

EFFECT OF METAKAOLIN POZZOLANIC ACTIVITY IN THE EARLY STAGES OF CEMENT TYPE II PASTE AND MORTAR HYDRATION

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The cement industry is one which most emits polluting gases to the environment, due to the calcium carbonate calcination, as well as to the burning of fossil fuels during the manufacturing process. Metakaolin (MK), in partial substitution to cement in its applications, is having a special worldwide growing role, for the technological increment due to its pozzolanic activity and mainly to the reduction of those emissions. In the present paper, the effect of pozzolanic activity of metakaolin was analyzed by thermal analysis in pastes and mortars of type II Portland cement in the first three days of the hydration, during which, relevant initial stages of the hydration process occur.

By non-conventional differential thermal analysis (NCDTA), paste and mortar samples containing 0, 10, 20, 30 and 40% of metakaolin in cement mass substitution and using a 0.5 water/(total solids) mass ratio, were evaluated. The NCDTA curves, after normalization on cement mass basis and considering the heat capacity of each reactant, indicate that the pozzolanic activity behavior of metakaolin is different in pastes and mortars. Through the deconvolution of the normalized NCDTA curve peaks, it can be seen that ettringite formation increases as cement substitution degree (CSD) increases, in both cases. Tobermorite formation is more enhanced in mortars than in pastes by MK, with a maximum formation at 30% of CSD. In the pastes, tobermorite formation increases as CSD increases but it is practically the same at 30 and 40% of CSD.

Keywords: cement, metakaolin, mortars, NCDTA, pastes, pozzolanic activity

Introduction

The cement industry is one which most emits polluting gases to the environment, due to the calcium carbonate calcination, as well as to the burning of fossil fuels during the manufacturing process, being responsible for 7% of the worldwide CO₂ emissions [1]. From Brazilian cement industry data it is estimated that 0.67 tons of CO₂ are emitted per ton of produced cement [2]. In the last decades, environmental challenges due to the necessity to reduce worldwide levels of CO₂ emissions, the energy consumption and the use of natural raw materials, besides the application of Quioto Protocol, promoted an expressive increase in research efforts to find viable alternatives to minimize the pollution effects of the main productive processes.

To attain this goal the use of activated clays as aggregates in pozzolanic cement manufacture is being stimulated, because, besides their use contributes to decrease those emissions, usually it promotes a better performance to cement pastes and concretes which are made from. Among those modified clays metakaolin (MK), which is obtained from thermal processing of kaolinitic clays [3, 4] is having a special worldwide

growing role, because it presents a higher pozzolanic activity, when compared to other activated clays.

When pozzolanic materials are added to the cement matrix, in partial substitution to it, they react with the calcium hydroxide formed during cement hydration, producing additional hydrated crystalline phases [5, 6]. The pozzolanic activity may not necessarily occur in the early stages of hydration, even when it occurs after some days of hydration [7]. Usually thermogravimetry (TG) has been used to evaluate the activity of pozzolanic materials in mixtures with cement for long hydration periods [8–10], as well as differential thermal analysis (DTA) in the study of the pozzolanic properties of calcined clays [3], MK [11–13] and calcined kaolin [14]. To evaluate the effects on the early stages of cement hydration, conduction calorimetry and non-conventional DTA (NCDTA) have been used to study the pozzolanic action of metakaolin [15], silica fume [16] and residual FCC catalyst [17, 18], from the additional heat promoted by respective pozzolanic reactions.

In this paper, the pozzolanic effect of a commercial metakaolin manufactured in Brazil, used in substitution to a type II Portland cement in different degrees, was studied in real time by NCDTA for the early stages of

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hydration of respective pastes and mortars, considering the effect of different specific heats of the raw materials.

Experimental

Materials and methods

The Portland cement (PC) used in this study is a commercial type II one, code CPII- F32, manufactured by Lafarge, RJ, Brazil. The commercial MK is manufactured by Metacaulim do Brasil, SP, Brazil. Samples of pastes and mortars containing MK were prepared in proportions from 0 to 40% mass substitution of cement. The pastes were named as MK0%, MK10%, MK20%, MK30% and MK40%, and the mortars as MKSA0%, MKSA10%, MKSA20%, MKSA30% and MKSA40%, according to the used cement substitution degree.

The quantity used for the paste NCDTA analyses was 100 g of solids (cement+MK), as indicated by previous work using NCDTA by Dweck *et al.* [19]. For the mortars 150 g of sand was added to the corresponding paste solid composition and in all cases a water to total solids mass ratio equal to 0.5 was used.

