Materials and Structures (2009) 42:983–992
DOI 10.1617/s11527-008-9437-z

ORIGINAL ARTICLE

Use of ultrafine rice husk ash with high-carbon content as pozzolan in high performance concrete

Guilherme Chagas Cordeiro ·
Romildo Dias Toledo Filho ·
Eduardo de Moraes Rego Fairbairn

Received: 18 January 2008 / Accepted: 30 September 2008 / Published online: 12 October 2008

Abstract Rice husk ash (RHA) has been generated in large quantities in rice producing countries. This by-product can contain non-crystalline silica and thus has a high potential to be used as cement replacement in mortar and concrete. However, as the RHA produced by uncontrolled burning conditions usually contains high-carbon content in its composition, the pozzolanic activity of the ash and the rheology of mortar or concrete can be adversely affected. In this paper the influence of different grinding times in a vibratory mill, operating in dry open-circuit, on the particle size distribution, BET specific surface area and pozzolanic activity of the RHA is studied, in order to improve RHA's performance. In addition, four high-performance concretes were produced with 0%, 10%, 15%, and 20% of the cement (by mass) replaced by ultrafine RHA. For these mixtures, rheological, mechanical and durability tests were performed. For all levels of cement replacement, especially for the 20%, the ultra-fine RHA concretes achieved superior performance in the mechanical and durability tests compared with the reference mixture. The workability of the concrete, however, was reduced with the increase of cement replacement by RHA.

Keywords Rice husk ash · Pozzolan · Grinding · Rheology · Materials processing · High-performance concrete

G. C. Cordeiro (✉)
Laboratory of Civil Engineering, Universidade Estadual do Norte Fluminense Darcy Ribeiro, Av. Alberto Lamego, 2000 Parque Califórnia CEP, CEP 28013-602 Campos dos Goytacazes, RJ, Brazil
e-mail: gcc@uenf.br

R. D. Toledo Filho · E. de Moraes Rego Fairbairn
Program of Civil Engineering, COPPE/Universidade Federal do Rio Janeiro, Rio de Janeiro, RJ, Brazil

1 Introduction

Rice husk ash (RHA) is an abundant by-product generated by the burning of rice husk. RHA is composed mostly of silica (80–95%). It has a highly microporous cellular structure, which helps its pozzolanic reaction in mixtures containing portland cement. According to the Food and Agriculture Organization of the United Nations [1], the quantity of rice (in husk) produced in the world is about 600 million tonnes/year. From this, a huge amount of RHA, estimated to be about 10 million tonnes, is generated worldwide, each year.

The use of reactive RHA as supplementary cementitious material may lead to reduction of the emissions of carbon dioxide caused by the cement production. It can also improve the mechanical and durability properties of concretes [2–4]. Moreover, the replacement of cement by RHA has another environmental advantage: the carbon remaining in the ash, which could be released to the atmosphere during a long storage period, is trapped in the concrete. Studies on RHA for use as a pozzolan have been carried out during the last three decades [2, 5–8]. Most of these studies concern ashes produced by controlled burning conditions, at specified temperature, time of burning, heating rate, type of furnace, and oxidizing conditions. In such conditions, a white highly reactive pozzolan with non-crystalline silica, small carbon content, and high specific surface area is produced.

Recently, a large amount of rice husk has been used as fuel to power the boilers of modern rice milling factories. It is used to produce steam, either for drying and parboiling (i.e., precooking) of the rice grains, or for the production of electricity in co-generation systems. Within these processes, the RHA generally has physical-chemical characteristics different from those of the ones produced under controlled conditions [9]. For example, the burning temperature in the boiler, which should be less than 900°C to avoid the formation of α-cristobalite (a crystalline polymorph of quartz) [6], is not always effectively controlled. Moreover, if sufficient oxygen is not available, and if the residence time for the husk in the boiler is not long enough, organic material in the form of unburnt or partially burnt rice husk, will remain within the bulk RHA after the burning process. It was indicated by X-ray diffraction analyses [10] that RHA by-products from different parts of India presented silica in distinct phases. Another study [11] demonstrated the great variability in the RHA characteristics, mainly carbon content and silica structure, of the by-products generated in different rice plants in Brazil. Hence, RHA produced in unsatisfactory conditions usually presents high-carbon content and a part of silica in crystalline state, which could compromise its pozzolanic activity. In this particular case, the mechanical ultrafine grinding of the RHA may minimize the effect of the residual carbon and presence of the crystalline compounds.

In this paper a study is presented on the production of ultrafine RHA from the residual by-product using vibratory grinding procedures. The experimental program demonstrates the possibility of using ultrafine residual RHA, containing high-carbon content, in high-performance concrete. Initially, different RHAs were produced by dry grinding in a pilot-scale open-circuit. It was expected that the reduction of RHA particle size could improve the pozzolanic reactivity, reducing the adverse effect of the high-carbon content in the ash, and increasing the homogeneity of the material. Detailed measurements of the particle size distribution, specific surface area, and pozzolanic activity using mechanical and chemical methods (pozzolanic index [12], Fratini's test [13] and Chapelle activity [14]) were carried out in order to compare the performance of the different RHAs. One optimal RHA was selected to be used in concrete production. Four types of concretes with RHA-cement ratios of 0.2–0.8, 0.15–0.85, 0.1–0.9, and 0–1 (by mass) were produced. Experiments were performed to investigate the rheology (with BTRHEOM rheometer), compressive strength (at 7, 28, 90, and 180 days), splitting tensile strength (at 28 days), Young's modulus (at 28 days), rapid chloride-ion penetrability, and pore size distribution.

