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Influence of particle size and specific surface area on the pozzolanic activity of residual rice husk ash

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ABSTRACT

The effect of the particle size distribution and specific surface area on the pozzolanic activity of a residual rice husk ash (RHA) was investigated in this work. Different samples of RHA obtained from ultrafine grinding were characterized with respect to particle size analyses by laser granulometry, BET and Blaine specific surface areas, pore volume distribution by mercury intrusion porosimetry, surface texture by scanning electron microscopy, pozzolanic activity using the cement mortar method and activity with lime using the Chapelle method. From the results, it was concluded that a good correlation exists between the 'external' specific surface area, that is, the surface area associated with the measured particle size distribution, and the pozzolanic activity of the residual RHA. On the other hand, nearly no correlation was identified between the pozzolanic activity and the specific surface area measured using the BET method, an observation that is particularly related to the cellular nature of the internal structure of this RHA.

1. Introduction

A cellular material is made up of an interconnected network of solid struts or plates which form the edges and faces of cells [1]. In general, cellular materials present high specific surface area due to external and internal pores of different sizes. Several types of cellular materials are predominantly composed of silica, such as rice husk ash (RHA) and sugar cane bagasse ash (SCBA), which are agro-industrial by-products generated by burning of rice husk and sugar cane bagasse, respectively. Considering these characteristics, both cellular materials have been employed as partial replacements of Portland cement in paste, mortar and concrete [2–9].

In regard to RHA, a number of studies have reported [9–13] that its pozzolanic activity depends basically on three factors: content of amorphous silica, particle specific surface area and particle size distribution. Indeed, when obtained from combustion at moderate temperatures (below about 800 °C), RHA presents mostly non-crystalline silica (a disordered Si–O structure), along with some carbon and metallic impurities [14,15]. Furthermore, RHA typically presents a very high specific surface area (30–80 m^2/g) due to the burn-off of carbon and the opening of the micropores in its skeleton which is essentially composed of silica. The particle size distribution of the RHA is another important characteristic that can affect its reactivity.

Although it is well recognized that there is a relationship between the specific surface area and the pozzolanic activity of RHA, it is not clear if RHAs that present, at the same time, high specific surface area and a coarse particle size, can be appropriately used as a pozzolan. This is particularly evident in ashes derived from uncontrolled combustion processes, which can produce high carbon contents and wide particle size distributions [4]. In this case, the specific surface area and the particle size distribution, which are usually inversely related for monolithic materials, can become independent of one another.

The relationship between surface activity and particle size may not be well defined for ashes produced in industrial units, called residual RHAs. As such, the effect of changes of particle size and specific surface area of the residual RHA on its pozzolanic activity was investigated in the present work. Different samples of RHA were obtained from controlled ultrafine grinding to enable as assessment of the role of the inner and outer porosity on their activity. Measurements using laser granulometry, BET specific surface area, Blaine specific surface area, mercury intrusion poros-

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imetry, microscopy and pozzolanic activity were performed in order to aid in understanding the factors with greatest relevance in residual RHA performance as a cement replacement. Since rice husk is used as biomass to produce steam and electricity in co-generation systems in different parts of the world, such study of the residual RHA properties is worthwhile.

2. Materials

The residual RHA (named as-received RHA or AR-RHA) was obtained from a rice processing unit in the State of Santa Catarina, Brazil. In the industry, the rice husk is burnt in boilers at temperatures between 600 °C and 850 °C. Table 1 shows the chemical composition of AR-RHA measured using the X-ray fluorescence method (Philips PW 2440 with Rh tube target and 3 kW) and its loss on ignition. Of particular interest in Table 1 is the high silica content (82.6 wt.%) and high loss on ignition (11.9 wt.%) of the ash. Fig. 1 presents the X-ray diffraction (Bruker D8 Focus with Cu $_{k\alpha}$ tube, 30 kV and 35 mA) pattern of the AR-RHA, where the presence of cristobalite is detected. Quantitative XRD analysis using the Rietveld method was performed with the aid of the Autoquan software from which it is possible to observe that the non-crystalline and crystalline (α-cristobalite) phases represent 66.0 ± 2.2 wt.% and 34.0 ± 2.2 wt.% of the sample, respectively. The corresponding quantitative XRD patterns were measured using a Seifert 3003 TT diffractometer equipped with a Cu $_{k\alpha}$ tube, at 30 kV and 40 mA.