Normalized NCDTA curves

The temperature difference $(T_s - T_{ref})_{mes}$, between the sample and the reference measured in real time during NCDTA analysis, is due to the exothermal effect of cement and metakaolin hydration reactions which occur and is directly proportional to the generated heat rate at a time t . For a same amount of generated heat, the higher is the heat capacity of the reacting media, the lower will be the resulting sample temperature and consequently, the value of $(T_s - T_{ref})_{mes}$. The higher are the reaction rates of cement and metakaolin, the higher is $(T_s - T_{ref})_{mes}$. For practical purpose, usually it is assumed that the heat capacity of the compositions does not change significantly, assuming that they have similar contents of components or that the different components have similar values of specific heat capacity (c_p). However, for more precise and correct analysis, the specific heat capacities of the components must be known. When they are significantly different, a normalized temperature difference $(T_a - T_{ref})_{norm}$ must be estimated, as was done in the present work. Considering as the control NCDTA curve, the MK0% sample, using 100 g of cement and 50 g of water, Eq. (1) was used to estimate $(T_a - T_{ref})_{norm}$:

$$(T_a - T_{ref})_{norm} = \frac{(T_a - T_{ref})_{mes} [\Sigma(m_i c_{pi})_{sample} / \Sigma(m_j c_{pj})_{control}]}{(m_{cim_control} / m_{cim_s})} \quad (1)$$

where $(\Sigma(m_i c_{pi})_{sample} / \Sigma(m_j c_{pj})_{control})$ = heat capacity correction factor; $(m_{cim_control} / m_{cim_s})$ = cement mass correction factor; $\Sigma(m_i c_{pi})_{sample}$, ($i=1$ to 4) = estimated heat capacity of the 4 components (cement, metakaolin, sand and water) of the partially cement substituted sample; ($i=1$ to 3 for pastes and 4 for mortars); $\Sigma(m_j c_{pj})_{control}$ ($j=1$ to 2) = estimated heat capacity of the 2 components (cement and water) of the control sample; m_{cim_s} = sample cement mass; $m_{cim_control}$ = control sample cement mass; m_i = sample component i mass; m_j = control sample component j mass.

To estimate the above heat capacities, the initial mass of each component was considered and the respective values of specific heat capacity (c_p) were calculated at the respective paste or mortar temperature at a time t , by using c_p measurements of the cement, MK and sand. These were obtained from respective modulated respective differential scanning calorimetry (MDSC) analysis, performed in a TA Instruments 2920 MDSC Model, previously calibrated with standard sapphire. Using sealed aluminum pans, the operating conditions were: cooling at 2°C min^{-1} from ambient temperature to -15°C , then heating at 4°C min^{-1} up to 60°C , with $\pm 0.5^\circ\text{C}$ temperature modulation, and a modulating period of 100 s. A constant value of $c_p = 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ was admitted for water.

For the study of the early stages of hydration, a non-conventional DTA (NCDTA) system was used [20], which presents the same principle as DTA but with no external heating or cooling system. The inert reference consists of a previously solidified cement paste with more than 28 days of hydration. Both sample and reference are kept in a closed polystyrene flask maintained in a styrene foam cup. Respective thermistors with 0.03°C resolution are inserted into the sample and reference inside the cup. The temperature data are collected and sent on real time through a Vernier Lab Pro interface to a computer, being saved as a function of time. The samples are prepared into the polystyrene cup, mixing the cement and metakaolin amounts and adding afterwards to the respective amount of water of each sample. More details of the measuring system can be found in a previous paper [20].

Deconvolution of NCDTA curves

NCDTA curves show the sum of exothermic effect due to the simultaneous reactions that occur during paste or mortar component hydration process on cement mass basis. The main characteristic peaks were obtained by deconvolution of NCDTA curves, by using Peak FitTM software, which allows one to use several mathematical functions to obtain a set of peaks which sum must be the same than the original NCDTA curve. The tri-calcium aluminate (C_3A) hydration characteristic peaks were obtained by using

the non-linear chromatography function (NLC) and for the other peaks the best fit was obtained by using Gaussian function. The total evolved heat on cement mass basis was estimated from the accumulated peak area of NCDTA normalized curves.

Results and discussion

Figure 1 shows the specific heat capacity curves of the raw materials, which were obtained by MDSC. As can be seen, for a same temperature, metakaolin c_p values are practically twice of sand c_p values, which in turn presents lower c_p values than cement c_p values.

