate and acid resistance. The results were compared with those of cementitious materials without RHA. It is concluded from the tested properties that the incorporation of both RHAs in concretes show different behaviors for air permeability and chloride ion penetration depending on the water/cementitious materials ratio used; in mortars, it reduces the mass loss of specimens exposed to hydrochloric acid solution and decreases the expansion due to sulfate attack and the alkali-silica reaction. The results of durability aspects due to physical or pozzolanic effects after the addition of both RHAs, and its chemical composition, in general indicate an enhanced performance, proving the feasibility of its rational utilization as a supplementary cementing material.

## 1. Introduction

The Food and Agriculture Organization's forecast of global rice production over the 2009 season was 678 million tonnes [1], about 20% of which is rice husk [2] which is typically a waste material from the point view point of industrial and agricultural processes. Even after its incineration, 20% of rice husk's weight remains as a waste material in the form of rice-husk ash (RHA) [2,3].

As an example, in Uruguay, where rice production has had a dramatic increase over the past ten years (becoming the most important crop since 2001), the main use of rice husk is as fuel in the rice paddy milling process. But the use of this fuel generates a huge volume of ash which has no immediate useful application and is usually dumped into water streams causing pollution and contamination of springs. As a result, the use of RHA has aroused great interest.

The chemical composition of RHA depends on temperature and burning time, but the variations in the components are not significant. The ash from open-field burning (or from non-controlled combustion in industrial furnaces) usually contains a higher proportion of non-reactive silica minerals such as cristobalite and tridymite, and it should be ground into very fine particles to develop pozzolanic activity. In addition, highly pozzolanic ash can be produced by means of controlled combustion when silica is kept in non-crystalline form. Such silica can react when added to cement in the presence of water (with calcium hydroxide) resulting in cementitious compounds [3]. Most research confirms the fact that burning temperature is a critical point in the production of amorphous reactive ash [4].

Rice-husk ash is a mineral admixture for cement and concrete [2,5]; the behavior of cementitious products varies with the source of RHA [3,4]. Most mineral admixtures have a favorable influence on the strength and durability of concrete. In the case of RHA, its chemical effect is related to the fact that when produced by controlled combustion it is a highly pozzolanic material which combines quickly with calcium hydroxide forming a secondary C–S–H; the physical effect is linked to particle size (less than 45 μm on average), which produces a refinement on the pore structure, acts as nucleation point for hydration products, and restricts the growth of crystals generated in the hydration process. Mehta [6] has argued that the grinding of RHA to a high degree of fineness should be avoided, since it derives its pozzolanic activity mainly from the internal surface area of the particles; for use in preparation of concrete and mortar products, at least about 75% of RHA particles are in a size range at from about 4 μm to about 75 μm, with a mean particle diameter between 8 μm and 6 μm, and a surface area of at least 20 $m^2/g$ [7].

Much data has been published concerning the influence of amorphous RHA produced by controlled combustion (CRHA) on the behavior of pastes, mortars, and concretes [2,3,6–24]; but less data is available on the effect of partially crystalline RHA not produced by controlled burning (RRHA), with most of this data being relatively recent [25–33]. This current interest is because an

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increasing amount of rice husk is used as fuel to power the boilers of modern rice milling factories, in order to produce steam, either for drying and parboiling of rice grains or for production of electricity.

A huge amount of RHA, estimated to be about 10 million tonnes, is generated worldwide each year. The RHA obtained generally has characteristics that differ from those of a CRHA. This may be due to different factors, such as an ineffective boiler burning temperature control (higher than 900 °C) [34], a not long enough residence time for the husk in the boiler, or insufficient oxygen content [31].

Limited data is available comparing the effects of CRHA and RRHA as a replacement of Portland cement, and on it only mechanical properties and autogenous shrinkage have been studied [35,36]. For instance, the literature provides separate studies of the durability of cementitious materials with CRHA [2,3,7–18,20–23] or partial aspects of durability with RRHA [25,27–32], but there are no previously published investigations comparing the effects of both ashes on durability. For this reason, the purpose of this investigation is to determine and compare the effects of both RHAs (CRHA and RRHA) in cementitious products exposed to hostile environments.

This paper presents a study of the influence of both RHAs in durability properties with different water/(cement + RHA), materials ratios and replacements of cement by RHA. The results are compared with those of cementitious materials without RHA.

