Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 35 (2005) 1292–1298

Cement and Concrete Research

Influence of metastable hydrated phases on the pore size distribution and degree of hydration of MK-blended cements cured at 60 °C

Moisés Frías Rojas*, M.I. Sánchez de Rojas

Eduardo Torroja Institute (CSIC), c/ Serrano Galvache, n.4, 28033 Madrid, Spain

Received 19 January 2004; accepted 20 October 2004

Abstract

When MK reacts with calcium hydroxide, cementitious products are formed. It has been reported that CSH, C_2ASH_8 and C_4AH_{13} are the most important hydrated phases formed. These phases are stable at 20 °C. However, some of them (C_2ASH_8 and C_4AH_{13}) are metastable phases, converting to hydrogarnet (C_3ASH_6) for long curing times at elevated temperatures. The partial or total conversion reaction could produce a negative effect on the performance and durability of blended cements, due to a volume decrease associated with the process of transformation.

Due to the influence that this conversion could have on the microstructure and durability of a cement paste containing MK, the current paper presents the results of a research programme carried out on blended cements containing 10%, 20% and 25% of MK, cured at 60 °C up to 124 days of hydration.

The total, partial porosity and average pore diameter evolution vs. time is determined using mercury intrusion porosimetry (MIP). An estimated degree of hydration of MK-blended cements cured at 60 °C is proposed.

The results show that there is no increase in porosity values and average pore diameters with time. Therefore, the hydrated phases produced in MK-blended cements under the test conditions used do not have a negative effect on the microporosity. A suitable correlation between porosity and degree of hydration has been found.

Keywords: MK-blended cement; High temperature; Metastable phases; Pore size; Hydration degree

1. Introduction

Natural pozzolans have been used since antiquity with excellent results for the production of durable concrete [1]. By-products as pozzolanic additions are also routinely used for the manufacture of commercial portland cements and high-performance concretes, due to their positive influence on the microstructure and durability of blended concretes [2–4].

Recently, some activated materials such as metakaolin (MK), which is obtained by thermal activation of kaolinite, have been shown to be excellent pozzolans [5–7]. Frías et al. [8] and subsequently Bai and Wild [9] reported that, due to its high pozzolanic activity, the temperature rise in MK-blended pastes can be greater than that observed in plain OPC at early ages, due to the double exothermic effect of the pozzolanic and hydration reactions. This phenomenon could lead to negative influences on durability aspects, particularly in large volume mass concrete causing thermal stress, cracking and loss of strength.

The pozzolanic reaction between MK and lime at 20 °C produces the cementitious compounds C_2ASH_8 and C_4AH_{13} and CSH gel. The proportion, appearance, evolution and stability of these phases depend on different factors including the chemical and mineralogical composition of MK, the MK/lime ratio, the presence or absence of activators and the temperature [10–16].

MK has been shown to modify the pore size distribution of mortars and pastes cured at 20 °C. Khatib and Wild [17]

---

* Corresponding author. Tel.: +34 91 30 20 440x220; fax: +34 91 30 20 700.

E-mail address: mfrias@ietcc.csic.es (M.F. Rojas).

0008-8846/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2004.10.038

reported a refinement of the pore structure and a total intruded pore volume increase between 14 an 28 days for pastes with 5%, 10% and 15% of MK. Subsequently, Frías and Cabrera [18 19] reported that MK has a positive effect on the pore size distribution of pastes with 10%, 15%, 20% and 25% of MK cured at 20 °C for up to 360 days and demonstrated a good statistical relationship between the degree of hydration and the porosity.

In spite of the excellent qualities developed by MK as pozzolanic material, the possible conversion of some hexagonal hydrates (C_2ASH_8 and C_4AH_{13}) at elevated temperatures could result in problems in its use. De Silva and Glasser [20] have reported, for the MK–lime-water system, significant changes in the phase development pattern with curing temperature (from 20 °C to 55 °C). The C_2ASH_8 and C_4AH_{13} are metastable phases and can convert to hydrogarnet (C_3ASH_6) over long curing periods at elevated temperatures. The consequence of a partial or total conversion reaction would be an increase of porosity and, therefore, a loss in performance and durability. The maximum volume reduction associated with the process of conversion was calculated to be 13.3%.

