

# LIME-METAKAOLIN HYDRATION PRODUCTS: A MICROSCOPY ANALYSIS

## PRODUKTI HIDRACIJE APNO-METAKAOLIN: MIKROSKOPSKA ANALIZA

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Metakaolin (MK) is nowadays a well-known pozzolanic material being used in cement-based materials, like mortars and concretes. The reaction of MK with calcium hydroxide yields cementitious products, being calcium silicate hydrate (CSH), stratlingite ( $C_2ASH_8$ ) and tetra calcium aluminium hydrate ( $C_4AH_{13}$ ) the main phases formed at ambient temperature. The transformation of stratlingite and  $C_4AH_{13}$  into hydrogarnet at long term is an important issue that may result in an increase in the porosity and a loss of compressive strength that can induce a complete material degradation.

With the objective of studying the compounds formed in lime/MK pastes and their stability during time, blended pastes were prepared with several substitution rates (in weight) of lime by MK, and maintained at RH > 95 % and  $23 \pm 2$  °C. XRD and TGA-DTA were used to follow the kinetics of the lime/MK hydration as well the reaction products. Microscopic tests (SEM-EDS) results are performed and compared with the thermal and mineralogical data. The results obtained show that the quantity of the hydration products formed changes with the lime replacement, being the aluminum and calcium silicates more abundant in the higher MK content pastes, and  $C_4AH_{13}$ ,  $C_4ACH_{11}$  and  $C_2ASH_8$  the major phases formed up to 90 days of curing.

Keywords: microscopy, XRD, TGA-DTA, lime, metakaolin

Metakaolin (MK) je danes dobro poznan pocolanski material in se uporablja v gradivih na podlagi cementa, npr. malta in beton. Reakcija MK s kalcijevim hidroksidom ustvari cementne proizvode: kalcijev silikatni hidrat (CSH), stratlingit ( $C_2ASH_8$ ) in tetra kalcij aluminijev hidrat ( $C_4AH_{13}$ ) kot glavne faze, ki nastanejo pri temperaturi okolice. Transformacija stratlingita in  $C_4AH_{13}$  v hidrogarnet po dolgem času je proces, ki lahko poveča poroznost in zmanjša tlačno trdnost ter lahko povzroči popolno degradacijo materiala.

S ciljem raziskave spojini, ki so nastale v zmesih apna-MK, in njihove časovne stabilnosti smo pripravili mešane mase z več deleži zamenjave (v masi) apna z VK in zorili pri RH > 95 % in  $23 \pm 2$  °C. XRD in TGA-DTA so bile uporabljene za spremljanje kinetike hidracije apna-MK in reakcijskih produktov. Rezultate mikroskopskih opazovanj (SEM-EDS) smo primerjali s termalnimi in mineraloškimimi podatki. Dobljeni rezultati kažejo, da količina hidracijskih produktov z nadomestitvijo količine apna količina aluminijevih in kalcijevih silikatov raste z vsebnostjo MK v masi in so  $C_4AH_{13}$ ,  $C_4ACH_{11}$ ,  $C_2ASH_8$  glavne faze, nastale po 90 dneh zorenja.

Glavne besede: mikroskopija, XRD, TGA-DTA, apno, metakaolin

## 1 INTRODUCTION

During the past decade, metakaolin (MK), a thermally activated aluminosilicate material ( $Al_2O_3 \cdot 2SiO_2$ ) obtained by calcination of clay or soil rich in kaolinite ( $Al_2(OH)_4Si_2O_5$ ), within the temperature range of 700–850 °C<sup>1</sup>, has been the objective of several research studies, mainly due to its capacity to react vividly with calcium hydroxide (pozzolanicity). Recent studies<sup>2</sup> showed that MK is a very effective pozzolan, altering the pore structure of the lime and cement pastes and greatly improving its resistance to the transport of water and diffusion of harmful ions through the matrix, supporting the idea of its beneficial addition in blended mortars, cement pastes and concrete.