## 2. Experimental program

### 2.1. Materials

The following materials were used in the preparation of the specimens: a Portland cement type I (normal Portland cement); natural siliceous river sand with maximum aggregate size of 4.75 mm; coarse aggregate (crushed granite) with maximum aggregate size of 12.5 mm; and a sulfonated naphthalene formaldehyde condensate based superplasticizer (solids content 42%). Two sources of RHA were considered: a residual RHA produced in parboiling process with burning temperature not effectively controlled (from the only factory of parboiled rice in Uruguay); and a homogeneous ash produced by controlled incineration from the United States (CRHA). The residual RHA used in this research was a processed waste which was dry-milled for the necessary time to obtain a median particle size of 8 μm, a defined specific surface by nitrogen absorption [7], and the maximum activity index according to ASTM C311-98b. The procedure for residual RHA optimization is presented in previous research [26,27]. The optimized residual RHA is named as RRHA. Both ashes, RRHA and CRHA, are the same as used in [26,27,35,36].

The physical and chemical characteristics of Portland cement and the two ashes are given in Table 1. Chemical analyses indicate that both ashes are mainly composed of $SiO_2$. Both ashes have the same median particle size and activity index. X-ray diffraction (Fig. 1) indicates that CRHA can be considered as an amorphous RHA; but RRHA showed crystalline structures, which were identified as cristobalite. A rapid analytical method for evaluating amorphous silica in RHA (according to Paya et al. [37]) has been used. Since the percentage of reactive silica contained in CRHA was 98.5%, and in residual RRHA was 39.55%, RRHA can be considered partially crystalline.

### 2.2. Experimental details

For studying the effects of RHA on durability of cementitious materials, concretes and mortars were made. The investigated durability aspects of the hardened concrete were air permeability and chloride ion penetration. Alkali-silica expansion, acid and sulfate attack in mortar specimens are also studied in this work.

**Table 1**
Physical properties and chemical analyses of the cement and RHA used.

| | Cement | RHA | |
|---|---|---|---|
| | | RRHA | CRHA |
| *Physical tests* | | | |
| Specific gravity | 3.14 | 2.06 | 2.16 |
| Fineness | | | |
| Specific surface, Blaine, $m^2/kg$ | 309 | – | – |
| Nitrogen adsorption, $m^2/kg$ | – | 28800 | 24300 |
| *Setting time, min,* | | | |
| Initial | 145 | – | – |
| Final | 275 | – | – |
| *Compressive strength, MPa* | | | |
| 1-day | 10.1 | – | – |
| 3-day | 22.8 | – | – |
| 7-day | 33.1 | – | – |
| 28-day | 45.1 | – | – |
| *Chemical analyses, %* | | | |
| Silicon dioxide ($SiO_2$) | 21.98 | 87.2 | 88 |
| Aluminum oxide ($Al_2O_3$) | 4.65 | 0.15 | – |
| Ferric oxide ($Fe_2O_3$) | 2.27 | 0.16 | 0.1 |
| Calcium oxide (CaO) | 61.55 | 0.55 | 0.8 |
| Magnesium oxide (MgO) | 4.27 | 0.35 | 0.2 |
| Manganese oxide (MnO) | – | – | 0.2 |
| Sodium oxide ($Na_2O$) | 0.11 | 1.12 | 0.7 |
| Potassium oxide ($K_2O$) | 1.04 | 3.60 | 2.2 |
| Sulphur oxide ($SO_3$) | 2.19 | 0.32 | – |
| Loss on ignition | 2.30 | 6.55 | 8.1 |
| *Compounds* | | | |
| Tricalcium silicate $C_3S$ | 44.0 | – | – |
| Dicalcium silicate $C_2S$ | 29.9 | – | – |
| Tricalcium aluminate $C_3A$ | 8.5 | – | – |
| Tetracalcium aluminoferrite $C_4AF$ | 6.9 | – | – |
| *Activity index* | | | |
| ASTM C311-98b | 100 | 92.93 | 92.4 |

In order to assess the effect of RHA on concrete durability, water–cementitious materials ratio of 0.50, 0.40 and 0.32 were selected to characterize normal and high performance concrete. Based on previous research [32], concrete mixes with 5%, 10% and 15% of cement replacement by RHA were studied in this investigation. Concrete mixes with RRHA, CRHA and control Portland cement concrete mixes, without RHA, were made. Table 2 shows the mixture proportions in weight of the materials. Concrete was mixed in a concrete mixer for 3 min. The slump test was immediately performed after the material was blended. The values obtained are summarized in Table 2, where superplasticizer percentages are used in relation to weight of (cement + RHA). Superplasticizer was used in very low percentages, according to the results obtained in the slumps, to allow consistency adjustments without changing the proportion of the other materials (trying to make the change in superplasticizer content in the concretes with RHA as small as possible).

