Microstructure of cement pastes with residual rice husk ash of low amorphous silica content

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HIGHLIGHTS

- Residual rice husk ash (RHA) produced in Brazil was characterized.
- Pastes with RHA with low amorphous silica content have strong consumption of $Ca(OH)_2$.
- There is a refinement of the pore structure of the pastes with this kind of RHA.
- RHA with low amorphous silica content, when finely divided, shows adequate pozzolanic activity.

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ABSTRACT

Residual rice husk ash (RHA) has been frequently suggested as possible mineral addition in cements. However, the characteristics of residual RHAs produced by different manufacturers and the effect of residual RHA with low amorphous silica content in addition in cement pastes are poorly understood. This paper aims at characterizing the different varieties of residual RHA produced in Brazil and at investigating the microstructure of cement pastes with 20% replacement of ordinary cement by RHAs which presents high and low amorphous silica content. A broad array of techniques was employed in the characterization, such as X-ray diffraction (XRD), thermogravimetric analysis (TG), scanning electron microscopy (SEM), X-ray microanalysis, and porosimetry by mercury intrusion (PMI). The results demonstrate that RHA with low amorphous silica content, finely divided, reduces the calcium hydroxide content and the Ca/Si ratio of calcium silicate hydrate (C–S–H), and also refines the porous structure of the pastes. Residual RHAs with low amorphous silica content thus proved to be suitable mineral addition for cements.

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1. Introduction

Rice husk ash (RHA) produced by controlled burning processes has a high amorphous silica content and is used as a mineral addition to the in cements, with properties similar to silica fume. Rice processing industries also use rice husks as fuel to generate the heat or electricity required by the various internal processes. As the combustion is carried out without control of the burning process, it generates large amounts of residual RHA by-products, whose proper disposal represents an important environmental issue [1,2]. Residual RHA is produced in many countries, and studying its properties is becoming increasingly important [3–5]. The residual RHA usually contains residual carbon and partly crystallized silica [6,7]; its main difference from the RHA produced by controlled burning is a lower content of amorphous silica. Several

authors have suggested the use of finely divided residual RHA as a mineral addition in cements [1–21]. However, only few studies have evaluated the characteristics of residual RHAs produced by different burning processes, and compared the effects of adding RHAs with high (>80%) and low (<20%) amorphous silica content to the cement, assessing the pozzolanic activity and the microstructure of the pastes [17].

Isaia [8] criticized the preconceptions against RHA produced without control of the burning process, noting: "how important is the presence of these crystalline phases in pozzolans, analyzed separately, for the performance of concrete or mortar? In fact, what matters is the final result that the specific pozzolan or mix with another pozzolan can provide when one or more levels of substitution are studied, in relation to the reference mixture." When dispersed in the paste, the small pozzolan particles generate a large number of nucleation sites for precipitation of cement hydration products. Additionally, the microfiller (physical) effect of the finer grains ensures a denser packing within the cement paste and

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reduces the wall effect in the paste-aggregate transition zone. This reinforces the effect of the pozzolanic reaction between the amorphous silica present in the pozzolan and the calcium hydroxide produced by cement hydration reactions. These behaviors highlight the synergy between Portland cement hydration, pozzolanic reaction, and, mainly, microfiller effect, whose combination leads to a improvement of the compressive strength compared to Portland cement mixtures [11].

Reducing the particle size of RHAs with low amorphous silica content influences their pozzolanic activity [7,8] and increases the their Ca(OH)$_2$ consumption [4,21]. The ultrafine grinding of residual RHA, that reduces the average particle diameter below 10 μm, was found to be sufficient for generating high pozzolanic activity [1,12]. Concrete with up to 25% replacement of the cement by finely divided residual RHA exhibited improved mechanical properties, compared to a reference concrete [16,18], although the improvement was more significant for RHAs produced by controlled burning [13]. The use of residual RHA and RHA produced by controlled burning has a positive effect on autogenous shrinkage, owing to their porous cellular structure. RHA probably acts as an internal reservoir, providing a local source of water to the paste volume [14]. Depending on the level of substitution in the cement, the finely divided residual RHA can inhibit or enhance the alkali-aggregate reaction in concrete [6]. The partial replacement of the cement by residual RHA improves the decreased expansion, the weight loss and the loss of compressive strength resulting from acetic acid and nitric acid attack [19]. Sensale (2010) [17] concluded that the finely divided residual RHA is effective for producing more durable concrete, compared to the reference concrete. The RHA produced without control of the burning process was deemed adequate for the production of self-compacting concrete with normal resistance, containing up to 40% RHA [20].