However, Cabrera and Frías [21] and subsequently Frías et al [22] have reported, in MK/lime systems cured at 60 °C, that hydrogarnet can be formed directly from the reaction between MK and lime and not from a transformation reaction. Furthermore, they have stated that the matrix plays an important role in the formation of hydrogarnet. So, in MK-blended cement matrices cured at 60 °C, there was no clear evidence of hydrogarnet formation [23]. These analytical results are not in agreement with the predictions of De Silva and Glasser [20].

From an engineering point of view, the use of MK in the manufacture of blended cement matrices is practically limited to laboratory studies due to the absence of experimental data that confirm technically the stability of theses matrices at high temperatures. The nature and development of porosity can be a good indicator of performance and this can be assessed by analysing the evolution of pore structure of blended cement pastes when curing at high temperatures.

Therefore, an investigation was undertaken on the influence of MK on the pore size distribution of blended cement pastes containing 10%, 20% and 25% MK, cured at 60 °C. In addition, an estimated degree of hydration is roughly proposed for these MK-blended cement pastes.

2. Experimental

2.1. Preparation of specimens and curing

A commercial metakaolin and a white portland cement (PC) available in UK were used for this study. The compositions of MK and cement are given in Table 1 as well as some physical properties.

Table 1
Chemical composition and physical properties of the cementitious materials used

Oxide(%)/physical properties	White cement	Metakaolin
SiO_2	20.40	51.60
Al_2O_3	5.02	41.30
Fe_2O_3	0.30	4.64
CaO	64.25	0.09
MgO	2.83	0.16
SO_3	2.63	–
Na_2O	0.39	0.01
K_2O	0.84	0.62
TiO_2	0.21	0.83
LOI	1.70	0.60
Rel. density (g/cm^3)	3.27	2.66
BET surface area (m^2/g)	1.04	15.00

Four different pastes were prepared. PC was partially replaced by 0%, 10%, 20% and 25% of MK. The water/binder ratio was 0.55 by weight. The mixtures were placed in plastic airtight containers and then left in an oven at 60 °C. After the predetermined curing time (1.25, 3, 9, 34 and 124 days), the hydration reaction was stopped using two different techniques, depending on the parameter to be studied:

(a) Vacuum oven drying. The samples were dried in air at 50 °C and a maximum vacuum of −1 bar to constant mass (after 3 days). This method was used for mercury porosity tests (MIP).
(b) Microwave oven drying. This procedure described in Ref. [19] was suitable for rapid drying of samples. This method was used for DTA and TG tests.

2.2. Techniques of testing

Total and partial porosities and pore size distribution measurements were made using a Micromeritic Autopore Model 9320 instrument. This Mercury Intrusion Porosimetry (MIP) instrument is capable of measuring pore size diameters down to 6.0 nm.

Free calcium hydroxide contents were determined by thermogravimetric analysis (TGA) using an STA 780 Thermal Analysis Instrument. Samples of between 12 and 16 mg of powder were heated at a heating rate of 20 °C min^{-1} in an N_2 atmosphere.

3. Results and discussion

3.1. Evolution of the total and partial porosities.

The total and partial porosities vs. hydration time for all pastes are shown in Fig. 1. In this work, the partial porosity is defined as the porosity in each of two fixed pore size intervals (between 1 and 0.1 μm and below 0.1 μm).

