Pergamon

Cement and Concrete Research 30 (2000) 561–569

CEMENT AND CONCRETE RESEARCH

Pore size distribution and degree of hydration of metakaolin–cement pastes

Moisés Frías*, Joseph Cabrera[1]

Civil Engineering Materials Unit (CEMU), School of Civil Engineering, University of Leeds, Leeds LS2 9JT, UK

Received 20 September 1999; accepted 27 December 1999

Abstract

The current paper shows the results of an investigation focussing on the effect of metakaolin (MK) on the microstructure of MK blended pastes. Pastes containing 0%, 10%, 15%, 20% and 25% of MK were prepared at a constant water/binder ratio of 0.55 and cured at 20°C for hydration periods from 1 to 360 days. On the one hand, the total, capillary, and gel porosity evolution with the curing time has been investigated. On the other hand, a method to estimate the degree of hydration in MK/OPC mixes is proposed in this paper. The values of the degree of hydration are calculated from the amount of $Ca(OH)_2$ present in the paste and from the data of differential thermal analysis (DTA) and thermogravimetry (TG). A good correlation between porosity and degree of hydration has been found. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Metakaolin; Blended cement; Porosity; Degree of hydration

1. Introduction

The use of mineral additions for the manufacture of mortar and concrete includes generally natural pozzolans from volcanic origin and by-products like fly ash and silica fume.

In most of the cases, mortars and concrete containing material with pozzolanic characteristics have (in normal condition), porosity values equal or superior to that of OPC concrete [1]. This evolution of the porosity depends on the characteristics of pozzolanic materials, such as fineness, mineralogy, loss of ignition, chemical composition and an important aspect to point out is the water/binder used [2].

This fact provokes the pozzolanic material to have a different influence on the microstructural properties. In a recent work, Frías and Sánchez de Rojas [3] reported an abnormal behavior on the evolution of porosity in fly ash (PFA)/cement (OPC) mortars with PFA contents between 0% and 40% at 28, 90, and 360 days of curing time. That work indicated that fineness, particle shape, and pozzolanic reaction rate play an important role on this particular behavior with respect to other pozzolanic materials.

However, it is well known that the critical factor affecting the performance and durability of concrete structure is the pore size distribution, rather than the total porosity. In this aspect, every pozzolanic material (even PFA) experiments a refineness in their capillary porosity structure, giving place to a more tortuous pore net [4]. It is due to the pore structure of concrete, which is not a static quantity but a time-dependent property [5]. The motive of this evolution is to determine whether hydration reaction or pozzolanic reaction play an important role in the development of the pore structure.

In the last years, a new material (metakaolin, MK) is being studied because of its high pozzolanic properties [6–10]. Owing to its fineness and chemical composition, MK shows a closer behavior to silica fume than to PFA [11]. One of the more important aspects to point out is its pozzolanic reaction rate constant (K). The authors of the present paper [12] reported a value of 27.10^{-4} for silica fume, 20.10^{-4} for MK, whereas it was only of 7.10^{-4} for PFA, in pozzolan/lime mixes cured at 60°C. This difference in MK mixes will have its repercussion on pore size distribution and on the degree of hydration as well, mainly, short-term.

---

* Corresponding author. Eduardo Torroja Institute (CSIC), c/ Serrano Galvache, s/n 28033 Madrid, Spain. Tel.: +34-90-30-30-440; fax: +34-90-30-20-700.

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

[1] Dr. J. Cabrera died prior to the publication of this article.