The particle size distribution in Fig. 2 shows that the original AR-RHA presents a reasonably wide range of particle sizes, with coarse particles of up to 1 mm and a median particle size (D_{50}) of 224 μm. The density of the AR-RHA is 2290 kg/m^3.

Portland cement (whose chemical composition is summarized in Table 1) with 3170 kg/m^3 density and 308 m^2/kg Blaine fineness, standard natural sand [16], and deionized water were used in mortars for the analyses of pozzolanic activity. Moreover, chemically pure calcium hydroxide was used in the Chapelle activity tests [17].

3. Methods

Ground RHAs were obtained by dry vibratory grinding using a mill manufactured by Aulmann & Beckschulte Maschininfabrik (Germany). Vibratory grinding tests were carried out in batch mode, simulating continuous open circuit operation with grinding times varying from 8 min to 240 min. They were conducted with a sample volume of 8 L using 16 L of grinding media, which corresponded to a mill filling of 48% [7]. The different ground ashes are designated as RHA-*X*, where *X* represents the grinding times in minutes.

Particle size distributions were measured using a laser diffraction particle size analyzer (Malvern Mastersizer) in liquid mode with analytical-grade ethyl alcohol as the dispersant and ultrasonic agitation for 60 s. The particle size distributions generated were characterized using D_{50}, which is the 50% passing size in the cumulative distribution. BET specific surface area was measured using a nitrogen adsorption apparatus (Gemini 2375V. 5.0). The specific surface area was also determined by Blaine's method [18] with an air-permeability apparatus. The morphology of RHA particles was investigated with the aid of images from an environmental scanning electron microscope (Philips, XL 30 ESEM), in which the samples were observed in natural conditions, without application of a conductive layer.

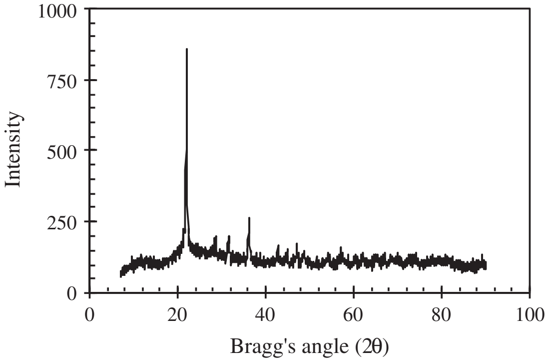

Fig. 1. X-ray diffraction pattern of AR-RHA (all peaks correspond to α-cristobalite phase).

Mercury intrusion porosimetry (MIP) measurements were performed using low and high pressure mercury porosimeters (Thermo Electron). The low pressure device was used to measure the larger pores, with pore diameters of up to about 112 μm, whereas the high pressure device (pressure range from 0.1 MPa to 400 MPa) permitted measurement of pore sizes down to 3.75 nm. The mercury intrusion test results are presented in Fig. 3 for a sample of RHA ground for 30 min. As is evident in the figure, RHA-30 showed a pronounced agglomerate volume, characterized by the linear slope of the mercury intrusion curve (see the "first run" curve in Fig. 3). This volume is the first to be filled by mercury at low pressure. With the additional increase in pressure, the void spaces that exist between the particles are filled with mercury. In the range of the interparticle spaces shown in Fig. 3, pores can additionally be filled. However, the shape of the measuring curves does not allow distinguishing between pores and interparticle volume. In order to eliminate the effect of the agglomerate fragmentation from the test results as much as possible, the low pressure measurement has been repeated. After that, the high pressure measurement is conducted, the two files are combined, and the resulting file is created by the instrument software (the dotted line curve in Fig. 3 – named "second run"). The values for the surface tension of mercury and the contact angle between mercury and silica were assumed to be 0.485 N/m and 140° [19], respectively.