The reaction between MK, calcium hydroxide and water results in the formation of hydraulic products. At ambient temperature the main phases/products formed are calcium silicate hydrate gel (CSH), stratlingite ( $C_2ASH_8$ ) and tetra calcium aluminium hydrate ( $C_4AH_{13}$ ). According to literature<sup>3</sup>, it is possible to

assume that these hydration phases are linked to lime/MK ratio, temperature, and also to the presence of various activators. However, reference to variations regarding these phase's stability has been shown in literature<sup>4</sup>. As stated by P. S. Silva and Glasser, transformation of stratlingite and  $C_4AH_{13}$  into hydrogarnet ( $C_3AH_6$ ) at long term may lead to a volume reduction, producing an increase in porosity and a loss of microstructural compactness, i.e., less mechanical strength.

Having the aim of studying the compounds obtained in lime/MK pastes and their stability overtime, it is important to discuss a possible conversion of metastable hexagonal hydrates ( $C_2ASH_8$  and  $C_4AH_{13}$ ) to stable cubic phase (siliceous hydrogarnet with variable composition,  $C_3AS_xH_{6-2x}$ ), when samples are submitted to ambient curing temperatures at long term ages, negatively influencing the performance of MK blended matrixes, especially on durability<sup>5</sup>.

Most of the works published up to now on lime/MK systems are focused on reaction kinetics and on its interaction with Portland cement<sup>3,5,6</sup>. However, there is

little information on microstructure and mechanical characteristics of the lime/MK pastes<sup>6</sup>.

In order to study the development of hydration phases of the lime/MK systems, pastes with different mixing mass ratios of lime/MK were prepared and afterwards cured at 23 °C and RH > 95 %.

At certain curing ages, XRD and TGA-DTA were used to follow the kinetics of the blended MK pastes as well the reaction products formed, while microscopic tests (SEM-EDS) results are performed and compared with the thermal and mineralogical data.

## 2 EXPERIMENTAL

The mix procedure consisted in mixing the amount of lime with the total amount of water, which was stirred for about 3 min using an external mixer, after which MK was added slowly, maintaining the mixing for further 20 min.<sup>7</sup> The pastes were then stored in open plastic containers and introduced in a sealed chamber at RH > 95 % and 23 ± 2 °C, to maintain on-going hydration reactions. The hydration was stopped after each predetermined curing time, subjecting the samples to acetone for complete removal of the free water, after which they were then dried at 40 °C, in order to be tested by XRD, TGA-DTA and SEM-EDS. The metakaolin used was ARGICAL M1200S from IMERYS with the mass fractions SiO<sub>2</sub> ≈ 55 % and Al<sub>2</sub>O<sub>3</sub> ≈ 39 % regarding chemical composition, while the lime used was a commercial Portuguese (Lusical H100) hydrated lime with a chemical composition of Ca(OH)<sub>2</sub> ≥ 93 and MgO ≤ 3, with classification CL90, according to the NP EN 459-1(2002) standard.

The evolution of the kinetic reactions as well as the phases formation was evaluated by X-ray diffractometry (XRD), thermogravimetric and differential thermal analysis (TGA-DTA) and scanning electron microscopy with X-ray microanalysis (SEM-EDS). The experimental conditions used are previously published<sup>8</sup>.

## 3 RESULTS AND DISCUSSION

In order to illustrate the main results obtained two pastes were selected with lime/MK mass ratios of 1/1 and 1/0.2.