0008-8846/00/$ – see front matter
PII: S0008-8846(00)00203-9

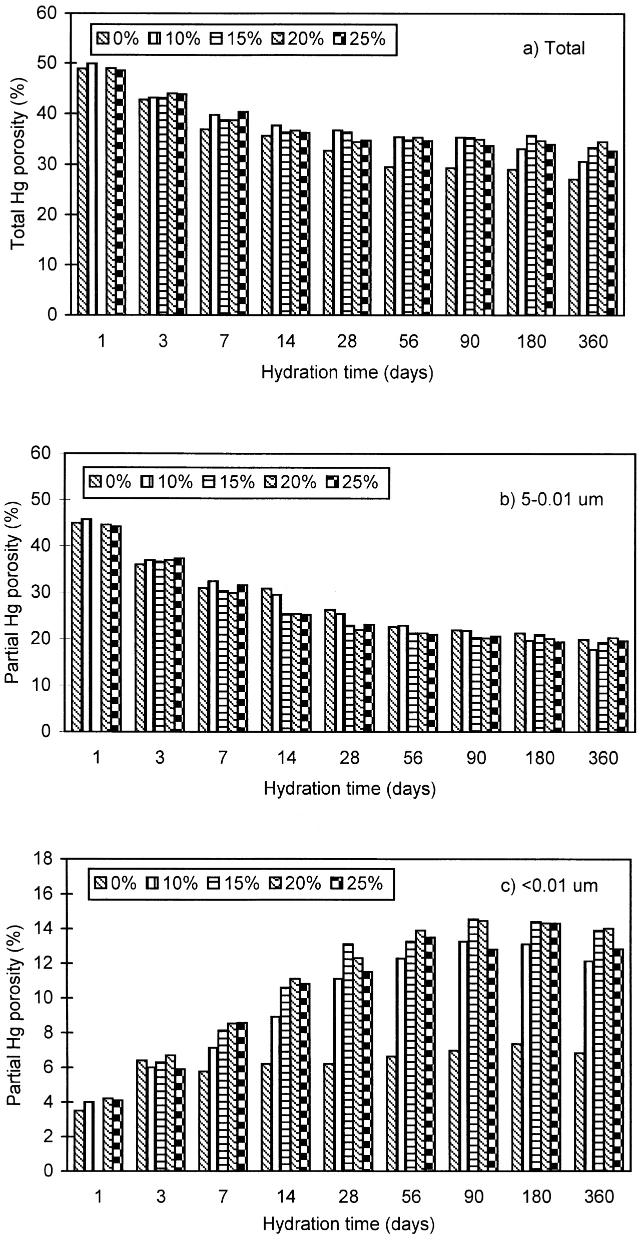


Fig. 1. Evolution of porosity with the hydration time.

In the literature, a few researches have been reported about the role of MK in modifying the pore size distribution. In this respect, Khabit and Wild [13] reported a refineness of the pore structure and a total intruded pore volume increase between 14 and 28 days for pastes with 5%, 10%, and 15% of MK.

Also, in the bibliography, no references have been found about the effect of MK on the degree of hydration. This lack of experience could be motivated by the complexity of pozzolan/cement systems, which are much more complicated than the OPC system. The progress of reaction between pozzolan and cement depends upon various factors and it is highly related to the properties of pozzolan and curing conditions.

A previous work [14], reported that the effect of PFA on the degree of hydration could be estimated using the method suggested by Cabrera, expressing the lime content of the PFA pastes as a percentage of OPC rather than of PFA/OPC.

In the present paper, these fundamental aspects are stressed because of the importance that MK can have on the performance of MK blended systems. Therefore, on the one hand, an investigation about the influence of MK on the pore size distribution between 0% and 25% of MK is made. On the other hand, a new methodology is proposed in order to estimate the effect of MK on the degree of hydration.

A relationship, total, capillary, and gel porosity vs. the degree of hydration is carried out in order to know the influence of MK on the microstructure of the pastes.

2. Experimental

2.1. Preparation of specimen and curing

A commercial MK was used in the present work [12]. The BET surface area of MK was 15.5 m^2/g, a value slightly lower than the silica fume value (20 m^2/g).

Five different pastes were prepared. White OPC was partially replaced with 0%, 10%, 15%, 20% and 25% of MK.

The water/binder was 0.55 by weight. The mixtures were placed in plastic airtight containers and then left in a curing room at 100% RH. After the predetermined curing time (1, 3, 7, 14, 28, 56, 90, 180 and 360 days), the hydration reaction was stopped using two different ways, depending on the parameter studied: (a) Vacuum oven method: the samples were left at 50°C and 1 bar. After 3 days, a constant mass was detected; method used for mercury porosity tests (MIP). (b) Microwave method: this procedure was good and quick to dry the samples. Further information can be found in a previous paper [12]; method used for differential thermal analysis (DTA) and thermogravimetry (TG) tests.

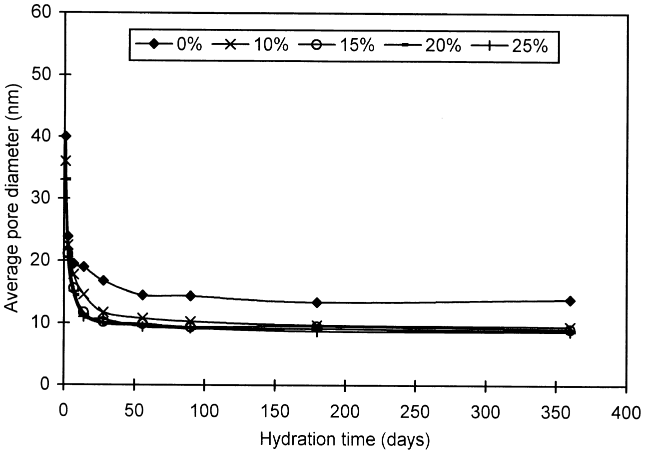


Fig. 2. Average pore diameter.

2.2. Techniques of testing

Total, capillary, and gel porosity and pore size distribution measurements were carried out using mercury intrusion porosimeter (MIP), with a Micromeritic Autopore Model 9200 instrument. The mercury porosimetry is capable of measuring pore size diameters up to 30 A.