2 Materials

2.1 Rice husk ash

The RHA (as-received) was collected at a local rice milling plant in the State of Santa Catarina, Brazil. In the plant, the rice husk was partially burnt in boilers at temperatures varying from 600 to 850°C. Table 1 presents the chemical composition of the RHA, determined by X-ray fluorescence method and loss on ignition. High values of silica content and loss on ignition (associated with the presence of residual carbon) and metallic impurities can be observed. This ash contains a significant quantity of K_2O that contributes to the formation of black particles during the burning [15], which causes the dark gray color of the ash. Figure 1 illustrates the X-ray powder diffraction (XRD) pattern of the RHA as-received. As can be seen, the RHA is partially crystalline and consists of α-cristobalite and amorphous compounds.

Table 1 Chemical composition (%, by mass) of the RHA and portland cement

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	SO_3	LOI[a]
RHA	82.6	0.4	0.5	0.9	0.1	1.8	0.1	11.9
Cement	20.9	4.2	5.3	63.5	0.2	0.4	2.4	1.1

[a] *LOI* loss on ignition

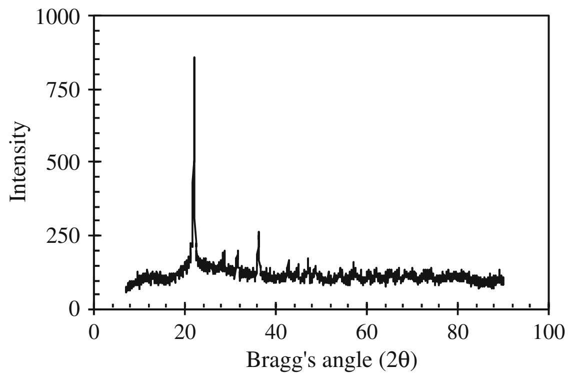

Fig. 1 X-ray diffraction pattern of as-received RHA (all peaks correspond to α-cristobalite)

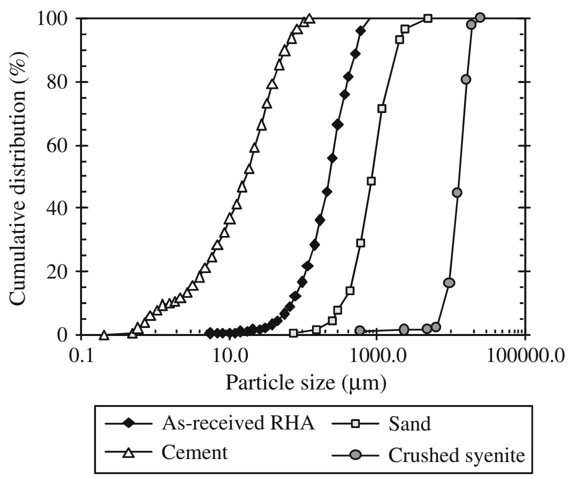

Fig. 2 Particle size distribution of as-received RHA, portland cement, and aggregates

The presence of α-cristobalite is evidence that the biomass was burnt at a temperature higher than 800°C [6]. The quantitative XRD analysis was performed using Bruker's Topas® v. 3 software [16], which is based on the Rietveld method. The mass percent values of calculated phases are 34% of α-cristobalite and 66% of amorphous with a tolerance of 1%. Considering a maximum silica content of 82.6%, this RHA sample contains approximately 49% of amorphous silica. The RHA presents BET specific surface area and specific gravity of 42738 m^2/kg and 2293 kg/m^3, respectively. The particle size distribution in Fig. 2 shows that the collected RHA presents a reasonably wide distribution of particle sizes, ranging from 1 mm to 1 µm, with an average size (D_{50}) of 224 µm. As RHA consists to a great part of coarse particles (Fig. 3a), an ultrafine grinding is necessary in order to reduce and control its particle size distribution. The scanning electron microscopy (SEM) image in Fig. 3a displays morphological aspects of the RHA as-received. It can be seen that the ash presents grains with porous structures, which explains its high specific surface area.

2.2 Complementary materials

Standard natural sand [17], deionized water and portland cement without mineral addition (similar to ASTM Type I) with 3170 kg/m^3 density and 308 m^2/kg Blaine fineness were used for preparing the mortar samples to determine the pozzolanic activity index of the RHAs (mechanical method). Table 1 presents the chemical composition of the cement. Coarse aggregate of crushed syenite (fineness modulus of 6.8), fine aggregate of siliceous river sand (fineness modulus of 2.1), water-reducing high-range admixture polycarboxylate-based with 33% solids content and density of 1210 kg/m^3, deionized water, and portland cement were also used for the concrete production. The particle size distribution of the cement and both aggregates are shown in Fig. 2.

