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Pozzolanicity of the material obtained in the simultaneous calcination of biomass and kaolinitic clay

Juan S. Uchima *, Oscar J. Restrepo, Jorge I. Tobón

Grupo del Cemento y Materiales de Construcción (CEMATCO), Calle 75 # 79A-51, Bloque M17-101, Departamento de Materiales y Minerales, Facultad de Minas, Universidad Nacional de Colombia, Medellín, Colombia

HIGHLIGHTS

- Kaolinitic clay was thermally treated in presence of rice husk.
- Calorimetry, X Ray Diffraction and thermogravimetric measures on blended cement pastes were performed.
- Compressive strength was determined on blended cement mortars.
- Pozzolanic activity of metakaolin obtained by calcinations in presence of rice husk was evaluated.

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ABSTRACT

The scope of this paper is to study the pozzolanic activity of metakaolin obtained in simultaneous calcinations with rice husk. Isolated calcinations of kaolinitic clay and rice husk were also performed for comparison. The raw materials were subjected to thermal treatments in a gas furnace at 670, 700 and 750 °C for 2.0, 2.5 and 3.0 h. Based on the loss of crystallinity of the materials obtained, two of them were selected and ground in a ceramic ball mill to prepare pastes with ordinary Portland cement (OPC) with levels of substitution of 10% and 20%, with a water/binder ratio of 0.4 and mortars with a water/binder ratio of 0.5 in order to evaluate the pozzolanic activity of the materials by X Ray Diffraction analysis, isothermal calorimetry, thermogravimetric analysis and compressive strength measurements. The curing ages were 1, 3, 7 and 28 days at normal curing conditions. Based on the results it was concluded that, the cement mixed with the supplementary cementitious materials (SCMs) obtained in simultaneous calcinations, present a slow pozzolanic activity with an improvement in compressive strength of up to 20.1% in relation to the OPC and of 5.5%, at 28 days of normal curing, in relation to the highest value found for the cement substituted with materials obtained in isolated calcinations. In general, good linear correlations were found between compressive strength values in mortars and fixed lime in cement pastes suggesting a strong dependence of compressive strength on the amount of fixed lime by the pozzolans.

1. Introduction

The use of supplementary cementitious materials (SCMs) has been increasing in recent years, in part due to the need of reducing the amount of carbon dioxide emissions associated with cement manufacturing, but also because of the positive impact it can have on the performance of cement, such as volumetric stability, increased mechanical strength, durability, among others.

Metakaolin (MK) and rice husk ash (RHA) are two SCMs of which the effects on cement and concrete have been investigated by several authors [1–4], and are the focus of this investigation. Kaolinitic clay is an aluminum silicate hydrate ($Al_2Si_2O_5(OH)_4$), which suffers dehydroxylation when submitted to calcination at a temperature range of 500–800 °C [5,6]; in this process the clay loses its long range order and becomes an amorphous, reactive material known as metakaolin ($Al_2O_32SiO_2$) [1,7,8]. The use of metakaolin (MK), has been found to have several benefits on concrete performance, such as increased resistance to sulfate attack, improved early mechanical strength and reduction of alkali-silica induced expansion [5,9].

Rice husk (RH), is an agro industrial by-product that is generated in great volumes and whose disposal is problematic so its use as a partial substituent (after burning) of cement or as an energy source is advantageous from an environmental viewpoint. Under controlled burning conditions rice husk transforms into a

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* Corresponding author.
E-mail address: jsuchimaq@unal.edu.co (J.S. Uchima).

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silica rich amorphous material of high reactivity [10,11]. The typical range of temperatures to obtain rice husk ash suitable for use as a SCM is 500–700 °C [12,13]; inferior temperatures might not be enough to expel the carbonaceous content from the material, and temperatures superior to approximately 700 °C might cause recrystallization of the material, which could negatively affect its reactivity. Cooling conditions of the ash are also important; quick cooling yields the best results regarding the amorphicity of the ash [12].

Rice husk ash (RHA), used as a partial substituent of cement, has several benefits on the performance of the material, for example, when used to manufacture concrete, improving its mechanical strength, reducing its porosity, due to, its filler effect and the pozzolanic reactivity [14].

Ternary blends containing OPC, MK and RHA, have also been studied. Shatat et al. [15] found increased compressive strengths in cement pastes when MK (15–20%) and RHA (5–10%) are used simultaneously. Durability and mechanical strengths in self compacting concretes containing combinations of MK and RHA were studied by Kannan et al. [16], and found that there were no adverse effects on durability up to 40% of substitution; in regard to compressive strength, the best results were achieved with 15% MK and 15% RHA.

No extensive studies have been done regarding the pozzolanicity of a combination of RHA and MK obtained in simultaneous calcination, an interesting possibility considering that part of the biomass calorific power can contribute to the activation of the kaolinitic clay to produce metakaolin, which is an endothermic process, and the pozzolanic properties of the metakaolin could benefit from the rice husk ash obtained in the same process, as this material is rich in amorphous silica. The aim of this work is, then, to compare the pozzolanicity of the material obtained in simultaneous calcination of the raw materials, with the pozzolanicity of the materials obtained in isolated calcinations; the properties analyzed were the heat evolution and heat released in cement pastes hydration, lime fixation capacity, compressive strength in mortars and the mineralogical evolution in the substituted pastes at different curing ages.