In order to determine the calcium hydroxide contents, thermal analysis methods such as DTA and TG have been used with a STA 780 thermal analysis. The analysis used between 12–16 mg of powder and heated at $20^{\circ}C\ m^{-1}$ in an N_2 atmosphere.

3. Results and discussion

3.1. Porosity and pore size distribution by MIP

The total, capillary, and very fine pore porosity vs. hydration times for all pastes are shown in Fig. 1.

At 24 h (Fig. 1a), the pastes show a very similar total porosity in all cases. Values between 49–50% are obtained. Subsequently, there is a continuous reduction in porosity with hydration time up to 28 days. Beyond this age, the total porosity is practically constant and a clear difference between OPC and MK mixes can be observed. MK mixes

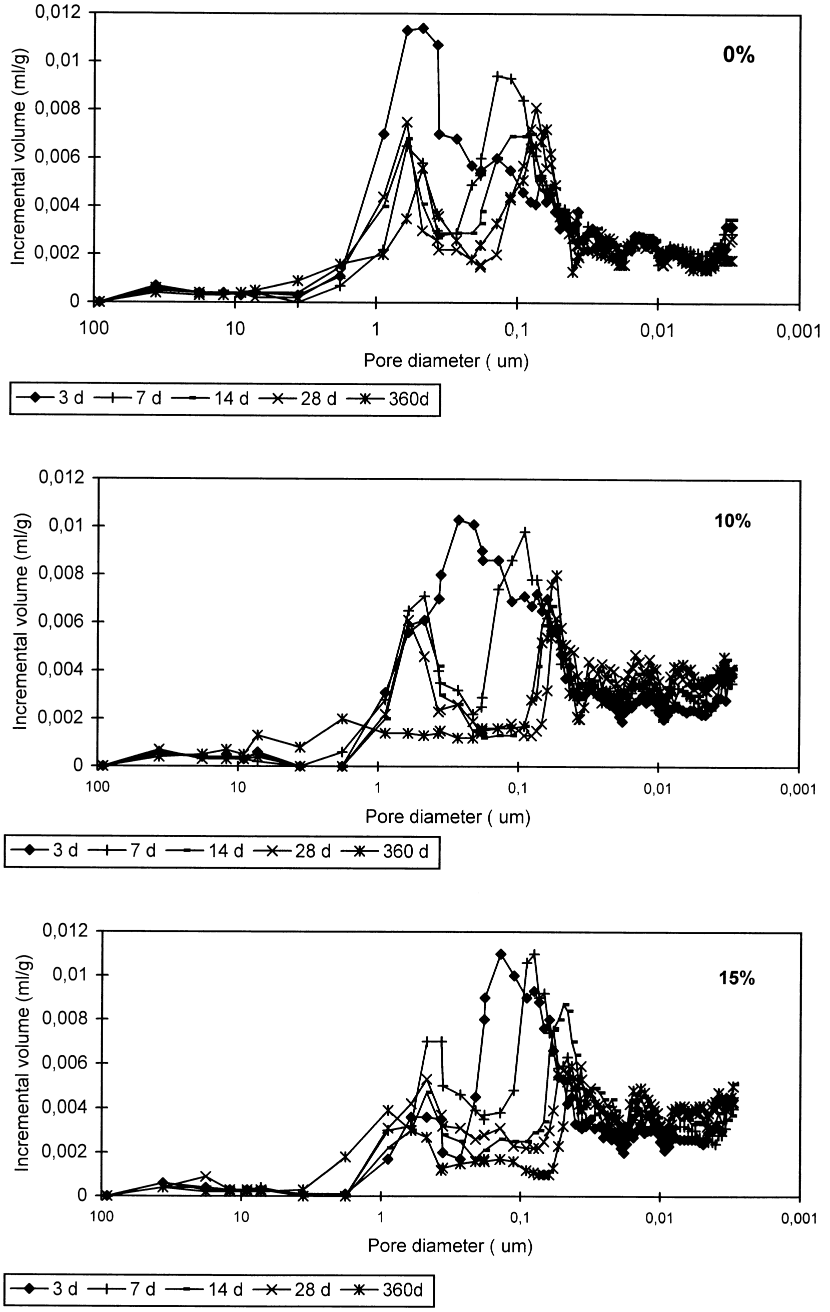


Fig. 3. Incremental volume vs. curing time for blended OPC pastes, containing 0%, 10%, and 15% of MK.

show a greater total porosity than the OPC paste and an increase of about 16% is obtained. MK contents have no important effect on the total porosity. This fact can probably be related to the high water/binder ratio used.

As for the capillary porosity (5–0.01 μm) (Fig. 1b), a clear difference is observed. During the first 7 days, an important difference between pastes with or without MK contents is not detected. However, at 14 days, the capillary porosity from OPC paste and pastes containing a 10% of MK showed a slight increase with respect to the other MK pastes. In this respect, it is important to point out that there is no difference of capillary porosity in pastes containing between 15% and 25% of MK with longer hydration time.