According to Table 2, CRHA concrete requires more superplasticizer that RRHA concrete; this is because CRHA presents greater loss on ignition that RRHA, as shown in Table 1, and therefore higher unburnt carbon content [38,39]. Unburnt carbon has very large surface area, and water demand is higher, so CRHA needs higher superplasticizer dosage for a given level of workability [38].

For concretes, three test specimens were prepared for each type of analyzed variable. All the specimens were cast following the directions of the Mercosur Code (called NM); then, they were labeled and cured in molds for 24 h. Afterwards, they were demolded and cured according to the test method used for each durability aspect studied.

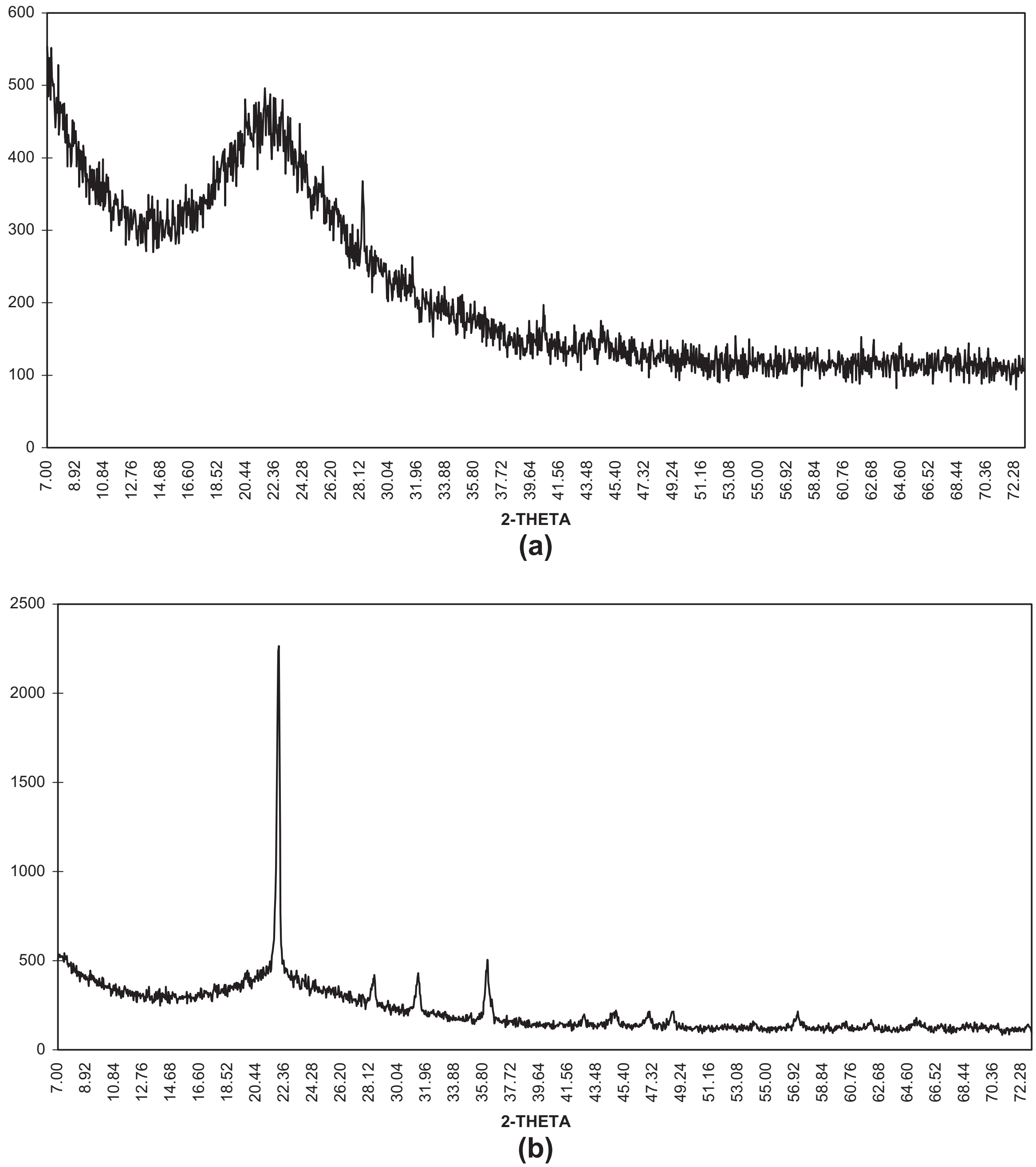

**Fig. 1.** X-ray diffraction of the rice-husk ashes used: (a) CRHA and (b) RRHA.

For mortars, five specimens were prepared for each type of analyzed variable according to the test method used. Mortars for the study of acid and sulfate attacks were made with an aggregate fine-cementitious materials ratio of 2.75, water–cementitious materials ratio of 0.50, 0.40 and 0.32, and 0%, 5%, 10% and 15% of cement replacement by RHA; for the alkali-silica reaction (ASR), according to ASTM 1260–01, a water–cementitious materials ratio of 0.47 was used (details will be presented later). Mortars with RRHA, CRHA and without RHA were study. The flow was measured according to ASTM C109, and superplasticizer was used to achieve the same flow as the reference mixture without RHA.

### 2.3. Test methods

In hardened state the evaluated properties were:

*Air permeability:* on concrete cylinders of 150 × 300 mm at 28 days of age was determined by the "Torrent Permeability Tester" method [40,41] according to the Swiss Standard SIA 262/1:2003. The particular features of the Torrent method are a two chamber vacuum cell and a pressure regulator, which ensure that air flows at right angles to the surface directed towards the inner chamber; this allows the calculation of the permeability coefficient $K_t$ on the basis of a simple theoretical model. By comparing the results [40] of gas permeability measured by the Torrent Permeability Tester ($K_t$) and oxygen permeability obtained for the Cembureau method ($K_0$) is $K_0 = 2.5K_t^{0.7}$ in E-16 m$^2$.

C*hloride ion penetration*: in 10 by 20 cm concrete cylinders at 28 days. All the specimens were cast following the directions of Mercosur Code; then they were labeled and cured in molds for 24 h. Afterwards, they were demolded and cured in a moist-curing

**Table 2**
Mix proportions of concrete.