From Fig. 1 data, c_p values in $J g^{-1} °C^{-1}$ in the stabilized temperature range from 10 to 50°C, are re-

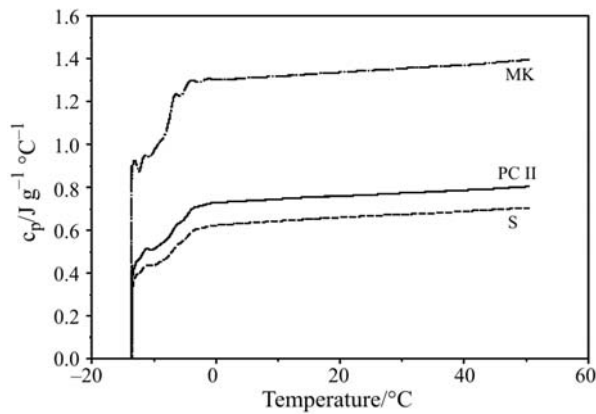


Fig. 1 Specific heat capacity values of the cement (PC II), metakaolin (MK) and sand (S)

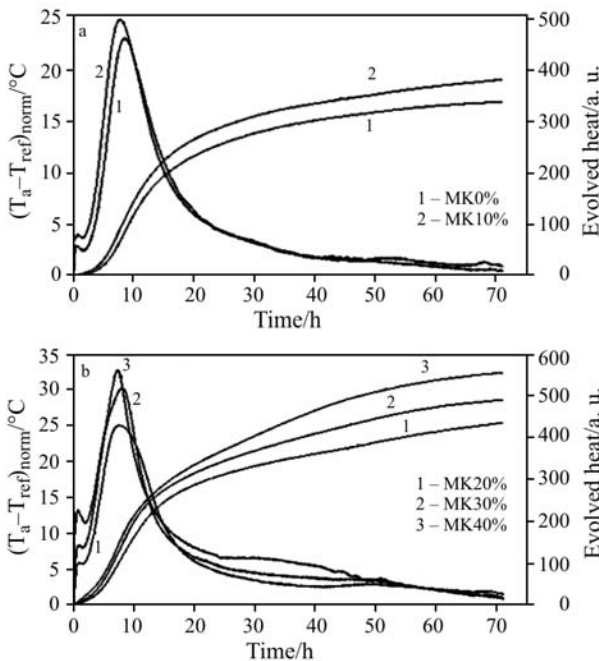


Fig. 2 Paste normalized NCDTA curves and respective accumulated evolved energies

spectively given by: $c_{pPCII}=0.0014T+0.7312$; $c_{pMK}=0.0019T+1.2998$ and $c_{pS}=0.0157T+0.682$, where T is the temperature in °C.

Figures 2a and b show the normalized NCDTA curves of the pastes and respective cumulative integral, which show the energy evolved as a function of time, in arbitrary units. The first peak of each curve, which occurs during the first 4 h, is characteristic of tricalcium aluminate (C_3A) hydration reactions and the second higher exothermic peak, which appears after 5 h of hydration, is characteristic to the tricalcium silicate (C_3S) hydration reactions [19]. During the first hours, the presence of metakaolin (MK), in partial substitution to cement, increases the calcium aluminate hydration reactions, which is evidenced by the higher peaks and accumulated energy generated in this period. The C_3S hydration reactions, represented by the second main peak are also enhanced by the partial substitution of cement by MK.

The accumulated evolved energy during the first 72 h of analysis evidences the pozzolanic activity of the metakaolin during the early hydration stages of the pastes. A 10% cement substitution degree by MK promotes an increase of almost 12% of the total evolved energy when compared to MK0% case. This increase of evolved energy is proportional to the cement mass substitution degree (CSD) and attains to almost 60% of the total energy of MK0% case, when CSD is 40%.