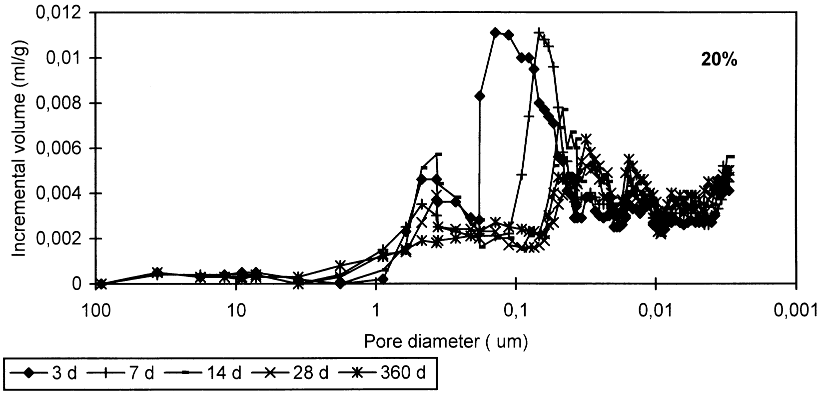
The positive effect of the incorporation of MK in the elaboration of blended pastes is that porous size is less than 100 A. A gradual increase in the very fine pores is observed with age. Fig. 1c shows two important moments on the evolution of the porosity at 7 and 90 days, respectively. This period of time corresponds with the start and the end of the pozzolanic reaction.

The clear shift towards finer pore structure can be quantified by expressing the pore size distribution in terms of the average pore diameter. The evolution of the average pore diameter (nm) with age is shown in Fig. 2.

A strong reduction on the average pore diameter is observed in the first days. Depending on MK contents, the evolution of this parameter is different. In the case of OPC paste, the average pore diameter decreases from 40 to 14.5 nm for a hydration time between 1 and 56 days. Subsequently, the average pore diameter is almost a constant value. In pastes with 10% of MK, the reduction of average pore diameter finishes at 28 days while for the 15%, 20%, and 25% MK pastes, this phenomenon occurs at 14 days. Above 10% of MK, the average pore diameter curves do not show any difference.

These findings are not totally in agreement with a previous paper. Khabit and Wild [13] reported that the refinement process seems to terminate at 14 days in pastes with 5%, 10%, and 15% of MK. On the other hand, they also reported a small increase in pore volume between 14 and 28 days of curing time and a renewed increase in calcium hydroxide level. These phenomena were explained on the basis of the formation of an inhibiting layer of reduction product on MK pastes and/or to the transformation from the less dense C_2ASH_8 and C_4AH_{13} and dense hydrogarnet.

Authors of the present paper do not detect any increase in calcium hydroxide content between 14 and 18 days and, therefore, there is no increase of total pore



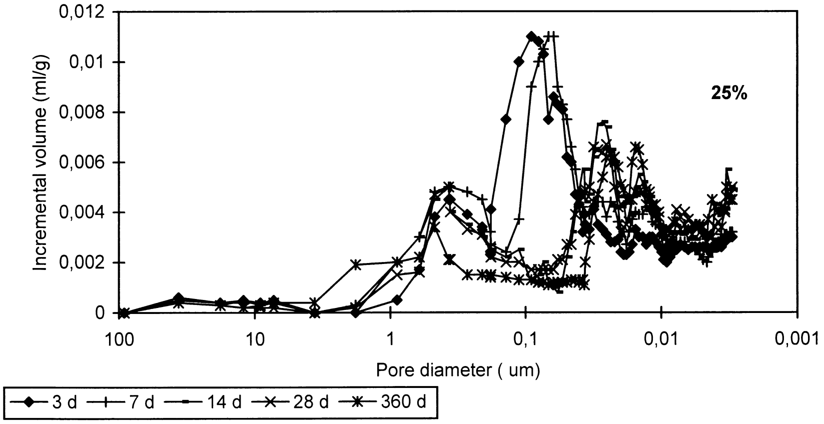


Fig. 4. Incremental volume vs. curing time for blended OPC pastes, containing 20% and 25% of MK.

volume at this period. A possible explanation for the difference found in MK pastes might be related to the nature, composition, and fineness of the cement and MK used. The study is being carried out in MK pastes, there is no evidence of formation of the hydrogarnet at 20°C and at short curing time.

Figs. 3 and 4 show the frequency of pore size as a function of hydration time for the five pastes tested. At early ages (3 days), a different behavior in pastes with or without MK is detected. For the 0% and 10% MK samples, a modal distribution is showed. An extensive interval of capillary pore size is localized between 5 and 0.05 μm. However, for the samples with MK contents up to 10%, two maxima appear, one at 0.6–0.7 μm and another is situated at about 0.1 μm.