3 Methods

3.1 Production of ultrafine RHA

Grinding of RHA was carried out in open circuit simulating continuous operation using a vibratory mill manufactured by Aulmann & Beckschulte Maschininfabrik (Germany). This grinding equipment works through friction and impacts caused by high-frequency movement of the grinding media. The mill shell, the grinding media and the solid particles influence directly the outcome of size reduction. In each batch, the 66 l mill internal volume was partially filled with 33 l of the grinding media (cylpebs with 13 mm diameter and 13 mm height) and 16 liters of the as-received RHA. The grinding times were 8, 15, 30, 60, 120, and 240 min. For each sample of RHA produced, particle size distributions and BET specific surface area were measured using a laser diffraction particle size analyzer (Malvern

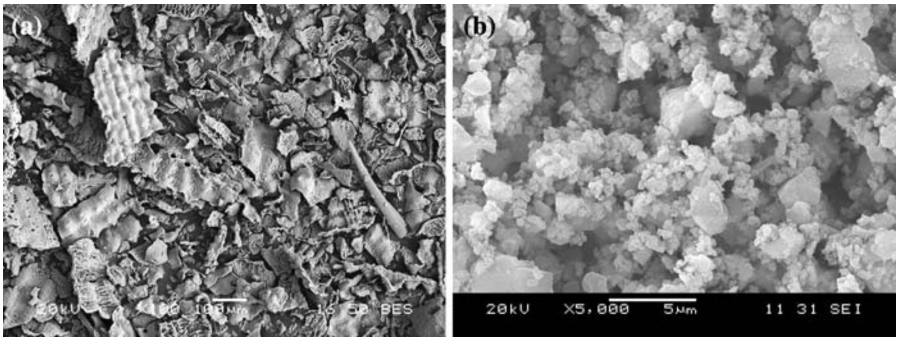

Fig. 3 SEM images of the as-received RHA (**a**) and RHA ground in the vibratory mill during 120 min (**b**)

Mastersizer 2000) and BET nitrogen adsorption apparatus (Gemini 2375 V. 5.0), respectively.

The pozzolanic activity of each respective ash was the main parameter used in the selection of the more adequate pozzolan to be used in concrete production. It was determined based on mechanical and chemical methods. The used mechanical method allows calculating of the pozzolanic activity index described by Brazilian standard NBR 5752 [12]. The pozzolanic index is the ratio between the compressive strengths at 28 days of mortars with RHA, and an ISO mortar. The ISO mortar was prepared using a constant 1:3 (weight basis) cement-sand ratio and the amount of water required (water-cement ratio of 0.52) to achieve a consistency index [18] in the range of 225 ± 5 mm. In all mixtures with RHA, 35% in volume of the cement was replaced by the ash. Moreover, adequate quantities of polycarboxylate superplasticizer (solid mass varying from 0.12% to 0.18% in relation to cement quantity of the ISO mortar) was added in order to keep the consistency without changes in water/cementitious materials ratio. After mixing and molding, mortar specimens (cylinders with 50 mm diameter and 100 mm height) were kept in a moist chamber during the first 24 h at temperature of 22°C. Then the specimens were demolded, sealed with plastic film and stored in hermetically closed containers at 38 ± 1°C and cured for 28 days. At the end of the curing process, the specimens (4 per mixture) were tested until failure in a servohydraulic press (Shimadzu UH-F1000kNI) operating at 0.1 mm/min.

The pozzolanic activity was also assessed using the Fratini and modified Chapelle tests. The Fratini's pozzolanicity tests were performed according to the Brazilian standard NBR 5753 [13] using mixtures with cement-RHA ratio of 1.86 (by volume). This test consisted of adding 20.00 g of cement-RHA blend to 250.0 ml of water. The solution was kept for 7 h in an oven at 40°C. After this period, 50 cm^3 of solution was withdrawn for filtration and the quantity of calcium cation (Ca^{2+}) and hydroxyl anion (OH^-) in solution was determined. The quantity of Ca^{2+} was determined by titration with EDTA-Na (0.02 M) solution using hydroxyl naphthol blue (10 g/l) as indicator, while the quantity of the OH^- was determined by titration with hydrochloric acid (HCl 0.1 N) solution using methyl orange (0.1 g/l) as indicator. The pozzolanicity of the blend materials was obtained by comparison between the quantity of calcium hydroxide ($Ca[OH]_2$) in the contact water and the solubility isotherm of $Ca(OH)_2$ in an alkaline solution at the same temperature. The modified Chapelle method [14] consisted of adding 1.000 g of mineral admixture and 1.000 g of calcium oxide in 250.0 ml of water. The solutions were kept for 16 h in an oven at 90°C. At the end of the period, the CaO content was determined by titration with hydrochloric acid (HCl 0.1 N) solution using phenolphthalein (1 g/l) as indicator. The results were expressed by fixed CaO, which is equal to the difference between 1.000 g and the mass of CaO obtained from titration. The optimal ultrafine RHA selected to be used in concrete production was the one ground during 120 min (see Sect. 4.1).

3.2 Concrete mix design, production and tests

A reference concrete was formulated within the framework of the Compressible Packing Model [19] using the computer code Betonlab Pro2 [20]. This model considers that the packing density of a granular mix depends on the size and shape of the grains, and on the adopted method of packing. The software Betonlab Pro2 optimizes the packing density of the mix considering the restriction of certain parameters such as strength and workability. The dosage parameters used were: (1) compressive strength of 60 MPa at 28 days; (2) slump of 150 ± 20 mm. The incorporation of the ultrafine RHA was made by replacing 10%, 15% and 20% of the cement mass by ash. Table 2 summarizes the mixture proportions for a constant volume of 1 m^3. It can be observed that the dosage of superplasticizer in RHA concretes was increased to maintain the slump consistency in the specified range.