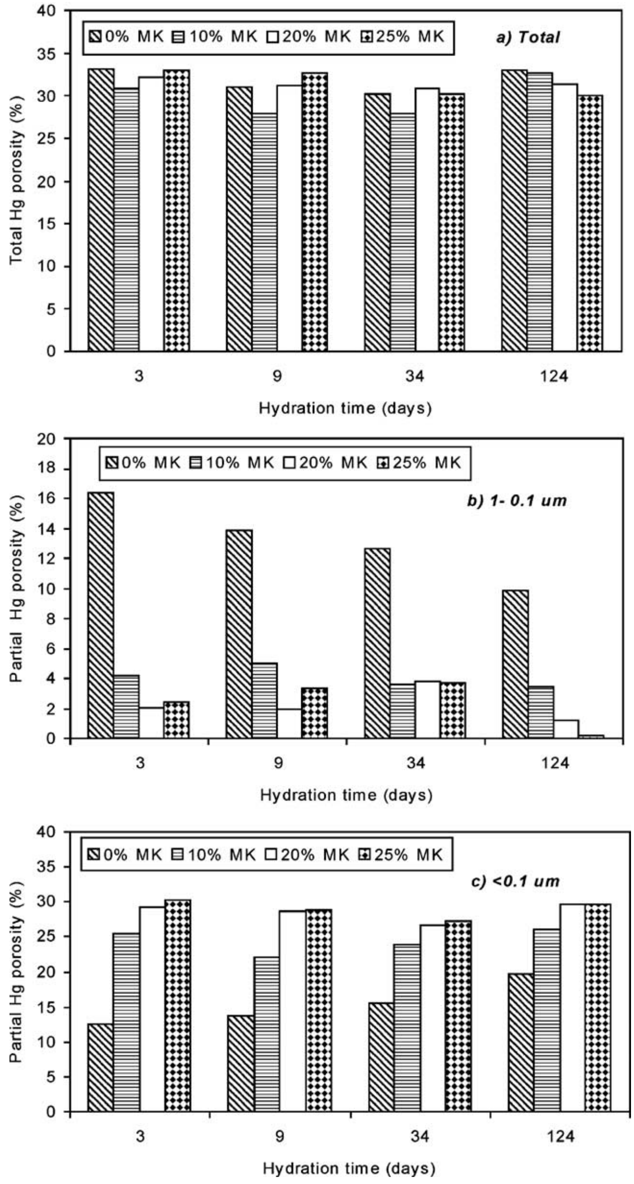

Fig. 1. Evolution of porosity with the hydration time.

After 3 days (Fig. 1a), all pastes show very similar total porosity (31–33%). The lowest value of porosity corresponds to the blended paste containing 10% MK (31% total porosity), the value increasing with an increase in MK content. With 25% MK, the total porosity is the same as that obtained for the control paste (33.02% and 33.06%, respectively).

Beyond 3 days, the differences in the total porosity between control paste and the MK-blended pastes vary very little. So, between 3 days and 124 days of curing, MK-blended pastes cured at 60 °C show no significant or systematic changes in their total porosity. This suggests that the most important microstructural changes occur in the early hours of hydration.

It is well known that an increase in curing temperature accelerates the hydration reaction. Comparing the data obtained at 60 °C in the current study with those obtained by Frías and Cabrera at 20 °C [18] reveals differences in the development of total porosity. In MK-blended pastes cured at 20 °C, there was a continuous reduction in porosity with hydration time up to 28 days; while for the same blended pastes cured at 60 °C, the total porosity values show small non- systematic variations for hydration times above 3 days.

With respect to the partial porosities of pastes cured at 60 °C a clear difference is observed between pastes with and without MK. From Fig. 1b and c, it appears that for each curing period, as the MK content increases the proportion of coarse porosity (d=1–0.1 μm) decreases and the proportion of fine porosity (d<0.1 μm) increases. It is also apparent (both from Fig. 1b and c) that when increasing the curing time, the control PC shows continuous pore refinement, whereas the PC-MK blends show little systematic change in porosity for hydration periods between 3 days and 124 days. This indicates that the incorporation of MK affects the microporosity of blended pastes at very early ages (below 3 days of curing); beyond this age, the microporosity of MK-blended pastes do not show any significant changes.

This very early pore refinement process in MK-blended pastes is also apparent from the average pore diameter data (Fig. 2). For PC paste, the average pore diameter decreased from 67 nm to 33 nm for curing times between 3 and 124 days. The incorporation of MK modifies substantially the pore structure, and a strong reduction in the average pore diameter is observed for all MK-blended pastes. Values of average pore diameter between 20 and 30 nm were detected.

It is important to point out that a slight increase of this parameter was observed between 3 and 9 days of curing for MK-blended pastes. This could be related to the end of the acceleration stage of the pozzolanic reaction, as will be mentioned later. For longer hydration times (>9 days), the average pore diameters showed little variation in MK-blended pastes, and after 124 days, the values found are similar to those found at the beginning of hydration (3 days).

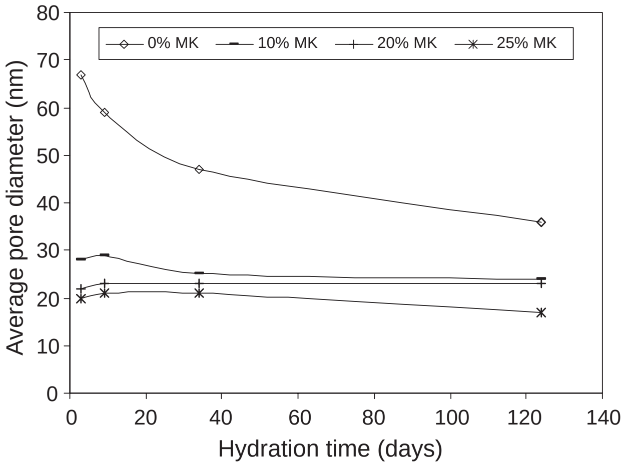

Fig. 2. Evolution of average pore diameter with the hydration time.