From 28 days of curing, an important shift can be observed. The pore size distribution of MK pastes changes toward smaller pore size, while the second maximum practically disappears.

As mentioned before, in the graphics of incremental volume, the influence of MK contents on the refinement of pore size, below 0.04 μm can be appreciated (Fig. 5). In them, the evolution of the finest pore size between 3 and 360 days of curing time can be clearly seen. The studies carried out on pore size show that important changes between 3 and 90 days happen. However, no refinement of pore size is detected for hydration periods above 90 days.

Variations of the pore sizes with curing time are not observed in OPC paste during selected hydration period

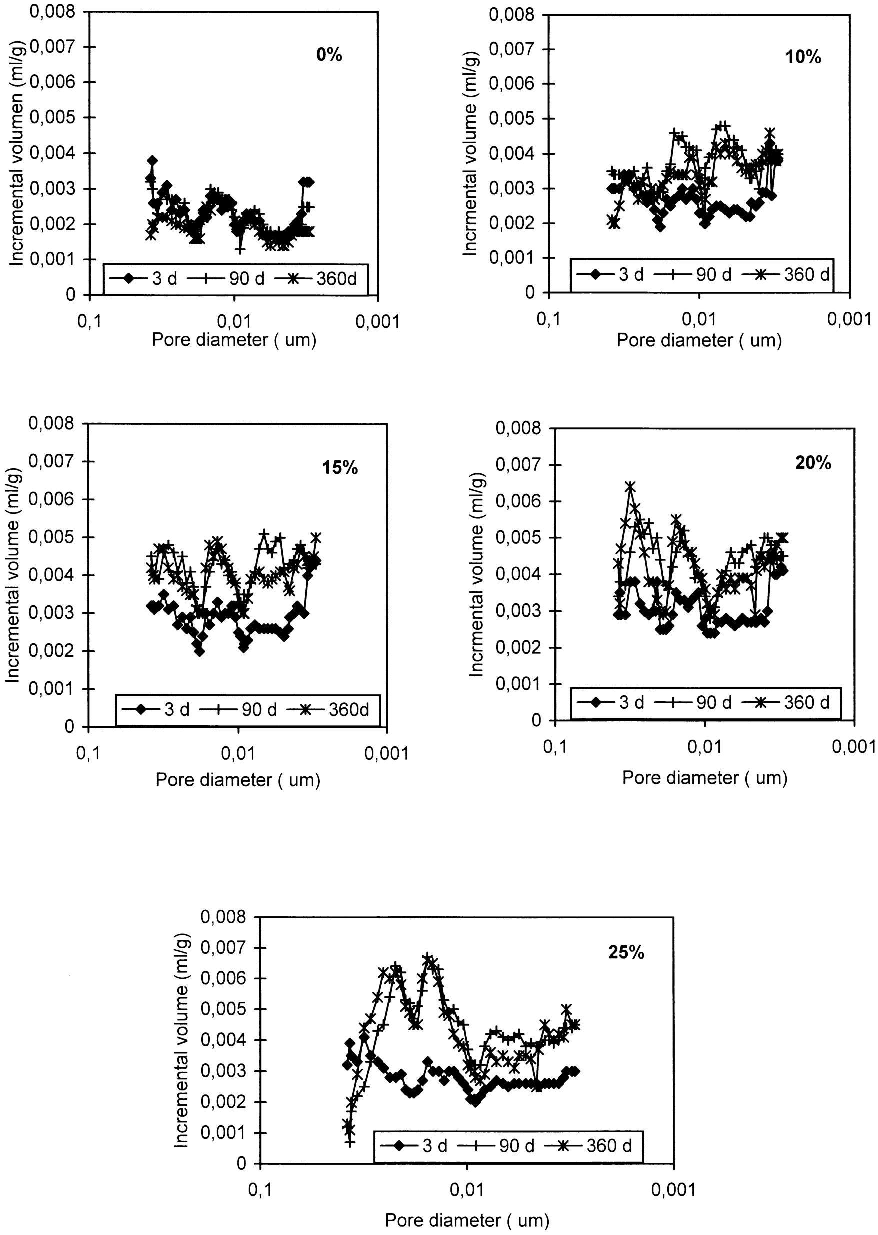


Fig. 5. Evolution of the finest pore sizes.