All concretes were prepared in a 150-l planetary mixer at lab-conditions (temperature of 21°C) for 8 min. After molding and compaction using a vibratory table, the specimens with 100 mm diameter and 200 mm height were left to cure for 24 h under a damp cloth, and then demolded and cured in a moisture controlled room with 100% relative humidity and 21°C. Besides the slump test, the concrete workability was measured with a BTRHEOM rheometer [21]. In this case, it was assumed that the fresh concrete behaves as a Bingham fluid, which exists a linear relationship between shear stress and shear velocity gradient. Due to a linear pattern of the flow gradient it was possible to determine directly the values of yield stress and plastic viscosity from the curves relating the torque to the rotation speed [19]. The compressive strength was determined after 7, 28, 90, and 180 days of curing using a servohydraulic machine (Shimadzu UH-F1000kNI). Young's modulus was calculated considering the linearity of the stress-strain curves until 0.4 of the compressive strength. For the splitting tensile tests, concrete disks 100 mm diameter and 25.4 mm thick were subjected to diametrically opposite compressive load until failure, according to ASTM C496-96 standard [22]. The results were validated by the analysis of variance (ANOVA) and Duncan's multiple range tests. Differences were considered significant when the probability $P \leq 0.05$. Four specimens were tested for each mixture.

In the rapid chloride-ion permeability test, according to ASTM C1202-97 [23], a concrete disc of 100 mm diameter and 50.8 mm height was assembled between two chambers. One chamber was filled with 3% sodium chloride (cathode) and the other with 0.3 M sodium hydroxide (anode). During the test, the specimens were subjected to a 60 V DC for a period of 6 h. The specimens were cut out from the mid-portion of the cylindrical specimen with 100 mm diameter and 200 mm height using a fine saw, after 28 days of curing. Duplicate specimens were tested. The value of the total charge is used to qualify the ability of the tested concrete to resist to chloride-ion penetrability according to ASTM C1202-97 classification [23]. This methodology is very criticized mainly because of the high voltage used during the test [24]. However, the rapid chloride-ion test is widely used in the durability studies and in this work the results were only used for evaluation of the performance of the RHA concrete in comparison to the reference mixture. Pore size distribution studies were performed using a Micrometics Autopore II 9215 mercury intrusion porosimeter. The equivalent pore radius was calculated using the Washburn equation [25] from five samples of about 1 cm^3 cut out from the mid-portion of cylinders with 100 mm diameter and 200 mm height after 180 days of curing.

4 Results

4.1 Characteristics of the ultrafine RHA samples

The effect of grinding in vibratory mill on the particle size distribution of the RHA samples can be observed in Fig. 4. The reduction of the particle sizes in relation to grinding time is evident and demonstrates the efficiency of the grinding procedures. Figure 5 shows

Table 2 Mixture proportions of concretes in kg/m^3

Concrete	Cement	RHA	Sand	Gravel	Water	Superplasticizer[a]
Reference	478	–	860.0	905.3	167.4	1.43
10% RHA	430.2	47.8	858.8	904.1	167.4	1.91
15% RHA	406.3	71.7	858.1	903.4	167.4	2.20
20% RHA	382.4	95.6	857.7	902.9	167.4	2.39

[a] The superplasticizer is specified as the solid mass

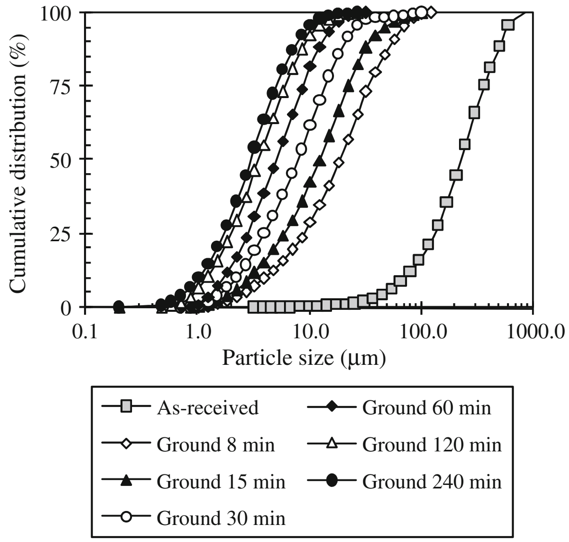

Fig. 4 Particle size distribution of as-received RHA and ground RHAs produced by vibratory grinding

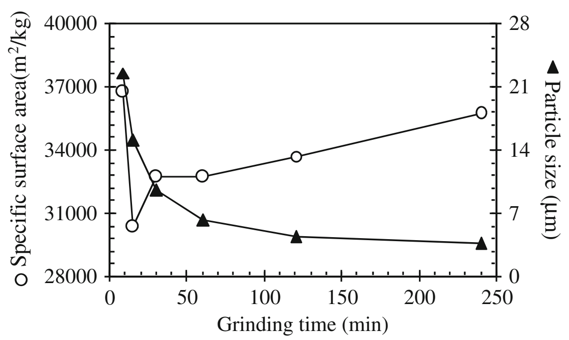

Fig. 5 Values of BET specific surface area and average particle size of the ground RHAs produced by vibratory grinding