Mortar mixtures containing RHA (AR-RHA and ground RHAs) were prepared in a laboratory bench mixer according to Brazilian standards in order to examine the pozzolanic activity index with Portland cement [20]. This index was calculated from the ratio between the compressive strengths at 28 d 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-to-cement ratio of 0.52) to achieve a consistency index in the range of 225 ± 5 mm based on the Brazilian Standard NBR 7215 [21]. In the Brazilian Standard, the mortar is placed in-

Table 1
Chemical composition (%) of AR-RHA and Portland cement.

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MnO	TiO_2	MgO	P_2O_5	LOI*
AR-RHA	82.6	0.4	0.5	0.8	0.1	1.8	0.3	–	0.7	0.8	11.9
Cement	20.9	4.2	5.3	63.5	0.2	0.4	–	–	–	–	1.1

* LOI – loss on ignition.

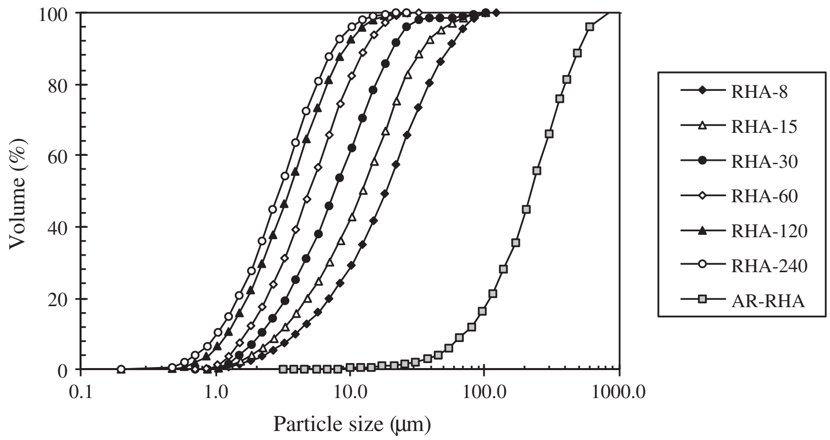

Fig. 2. Particle size distribution of the AR-RHA and ground RHAs after different times of grinding (in minutes).

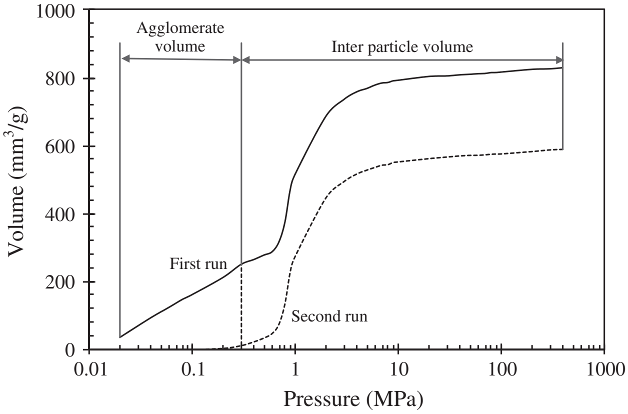

Fig. 3. Mercury intrusion porosimetry measurement of the RHA-30 with identification marks of the characteristic segments.

side a conical mold (125 mm base, 80 mm top and 65 mm height) on a flow table that drops 12.5 mm for 30 times in 30 s. The consistency index is reported as the average of two orthogonal diameters obtained after the flow. In all mixtures with RHA, 35% by volume of the cement was replaced by the mineral admixture. Moreover, appropriate quantities of polycarboxylate superplasticizer (varying from 0.12% to 0.18% of solid mass in relation to the cement quantity in the ISO mortar) were added in order to keep a constant consistency without changes in the 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 22 °C. The specimens were then demolded, sealed with plastic film and stored in hermetically closed containers at 38 ± 1 °C and cured for 28 d. At the end of the curing process, the specimens (four per mixture) were tested in compression until failure in a servohydraulic machine (Shimadzu UH-F1000kNI) operating at 0.1 mm/min.

The pozzolanic activity was also assessed using the modified Chapelle test [17], which consisted of adding 1.000 g of mineral admixture and 1.000 g of calcium oxide to 250 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 a hydrochloric acid (HCl 0.1 N) solution using phenolphthalein (1 g/L) as the indicator. The results were expressed as the amount of fixed CaO, which is equal to the difference between 1.000 g and the mass of CaO obtained from titration.