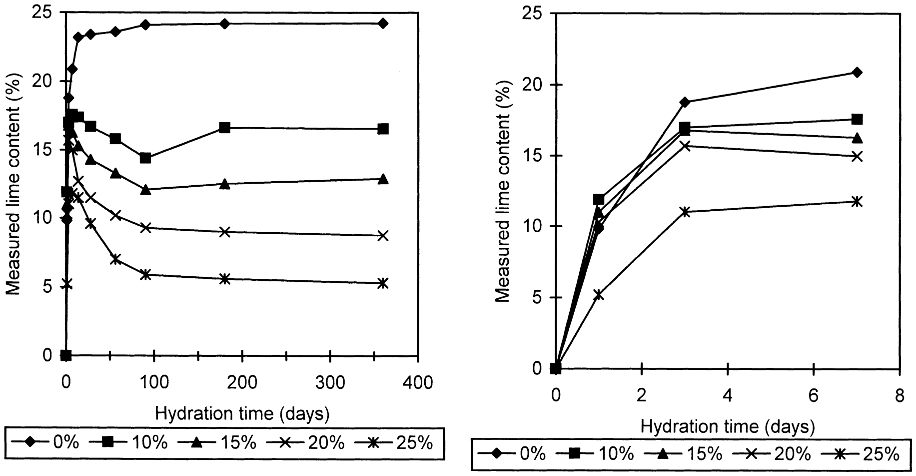


Fig. 6. Evolution of calcium hydroxide with hydration time.

(Fig. 5, 0%). However, in other cases, an important increase in HG incremental volume can be detected with the increase of MK content (Fig. 5, 10–25%).

3.2. Evolution of the calcium hydroxide content with time

In order to determine the degree of hydration of MK pastes, it is necessary to know the total amount of calcium present in the hydrated MK/OPC systems. The total calcium hydroxide was calculated taking into account the weight loss due to the dehydroxylation of $Ca(OH)_2$ and the decomposition of $CaCO_3$.

Fig. 6 shows the percentage of calcium hydroxide with the curing time up to 360 days. Here, different phenomena can be observed: (a) Calcium hydroxide contents of MK/OPC samples increase with age until 3–7 days. (b) Subsequently, the values start reducing, more or less depending on MK content. (c) In the cases of mixtures with 10% and 15% of MK, an inflexion point at 56 and 90 days, respectively can be clearly seen. Beyond this point, the calcium hydroxide content experiments a progressive increase.

This behavior of calcium hydroxide content is due to different hydration mechanisms: the increase in the $Ca(0H)_2$ amounts is due to the OPC hydration, while the decrease in the values is related with the pozzolanic reaction of MK. The inflexion points (for 10% and 15% of MK) represent the end of the pozzolanic reaction, due to the total consumption of MK.

These findings are in agreement with researches carried out by the same authors in a previous work. Frías and Cabrera [15] reported that in MK/lime mixes at 20°C, the reaction rate constant was very low ($k = 0.18 \times 10^{-4}$) in the first moments of the pozzolanic reaction, increasing quickly after 7 days (2.5×10^{-4}).

An important aspect to point out in MK/OPC mix is the accelerating effect of MK on the hydration reaction (Fig. 6). This is probably due to the dispersing effect of MK on the agglomerated cement grains that act as nucleating agent. At 1 day, $Ca(OH)_2$ content is higher than OPC value, except for the mixture with a 25% of MK. Subsequently, the pozzolanic reaction is the predominant effect. A similar phenomenon has been observed by another researcher [16] who worked with silica fume pastes.

3.3. Degree of hydration

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

The starting point of this study was the application of the method suggested by Cabrera [17] in which the $Ca(OH)_2$ content of the PFA pastes was expressed as a percentage of OPC rather than of PFA/OPC. Subsequently, Abdelrahim [14] and Cabrera reported a valid statistical relationship between the degree of hydration calculated from specific gravity and the degree of hydration calculated from $Ca(OH)_2$ ($R^2 = 0.86$).

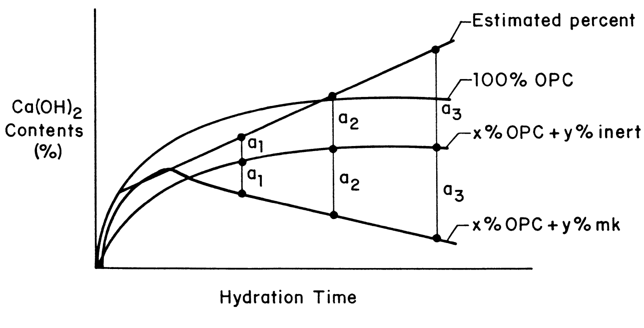


Fig. 7. Schematic diagram for the estimation of the amount of $Ca(OH)_2$.

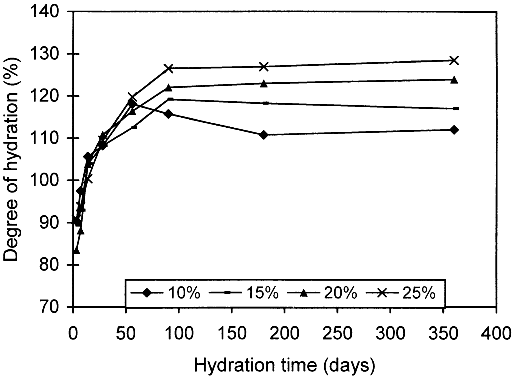


Fig. 8. Evolution of the estimated degree of hydration.

