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Effects of metakaolin on autogenous shrinkage of cement pastes

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Abstract

The effects of partial replacements (5%, 10%, 15% and 20%) of Portland cement by high-purity metakaolin (MK) on the autogenous shrinkage of pastes (water/binder ratios 0.3 and 0.5) were investigated. In order to distinguish the effect of heterogeneous nucleation and pozzolanic activity from the dilution effect, some mixes were prepared using a coarse powder (Q_{ref}) instead of MK (10% and 20% for both w/b ratios). The hydration of cement–MK pastes was followed qualitatively by differential thermal analysis (DTA). DTA showed that C–S–H and gehlenite (C_2ASH_8) were the main compounds produced by MK pozzolanic reaction. Results showed that the long-term autogenous shrinkage of cement–MK pastes, for both w/b ratios, decreased as the cement replacement level by MK increased. No expansion was observed at early ages, contrary to the findings of other authors. With the elimination of the dilution effect, it was shown, at early ages, that the increase of autogenous shrinkage of the cement–MK pastes relative to cement–Q_{ref} mixes was due to heterogeneous nucleation. At later ages, autogenous shrinkage became lower for cement–MK pastes than for cement–Q_{ref} pastes, surely because the pozzolanic activity of MK became predominant. This behavior i.e. reduction of autogenous shrinkage, is one more benefit confirming the interest of using MK in concrete.

Keywords: Metakaolin; Autogenous shrinkage; Dilution effect; Heterogeneous nucleation; Pozzolanic reaction

1. Introduction

It is well known that pozzolana such as silica fume, fly ash and blast-furnace slag are industrial by-products that present great variations of properties, which can sometimes compromise their use. On the other hand metakaolin (MK) is an artificial pozzolana produced by burning selected kaolinite clay within a specific temperature range (between 650 and 800 °C). The production process is closely controlled and thus higher purity and reactivity can be obtained. MK is basically made up of silica and alumina in an amorphous state, that react with calcium hydroxide (CH) produced by Portland cement hydration to form calcium hydrosilicate (C–S–H) and calcium hydroaluminosilicate (essentially gehlenite – C_2ASH_8) [1].

There is a consensus in the literature that the pozzolanic reaction between MK and CH helps to refine the binder capillary porosity [2–7], with the direct consequence of improving the mechanical characteristics [5–15] mainly at early ages [16–19], and durability e.g. resistance to sulfate attack [3,13,20,21], chloride ingress [15,16,21–27] and alkali silica reaction [22,28,29]. The replacement of part of the cement by MK (up to 15%) reduces drying shrinkage in comparison with concrete without MK [15,16,30] and with silica fume [15,16].

However, conflicting results are found concerning autogenous volume changes in cement-based materials due to the presence of MK. Brooks and Megat Johari [30] found that, at very young ages, from the initial setting to up to 20 h, the autogenous shrinkage of concrete (water/binder of 0.28) decreased with the substitution of 5%, 10% and 15% of cement by MK. However, they also found that the long-term autogenous shrinkage increased when measured from

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24 h. In their study, Wild et al. [31] showed that, for cement–MK pastes (w/b = 0.55), autogenous shrinkage increased for MK content up to a maximum of 10%; then, it appeared to be comparable to that of the control cement paste for MK content above 15%. An expansion up to 14 days for all the compositions (0–25% MK) was also observed, except for 10% MK [31]. Kinuthia et al. [32] also found, in cement–MK pastes (w/b = 0.50), that 5% and 10% MK increased the autogenous shrinkage of cement pastes, while at 15% and 20% MK, they observed a significant decrease.

As can be seen, literature regarding the effect of the MK on autogenous shrinkage is scarce and somewhat contradictory. Moreover, it is not clear if the reduction of autogenous shrinkage at higher MK replacement levels observed by Brooks and Megat Johari [30], Wild et al. [31] and Kinuthia et al. [32] is due to MK pozzolanic reaction or dilution of the cement or both. Indeed, the effect of MK on autogenous shrinkage of cement pastes can be the consequence of four phenomena: (i) cement dilution by MK, less cement generating less shrinkage, (ii) heterogeneous nucleation of hydrates on the surface of MK particles, accelerating cement hydration and, consequently, increasing shrinkage, (iii) pozzolanic reaction of MK with CH produced by cement and, (iv) increase of capillary tension, due to the refinement of pore size distribution, leading to an increase in autogenous shrinkage. This work intends to clarify the part of the autogenous shrinkage involving cement and metakaolin.

2. Materials and methods

The cement used was a standard CEM I 52,5 as specified in European Standard EN 197-1, with a specific gravity of 3.1 and a surface area (Blaine) of 400 m^2/kg. The MK was high-purity MK with a surface area (BET) of 23,000 m^2/kg and an average particle size of 4 μm. The composition of cement and MK are given in Table 1. Cement–MK pastes were prepared with levels of cement replacement by MK at 0% (control), 5%, 10%, 15% and 20% and with two w/b ratios (0.3 and 0.5). For the low-water mixtures, a polycarboxyl acid based superplasticizer was added at 0.86% of the cement weight. Specimens were cast in two layers and carefully compacted on a vibrating table to avoid excess bleeding. The molds (three for each mixture) measured $2 \times 2 \times 16$ cm and had shrinkage bolts in the two extremities. After casting, specimens were covered and maintained in a climate chamber during the setting process. Immediately after demoulding (24 h after mixing), all specimens were wrapped in aluminum waterproof tape, which was found to be very effective since the specimens showed minimal weight loss (less than 0.0025%/day). After initial length measurement, the specimens were stored in the curing room maintained at 20 °C. At prescribed ages, the autogenous shrinkage of the specimens was measured using the scale micrometer method. Although shrinkage took place in the first few hours after mixing, it was not possible to measure the length changes with this apparatus before 24 h. The autogenous shrinkage reported is therefore that which occurred subsequently to the first 24 h after mixing. Each length change value reported is the mean of three values from three replicate specimens. In order to verify the reproducibility of the measurements, some mixtures were repeated at intervals of several weeks: the differences observed were less than 5%.