4. Results

Fig. 2 shows the cumulative size distributions of ground RHAs in comparison to the AR-RHA. Each curve of ground RHA corresponds to the individual adopted grinding times (varying from 8 min to 240 min). The ground RHA curves show very similar shapes, indicating that particles of all sizes were broken down as a result of the grinding action. As expected, the results indicate significant reductions in particle size with the increase in grinding time and the ground RHAs present values of D_{50} between 3.6 μm and 22.5 μm, whereas the AR-RHA presents a D_{50} of 224 μm.

Results on the influence of particle size reduction on the BET specific surface area of the RHA samples are presented in Fig. 4. They show that, as samples became finer as a result of grinding, BET specific surface areas do not necessarily increase monotonically, as would be expected, and as is observed with the Blaine specific surface area measurements that are also included in Fig. 4. This is particularly evident in the case of samples RHA-8 and RHA-15, which present lower BET specific surface areas than the as-received material. Although for samples subjected to longer grinding times (exceeding 15 min) the BET specific surface area increases again with grinding time, the original value of the specific surface area of the rice husk ash (AR-RHA) is not reached, even after 240 min of grinding. These results suggest that a certain independence exists between D_{50} and BET specific surface area for the RHA, which generally contradicts the well-known inverse relationship between specific surface area and particle size. Therefore, results from the present work suggest that the breakage of the very porous cellular structure material does not only result in the creation of new surfaces, as is observed in most monolithic materials. In this case, the grinding action breaks down fragile silica walls within the residual RHA microstructure, resulting in the collapse of pores, which may be filled by submicron-sized particles, as demonstrated by MIP and SEM analyses, which may result in a decrease in specific surface area.

Fig. 5 shows the overlaid mercury pore size against volume curves of the ground RHAs and AR-RHA. It is evident that with increasing grinding time there is a continuous decrease in particle size and the proportion of agglomerates (linear part of the curves) increases for the ashes. However, the cumulative volume (agglomerate volume plus interparticle volume) is nearly the same for all ground RHAs. On the other hand, the intrusion curve of the AR-RHA indicates a very large amount of internal pores in the material. The pore volume for the AR-RHA is about 1890 mm^3/g, which is equivalent to 63 vol.% porosity. As seen in Fig. 5, the entire pore volume of AR-RHA consists of pores in the range from 10 μm to

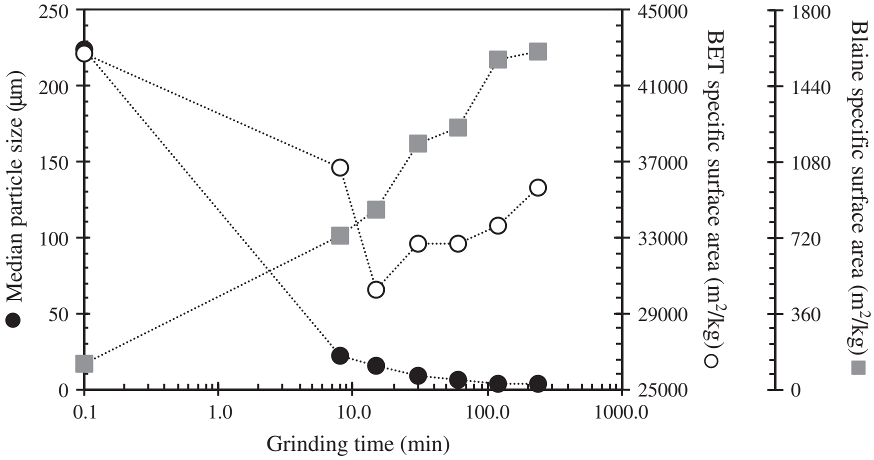

Fig. 4. Variation of the median particle size (D_{50}) and BET specific surface area due to grinding. (*The X-axis equal to 0.1 refers to the AR-RHA - sample without grinding*).