the change in D_{50} sizes and BET specific surface area with respect to grinding time carried out in the mill. As expected, D_{50} decreases and specific surface area increases with a continuing grinding process. The ashes produced under different grinding times present a wide range of particle sizes, with D_{50} values ranging from 3.6 to 22.5 μm. It can be observed that the reduction of the particle sizes is less expressive for greater grinding times. This behavior can be attributed to the limit of grinding for the adopted grinding procedures. It is due to the inherent difficulty of grinding fine particles associated with their higher strength, low capture probability and their tendency to agglomerate [26]. The BET specific surface area decreases significantly after 15 min of grinding. This initial reduction of BET may be explained by the collapse of the cellular structure with high internal micropores. In this case, pores originally accessible to N_2 are probably compacted and/or filled by fine particles [9]. After 15 min of grinding, the BET area increases continually. It is important to emphasize that BET area >32,000 m^2/kg and D_{50} smaller than 10 μm are obtained by RHA products with grinding times between 30 and 240 min. Besides porous structures, the exceptionally high specific surface area values of the as-received and ground RHAs can be attributed to the high-carbon content of the ash. The carbon particles present greater specific surface area when compared to silica particles [3]. Figure 3b shows the grains of RHA product after 120 min of grinding (examined by SEM). For this grinding time, the RHA sample presents ultrafine particles, when the coarse grains present in the as-received material were totally broken down by the grinding media.

The relationship between the pozzolanic activity index and grinding times is shown in Fig. 6. It is clearly demonstrated that the grinding increases the RHA reactivity. All ground RHAs present pozzolanic indices higher than 75%, the minimum value established by Brazilian standard NBR 12653 [27] (in accordance with the ASTM C618-05 [28]) irrespective of grinding time. As expected, the highest pozzolanic indices are obtained by RHAs generated by long periods of grinding (120 and 240 min). However, there is no significant difference between the 120 and 240 min ground ashes. The results of

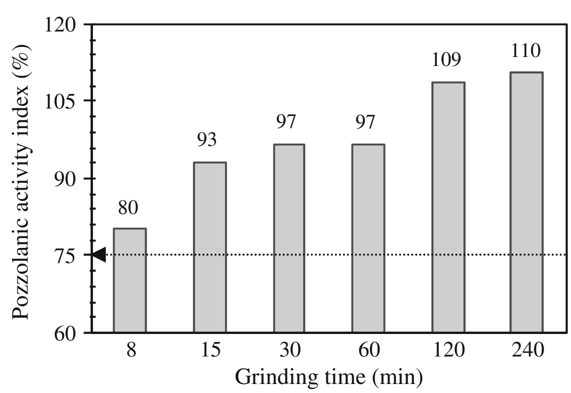

Fig. 6 Relationship between grinding time and pozzolanic activity index of the ground RHAs (the dotted line represents the minimum value that characterizes a material as pozzolanic according to the Brazilian standard NBR 12653 [27])

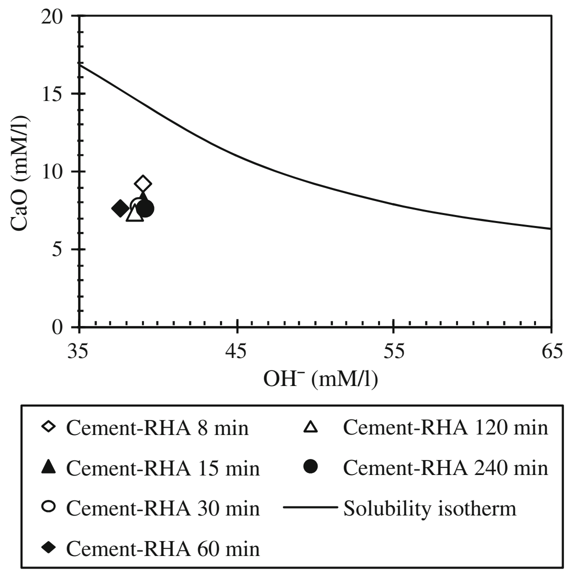

Fig. 7 Results of the Fratini's tests for different RHAs

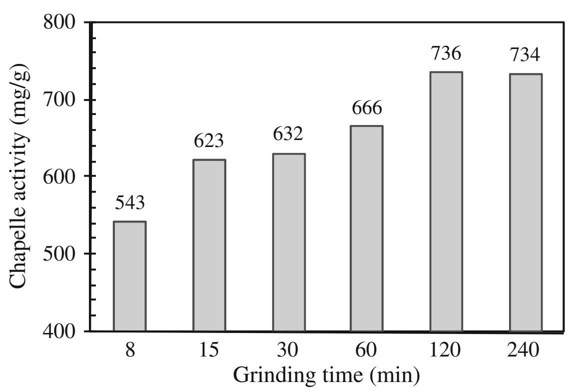

Fig. 8 Relationship between grinding time and Chapelle activity of the ground RHAs

Fratini's tests (see Fig. 7) show that all ground RHAs present OH^- to CaO coordinate points localized below the solubility isotherm of CH. This behavior confirms the pozzolanic activity of the ultrafine RHAs. Nevertheless, the results show that the Fratini's test was not appropriate to display the differences between the distinct RHAs, which are verified in the mechanical tests. This distinction is very clear from results of the Chapelle activity, when the RHAs exhibit a similar trend comparing to pozzolanic activity indices, as shown in Fig. 8. In this case, the increase in lime fixed during the pozzolanic reactions is directly proportional to the grinding time. The activities of the ashes varying from 543 to 734 mg/g (mg of CaO to g of pozzolan) are indicative of the high reactivity. The RHAs produced after 120 and 240 min of grinding also present the highest values of the activity and no significant difference is observed between them. In accordance with the experimental procedures, the RHA ground in vibratory mill during 120 min in batch mode is selected for application in concrete, since this ash presents excellent pozzolanic activity with a moderate grinding time.