3.2. Evolution of the pore size distribution

Fig. 3 shows the frequency of pore sizes as a function of hydration time for the four pastes tested. A different behaviour in pastes made with or without MK was detected. For the 0% MK paste at 3 days of curing, a modal distribution is observed. An extensive interval of pore sizes was localised between 4 and 0.06 μm. For longer ages, a refinement of pore sizes was detected. At 124 days of curing, a well-defined maximum was localised about 0.1 μm.

For the MK-blended pastes, the same modal distribution was also observed in all cases. With the incorporation of MK in blended pastes, a refinement of pore sizes was observed with respect to the control PC paste. This refinement is closely related to the MK content. So, for the 10% MK pastes, an extensive interval was localised between 0.1 and 0.01 μm. For pastes with 20% and 25% of MK, a similar tendency was observed with curing time but the maximum value appeared at 0.035 μm and 0.016 μm, respectively. Therefore, the addition of 25% of MK produces the finest porous structure.

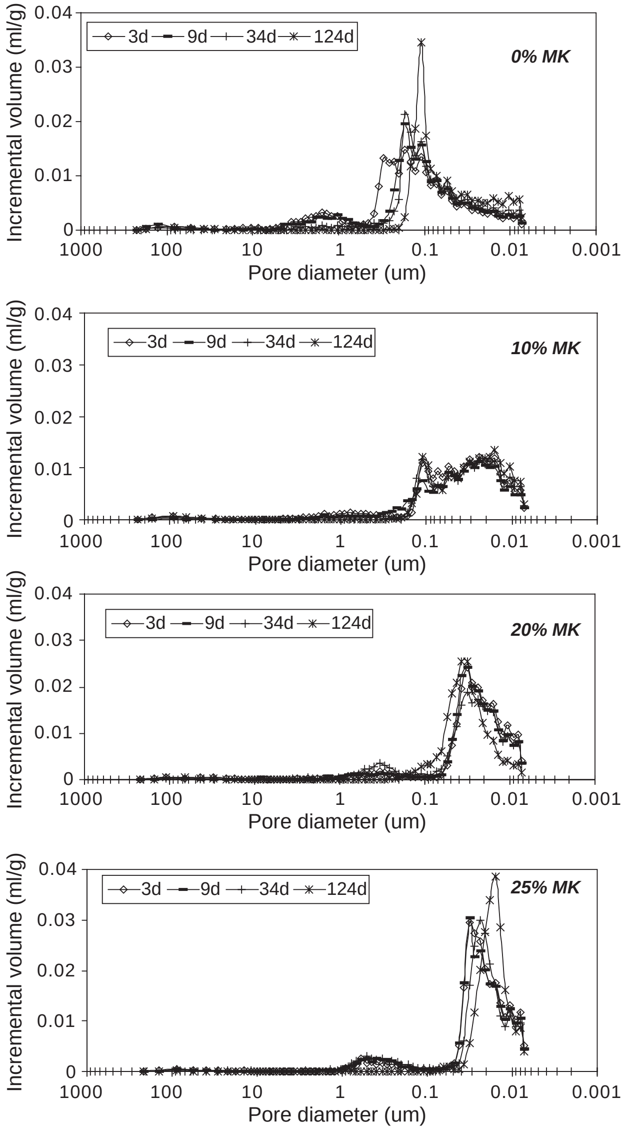

Fig. 3. Pore size distribution for blended pastes containing 0%, 10%, 20% and 25% of MK.

The data clearly confirm the existence of a refinement of the pore structure with the incorporation of MK. A more detailed study carried out on the finest pore sizes (between 0.1 and 0.01 μm) (Fig. 3) found little significant change of pore size distribution after 3 days of curing and no change of the pore size distribution towards coarser pore sizes was detected.