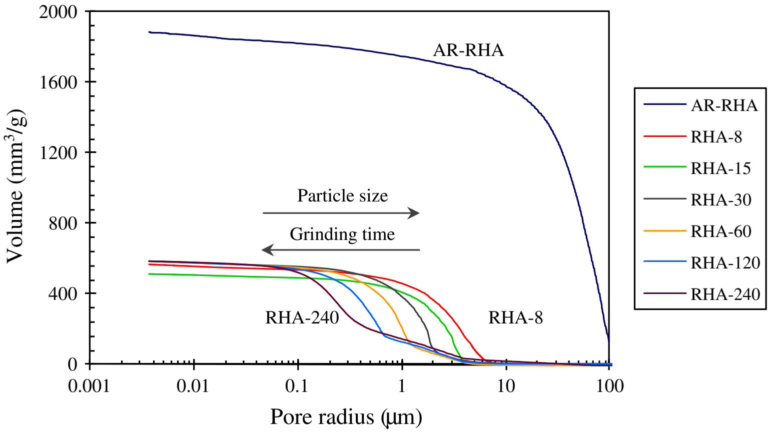

Fig. 5. Pore size distribution of AR-RHA and ground RHAs.

100 µm, while the pores of ground RHA varied from 0.1 µm to 10 µm. It is evident in Fig. 5 that a significant proportion of the pore volume in the AR-RHA sample corresponds to pores with sizes larger than 10 µm. Such porosity disappears after grinding, given that such large pores collapse as a result of the collisions between grinding media.

These conclusions from MIP are confirmed by the SEM images presented in Figs. 6 and 7. Fig. 6 demonstrates that the AR-RHA presents grains with very porous structures. Figs. 6a and b show the outer and inner epidermis of the RHA, respectively, whereas pores in the silica skeleton are visible in Fig. 6c. It is important to note that the pore sizes of AR-RHA in these images are consistent with the values identified in the MIP tests. The cellular structure of the ash has been gradually broken down during grinding, as can be seen in Fig. 7. Although highly porous particles have been observed in RHA-8 (Fig. 7a) with pore radii smaller than 20 µm, RHA-30 presents only a limited proportion of particles with the original structure (Fig. 7b). After 120 min of grinding, however, the cellular skeleton is apparently completely broken down by the action of the grinding media (Fig. 7c).

In order to understand the role of microstructure changes on the reactivity of RHA, pozzolanic activity measurements have been performed (pozzolanic activity index and Chapelle method) and results are summarized in Fig. 8. It is important to note that the pozzolanic activity index allows joining the physical and chemical effects of the RHA particles, since this test is based on results of compressive strength of mortars after 28 d of curing. Furthermore, there is apparently no change in the structure of silica by grinding for prolonged times, since the RHA-240 also presents 66 wt.% of non-crystalline phases according to the quantitative XRD analysis. As such, any change in pozzolanic activity produced by grinding must be associated with its effect on the internal and external structure of the particles.

An inverse logarithmic relationship ($R^2 = 0.9$) was identified between D_{50} and pozzolanic activity index values. Although caution is warranted in using the Chapelle test to assess reactivity of a pozzolanic material, given that the test is carried out at a high temperature [6], Fig. 8 also clearly demonstrates that the same behavior can be observed in the relationship between D_{50} and the Chapelle activity. It should be noted that the Chapelle activity can be represented by a logarithmic law with good correlation ($R^2 = 0.98$). As expected, the RHA reactivity increases as the particle sizes become finer.

An analysis of the relationship between pozzolanic activity measurements and BET specific surface areas (Fig. 9) does not lead to a similar conclusion. In this case, the pozzolanic activity indices or the Chapelle activities are not necessarily higher for the RHA with higher BET specific surface area. These results indicate that the pozzolanic activity of the residual RHA seems to be mainly associated to its outer specific surface area. Indeed, this poor correlation between BET surface area and pozzolanic activity is certainly associated with the well-known fact that the BET specific surface