4.2 Properties of concrete containing ultrafine RHA

The consistency (slump) of the reference concrete is reduced from 130 to 100 mm, 60 mm, and 20 mm, respectively, when 10%, 15% and 20% of ultrafine RHA is used as cement replacement. This decreasing in slump value occurs due to the high specific surface area and high-carbon content of the RHA. As already mentioned, to obtain the same consistency of the reference concrete it is necessary to increase the amount of superplasticizer in the mixtures containing RHA (see Table 2). A similar approach was used by Bui et al. [29] when using a RHA containing about 5% of carbon in its chemical composition.

The influence of the cement replacement by RHA on the rheology of the concretes of same consistency is shown in Fig. 9. It can be seen that the Bingham model is adequate to describe the rheological behavior of the concrete, since the results of the

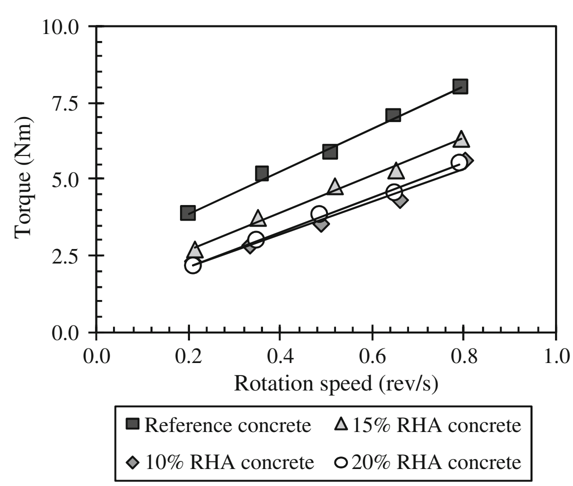

Fig. 9 Relationship between torque and rotation speed in BTRHEOM rheometer

Table 3 Fresh and hardened properties of concretes

Mixture	Yield stress (Pa)	Plastic viscosity (Pa s)	Young's modulus (GPa)	Splitting tensile (MPa)	Electrical charge (C)
Reference	693	306	34.2 (0.7)	5.5 (0.3)	1179 (25)
10% RHA concrete	296	235	32.7 (0.5)	5.9 (0.4)	585 (18)
15% RHA concrete	304	268	32.7 (1.2)	5.7 (0.3)	279 (19)
20% RHA concrete	285	250	33.9 (0.6)	5.8 (0.4)	261 (28)

Standard deviation is indicated within bracket

BTRHEOM rheometer show a linear relationship between torque and rotation speed. The linear fitting presents values of R^2 >96% for all mixtures. In fact, the Bingham model represents well the fresh behavior of concretes with consistency in the range studied, as it was verified by Sedran [30]. Table 3 summarizes the values of the Bingham parameters determined for all concretes. The incorporation of the ultrafine RHA reduces the yield stress and also the plastic viscosity, but to a lesser extent. There are no expressive differences between the three mixtures containing RHA. The results indicate that with an adequate correction in the mixture consistency, the ultrafine ash proportionates positive effects in the fresh concrete properties. The better behavior of the RHA mixtures can be attributed to the presence of ultrafine particles and the slightly higher paste-aggregates ratios, which tends to reduce the particle interlocking and internal friction. The paste-aggregates ratio increases due to the replacement of cement by RHA, since the density of the RHA (2293 kg/m^3) is significantly lower than the cement density.

The representative stress-strain curves obtained from compressive tests carried out after 28 days of curing can be seen in Fig. 10. The reference concrete presents compressive strength of 60.9 MPa, while the 20% RHA mixture presents 70.0 MPa of strength (increase of about 15%). There is no significant difference in the compressive strength of the mixture containing 10% RHA and the reference concrete. The 15% RHA concrete shows a slight increase (by about 4%) in its compressive strength when compared with that of the reference concrete. No significant interactions (ANOVA tests) are observed between average Young's modulus and type of concrete, as shown in Table 3. The evolution of strength with time is shown in Fig. 11. After 7 days of curing, all mixtures presented similar values of compressive strength according to the statistical analyses carried out. After