| w/(c + RHA) | RHA (%) | Cement (kg/m$^3$) | Fine agg. (kg/m$^3$) | Coarse agg. (kg/m$^3$) | Superplast (%) | | Slump (mm) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | RRHA | CRHA | RRHA | CRHA |
| 0.32 | 0 | 534 | 690 | 1050 | 0.52 | | 60 | |
| | 5 | 507.5 | 690 | 1050 | 0.55 | 0.70 | 80 | 70 |
| | 10 | 481 | 690 | 1050 | 0.81 | 0.90 | 65 | 70 |
| | 15 | 454 | 690 | 1050 | 0.95 | 1.00 | 40 | 65 |
| 0.40 | 0 | 462 | 723 | 1018 | 0.10 | | 50 | |
| | 5 | 439 | 723 | 1018 | 0.24 | 0.26 | 50 | 65 |
| | 10 | 416 | 723 | 1018 | 0.20 | 0.27 | 45 | 55 |
| | 15 | 393 | 723 | 1018 | 0.41 | 0.50 | 40 | 65 |
| 0.50 | 0 | 408 | 758 | 983 | – | | 70 | |
| | 5 | 388 | 758 | 983 | – | 0.20 | 100 | 80 |
| | 10 | 367 | 758 | 983 | – | 0.30 | 95 | 80 |
| | 15 | 347 | 758 | 983 | – | 0.40 | 40 | 60 |

room at 21 ± 2 °C and a relative humidity of more than 90–95% until testing. For the chloride ion penetration test, the Italian Standard 79-28 was used; $Cl^-$ was introduced from the outside of the hardened concrete (external $Cl^-$). Seven days after curing, the specimens were immersed in water, having a $Cl^-$ concentration of 5% for 21 days. After splitting tensile test, a silver nitrate solution was sprayed on the fractured surface to observe the color change boundary. In the zone penetrated by $Cl^-$, silver nitrate forms a white precipitate of silver chloride, while in the area not penetrated by $Cl^-$ it reacts with $OH^-$ ions to form silver oxide, which appears on the surface as a brown precipitate. Because of the appearance of contrasting colors at the color change boundary, the zone is clearly drawn. Based on this result, each fractured surface was scanned, each $Cl^-$ depth of penetration was evaluated with statistical analysis, and the diffusion coefficient was calculated.

*Acid attack:* the influence of RHA in the chemical deterioration of concrete was studied according to Mehta and Folliard [14] and ASTM C267 on mortar cylinders of 50 × 100 mm exposed to 1% HCl solution. The mass of the cylinders from each of the mixtures, after 7 days of moist-curing (temperature of 20 °C and a relative humidity of 100%), was determined in the saturated surface dry (SSD) condition, before immersion in the HCl solution. On a weekly basis, the test cylinders were cleaned by three quick rinses in running cold tap water and quick dried by blotting with a paper towel between each rinse. For each one of the test specimens prepared, the mass was determined after ½ h. The HCl solution was also changed on a weekly basis before resubmerging the cylinders. The mass was determined up to 84 days [14].