In the present paper we characterized residual RHAs produced in Brazil. Furthermore, we analyzed the compressive strength of mortars and microstructures of cement pastes with 20% replacement of ordinary cement by RHAs with high and low amorphous silica content, through X-ray diffraction (XRD), thermogravimetric (TG) analysis, scanning electron microscopy (SEM) with X-ray microanalysis, and porosimetry mercury intrusion (PIM).

2. Materials and methods

2.1. Materials

The different burning procedures used in industries producing residual RHAs in several states of Brazil were analyzed. We selected nine residual RHAs to represent the main burning processes. The residual RHAs 1–5 and 9 are produced by rice processing industries from different regions of the country, that use rice husk as fuel to generate power and heat for the rice drying and/or parboiling processes. These residual RHAs are burned in furnaces or boilers without control of the burning process, and are often dumped on the roadside or into rivers in close proximity to the industries. The residual RHAs 6, 7, and 8 were produced by thermal power plants using rice husk as fuel, again without control of the burning process. These power plants generate large amounts of residues, without proper disposal. The RHA 10 was produced in a power plant with a controlled burning process. Burning was performed in a furnace at a temperature of 700 °C for 2 h, with slow cooling at room temperature.

The milling process of the 10 RHAs was carried out for 5 h in a ball mill specified for the Los Angeles abrasion test in coarse aggregates (NBR NM 51/2001 [22]). Twelve (12) steel balls (6.0 kg) were used as abrasive weight, to process a total of 2.5 kg RHA. This specific procedure was adopted to ensure milling of all RHAs with the same energy, although this milling procedure is not the most suitable for RHA.

The chemical characterization of 10 RHAs was performed by Energy Dispersive X-ray Fluorescence (ED XRF) and Loss on Ignition analysis. The ED XRF data were obtained using a Shimadzu spectrometer (EDX-720) in high vacuum, that analyzes the range of elements from sodium ($_{11}$Na) to uranium ($_{92}$U) with a rhodium target X-ray tube. The particle size distribution of RHAs was measured using a laser diffraction particle size analyzer (Mastersizer S Standard Bench – Malvern Instruments) with ethyl alcohol as dispersant and ultrasonic agitation for 60 s. The BET specific surface area was measured using a nitrogen adsorption apparatus (Autosorb 1 – Quantachrome Nova2200). The X-ray diffraction (XRD) data were obtained by a Geigeflex T/Max RIGAKU diffractometer, operating with copper

radiation (CuKα = 1.5406 Å) and a nickel filter at 40 kV and 20 mA. The scanning speed was 2°/min in a 2θ range from 2° to 70°. The RHAs specific mass was obtained through the NBR NM 23 (2000) standard [23]. The Pozzolanic activity index (PAI) with cement of RHAs was obtained by NBR 5752/2012 [24].

In order to evaluate the effect of the amorphous silica content on the RHA pozzolanic activity, we compared the properties of two RHA samples with high (>80%) and low (<20%) amorphous silica content. It is important for RHAs with high and low contents of amorphous silica to have the same average diameter in order to facilitate the evaluation and comparison of the microstructures of pastes. A suitable grinding procedure was formulated to produce RHA grains of less than 10 μm average diameter and approximately equal size. The RHAs with high and low content of amorphous silica (2.5 kg) were ground in a ball mill for 7 and 6 h, respectively, with a load of 40 steel spheres giving a total weight of 10.50 kg. Ordinary Portland Cement (OPC) without mineral additions (similar ASTM Type I), obtained directly from a cement factory in a single batch, was employed as reference.