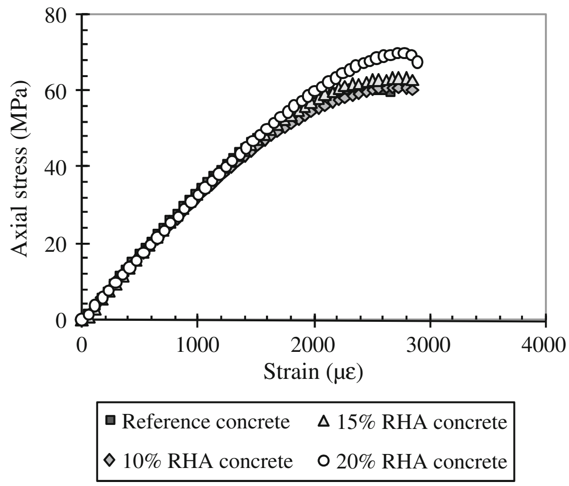

Fig. 10 Typical stress versus strain curves of concretes at 28 days of curing

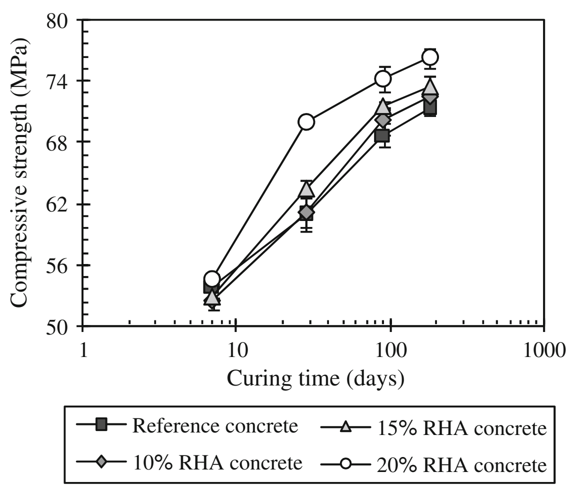

Fig. 11 Evolution of compressive strength of concretes against curing time

90 and 180 days of curing, the compressive strength of the concrete containing 10% and 15% of RHA present the same trend already observed at 28 days.

Regarding to the 20% RHA concrete, it can be seen that although it presents higher strength than that observed for the reference concrete at these ages, the increase (by about 7–8%) is slightly smaller than that observed after 28 days of curing. In relation to the splitting tensile strength after 28 days, no significant differences are observed for all mixtures according to statistical analyses, as can be verified in Table 3. The results of the mechanical tests indicate that the use of the ultrafine RHA with high-carbon content maintains or increases the behavior observed for the reference concrete.

With regards to the results of the chloride-ion penetrability, the incorporation of the ultrafine RHA causes expressive decreasing of the electrical charges passing of the concretes (as shown in Table 3). The average charge through the reference concrete is equal to 1179 C and this mixture is classified as having "low" penetrability according to ASTM C1202-97 [23] classifications. The cement replacement by RHA provides a change of classification. In this case, all concretes produced with RHA present "very low" penetrability, with a charge of 585 C for 10% RHA concrete and below 300°C for 15% and 20% RHA mixtures. Comparable results were verified in a study carried out with a RHA produced by controlled burning [31].

Regarding the pore size distribution presented in Fig. 12, the presence of RHA produces only a slight refinement in the pore structure of the reference concrete. Form the cumulative intrusion curves it is

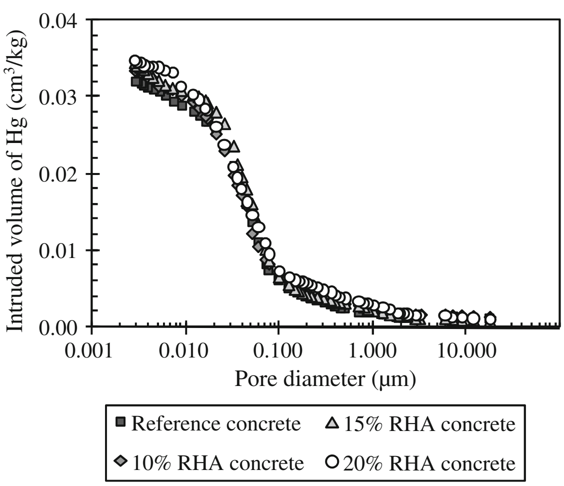

Fig. 12 Pore size distribution curves of concretes at 90 days of curing

determined that the amount of pores <0.02 μm in diameter of the reference mixture is increased from 3.7% to about 5% with the incorporation of the ultrafine RHA. It is worth to mention that no substantial differences in the pores distribution are expected, since the concretes in this study were proportionate for maximum packing density according to CPM. Nevertheless, the development of pore structure agrees well with the results of the compressive strength and chloride-ion penetrability.

5 Conclusions

Based on experimental results, the following conclusions can be drawn:

1. The grinding procedures adopted can be used to increase the homogeneity and pozzolanic activity of the RHA containing loss on ignition about 12%. A grinding time of 120 min was sufficient to generate an ultrafine ash with 6.8 μm average particle size, 33670 m^2/kg BET specific surface area, 109% pozzolanic activity index, and 736 mg/g Chapelle activity.
2. The slump consistency of the reference concrete was reduced due to the use of the ultrafine RHA as cement replacement. Thus, it was necessary to increase the amount of superplasticizer in the mixtures containing RHA to obtain the same consistency of the reference. After this correction, the ultrafine RHA concretes presented values of yield stress and plastic viscosity lower than those of the reference mixture.
3. The use of the ultrafine RHA maintained or increased the mechanical behavior of the reference concrete. The mixture containing 20% of RHA presented a superior performance for all ages. The results of Young's modulus and splitting tensile strength, at 28 days, indicated that the incorporation of the ultrafine RHA did not change these properties significantly.
4. For the chloride-ion penetrability tests, all concretes with ultrafine RHA reduced expressively the values of charge passing (up to 78%). The reference concrete was classified as having "low" penetrability, whereas the RHA mixtures had "very low" penetrability, which confirmed the beneficial effects of incorporating the ultrafine RHA in concrete.

5. Regarding to the pore size distribution, a slight increase in the volume of pores <0.02 μm in diameter was observed for the RHA mixtures as compared with that of the reference concrete, indicating a small pore refinement.