*Sulfate resistance:* mortar bars were prepared in accordance to ASTM C1012 and Refs. [14,28,30,42–45]. Ten specimens of 25 × 25 × 285 mm were prepared for each mixture. After casting, specimens were covered with moist paper towels (approx. 100% relative humidity) for 24 h, after which they were demolded, marked and placed in a saturated lime–water solution for 28 days [42–44]. After 28 days of lime–water curing, the initial length was measured and the specimens were divided into two categories for further curing: (a) curing in saturated lime–water (control), (b) curing in a solution of 5% sodium sulfate according to Refs. [14,28,30,42–45]. The sodium sulfate solution PH was controlled daily and corrected when needed with a 1 N sulphuric acid solution. On a weekly basis, the length change of the prisms was measured over time, up to 200 days (28 weeks).

*Alkali-silica expansion:* to study the influence of the two RHAs behavior concerning the ASR, tests were performed according to the ASTM C1260 method on mortar bars. Water–cementitious materials ratio of 0.47 was used with 10%, 20%, 30% and 40% of RRHA replacement by mass, and 10% and 20% of CRHA, respectively. Control Portland cement mortar mix, without RHA, were also included for comparison. Five prism samples for each batch of mixing proportions with dimensions of 25 × 25 × 285 mm were prepared. The samples were immersed in a 1 N NaOH solution at 80 °C. The length change of the prisms was measured over time, up to 16 days, 14 days of immersion in 1 N NaOH solution, according to ASTM C1260–01. The used sand was a very reactive fine aggregate, when tested using the above-mentioned method, composed of 95% (by weight) of natural siliceous sand from the River Plate and the remaining 5% was completed with sand obtained by crushing a clastic sedimentary rock from the Province of Chaco, Argentina, which consists of quartz grains in an amorphous siliceous matrix, with opal, chalcedony and microcrystalline quartz (the first two minerals should be considered as highly reactive); a micrograph of this sand is shown in Fig. 2. The mixture of both sands in determined proportions results in a very reactive finite aggregate [46].

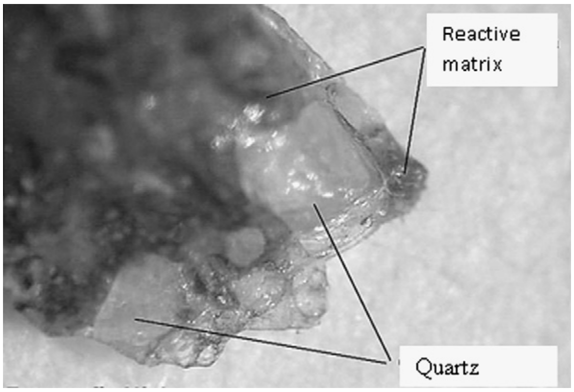

**Fig. 2.** Micrograph of the reactive sand used for the study of the ASR.

## 3. Test results and discussion

### 3.1. Air permeability

The results of the tests for concretes with and without RHA are given in Table 3, where $K_t$ represents gas permeability, $\rho$ electrical resistance, and the concrete quality class is determined from $K_t$ and $\rho$ in a nomogram [40,41] according the Swiss Standard SIA 262/1:2003.

For water–cementitious materials ratio of 0.50, the results of air permeability without RHA are higher than those with RRHA, and the concrete quality obtained is normal; with CRHA, the results

**Table 3**
Air permeability of concretes at the age of 28 days.

| w/(c + RHA) | RHA (%) | RRHA | | | CRHA | | |
|---|---|---|---|---|---|---|---|
| | | $K_t$ ($10^{-16}$m$^2$) | $\rho$ (kΩ cm) | Conc. quality | $K_t$ ($10^{-16}$ m$^2$) | $\rho$ (kΩ cm) | Conc. quality |
| 0.50 | 0 | 0.079 | 10 | Good | 0.079 | 10 | Good |
| | 5 | 0.167 | 8 | Normal | 0.046 | 11 | Good |
| | 10 | 0.303 | 11 | Normal | 0.074 | 11 | Good |
| | 15 | 0.459 | 12 | Normal | 0.062 | 13 | Good |
| 0.40 | 0 | 0.018 | 13 | Good | 0.018 | 13 | Good |
| | 5 | 0.006 | 13 | Good | 0.009 | 15 | Good |
| | 10 | 0.043 | 12 | Good | 0.007 | 14 | Good |
| | 15 | 0.017 | 12 | Good | 0.029 | 17 | Good |
| 0.32 | 0 | 0.019 | 17 | Good | 0.019 | 17 | Good |
| | 5 | 0.029 | 15 | Good | 0.026 | 18 | Good |
| | 10 | 0.016 | 18 | Good | 0.001 | 17 | Very Good |
| | 15 | 0.011 | 17 | Good | 0.002 | 20 | Very Good |