Based on that method, Fig. 7 shows three curves corresponding to 100% OPC, x% OPC + y% inert and x% OPC + y% MK. From these data, it is possible to calculate the estimated percent line, as follows:

$$(x\% \text{ OPC} + y\% \text{ inert}) - (x\% \text{ OPC} + y\% \text{ MK}) = a(a_1,\ a_2,\ a_3 \text{ at any age})$$

where a is the decrease of calcium hydroxide due to pozzolanic reaction; a + (x% OPC + y% inert) = estimated percent values.

The degree of hydration for MK/OPC pastes is calculated as the quotient between estimated percent values and 100% OPC values, being that this quotient approximates statistically better to the experimental data obtained by TG.

This form of estimating the degree of hydration for MK mixes presents a modification to the referenced method [17], in which, supposed that for fly ashes, the degree of hydration has been calculated as the quotient between estimated percent and x% OPC + y% inert.

The values and evolution of the degree of hydration for MK mixes are represented in Fig. 8. The degree of hydration values below 100% (value corresponding to the OPC) are detected up to 8–9 days of hydration time. Subsequently, these values increase above 100% with hydration time and MK content.

At first sight, the values of the degree of hydration above 100% could lead to false opinions about the behavior of MK. However, a detailed study of these results permits the acquisition of relevant information:

Up to 14 days of hydration time, the degree of hydration reaches values below 100%. It might be indicating the total absence of pozzolanic reaction. In this period, the predominant reaction is the hydration reaction, which is produced between cement particles and water.

Period between 14–90 days of curing: the degree of hydration values is situated above 100%. This fact might be indicating the overlap between both reactions (hydration and pozzolanic ones). In this case, calcium hydroxide produced during the hydration reaction is converted into other hydrated phases, such as C_2ASH_8, C_4AH_{13}. Therefore, total hydrated phases produced in

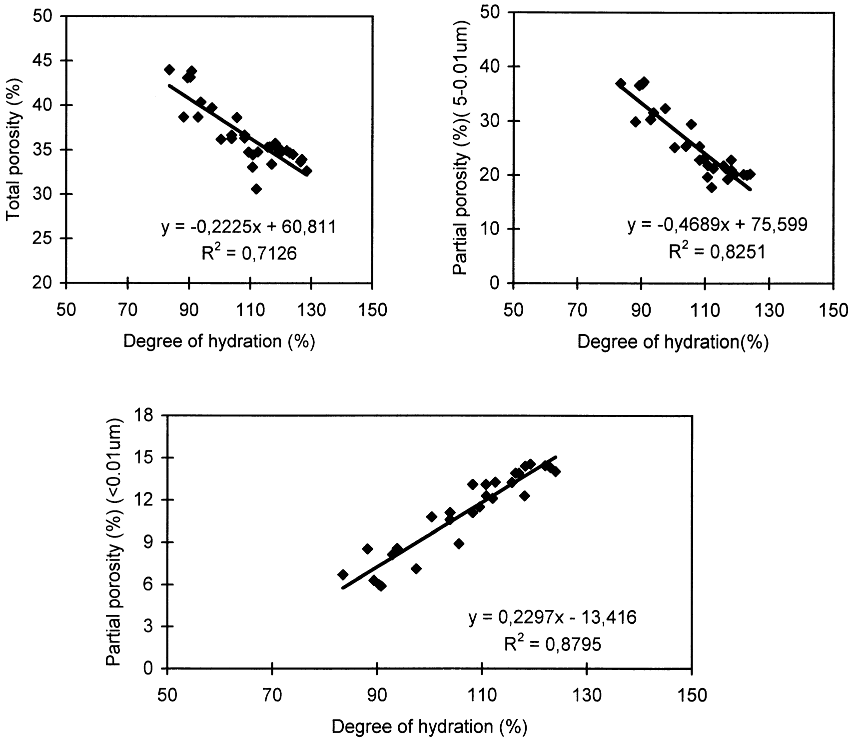


Fig. 9. Regression equations between porosity and degree of hydration.

MK/OPC pastes is higher than that in OPC (about 25% is calcium hydroxide).

Period above 90 days: the values of the degree of hydration are practically constants, with a slight decrease for mixes with 20% and 25% of MK.

Finally, an important decrease in the values between 90 and 180 days is detected in the blended paste with 10% of MK and less important for 15% of MK. Subsequently, these values increase with hydration time. This evolution of the degree of hydration values is closely related to the absence of MK in blended pastes due to the finishing of pozzolanic reaction and the consequent increase of calcium hydroxide again.

These findings are in agreement, on one hand, with the results mentioned above (Figs. 3 and 4) and, on the other hand, with the results obtained in a previous paper carried out by the same authors. They reported that the pozzolanic reaction is more important after 9 days of hydration time in MK/lime mix at 20°C.