Acknowledgements The authors wish to thank FAPERJ, CAPES and CNPq for the financial support to this investigation. The authors are also indebted to Centro de Tecnologia Mineral (CETEM), where the grinding experiments were conducted.

References

1. Food and Agriculture Organization of the United Nations (2007) http://www.fao.org. Cited 12 May 2007
2. Metha PK (1977) Properties of blended cements made from rice husk ash. ACI Mater J 74:440–442
3. Salas J, Castillo P, Sanchez Rojas MI, Veras J (1986) Empleo de cenizas de cáscara de arroz como adiciones en morteros. Mater Construcc 36:21–39
4. Zhang M-H, Malhotra M (1996) High-performance concrete incorporating rice husk ash as a supplementary cementing material. ACI Mater J 93:629–636
5. Pitt N (1976) Process for preparation of siliceous ashes. US Patent 3,959,007 25 May 1976
6. Hamad MA, Khattab IA (1981) Effect of the combustion process on the structure of rice hull silica. Thermochim Acta 48:343–349. doi:10.1016/0040-6031(81)80255-9
7. Sugita S (1994) On the burning principle and the furnace design based on the principle for producing highly active rice husk ash. Paper presented at the 3e international conference on the concrete future, Kuala Lumpur
8. James J, Subba Rao M (1986) Reactivity of rice husk ash. Cement Concr Res 16:296–302. doi:10.1016/0008-8846(86)90104-3
9. Cordeiro GC (2006) Use of sugar cane bagasse ash and rice husk ashes as mineral admixture in concrete. DSc Thesis, Universidade Federal do Rio de Janeiro, Brazil
10. Yoganda MR, Jagadish KS (1988) Pozzolanic properties of rice husk ash, burnt clay and red mud. Build Environ 23:303–308. doi:10.1016/0360-1323(88)90036-4
11. Rego JHS (2004) As cinzas de casca de arroz (CCAs) amorfa e cristalina como adição ao concreto—Aspectos de microestrutura das pastas. DSc Thesis, Universidade de Brasília, Brazil
12. Associação Brasileira de Normas Técnicas (1992) Pozzolans—Pozzolanic activity—determination of pozzolanic activity index with portland cement: NBR 5752. Rio de Janeiro
13. Associação Brasileira de Normas Técnicas (1992) Portland pozzolanic cement—Pozzolanicity test—method of test: NBR 5753. Rio de Janeiro
14. Raverdy M, Brivot F, Paillère AM, Bron R (1980) Appréciation de l'activité pouzzolanique de constituents secondaires. Paper presented at the 7e Congrés International de la Chimie des Ciments. Paris
15. Chandrasekhar S, Satyanarayana KG, Pramada PN, Raghavan P (2006) Effect of calcination temperature and heating rate on the optical properties and reactivity of rice husk ash. J Mater Sci 41:7926–7933. doi:10.1007/s10853-006-0859-0
16. Bruker (2005) Topas version 3.0: diffract plus tutorial. Bruker, Karlsruhe
17. Associação Brasileira de Normas Técnicas (1982) Standard sand for cement test: NBR 7214. Rio de Janeiro
18. American Society for Testing and Materials (2004) Standard test method for compressive strength of hydraulic cement mortars (using 2-in. or [50-mm] cube specimens). ASTM C:109-05. Philadelphia
19. De Larrard F (1999) Concrete mixture proportioning: a scientific approach. E&FN Spon, London
20. Sedran T, De Larrard F (2000) Betonlab Pro2, Computer-aided mix-design software pub. Ecole Nationale des Ponts et Chaussées, Paris
21. Hu C, De Larrard F, Sedran T, Boulay C, Bosc F, Deflorenne F (1996) Validation of BTRHEOM, the new rheometer for soft-to-fluid concrete. Mater Struct 29:620–631. doi:10.1007/BF02485970
22. American Society for Testing and Materials (2004) Standard test method for splitting tensile strength of cylindrical concrete specimens: ASTM C496/C-04. Philadelphia
23. American Society for Testing and Materials (1997) Standard test method for electrical indication of concrete's ability to resist chloride ion penetration: ASTM C1202-97. Philadelphia
24. Andrade C (1993) Calculation of chloride diffusion coefficients in concrete from ionic migration measurements. Cement Concr Res 23:724–742. doi:10.1016/0008-8846(93)90023-3
25. Winslow DN, Lovell CW (1981) Measurements of pore size distributions in cements, aggregates and soils. Powder Technol 29:151–165. doi:10.1016/0032-5910(81)85013-9
26. Austin LG, Concha F (1994) Diseño y simulación de circuitos de molienda y clasificación. CYTED, Concepción
27. Associação Brasileira de Normas Técnicas (1992) Pozzolanic materials: NBR 12653. Rio de Janeiro
28. American Society for Testing and Materials (2005) Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete: ASTM C618-05. Philadelphia
29. Bui DD, Hu J, Stroeven P (2005) Particle size effect on the strength of rice husk ash blended gap-graded portland cement concrete. Cement Concr Compos 27:357–366. doi:10.1016/j.cemconcomp.2004.05.002
30. Sedran T (1999) Rheologie et rheometrie des betons. Application aux betons autonivelants. These de Doctorat, École Nationale des Ponts et Chaussées
31. Nehdi M, Duquette J, El Damatty A (2003) Performance of rice husk ash produced using a new technology as a mineral admixture in concrete. Cement Concr Res 33:1203–1210. doi:10.1016/S0008-8846(03)00038-3