of air permeability are better than those without RHA, and the concrete quality obtained is good.

For high performance concrete with water/cementitious materials ratio of 0.32 and 0.40, the concrete quality class results for RHA concrete and control concrete without RHA do not differ one to another, both are good; but for water/cementitious ratio of 0.32 with 10% and 15%, CRHA results are better (very good).

The air permeability results show a better air permeability for the CRHA than for the RRHA concretes. This is mainly due to the pozzolanic effect of CRHA [35], which produces a decrease in the total porosity attributed to the change occurring in pore size distribution (being a consequence of the fact that CRHA could react with calcium hydroxide to form CSH [47]).

### 3.2. Chloride ion penetration

Table 4 shows the results for $Cl^-$ depth of penetration and the diffusion coefficient ($D$) by immersion in water, having a $Cl^-$ concentration equal to 5% for 21 days. The results show different behaviors depending on the water/cementitious materials ratio.

It can be seen that the $Cl^-$ depth of penetration and the diffusion coefficient in concretes with water/cementitious materials ratio of 0.50 decreases with both RHAs; the best results are obtained with 15% CRHA.

For concretes with water/cementitious materials ratio of 0.40, a decrease of chloride penetration is obtained with RRHA and with 15% substitution of Portland cement by CRHA. The results obtained with 5% and 10% CRHA are not smaller than those of the control mixture (100% Portland cement).

For concretes with water/cementitious materials ratio of 0.32, a decrease of the chloride penetration is obtained only with 15% substitution of Portland cement by RRHA.

In this paper the best resistance to chloride ion penetration is obtained with 15% substitution of Portland cement by RHA; in water/cementitious materials ratio of 0.50, the best resistance is obtained with CRHA, while in 0.40 and 0.32 it is obtained using RRHA. This is mainly due to the pore-refining capacity of RHA in concrete [20,29,48,49].

### 3.3. Hydrochloric acid attack

The specimens containing RHA were found to be more resistant to the HCl solution than those without RHA; as shown by the reduced mass loss on Fig. 3 for RRHA with water–cementitious material ratio of 0.40 during immersion on 1% HCl where each value represents the average of five experimental observations.

Independently of the mixture, the mass loss of the mortars increases with immersion time, and the percentage of mass loss of the reference mortars increases rapidly when compared to that of RHA mortars. Similar behavior was reported by Refs. [14,17,50].

The mass loss decrease with increasing RHA content in mortars (Ref. [17] also reports a similar observation) shows that the acid attack decreases with increase cement substitution with RHA.

At the final immersion period the mass loss of the RHA mortars is less than that of the control, demonstrating higher resistance to HCl solution.

The improved acid resistance of the specimens containing RHA can be attributed in part to the pozzolanic reaction by the use of

**Table 4**
Chloride ion penetration of concretes.

| w/(c + RHA) | RHA(%) | RRHA | | CRHA | |
|---|---|---|---|---|---|
| | | Depth $Cl^-$ (mm) | $D$ ($10^{-6}$ mm$^2$/s) | Depth $Cl^-$(mm) | $D$ ($10^{-6}$ mm$^2$/s) |
| 0.50 | 0 | 12.80 | 5.60 | 12.80 | 5.60 |
| | 5 | 12.40 | 5.30 | 12.06 | 5.01 |
| | 10 | 11.54 | 4.59 | 12.23 | 5.15 |
| | 15 | 11.88 | 4.86 | 11.43 | 4.50 |
| 0.40 | 0 | 9.59 | 3.17 | 9.59 | 3.17 |
| | 5 | 8.46 | 2.47 | 9.63 | 3.19 |
| | 10 | 8.82 | 2.68 | 9.78 | 3.29 |
| | 15 | 7.60 | 1.99 | 9.16 | 2.89 |
| 0.32 | 0 | 7.36 | 1.86 | 7.36 | 1.86 |
| | 5 | 8.48 | 2.48 | 7.76 | 2.07 |
| | 10 | 8.01 | 2.21 | 7.77 | 2.08 |
| | 15 | 6.90 | 1.64 | 7.33 | 1.86 |

