Construction and Building Materials 118 (2016) 286–293

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

# Mineralogical evolution of portland cement blended with metakaolin obtained in simultaneous calcination of kaolinitic clay and rice husk

Juan S. Uchima *, Oscar Jaime Restrepo-Baena, 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

- Hydrated cement phases quantities in blended cement pastes were estimated.
- A deconvolution method in DTG curves was used to avoid peak overlapping.
- Correlation between mineralogical evolution and compressive strength was established.

## ARTICLE INFO

*Article history:*
Received 31 October 2015
Received in revised form 3 May 2016
Accepted 6 May 2016
Available online 14 May 2016

*Keywords:*
Metakaolin
Rice Husk ash
Compressive strength
Thermogravimetric analysis
Pozzolans
Calcium silicate hydrates

## ABSTRACT

Mineralogical evolution of blended cement pastes was studied. The supplementary cementitious materials (SCMs) used, were metakaolin (MK) and rice husk ash (RHA). The MK used was obtained by calcination in presence of rice husk; kaolinitic clay and rice husk were also thermally treated in an isolated manner for comparison purposes. The mixed 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. Mortars with a water /binder ratio of 0.5 were prepared with the same supplementary cementitious materials (SCMs) and substitution levels. Llime-pozzolan pastes were also prepared with the same levels of substitution with a water/lime-pozzolan ratio of 1.0. The ages of analysis were 1, 3, 7 and 28 days. Hydrated cement phases (C-S-H, C-A-S-H) were identified and their quantities estimated with the aid of thermogravimetric (DTG) and X ray diffraction analyses (XRD). The impact of mineralogical evolution on compressive strength development was assessed by means of the correlation between the quantities of hydrated cement phases in blended cement pastes and compressive strength measurements in the corresponding blended cement mortars.



## 1. Introduction

Thermogravimetric analysis has been used with success to research cement hydration, specifically the formation and evolution of the different hydrated phases [1–4]; using DTG curves, it is possible to quantify Portlandite in cement pastes at different curing ages, something that cannot easily be done with phases such as calcium silicate hydrates (C-S-H), calcium aluminate silicate hydrates (C-A-S-H) and calcium aluminate hydrates (C-A-H), as their decomposition temperatures are close to one another, something that causes peak overlapping in DTG curves [5] [6]. Deconvolution methods have been used to separate peaks associated with decomposition events that occur at close temperatures, which allows then, identification and quantification of different hydrated cement phases. Dweck et al. [7] used a deconvolution method to separate overlapped peaks in DTG curves of type II cement pastes at several curing ages, with the aim of studying the evolution of ettringite during hydration. In other works, to avoid the problem posed by peak overlapping, high resolution thermogravimetry has been used [8].

One of the factors that influences greatly the development of mechanical strengths and durability of cement is the quantity of hydrated phases such as calcium silicate hydrates [9]. The use of pozzolanic materials can contribute to the formation of such hydrated phases. Metakaolin (MK) is a pozzolanic material whose effects on cement have been widely studied [10–12]; the pozzolanic reactions taking place in cement pastes containing MK

* Corresponding author. Tel.: +574 4255364.
*E-mail address:* jsuchimaq@unal.edu.co (J.S. Uchima).

http://dx.doi.org/10.1016/j.conbuildmat.2016.05.063
0950-0618/

have C-A-S-H, C-S-H and to a lesser extent, C-A-H as main products [13] [14]. Rice husk ash (RHA) has also been researched as a pozzolan by several authors [15–17]. Both MK and RHA are obtained after thermal treatments of raw materials (kaolinitic clay and rice husk, respectively), at appropriate temperatures that allow the obtaining of an amorphous and therefore reactive material; the typical temperature ranges suitable for such thermal treatments are $500-800\,^{\circ}C$ for MK [12] [18] [19], and $500-700\,^{\circ}C$ for RHA [20] [21]. The effects of the material obtained in simultaneous calcination of kaolinitic clay and rice husk on cement properties, lack of extensive research [22].

This is a possibility that has, in principle two advantages, the first being the contribution of the combustion of the biomass to the energy required by the endothermic formation reaction of MK; the second is the modification in the properties of MK, caused by the presence of RHA, which contains typically more than 90% of amorphous silica if the calcinations conditions are appropriate [23]. The second aspect is the one explored in this work, specifically in regard to the relationship between mineralogical evolution of blended cement pastes and development of compressive strength in cement mortars prepared with the same pozzolanic materials.