Figure 3 shows an example of the application of the deconvolution software to the NCDTA curve for MK0% case, which was used as control sample. The upper curve is the original curve and the below deconvoluted set of peaks are those which sum is equal to the original one. During the first hours of cement hydration, the first deconvoluted peak (P1) is characteristic to C_3A hydration, in the presence of calcium sulfate forming ettringite. This stage, as corresponds to a pre-induction or dormant period [21], where the C_3S hydration rate is very low due to the presence of ettringite ($CaO \cdot Al_2O_3 \cdot 3SO_4 \cdot 32 \cdot H_2O$),

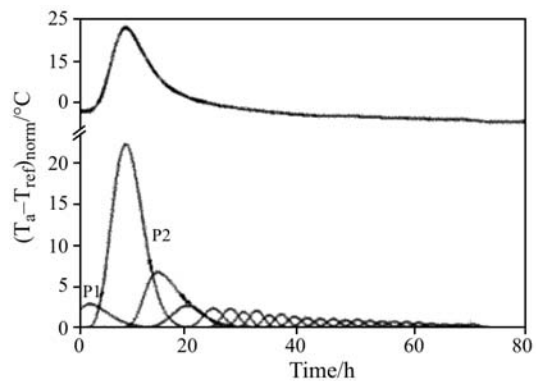


Fig. 3 Deconvolution of the NCDTA normalized curve of sample MK0%

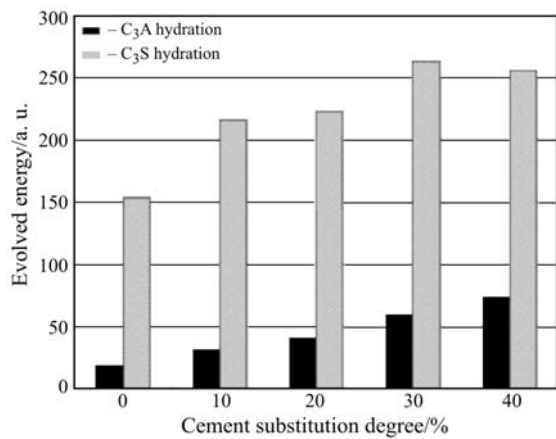


Fig. 4 Energy evolved by C₃A and C₃S hydration steps during the hydration of pastes at different cement substitution degrees by MK

which coats cement particles. Between 4 and 14 h a second and more higher peak (P2) is observed, due mainly to C₃S hydration and consequent tobermorite (3CaO·2SiO₂·xH₂O) and calcium hydroxide (Ca(OH)₂) formation. During this stage, which corresponds to the accelerating period, the reaction media attains a maximum energy release rate expressed by the maximum of the second NCDTA peak. The following shown peaks are due to the reactions that occur in the post-acceleration period.

Figure 4 shows the values of P1 and P2 peak area for the several analyzed pastes, which are proportional to the total heat, which is evolved during respectively C₃A and C₃S hydration stages. As can be seen, the presence of MK in the pastes provokes an almost linear increase of the C₃A hydration degree. There is also an increase in C₃S hydration but in MK40% case there is a decrease with respect to MK30% case, which presented the highest energy evolved in this step. This can be due to a lower available quantity of calcium hydroxide for the additional pozzolanic MK reaction, or to lower available water because of the higher amount consumed in the previous higher C₃A hydration, as observed by Dweck *et al.* [19] in a study by NCDTA of the solidification process of tannery waste by slag cement.

As shown by Figs 5a and b, the NCDTA curves of the mortar samples show a similar behavior to that of the pastes, but the total accumulated energy at the end of 72 h is higher than the paste cases.

The presence of a significant relative quantity of sand also promoted a higher water quantity available in the reacting system, due to the maintenance of the same water to total solid mass ratio than in the pastes.

Although this decision was taken to have a same operating parameter and because the additional water is effectively needed to maintain a good initial workability, this additional water may have enhanced the many simultaneous hydrations reactions. The addi-

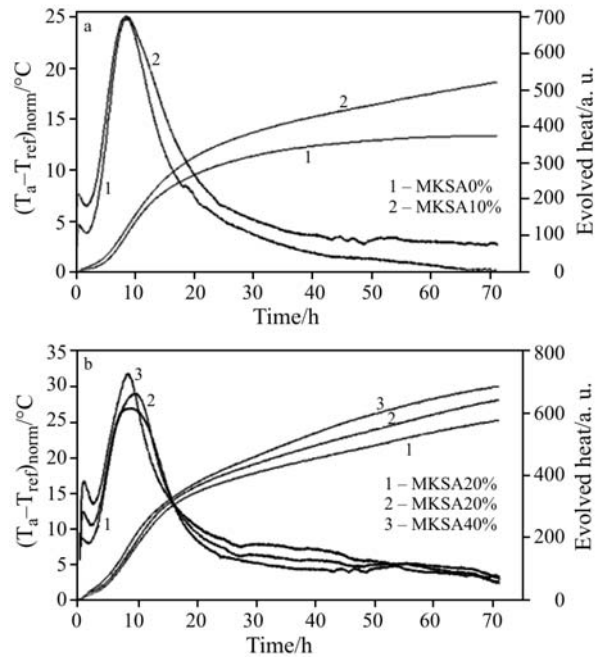


Fig. 5 Mortar normalized NCDTA curves and respective accumulated evolved energies