3.3. Evolution of the calcium hydroxide content with time

In order to estimate the degree of the hydration of the MK-blended cement pastes, it is necessary to know the total amount of free calcium hydroxide present in the hydrated system. The total free calcium hydroxide was calculated from the weight loss due to the dehydroxylation of $Ca(OH)_2$ and the decomposition of $CaCO_3$ (which was assumed to have formed from the carbonation of $Ca(OH)_2$). Fig. 4 shows the evolution of free calcium hydroxide with curing time up to 124 days. The principal features are:

(a) The free calcium hydroxide content of the control paste increased gradually with hydration time, as expected.

(b) For the MK-blended cement pastes, the free $Ca(OH)_2$ content showed two well-defined stages: the first stage corresponds to a decrease of free lime content, and the second stage shows an increase in free lime content. For the case of 10% and 20% of MK, the inflexion points of these two stages are located at 3 and 9 days, respectively. With 25% of MK, the free lime content maintains a small but unchanging value up to 9 days of hydration, and subsequently, its content increases with curing time.

The changes in gradients of the free lime content vs. hydration time curves are a result of the relative rates of lime consumption by the pozzolanic reaction and of lime production by PC hydration.

This evolution of free lime content in MK-blended pastes cured at 60 °C is very similar to that reported for the same pastes cured at 20 °C [18]; but in the first case, the inflexion points occurred at shorter times. This fact is in agreement with researches carried out by Frías and Cabrera [24]. They reported that in MK–lime mixes cured at 20 °C, the reaction rate constant was 0.18×10^{-4}, while at 60 °C of curing temperature was 15.1×10^{-4} for the same hydration period.

3.4. Degree of hydration

There are various methods for measuring the degree of hydration of OPC cements. However, the determination of

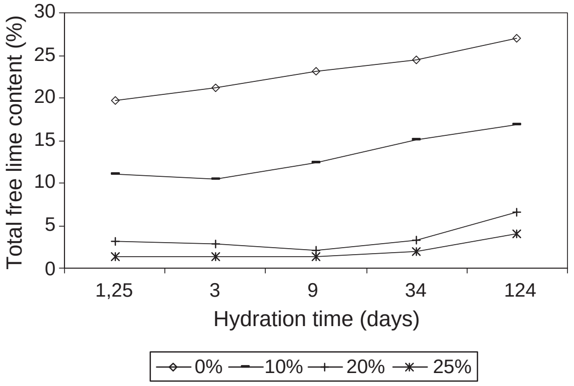

Fig. 4. Evolution of calcium hydroxide with hydration time.

the degree of hydration of blended cement systems is much more complicated. The progress of reaction between pozzolan and cement depends upon various factors and is highly related to the properties of pozzolans, hydration time and curing temperature.

The starting point of this study was the application of the method suggested by Cabrera for PFA–PC blended cements [25]. The decrease in the amount of $Ca(OH)_2$ present is an indication of the degree of hydration of a pozzolanic cement. The effect of PFA on the degree of hydration can be illustrated more clearly by expressing the $Ca(OH)_2$ content of PFA pastes as a percentage of OPC rather than of PFA–OPC. Recently, Frías and Cabrera [18] applied, for the first time, this method to MK-blended pastes cured at 20 °C. They reported a statistical relationship between the degree of hydration calculated from this method and the porosity from the MIP technique.

Based on this method, Fig. 5 shows a schematic representation of the CH percentages corresponding to 100% PC, x% PC+y% inert and x% PC+y% MK. Taking account of actual free lime contents obtained from the TG technique for the curves 100% PC and x% PC+y% MK and assuming that the curve x% PC+y% inert vs. time can be derived by reducing the CH(100%PC) curve by the fraction $y/100$; it is possible to estimate percent lime a_t consumed by the pozzolanic reaction as:

$$\mathrm{CH}_{(x\%\mathrm{PC}+y\%\mathrm{inert})_t} - \mathrm{CH}_{(x\%\mathrm{PC}+y\%\mathrm{MK})_t} = a_t$$

where a_t is the decrease of calcium hydroxide at time t due to the pozzolanic reaction. Therefore, the estimated total value of CH produced by the hydrating PC and expressed as a percentage of the PC content is:

$$a_t + (x\%\ \mathrm{PC} + y\%\ \mathrm{inert})_t.$$

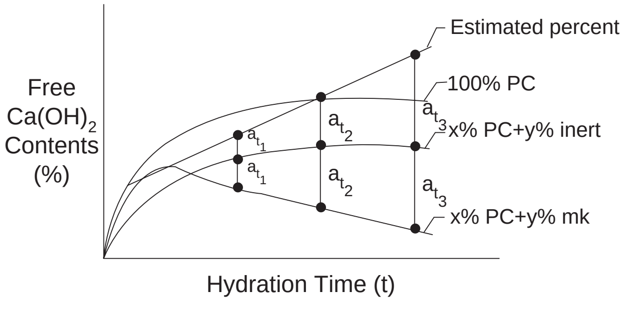

Fig. 5. Schematic diagram for the estimation of the amount of $Ca(OH)_2$.