The chemical characterization of the RHA of high amorphous silica content and RHA of low amorphous silica content and of OPC was performed by ED XRF and Loss on Ignition analysis. The particle size distribution of the RHAs was measured as described above; their amorphous silica content of the RHAs was measured by a rapid analytical method developed by Payá et al. [25], and the Ca(OH)$_2$ consumption of the RHAs was determined through the modified Chapelle method based on Raverdy et al. work [26]. For a material to be classified as pozzolanic, a minimum consumption of 330 mg CaO/g is required.

2.2. Methods for evaluating the microstructure of paste binders

Three binders were used in the study: OPC (employed as the reference binder) and two composite binders – RHA with a high amorphous silica content and RHA with a low amorphous silica content – each of which replaced 20 mass% of the reference OPC. According to Ganesan et al. [27], replacement levels of up to 30 mass% are considered appropriate for the production of concrete without any adverse effects on properties such as strength and durability compared to those of pure cement. The binders were homogenised in a ceramic container.

The compressive strength of the binders at 3, 7, 28, and 91 days was determined in mortars by NBR 7215/1996 [28] with a water to binder (w/binder) ratio of 0.48. This test was used to determine the compressive strength of binders.

A 2 L planetary mixer was used for the preparation of pastes with a w/binder ratio of 0.50. This specific w/binder ratio was used since it is close to the w/binder ratio that is used for determining the compressive strength of mortars.

The binders were mixed with water for 2 min at a low rotation speed; subsequently, there was a pause of 30 s, and then, high-speed mixing was performed for another 2 min. Cylinders with dimensions of 5 cm × 10 cm were prepared in moulds, covered with plastic wrap, and immersed in water-saturated Ca(OH)$_2$ for 91 days at 20 °C. The samples were then removed from the cylinders, and the hydration reaction was stopped by immersing the samples in acetone for 30 min and drying them in an oven at 100 °C for 1 h. Subsequently, the samples were packaged with soda lime and silica gel to prevent hydration and carbonation.

The samples prepared for XRD and thermogravimetric (TG) tests at 3, 7, 28 and 91 days were cracked with a hammer and then milled in a porcelain crucible.

TG experiments were performed in an instrument for simultaneous thermal analysis (DSC-TG, SDT 2960 model, TA Instruments). As portable samples, an aluminum crucible and an aluminum oxide crucible were used as references for analysis. All measurements were performed at a heating ratio of 20 °C/min, from 25 °C to 1000 °C under continuous N$_2$ flux (110 cm^3/min).

For the SEM analysis, including X-ray microanalysis, two test samples were removed at 91 days for preparation with polished section. All samples analyzed by SEM were subjected to a prior procedure of deposition of a thin layer of conductive material (Au) on their surfaces. The Ca/Si (C/S) ratio of C–S–H was determined by a LEICA S440i Scanning Electron microscope. The different phases were identified using backscattered electron detectors (BSE). For semiquantitative microanalysis of the C/S ratio of C–S–H, a spectrometry by X-ray scattered energy (XSE) was performed with an OXFORD Link device with 20 kV voltage. The microanalyses were amplified to 8000x, and 25 microanalyses were randomly determined in regions of possible C–S–H presence for each sample analyzed. The microanalysis instrument was calibrated with pure cobalt standard, with a 100 s acquisition time for each microanalysis.

The Mercury Intrusion Porosimetry was performed using a Quanta Chrome PoreMaster mercury intrusion porosimeter, with 0.485 N/m and 130° taken as the surface tension and the contact angle between mercury and pore and wall, respectively. After 91 days of curing in a controlled-moisture room and drying at 45 °C until constant mass, samples of about 1 cm^3 were cut from the mid-portion of the cylinders using a diamond cutter with 50 mm diameter and 100 mm height.

3. Results and discussion

3.1. Characterization of the residual RHAs produced in Brazil

It is important to determine the characteristics and properties of the residual RHAs produced by different burning processes in the industry, in order to enable their use as mineral addition in