tional available water increases the possibility of a higher degree of cement hydration, generating more calcium hydroxide. It also increases the available amount of dissolved calcium hydroxide, increasing the rate of pozzolanic activity of MK, forming more calcium aluminate and silicate hydrated products. All these enhanced exothermic reactions contribute to a higher evolved energy per unit mass of cement and as a consequence, higher reaction media temperatures and normalized NCDTA signals as well.

Figure 6 shows the energy evolved by C₃A and C₃S hydration steps during the hydration of the mortar prepared with different MK substitution degrees, from respective P1 and P2 deconvoluted peak area of NCDTA curves. As can be seen, the higher is the pres-

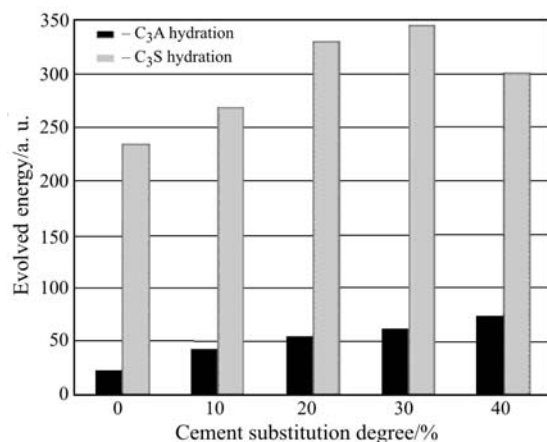


Fig. 6 Energy evolved by C₃A and C₃S hydration steps during the hydration of mortars at different cement substitution degrees by MK

ence of MK in substitution to cement in mortars, the higher is the C_3A hydration degree, and the higher is the C_3S hydration as well up to the case of 30% of CSD. As occurred in the pastes, when CSD is increased to 40%, this behavior is not seen, and a little reduction on the total evolved energy occurs, indicating that the total pozzolanic reactivity of MK with respect to the calcium silicates hydration is lower at these experimental conditions. This behavior also can be due to a lower calcium hydroxide present formed from the lower initial cement quantity present in the mortar, as occurred in the similar case of paste hydration.

Ambroise *et al.* [22] studying the system composed by C_3S and MK through isothermal conduction calorimetry at 25°C concluded that for values of C_3S substitution higher than 40% of MK, metakaolin acts as an inert in the C_3S hydration process.

This confirms the possibility of the decrease of pozzolanic activity of MK when present in the studied pastes and mortars at CSD values higher than 30% and indicates that the C_3S hydration peak evolved energy obtained by deconvolution of NCDTA normalized curves is a parameter that can be used as an indication of the evolution of the MK pozzolanic activity in cement pastes and mortars.

Conclusions

From NCDTA curves it can be noticed, in real time, that the substitution of cement by MK accelerates the early stages of hydration of cement pastes and mortars, which evidences the metakaolin pozzolanic activity during these stages.

Deconvolution of NCDTA curves allows one to obtain the respective NCDTA peaks of the first two main cement hydration steps (calcium aluminate and silicate hydration) and the relative energies generated from respective exothermic effects for each cement substitution degree (CSD).

When CSD is changed from 10 to 30% in pastes or mortars, the higher is the CSD by MK, the higher is the total evolved energy at 72 h of hydration, from calcium aluminate and calcium silicates hydration and other simultaneous reactions due to the pozzolanic reactions promoted by MK.

When CSD is increased from 30 to 40% the calcium aluminate hydration continues showing an increase of evolved energy but the opposite occurs with the total energy evolved from calcium silicate hydration showing a decrease on total MK pozzolanic activity.

Ettringite and tobermorite formation is more enhanced in mortars than in pastes for a same CSD degree by the presence of MK, with a maximum formation at 30% of CSD.

Obtained from the deconvolution of NCDTA normalized curves, the area of C_3S hydration peak, which is proportional to the total energy evolved from respective exothermic effect, is a parameter that can be used to study the evolution of the MK pozzolanic activity in cement pastes and mortars.

Acknowledgements

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