2. Materials and methods

Kaolinitic clay from La Unión, Antioquia, and RH from Córdoba, Colombia, were the raw materials used in this study; after mixing them manually, they were subjected to controlled combustion at 670, 700 and 750 °C for 2.0, 2.5 and 3.0 h, temperatures and times that fall within ranges found to be acceptable by several authors [5,13,17]. Chemical composition of the kaolinitic clay is shown in Table 1. A gas furnace with two atmospheric premix burners with liquefied petroleum gas fuel was used. The mix proportion for the thermal treatment of the materials was 91% kaolinitic clay and 9% rice husk; since the density of the former $(1.05\,\frac{g}{cm^3})$ is almost seven times the density of the latter $(0.16\,\frac{g}{cm^3})$, a given amount of mass of rice husk occupies almost seven times the volume occupied by the kaolinitic clay and given the fact that, the typical ash content of rice husk is only about 16% [18] and the corresponding value for kaolinitic clay is about 86% [19], kaolinitic clay was chosen to be the major component of the mix; in this proportion more than half the volume (60%) of the containers used is occupied by the kaolinitic clay and after each calcination, more than 80% of the mass initially loaded into the furnace is available to test as a potential pozzolan. The containers used were selected to allow a better supply of oxygen for the material, especially for an effective combustion of the rice husk, which during the calcination needs to be rid of the most possible carbonaceous content.

The raw materials were also burned in an isolated way; rice husk was burned at 670 °C and the kaolinitic clay was burned at 750 °C, both for 2 h. Two of the materials obtained during simultaneous calcinations of clay and biomass were selected according to the loss of crystallinity, determined by X Ray Diffraction (DRX) analysis of the ashes, in which the criterion used, was the disappearance of kaolinite peaks; these materials and the ones obtained in the isolated calcinations of biomass and clay were subjected to grinding in a ceramic ball mill for a maximum of 4 h, with the aim of increasing its specific surface area, and thus its reactivity. The mass of the milling balls was kept constant with respect to the mass of each sample being milled. Every sample was milled until at least 80% of it, passed through a #325 mesh.

The particle size distribution of each material was then determined by laser granulometry with a water media in a Mastersizer 2000 particle size analyzer.

OPC provided by Argos Cement Company, the composition of which is shown in Table 1, was blended with these materials (10%, 20%); cement pastes were then manually prepared with a water/binder ratio of 0.4, to analyze the mineralogical evolution by means of XRD and thermogravimetric analysis (TG); XRD analyses were performed in a *PANalyticalX'Pert PRO MPD*, with a $6^\circ - 70^\circ$ (2θ) range, 0.013 step and accumulation time of 59 s. TG analyses were performed in a TGA 2950 thermogravimetric analyzer, with platinum crucibles with no lid. The heating rate was 5 °C/min, with a nitrogen flow of 40 mL/min and the mass of each sample was (40 ± 1) mg. The chemical compositions of the materials were obtained by X ray fluorescence (XRF) in a *PANalytical AXIOS* spectrometer with a rhodium X ray tube.

After mixing, the pastes were stored and sealed in plastic bottles to avoid carbonation, kept partially submerged in water in the curing room until the day of testing, when they were ground in an agate mortar in presence of acetone to stop the process of hydration; the samples were then oven-dried at 60 °C for 90 min and stored in marked plastic microtubes for the XRD and TG analyses. The heat released rate, as well as the total heat released were monitored during the first 72 h of hydration, with isothermal calorimetry at a temperature of 25°C .Isothermal calorimetry measurements were performed in a TAM air isothermal calorimeter. Blended cement mortars were prepared with a water/binder ratio of 0.5 to analyze the effect of the SCMs in the development of compressive strength, according to ASTM C109 [20]; the testing ages for pastes and mortars were 1, 3, 7 and 28 days.

The nomenclature used for the different samples is as follows: rice husk ash: (RHA), metakaolin: (MK) and metakaolin obtained by simultaneous calcinations with rice husk: (MKR); the first three numbers following the letters correspond to the temperature at which the material was obtained and the rest of the numbers correspond to the percentage of substitution by pozzolan in the case of cement pastes and mortars; cement pastes or mortars blended with the materials are identified with a "C" as the first letter.

3. Results and discussion

3.1. Characterization

Diffractograms for the raw clay and several samples after the thermal treatment are shown in Fig. 1; in this figure the last numbers indicate the time of residence in the gas furnace in hrs. It can be observed in all of the ashes that, the peaks corresponding to kaolinite disappeared, which indicates dehydroxylation of the material, and formation of metakaolin [21].

The differences in the loss of crystallinity of the materials after the thermal treatment are not very significant, since all of the samples have in common the disappearance of kaolinite peaks, so it was decided to use MKR 670 2 and MKR 750 2 for preparation of pastes and mortars during the remainder of the study, having in this way a wider temperature range.

The diffractogram of the RHA obtained after the isolated thermal treatment, at 670 °C, is presented in Fig. 2; its low crystallinity can be inferred from the width of the main peak.

The granulometric distribution and mean particle sizes of the OPC and the different mineral additions used are shown in Fig. 3; it can be seen that there is a similarity in the distributions of all materials used.

Table 1
Chemical compositions of kaolinitic clay and OPC.

Parameter (%)	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	SO_3	Loss on ignition
Kaolinitic clay	63.80	21.86	0.82	0.13	2.94	0.14	0.29	0.38	0.18	9.31
Cement	17.98	4.92	3.25	2.22	64.06	0.19	0.23		2.57	4.59