The relative degree of PC hydration at time t for the MK/PC pastes is calculated as the quotient between the estimated percent CH values for the MK/PC paste (a) and the CH values for the 100% PC pastes (b) multiplied by 100 ($a/b \times 100$). The relative degree of PC hydration for MK/PC mixes cured at 60 °C vs. hydration time is represented in Fig. 6.

A detailed study of these results shows that the relative degree of hydration for the MK-blended cement pastes is above 100% for a hydration period between 1.25 and 124 days.

This fact is indicating the overlap between both reactions (hydration of cement particles with water and pozzolanic reaction between MK and calcium hydroxide produced during the hydration reaction of cement). The pozzolanic reaction forms well-known hydrated phases, such as CSH, C_2ASH_8, C_4AH_{13} and C_3ASH_6. Therefore, total hydrated phases produced in MK–PC pastes were higher than those in control cement paste (about 25% is free calcium hydroxide) and their contents will depend on the MK/lime ratio. So, with a 10% of MK, an increase of degree of hydration was observed between 1.25 and 3 days of curing. Subsequently, this value decreases with the hydration time. Pastes with a 20% of MK showed a higher degree of hydration. Up to 9 days of hydration time, a slight increase on the degree of hydration was observed, decreasing slowly for longer ages. A similar behaviour of the degree of hydration for the 25% MK paste is observed. In this case, the evolution of degree of hydration was practically constants up to 34 days of curing. Later than this age, a slight decrease was observed.

These inflexion points localised at 3, 9 and 34 days of hydration for contents of 10%, 20% and 25% of MK are closely related to the end of the acceleration stage of pozzolanic reaction and in consequence free calcium hydroxide content increased. This fact depends on different factors, which can be compatible at the same time: (a) to the total consumption of MK in some cases (10% of MK); (b) a

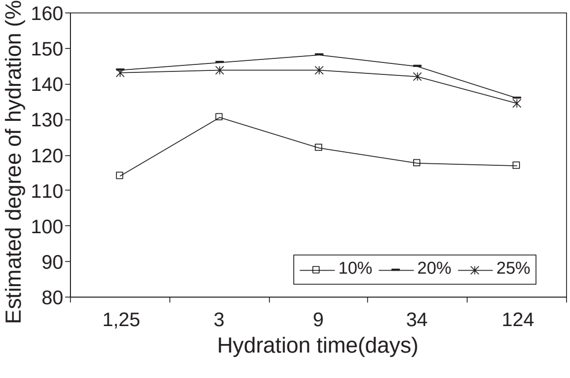

Fig. 6. Evolution of the estimated degree of hydration.

lack of mobility of Ca^{2+} ions in blended pastes with high MK contents (mainly with 20% and 25%), due to the refinement process of porous structure.

Therefore, it is possible to underline that from 1.25 to 124 days of hydration, the degree of hydration values increased or decreased in function of predominant reaction at each moment. An increase in the degree of hydration values means the pozzolanic reaction predominates over the hydration one and vice versa.

These findings are in agreement, on one hand, with the results mentioned above (Fig. 4) and, on the other hand, with the results obtained in a previous paper carried out by one of the authors of the current paper [21]. They reported that the pozzolanic reaction was more important before 9 days of hydration time in MK/lime mix at 60 °C (1:1 in weight).

The current authors would like to underline an important phenomenon shown in Fig. 6. The degree of hydration value corresponding to the blended pastes with a 25% of MK was slightly lower than that with a 20% of MK. At the first view, this value could lead to false opinions; however, this behaviour could be justified as a result of a large MK content. Two phenomena happen: (a) a replacement value above 20% of MK means that this acts as filler (inert material); (b) by dilution effect, an excess of MK in mix also produce a decrease of total available $Ca(OH)_2$ content coming from the hydration reaction of PC in blended pastes. A final result of both effects would be the production of a lower content of hydrated phases, mainly from pozzolanic reaction, and therefore, a slightly lower degree of hydration in blended pastes with a 25% of MK than that in 20% of MK was detected. This fact will be in agreement with a prior study, which reported that MK reacts with 1.2 times its mass of portlandite.