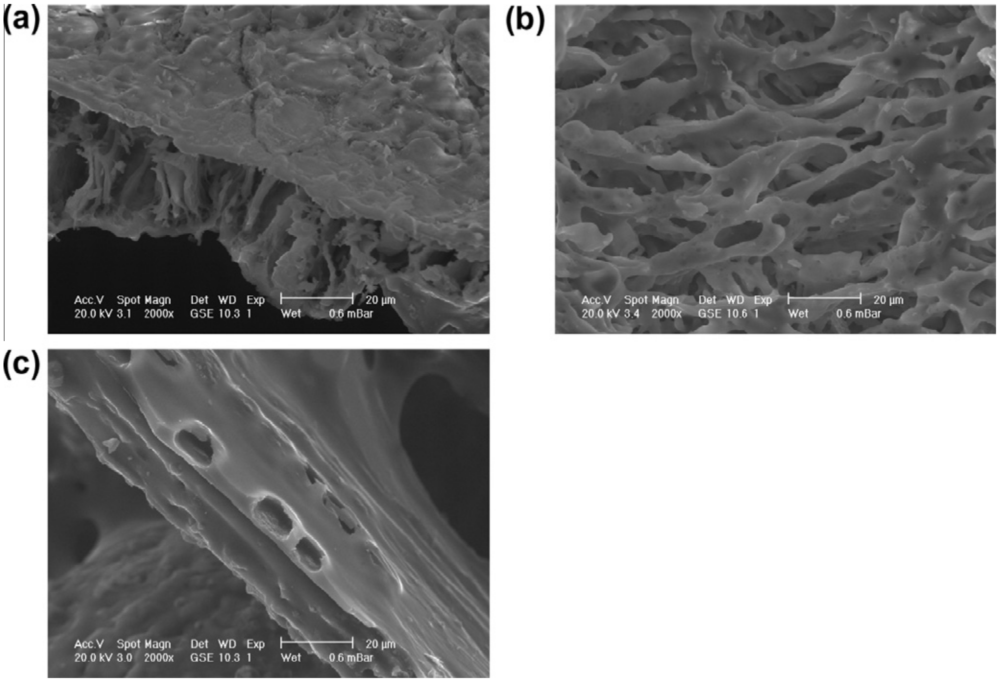

Fig. 6. SEM images of AR-RHA showing its microporous nature (a–c). Magnification of 3000×.

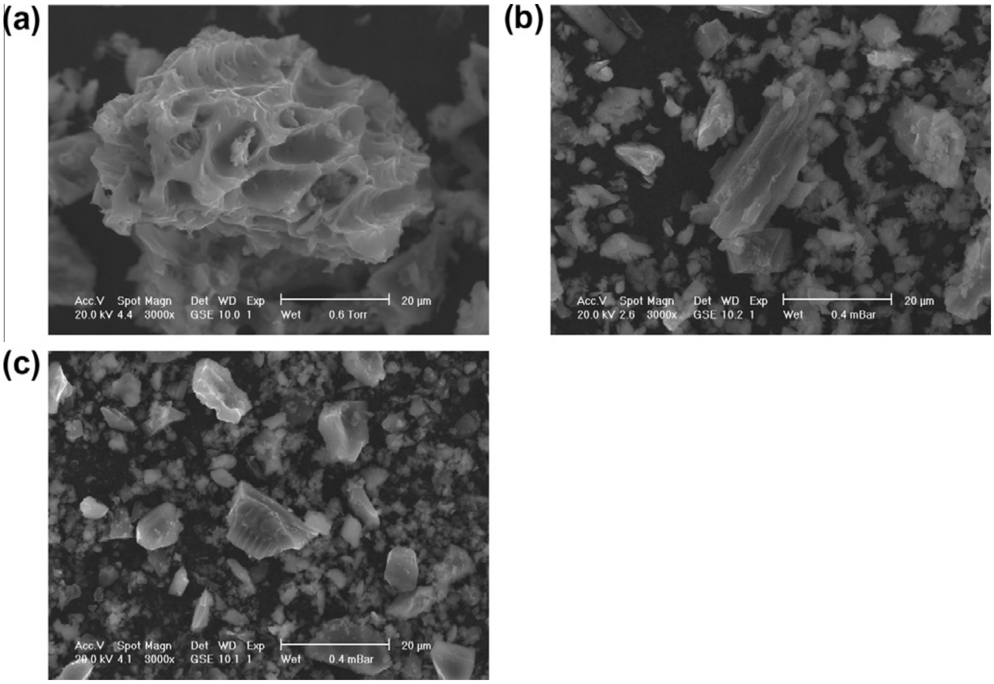

Fig. 7. SEM images of RHA-8 (a), RHA-30 (b) and RHA-120 (c). Magnification of 3000×.

area of the RHA is strongly influenced by the internal porous structure of the particles.