## 2. Materials and methods

The raw materials used in this work were kaolinitic clay from La Unión, Antioquia, Colombia and RH from Córdoba, Colombia; they were mixed manually, and were subjected to controlled combustion at temperatures and times that fall within ranges found to be acceptable by several authors: 670, 700 and $750\,^{\circ}C$ for 2.0, 2.5 and 3.0 h [18] [21] [23] [24]. Chemical composition of the kaolinitic clay is shown in Table 1 and CHN elemental analysis results for the biomass are shown in Table 2. The thermal treatment was administered to the raw materials by means of a gas furnace with two atmospheric premix burners with liquefied petroleum gas fuel. The mix proportion for the thermal treatment of the materials was 91% kaolinitic clay and 9% rice husk; since the density of the clay ($1.05\,\frac{g}{cm^3}$) is almost seven times the density of the biomass ($0.16\,\frac{g}{cm^3}$), a given amount of mass of rice husk occupies almost seven times the volume occupied by the kaolinitic clay and taking into account that, the typical ash content of rice husk is only about 16% [25] and the corresponding value for kaolinitic clay is about 86% [26], kaolinitic clay was chosen to be the major component of the mix; in this way 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 loaded into the furnace, is available to test for pozzolanic potential [22].

The raw materials were also burned in an isolated way; rice husk was burned at $670\,^{\circ}C$ and the kaolinitic clay was burned at$750\,^{\circ}C$, both for 2 h. Two of the materials obtained by simultaneous calcinations of clay and biomass were selected according to the loss of crystallinity, determined by X Ray Diffraction (XRD) 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 objective of increasing their reactivity, by means of increasing their specific surface area. Every sample was milled until at least 80% of it, passed through a #325 Tyler mesh [22].

The particle size distribution of each material was determined by laser granulometry with a water media in a Mastersizer 2000 particle size analyzer [22]. Specific surface area measurements were performed in a Gemini-Micrometrics equipment, based on BET theory.

OPC was provided by Argos Cement Company, the composition of which is shown in Table 1. OPC was blended with the SCMs (10 and 20%). Cement pastes were then manually prepared with a water/binder ratio of 0.4, to analyze the mineralogical evolution by means of thermogravimetric analysis (TG). TG analyses were performed in a TGA 2950 thermogravimetric analyzer, with platinum crucibles with no lid. The heating rate was $5\,^{\circ}C/min$, 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 [22]. CHN elemental analysis of the biomass was performed in an EXETER CE 490 elemental analyzer.

**Table 2**
CHN elemental analysis by percentage of dry mass, with standard deviation. C: Carbon, H: Hydrogen, N: Nitrogen.

| C %w/w ± SD | H %w/w ± SD | N %w/w ± SD |
|---|---|---|
| 37.10 ± 0.05 | 4.62 ± 0.04 | 0.55 ± 0.01 |

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 $60\,^{\circ}C$ for 90 min and stored in marked plastic microtubes for the TG analyses. 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 [27]; the testing ages for pastes and mortars were 1, 3, 7 and 28 days [22].

Lime–pozzolan pastes were also prepared with the materials obtained in the calcinations to perform thermogravimetric analyses on those lime pastes containing the materials which yielded the best compressive strength results in mortars; this, in order to establish a comparison with thermal analyses results from cement pastes, which could lead to clearer identification of mass loss events. The same procedure used for cement pastes was applied for lime-pozzolan pastes. XRD analyses were performed on these pastes at 3 and 28 days of curing to help identify the hydrated phases present at those ages. XRD analyses were performed in a *PANalytical X'Pert PRO MPD,* with a $6^0-70^0(2\theta)$ range, 0.013 step and accumulation time of 59 s.

For an estimation of hydrates quantities (C-S-H and C-A-S-H) in cement pastes at the different curing ages, it was necessary to clearly identify each peak in DTG curves, which in principle is not possible due to overlapping of peaks. With that purpose, the software PeakFit 4.12 was used. The software allows a separation of the overlapped peaks associated with each decomposition event, by means of a deconvolution performed on the DTG curves obtained experimentally for the cement pastes samples. As a result of the deconvolution, the software calculates a new DTG curve which is the result of adding the separated peaks, giving a coefficient of determination that indicates the effectiveness of the deconvolution process.

The nomenclature used for the different samples was 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 of cement by pozzolan. Cement pastes or mortars blended with the materials are identified with a "C" as the first letter. In lime-pozzolan pastes the letter "L" is used instead of "C".

## 3. Results and discussion

### 3.1. Characterization

The differences in the loss of crystallinity of the materials after the thermal treatment were not significant, since all of the samples have in common the disappearance of kaolinite peaks, which indicates dehydroxylation of the material, and formation of metakaolin [28]. It was decided then, to use MKR 670 2 and MKR 750 2 samples (the last digit in this case indicates the time of residence in the gas furnace in hours) for preparation of pastes and mortars during the remainder of the study, having in this way a wider temperature range. Diffractograms for the raw clay and the selected samples after the thermal treatment are shown in Fig. 1, where the PDF2 database was used for peak identification; it can be seen clearly in the marked region, that the main peak corresponding to kaolinite, is only present in the diffractogram for the raw material. The other peaks disappear as well after the thermal treatment.

**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 |