From data and observations presented here, it is logical to think that the degree of hydration in MK-blended pastes at high temperature can be estimated roughly with the methodology described earlier and the values obtained from this way are closely related to the amount of $Ca(OH)_2$ present in the paste and, subsequently, with the formation of secondary phases from pozzolanic reaction.

Using the porosity values in conjunction with the degree of hydration values, it is possible to find a statistical equation that describes the relationship between both parameters (Eq. (1))

$$Y = 0.1178x + 14.818. \tag{1}$$

The correlation coefficient (R^2) for this regression equation was 0.75. This value is not as high as that found for the MK-blended cement pastes cured at 20 °C (R^2=0.88) [18]. This fact could be indicating that, apart from the complexity to calculate the degree of hydration of blended cement matrixes in normal conditions, there is another factor added which has a direct effect in this line such as curing temperature. In general terms, the influence of curing temperature on the hydration reaction of cementing matrices and its effect on final performances is surrounded by contradictory opinions at the moment, due to the microstructural changes, stability and evolution of hydrated phases, produced by high curing temperatures. If, moreover, there is a total ignorance of its influence on the degree of hydration of matrices cured at high temperatures up till now as reflected in the absence of literature, obtaining a suitable correlation coefficient between porosity and degree of hydration could indicate that we are working on a correct way in order to deepen our knowledge in the determination of the degree of hydration in systems cured at 60° C, although further investigations will be necessary to understand the influence of curing temperature on porosity and degree of hydration of cementing mixes in order to improve the statistical parameters.

4. Conclusions

From the results obtained, the following conclusions can be drawn:

(1) Blended pastes containing MK cured at 60 °C exhibit a refinement of pore sizes as indicated by partial porosities, pore size distribution and average pore size.
(2) When a curing temperature of 60 °C is applied, the microporosity of MK-blended pastes did not give important changes after 3 days of curing.
(3) Measured lime content and its evolution with age is closely related to the MK content present at each moment of hydration.
(4) For the first time, the current paper proposes a way for calculate the degree of hydration of MK-blended cements cured at high temperatures (60 °C) from the calcium hydroxide contents in each moment of the reaction. These values are affected by the calcium hydroxide released by the hydration reaction of cement and MK content as well as secondary phases produced during pozzolanic reaction. An acceptable statistical relationship (R^2=0.75) has been found between porosity and degree of hydration. Its value is lower than that found for the same mixes cured at 20 °C (R^2=0.88).
(5) The results show the necessity of adding at least 20% of MK to obtain an important refinement of pore structure in order to get denser and homogeneous blended pastes.
(6) The hydrated phases produced during the pozzolanic reaction did not lead to any negative effect on the porous structure, stating that the hydrated phases formed during the pozzolanic reaction are stable in MK-blended pastes cured at 60 °C and up to 124 days of reaction. This fact is a fundamental aspect from the viewpoint of engineering and microstructural properties of new blended cements.

References

[1] F. Massazza, Pozzolanic cements, Cem. Concr. Comp. 16 (4) (1993) 185–214.

[2] J.G. Cabrera, A.R. Cusens, A. Ramezanianpour, The effect of curing conditions on the carbonation of mortars containing cement, pfa, silica fume and trass, 1st Inter Conference on Deterioration and repair of reinforced concrete in the Arabian Gulf, E&FN Spon, Bahrain, II, 1995, pp. 26–29.

[3] M.C. Andrade, M. Frías, B. Aarup, Durability of ultra-high strength concrete: compact reinforced composite, in: F. De Larrard, R. Lacroix (Eds.), 4th International Symposium on the Utilization of High Performance Concrete, Ecole Nationale des Ponts et Chaussées, Paris, vol. II, 1996, pp. 529–534.

[4] P.H. Metha, P. Schiessl, R. Raupach, Performance and durability of concrete systems, 9th Inter. Congress on the Chemistry of Cement, National Council for Cement and Building Materials, New Delhi, India, 1992, pp. 571–663.