### 3.1 X-ray diffraction analysis (XRD)

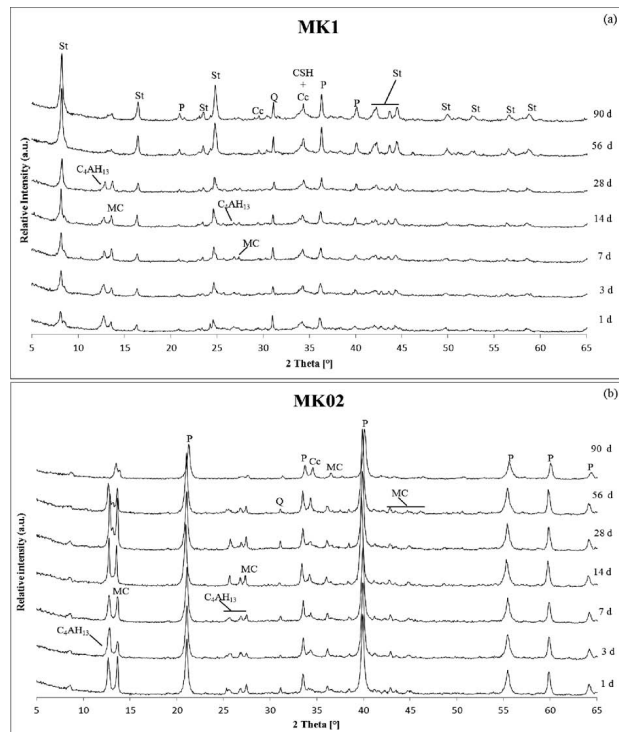
XRD patterns are illustrated in **Figures 1a** and **b**. A peak attributed to stratlingite (C<sub>2</sub>ASH<sub>8</sub>) is noted for paste MK1. The stratlingite tends to increase with the curing time, becoming the dominant phase, whereas significant amounts of monocarboaluminate (C<sub>4</sub>A $\bar{C}$ H<sub>11</sub>), quartz, calcite, calcium silicate hydrates (CSH) and calcium aluminate hydrates (C<sub>4</sub>AH<sub>13</sub>) are observed. Although in paste MK02 stratlingite is not detected by XRD, it is possible that it may be present in very low, undetected

quantity. An interesting result was also observed in paste MK1 up to 28 d of curing regarding the presence of calcium aluminates hydrates (C<sub>4</sub>A $\bar{C}$ H<sub>11</sub> and C<sub>4</sub>AH<sub>13</sub>), whereas at further ages (56 d and 90 d) only traces of these compounds are identified, presumably signifying that a decomposition of these phases may have occurred. Traces of crystallized CSH were detected in higher MK mixes.

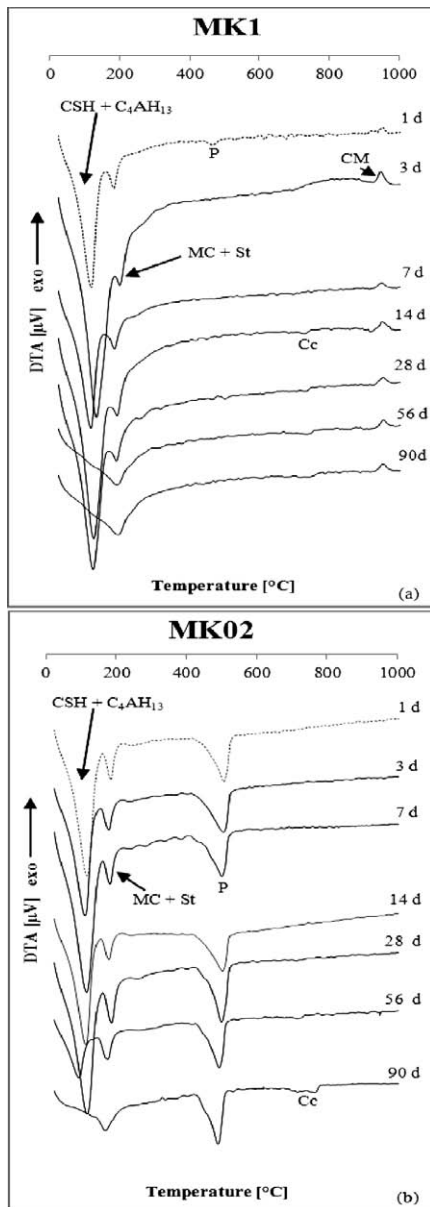
In MK02 paste high amounts of portlandite (CH) are observed, however a maximum peak is noticed for 56 d and 90 d of reaction, possibly due to the decomposition of C<sub>4</sub>AH<sub>13</sub> and monocarboaluminate, liberating more portlandite to the system, also observed for paste MK1. The XRD confirms also up to 90 d the non-formation of hydrogarnet phase for both pastes, which can be explained due to the fact that this compound is associated with higher curing temperatures. Reports of the absence of hydrogarnet until 270 d of curing time are shown by other authors<sup>6</sup>.