On the other hand, a comparison between the RHA pozzolanic activity and specific surface area values based on particle size and, thus, mainly external porosity, such as Blaine specific surface area, demonstrates that these are closely related, as can be seen in Fig. 10. Thus, the pozzolanic activity index and Chapelle activity linearly increase as the D_{50} increases. A good correlation is found for both curves ($R^2 > 0.9$) These results confirm the RHA particle size influence on its pozzolanic activity, demonstrated in Fig. 8. This issue is particularly relevant since particle size analyses and/or Blaine tests, which are more convenient to conduct than BET or MIP tests, are tools that give a more direct insight into the potential reactivity of the residual RHA. However, it is very important to recognize that the Blaine measurement has a number of known limitations and does not reflect the accurate RHA specific surface area, particularly as it becomes unreliable when its magnitude is larger than 500 m^2/kg [22].

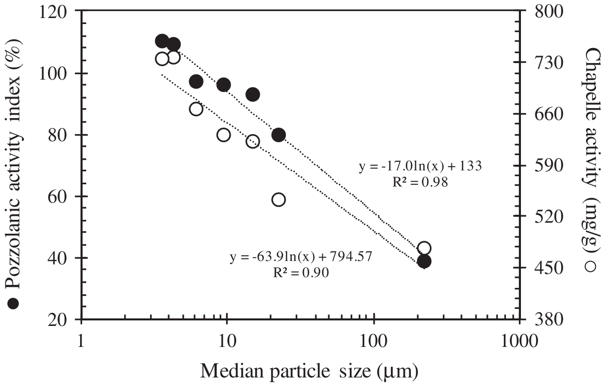

Fig. 8. Relationship between pozzolanic activity and median particle size of AR-RHA and ground RHAs.

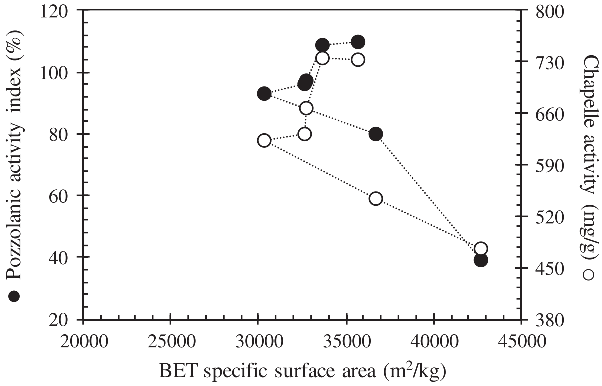

Fig. 9. Relationship between pozzolanic activity and BET specific surface area of AR-RHA and ground RHAs.

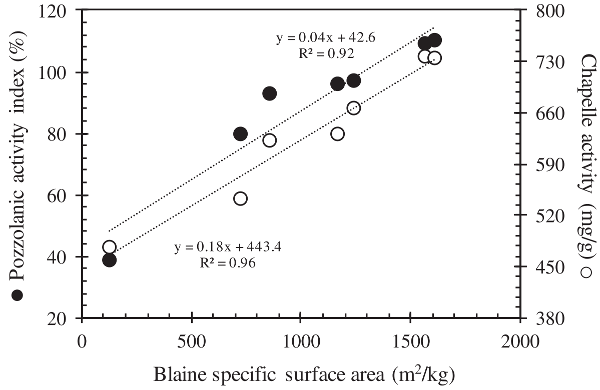

Fig. 10. Relationship between pozzolanic activity and Blaine specific surface area of AR-RHA and ground RHAs.

5. Conclusions

The following conclusions have been drawn from this study:

- The pozzolanic activity of the residual RHA evaluated by compressive strength tests and a chemical method was correlated to particle size through an inverse log-linear relationship.
- Since the residual RHA has high carbon content and its microporous structure is broken down as a result of the grinding action, the BET surface area is not a particularly useful tool to characterize its potential pozzolanic activity.
- Although the BET determination represents more accurately the complex specific surface area of the RHA, 'external' specific surface area, measured indirectly using Blaine's method, for instance, and/or particle size distribution can be used as tools to assess the potential pozzolanic activity of highly porous materials such as residual RHA.