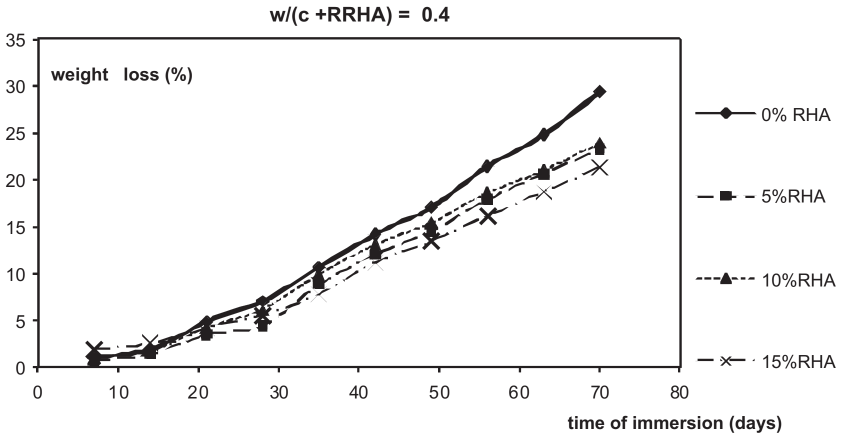

**Fig. 3.** Weight loss (%) of specimens immersed in 1% HCl solution.

RHA, resulting in the conversion of calcium hydroxide (which is readily attacked by HCl) to C–S–H, thus increasing the overall acid resistance of the RHA specimens [14,17,51].

### 3.4. Sulfate attack

The results of expansion reduction obtained at 196 days (28 weeks) of immersion in 5% sodium sulfate solution with the two RHAs used in relation to the reference without RHA are presented in Table 5. The specimens containing RHA were found resistant to the sodium sulfate attack. It can be observed that as the percentage of RHA was increased, a larger expansion reduction was obtained.

The results obtained with RRHA and CRHA in this manuscript are consistent with the ones obtained for CRHA [14] and RRHA [28,30], showing the effectiveness of the two RHAs incorporation in relation to sulfate attack.

The rise in sulfate resistance of RHA with increasing RHA replacement level is explained in the following paragraphs:

For the mechanism of sodium sulfate attack [52,53], calcium hydroxide from the hydration reaction of cement reacts with sodium sulfate and transforms to gypsum, leading to the expansion of an outer skin of the specimen; then gypsum reacts with the aluminum compounds to produce ettringite that increases in volume and instability. This causes the expansion of cement matrix, leading to further cracking of the interior of the mortar. Theoretical computations and experimental results show that the resistance of sulfates depends of the amount of $Al_2O_3$ available on the anhydrous cement [54]; the negative effects of high $Al_2O_3$ contents in slag are mentioned in literature [55,56].

From Table 1, the $Al_2O_3$ content of the cement is 4.65%, while for RRHA and CRHA are 0.15 and zero respectively. As replacing cement by RHA, either RRHA or CRHA, there is a decrease in $Al_2O_3$ content of the cementitious system and an improvement of the resistance to sulfate as a result. This explains the results in Table 5; also, increasing RHA percentage tends to reduce the expansion, and the best results are obtained with CRHA in higher water–cementitious material ratio.

**Table 5**
Reduction in sulfate expansion at 28 weeks.

| w/(c + RHA) | RHA (%) | RRHA | CRHA |
|---|---|---|---|
| 0.50 | 5 | 18 | 59 |
| | 10 | 29 | 69 |
| | 15 | 49 | 85 |
| 0.40 | 5 | 23 | 43 |
| | 10 | 31 | 53 |
| | 15 | 95 | 71 |
| 0.32 | 5 | 22 | 11 |
| | 10 | 33 | 15 |
| | 15 | 82 | 55 |

In denser cementitious matrices (water/cementitious material ratio = 0.32 or even 0.40 with 15% RHA), in addition to the $Al_2O_3$ content, the physical or pozzolanic effect of RHA play an important role in the resistance to sulfate. First, the durability of a hardened cement paste to sulfate is reduced due to the presence of calcium hydroxide [57]; second, in the pozzolanic reaction pozzolan reacts with calcium hydroxide (created during the cement hydration) and generates lower density calcium silicate hydrates (C–S–H) [57]; for this reasons the RRHA specimens have more calcium hydroxide than those CRHA specimens, being thus more resistant to sulfates in denser cementitious matrices.