From the observations presented here, it is obvious that the degree of hydration in MK/OPC systems can be estimated with the methodology described earlier and the values obtained this way are closely related to the amount of $Ca(OH)_2$ present in the paste at earlier hydration period and, subsequently, with the formation of secondary phases from pozzolanic reaction.

3.4. Relationship between porosity and degree of hydration

Using the total, capillary, and gel porosity values in conjunction with the values of degree of hydration, it is possible to find a valid statistical equation that describes the relationship between both parameters.

Fig. 9 shows the plots of porosity vs. degree of hydration and the regression equations. A good correlation is found. The correlation coefficient (R^2) for total, capillary, and gel porosity is 0.71, 0.82, and 0.88, respectively. Comparing these results, it is possible to observe that the best correlation coefficient corresponds to the gel porosity, followed by capillary porosity and, finally by total porosity.

This is a good indication that the values of degree of hydration above 100% are directly related to the refineness of the smallest pore sizes, mainly. It is due to an increase of the hydrated phase contents during the pozzolanic reaction.

4. Conclusions

The main conclusions of this paper can be summarized as follows.

(1) The total porosity decreases up to 28–56 days of curing time. The values show similar porosities in all mixes. Above this age, the total porosity of MK mixes increases with respect to the OPC paste.

(2) A similar phenomenon for the capillary porosity is also observed. In this case, the values obtained for MK mixes decrease with respect to OPC mix.

(3) The best evidence of the influence of MK on the refineness of the pore structure was detected in pores with radio smaller than 100 A. Between 7–90 days, the gel porosity of MK mixes increases, while the OPC mix remains practically constant.

(4) The results show the necessity of adding at least 15–20% of MK to obtain an important improvement in the porosity, reducing the average pore diameter (Fig. 2) and gel porosity (Figs. 3–5).

(5) Measured lime contents (Fig. 6) show the total consumption of MK (10% and 15%) at 90 days of hydration time.

(6) A valid model is proposed to estimate the degree of hydration from the calcium hydroxide contents. These values are affected by calcium hydroxide and secondary phases produced by the pozzolanic reaction in blended pastes.

(7) A good statistical relationship has been found between the degree of hydration (measured with the method proposed in the current paper) and the porosity. The best one is the one corresponding to the gel porosity ($R^2 = 0.88$).

Acknowledgments

The authors wish to thank the TMR Mari Curie grant (European Commission), which supported the present research.

References

[1] F. Massazza, G. Oberti, Durability of pozzolanic cements and Italian experience in mass concrete, in: V.M. Malhotra (Ed.), 2nd Inter Conference on Durability and Concrete, American Concrete Institute, Montreal, Canada, Vol. II, (1991) 1259–1283.

[2] O. Gjorv, High strength concrete, in: V.M. Malhotra (Ed.), Advances in Concrete Technology, American Concrete Institute, Montreal, Canada, (1992) 21–77.

[3] M. Frías, M.I. Sánchez de Rojas, Microstructural alterations in fly ash mortar, Cem Concr Res 27 (2) (1997) 50–57.

[4] N. Tenoutasse, A.M. Marion, The influence of silica fume on the hydration and microstructure of OPC pastes, in: V.M. Malhotra (Ed.), 2nd Inter Conference on the Use of Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, American Concrete Institute, Madrid, Spain, Supplementary Papers (1986) 1–23.

[5] A.K. Suryavanshi, R.N. Swamy, Cem Concr Aggregates 20 (1) (1998) 169–179.

[6] P.S. Silva, F.P. Glasser, Phase relation in the system $CaO–Al_2O_3–SiO_2–H_2O$ relevant to MK–lime hydration, Cem Concr Res 23 (1993) 627–639.

[7] J. Ambroise, S. Maximilien, P. Pera, Properties of MK blended cement, Adv Cem Based Mater 1 (1994) 161–168.

[8] N.J. Coleman, C.L. Page, Aspects of the pore solution chemistry of hydrated cement pastes containing MK,Cem Concr Res, 27 (1) (1997) 147–154.

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

[10] J. Bai, S. Wild, B.B. Sabir, J.M. Kinuthin, Workability of concrete in incorporating PFA and MK, Mag Concr Res 51 (3) (1999) 207–226.

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

[12] J. Cabrera, M. Frías, Mechanism of hydration of the MK–lime–water system, Cem Concr Res in press.

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

[14] K. Abdelrahim, The effect of environmental curing condition on the gas and water permeability of concrete, Doctoral Thesis, Department of Civil Engineering, University of Leeds, 1995, p. 307.

[15] M. Frías, J. Cabrera, The effect of temperature on the hydration rate and stability of the hydration phases of metakaolin–lime–water systems, Cem Concr Res submitted for publication.

[16] A.M. Sharara, H. Eldidamony, H. Ebied, A. Elaleem, Cem Concr Res 24 (5) (1994) 966–976.

[17] J. Cabrera, private communication, University of Leeds, UK, 1993, p. 185.