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References

[1] Gibson LJ, Ashby MF. Cellular solids: structure and properties. Cambridge: Cambridge University Press; 1997.
[2] James J, Subba Rao M. Reactivity of rice husk ash. Cement Concr Res 1986;16(3):296–302.
[3] Zhang M-H, Malhotra VM. High-performance concrete incorporating rice husk ash as a supplementary cementing material. ACI Mater J 1996;93(6):629–36.
[4] Cordeiro GC, Toledo Filho RD, Fairbairn EMR. Use of ultrafine rice husk ash with high-carbon content as pozzolan in high performance concrete. Mater Struct 2009;42:983–92.
[5] Martirena Hernández JFM, Middeendorf B, Gehrke M, Budelmann H. Use of wastes of the sugar industry as pozzolana in lime-pozzolana binders: study of the reaction. Cement Concr Res 1998;28(11):1525–36.
[6] Cordeiro GC, Toledo Filho RD, Tavares LM, Fairbairn EMR. Pozzolanic activity and filler effect of sugar cane bagasse ash in Portland cement and lime mortars. Cement Concr Comp 2008;30(5):410–8.
[7] Cordeiro GC, Toledo Filho RD, Tavares LM, Fairbairn EMR. Ultrafine grinding of sugar cane bagasse ash application as pozzolanic admixture in concrete. Cement Concr Res 2009;39(2):110–5.
[8] Cordeiro GC, Toledo Filho RD, Fairbairn EMR. Effect of calcination temperature on the pozzolanic activity of sugar cane bagasse ash. Constr Build Mater 2009;23(10):3301–3.
[9] Della VP, Kühn I, Hotza D. Rice husk ash as an alternative source for active silica production. Mater Lett 2002;57(4):818–21.
[10] Hanafi S, Abo-El-Enein SA, Ibrahim DM, El-Hemaly SA. Surface properties of silica produced by thermal treatment of rice husk ash. Thermochim Acta 1980;37(2):137–43.
[11] Wang L, Seals RK, Roy A. Investigation of utilization of amorphous silica residues as supplementary cementing materials. Adv Cement Res 2001;13(2):85–9.
[12] Payá J, Monzó J, Borrachero MV, Mellado A, Ordoñez LM. Determination of amorphous silica in rice husk ash by a rapid analytical method. Cement Concr Res 2001;31(2):227–31.
[13] Bui DD, Hu J, Stroeven P. Particle size effect on the strength of rice husk ash blended gap-graded Portland cement concrete. Cement Concr Comp 2005;27(3):357–66.
[14] Salas A, Delvasto S, Mejía de Gutierrez R, Lange D. Comparison of two processes for treating rice husk ash for use in high performance concrete. Cement Concr Res 2009;39(9):773–8.
[15] Hamad MA, Khattab IA. Effect of the combustion process on the structure of rice hull silica. Thermochim Acta 1981;48(3):343–9.
[16] ABNT NBR 7214. Standard sand for cement test. ABNT, Technical Standards Brazilian Association, Rio de Janeiro, Brazil; 1982.
[17] Raverdy M, Brivot F, Paillère AM, Bron R. Appréciation de l'activité pouzzolanique de constituents secondaires. In: Proceedings of 7e congrés international de la chimie des ciments, Paris, France; 1980.
[18] ASTM C204-07. Standard test methods for fineness of hydraulic cement by air-permeability apparatus; 2002.
[19] Lubda D, Lindner W, Quaglia M, du Fresne von Hohenesche C, Unger KK. Comprehensive pore structure characterization of silica monoliths with controlled mesopore size and macropore size by nitrogen sorption, mercury porosimetry, transmission electron microscopy and inverse size exclusion chromatography. J. Chromatogr. A 2005;1083(1–2):14–22.
[20] ABNT NBR 5752. Pozzolans – Pozzolanic activity – determination of pozzolanic activity index with Portland cement. ABNT, Technical Standards Brazilian Association, Rio de Janeiro, Brazil; 1992.
[21] ABNT NBR 7215. Portland cement – determination of compressive strength. ABNT, Technical Standards Brazilian Association, Rio de Janeiro, Brazil; 1996.
[22] Von Berg W. Influence of specific surface and concentration of solid upon the flow behaviour of cement pastes. Mag Concr Res 1979;31:211–6.