### 3.5. Alkali-silica expansion

According to the limits established by ASTM C 1260/01, at 16 days after casting, 14 days in 1 N NaOH at 80 °C, expansions of less than 0.10% are indicative of innocuous behavior, and expansions of more than 0.20% are indicative of potentially deleterious expansions [58–60]. Fig. 4 shows at the age of 16 days, 14 days in 1 N NaOH at 80 °C, the expansion results of mortar bars made with reactive aggregate and various amounts of both RHAs, where each value represents the average in five experimental observations.

The specimens without RHA present the highest expansions, while the use of RHA reduces the expansions. As reported in literature, the use of RHA is beneficial in reducing the alkali-silica reaction [14,17,18]. This may be because RHA produces less expansive alkali-silica gel from the reaction with the alkalis released from the cement hydration [17].

Lower RHA content reduces the expansions, but even 20% RRHA and 10% CRHA specimens exceeds the expansion limit of 0.10% after 14 days in 1 H NaOH at 80 °C. The specimens made with 20% CRHA passed the expansion criterion, and with 30% RRHA replacement was just at the limit at 14 days; for this reason were tested mortar bars with higher replacement levels (40% RRHA).

It is evident that CRHA specimens indicate a superior inhibiting effect of expansion due to alkali-silica reaction than RRHA specimens. This is due to the amorphous silica content of the RHA used in this work. Evidence of a point of equivalency between a higher replacement level of RRHA and a lower replacement level of CRHA can be seen in Fig. 4.

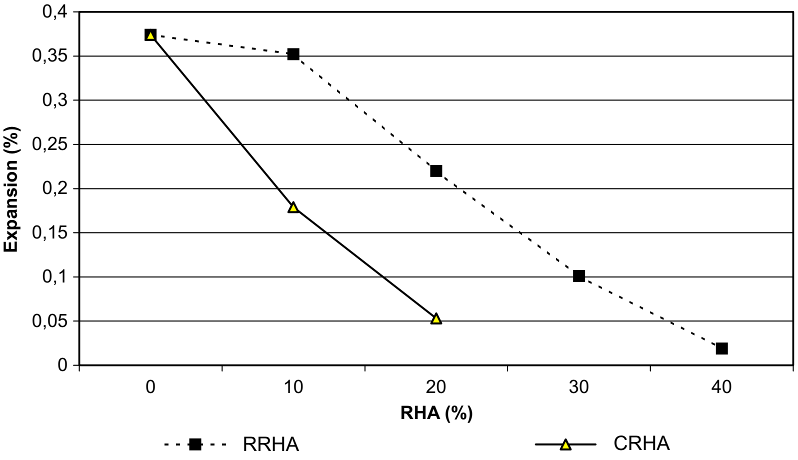

**Fig. 4.** Expansions vs RHA (%) at 14 days in 1 N Na OH at 80 °C, using reactive aggregate.

## 4. Concluding remarks

This paper analyzes aspects of durability of cementitious materials without rice-husk ash and with two rice-husk ashes: amorphous (CRHA) and partially crystalline optimized with dry-milling (RRHA). The main conclusions are as follows:

1. Results of air permeability and chloride ion penetration show different behaviors depending on the water/cementitious materials ratio used.
2. CRHA concretes show better air permeability than RRHA concretes.
3. The best resistance to chloride ion penetration is obtained with 15% substitution of Portland cement by RHA (for water/cementitious materials ratio of 0.50 with CRHA, and for 0.40 and 0.32 with RRHA).
4. The specimens containing RHA were found to be more resistant to HCl solution and sulfate attack than the specimens without RHA.
5. The use of RHA is beneficial in reducing the alkali-silica reaction (ASR). CRHA specimens inhibit expansion due to ASR to a much greater degree than the RRHA specimens.

The efficacy of the partially crystalline RHA optimized with dry-milling (RRHA) in the production of concretes and mortars is confirmed through durability performance evaluations of the studied specimens and by the presented results.

It is possible to establish an auspicious setting for the development of concretes and mortars from the incorporation of RHA, amorphous or partially crystalline optimized with dry-milling, as a supplementary cementing material. It has been verified that it is possible to obtain concretes and mortars with comparable or better properties to those of the control specimen (without RHA) with a lower consumption of cement, thus reducing the negative environmental impact that $CO_2$ emissions represent and the high cost of fossil fuel consumption in the production of clinker. Moreover, the incorporation of RHA in concrete materials resolves the current problems associated with RHA disposal.

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