[5] S. Wild, J.M. Khatib, A. Jones, Relative strength, pozzolanic activity and cement hydration in superplasticised MK concrete, Cem. Concr. Res. 26 (10) (1996) 1537–1544.

[6] F. Cursio, B.A. DeAngelis, S. Pagliolico, MK as a pozzolanic microfiller for high-performance mortars, Cem. Concr. Res. 28 (6) (1998) 803–809.

[7] B.B. Sabir, S. Wild, J. Bai, Metakaolin and calcined clays as pozzolans for concrete: a review, Cem. Concr. Comp. 23 (2001) 441–454.

[8] M. Frías, M.I. Sánches de Rojas, J. Cabrera, The effect that the pozzolanic reaction of MK has on the heat evolution in MK-cement mortars, Cem. Concr. Res. 30 (2) (2000) 209–216.

[9] J. Bai, S. Wild, Investigation of the temperature change and heat evolution of mortar incorporating PFA and MK, Cem. Concr. Comp. 24 (2) (2002) 201–209.

[10] M.A. Serry, A.S. Taha, S.A.S. El-Hemaly, H. El-Didamony, Metakaolin-lime hydration products, Thermochim. Acta 79 (1984) 103–110.

[11] M. Murat, Hydration reaction and hardening of calcined clays and related minerals: I. Preliminary Investigation on metakaolin, Cem. Concr. Res. 13 (2) (1983) 259–266.

[12] J. Ambroise, M. Murat, J. Pera, Hydration reaction and hardening of calcined clays and related minerals: IV. Experimental conditions for strength improvement on MK minicylinders, Cem. Concr. Res. 15 (1995) 83–88.

[13] D.S. Klimesch, A. Ray, Hydrogarnet formation during autoclaving at 180 °C in unstirred MK–lime-quartz slurries, Cem. Concr. Res. 28 (8) (1998) 1109–1117.

[14] M.S. Morsy, A.F. Galal, S.A. Abo-El-Enein, Effect of temperature on phase composition and microstructure of artifical pozzolana-cement pastes containing burnt kaolinite clay, Cem. Concr. Res. 28 (8) (1998) 1157–1163.

[15] S. Wild, J.M. Khatib, L.J. Roose, Chemical shrinkage and autogenous shrinkage of portland cement-MK pastes, Adv. Cem. Res. 10 (3) (1998) 109–119.

[16] P.S. De Silva, F.G. Glasser, The hydration behaviour of MK–$Ca(OH)_2$–sulphate binders, Proc. 9th Intr. Conf. on the Chemistry of Cement, National Council for Cement and Building Materials, New Dehli, vol. 4, 1992, pp. 671–677.

[17] J.M. Khatib, S. Wild, Pore size distribution of MK paste, Cem. Concr. Res. 26 (10) (1996) 1545–1553.

[18] M. Frías, J. Cabrera, Pore size distribution and degree of hydration of MK cement pastes, Cem. Concr. Res. 30 (4) (2000) 561–569.

[19] M. Frías, M.I. Sánchez de Rojas, Influence of the MK on porous structure of matrixes based in MK/cement, Mater. Constr. 50 (259) (2000) 57–67.

[20] P.S. De Silva, F.G. Glasser, Phase relations in the system $CaO–Al_2O_3–SiO_2–H_2O$ relevant to MK–calcium hydroxide hydration, Cem. Concr. Res. 23 (3) (1993) 627–639.

[21] J. Cabrera, M. Frías, Mechanism of hydration of the MK–lime-water system, Cem. Concr. Res. 31 (2) (2001) 177–182.

[22] M. Frías, M.I. Sánchez de Rojas, J. Rivera, The effect of the temperature on the formation of hydrogarnet in matrices made with MK/lime mixtures, in: V.M. Malhotra (Ed.), 7th CANMET/ACI Inter. Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Chennai (Madras), India, vol. 2, 2001, pp. 757–769.

[23] M. Frías, M.I. Sánchez de Rojas, The effect of high curing time on the reaction kinetics in MK/lime and MK-blended cement matrixes at 60 °C, Cem. Concr. Res. 33 (2003) 643–649.

[24] M. Frías, J.G. Cabrera, The effect of temperature on the hydration rate and stability of the hydration phases of MK–lime-systems, Cem. Concr. Res. 32 (2002) 133–138.

[25] J.G. Cabrera, Private communication, School of Civil Engineering, University of Leeds, UK, 1993.