An important reference must be attributed to the fact that for both pastes the calcite (CaCO<sub>3</sub>) content tends to increase up to 90 d of curing.

Several studies have reported the appearance C<sub>4</sub>AH<sub>13</sub> or C<sub>4</sub>A $\bar{C}$ H<sub>11</sub> and C<sub>2</sub>ASH<sub>8</sub> and CSH at 20 °C<sup>5</sup> as the reaction products of the lime/MK hydration reaction. In other studies<sup>4</sup>, C<sub>2</sub>ASH<sub>8</sub> and CSH are considered the main phases formed, however in this research, the formation



**Figure 1:** XRD patterns for a) MK1 and b) MK02; Cc – calcite; P – portlandite; MC – monocarboaluminate; St – stratlingite; CSH – calcium silicate hydrate; C<sub>4</sub>AH<sub>13</sub> – tetracalcium aluminium hydrate  
**Slika 1:** XRD-spektri za a) MK1 in b) MK02; Cc – kalcit, P – portlandit, MC – monokarboaluminat, St – stratlingit, CSH – kalcijev silikat hidrat, C<sub>4</sub>AH<sub>13</sub> – tetrakalcij aluminijev hidrat

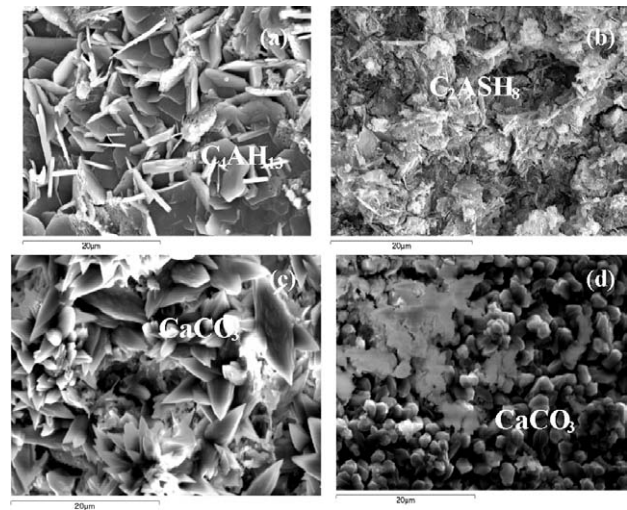


**Figure 2:** DTA curves for a) MK1 and b) MK02; P – portlandite; CM – cristoballite and mullite; St – stratlingite; CSH – calcium silicate hydrate; Cc – calcite; MC – monocarboaluminate;  $C_4AH_{13}$  – tetracalcium aluminum hydrate  
**Slika 2:** DTA-spektri za a) MK1 in b) MK02; P – portlandit, CM – kristobalit in mulit, St – stratlingit, CSH – kalcijev silikat hidrat, Cc – kalcit, MC – monokarboaluminat,  $C_4AH_{13}$  – tetrakalcijev aluminijev hidrat

of CSH,  $C_4AH_{13}$ ,  $C_4\bar{A}CH_{11}$  and  $C_2ASH_8$  have been identified.

### 3.2 TGA-DTA analysis

Figures 2a and b present the DTA curves of MK1 and MK02. The sharp peak observed at about 110 °C can be attributed to the presence of CSH and  $C_4AH_{13}$ , being sharper for 28 d, disappearing after 90 d of reaction. The characteristic peak of stratlingite, which appears as a sharp peak at about 190 °C, can be observed for MK1,



**Figure 3:** SEM micrographs of MK1 and MK02 at ages 28 d and 90 d: a) SEM image of MK1 paste at 28 d where the presence of hexagonal  $C_4AH_{13}$  is visible; b) SEM image of MK1 at 90 d where is visible the predominance of  $C_2ASH_8$ ; c) SEM image of MK02 at 28 d of curing; revealing the presence of  $CaCO_3$ ; d) SEM image of MK02 paste at 90 d of curing where is visible an increase in the paste carbonation rate  
**Slika 3:** SEM-posnetki MK1 in MK02 po zorenju 28 d in 90 d: a) SEM-posnetek MK1-mase po 28 d, kjer je viden heksagonalni  $C_4AH_{13}$ , b) SEM-posnetek MK1 po 90 d, kjer je vidna prevlada  $C_2ASH_8$ , c) SEM-posnetek MK02 po 28 d, ki dokazuje prisotnost  $CaCO_3$ , d) SEM-posnetek MK02, kjer se v masi vidi rast hitrosti karbonacije

however, a broader peak after 90 d of curing. In the same range of temperature ( $\approx 160\text{--}220$  °C) the dehydration of  $C_4\bar{A}CH_{11}$  (monocarboaluminate) occurs.

For paste MK1 a small broad peak at about 480 °C is present at 1 d reaction, indicative of the existence of free portlandite, being almost consumed after 1 d of curing (Figure 2a). Instead, for paste MK02, a sharper band can be seen at approximately 500 °C (Figure 2b), due to free portlandite in the reaction.

As referred above at about 950 °C, a sharp exothermic peak was only observed for paste MK1, attributed to the formation of high-temperature phases such as mullite and cristobalite, as described by Bakolas, appearing due to the existence of "free" MK. These peaks do not appear in paste MK02 due to the total amount of MK being rapidly consumed.

### 3.3 SEM results

Figures 3a, b, c and d show the main results of the SEM-EDS. Paste MK1 at 28 d of reaction presents (Figure 3a) a well-crystallized matrix, with large amounts of  $C_4AH_{13}$ ; instead at 90 d of curing (Figure 3b) the paste matrix is more "densified" and less crystalline with a large presence of stratlingite. In paste MK02 (Figures 3c and d), the microstructure "evolution" does not vary like in MK1 from 28 d to 90 d, remaining as a crystalline microstructure, revealing high amounts of calcite.

#### 4 CONCLUSIONS

The influence of the lime/MK ratio was studied at ambient temperature and RH > 95 %. According to the results obtained the products formed are the same for all blended mixes, while the amount formed changes with the MK content, being the aluminum ( $C_4AH_{13}$ ,  $C_4\overline{A}CH_{11}$ ) and calcium silicates ( $C_2ASH_8$ ) more abundant in the higher MK content pastes. SEM results show that for MK1 at 28 d the microstructure consists essentially of  $C_2ASH_8$  and  $C_4AH_{13}$  and  $C_4\overline{A}CH_{11}$ , while at 90 d of curing there is a significant decrease of the presence of calcium aluminate hydrates, and a predominance of stratlingite. On the contrary, the MK02 paste reveals a highly crystalline microstructure, with predominance of calcite. Up to 90 d of curing time, no hydrogarnet presence is detected, in any of the blended pastes studied. A decrease in the amount of  $C_4AH_{13}$  and  $C_4\overline{A}CH_{11}$  with curing time is verified, not followed by a decrease in microstructural porosity, that may influence for mixtures with low MK content a decrease in the mechanical resistance of the blended lime/MK mixes. The results show the formation of hydration products that may confer mechanical resistance to lime/MK mortars.

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