In order to verify that the effect of MK was not simply due to cement dilution, pastes were prepared in the same conditions, with replacement of 10% and 20% (percent by weight) of cement by an inert quartz powder Q_{ref} with a mean diameter of 215 μm, a fineness (Blaine) of 23 m^2/kg and a narrow particle size distribution. These characteristics gave the powder a very weak influence on cement hydration, whatever the cement replacement rate used [33]. It has already been shown by Lawrence et al. [33] that the quartz Q_{ref} characterizes only the dilution effect associated with the use of mineral admixture in cement based materials, since heterogeneous nucleation effect becomes non-significant for specific areas lower than 50–100 m^2/kg.

The cement–MK paste hydration was followed qualitatively by differential thermal analysis (DTA). The specimen preparation and conditioning were similar to that for autogenous shrinkage. At the ages of 1, 2, 3 and 7 days, fractions of the internal part of the specimens were ground to less than 80 μm and rapidly immersed in acetone to stop the hydration. The samples were dried at 60 °C for 4 h and then stored in a CO_2-free atmosphere. DTA runs were carried out from 20 to 750 °C, at a heating rate of 5 °C per minute under static air atmosphere. The endothermic peaks near 120, 140, 200 and 540 °C correspond to ettringite, calcium hydrosilicate (C–S–H), gehlenite (C_2ASH_8) and portlandite (CH), respectively [7,34]. Table 2 shows that, after 3 days, gehlenite, which is the main product of the reaction between MK and CH, was produced in smaller amounts in low-water mixtures than in high-water mixtures. This may be due to the lack of water decreasing ion mobility in the dense medium and thus slowing the pozzolanic reaction.

Table 1
Chemical composition of cement and metakaolin (% by mass)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	SO_3	LOI
Cement	20.1	5.6	2.0	62.5	3.1	n.d.	0.2	0.9	3.2	1.7
Metakaolin	52	44	1	0	0	2	0.4	0.2	0	1.1

Table 2
DTA of cement–MK pastes: gehlenite (C_2ASH_8) formation occurrence (the number of + marks indicate the relative amount of gehlenite)

% MK	Water/binder ratio = 0.3				Water/binder ratio = 0.5			
	5	10	15	20	5	10	15	20
1 day	–	+	+	+	–	–	+	+
2 days	–	+	+	+	–	–	+	+
3 days	+	++	++	++	++	++	++	++
7 days	+	+	++	++	+++	+++	+++	+++

3. Results and discussion

3.1. Autogenous shrinkage of cement pastes with MK

Fig. 1 shows the evolution of autogenous shrinkage with time for pastes containing up to 20% MK, at water–solid ratios of 0.3 and 0.5. It can be noted that for these two water contents:

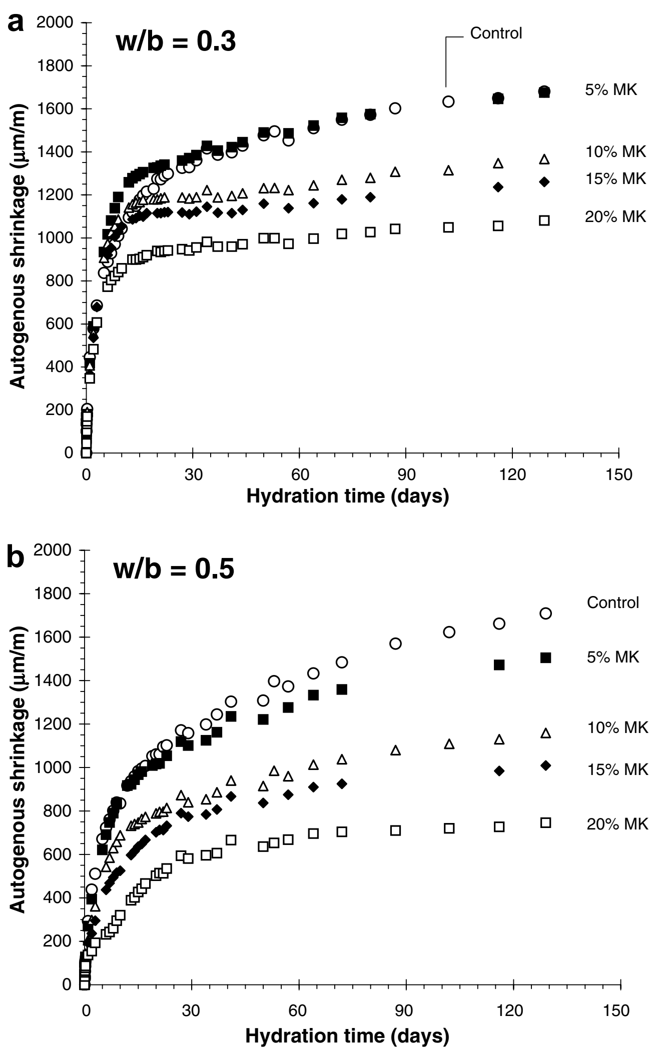

Fig. 1. Effect of MK on autogenous shrinkage of cement pastes, for water/binder ratios of (a) 0.30 and (b) 0.50.

- contrary to the findings of some authors [31], no global expansion was observed in the short term, all pastes showing a decrease in their length;
- the long-term autogenous shrinkage decreased with the increase of MK.

The water content had a significant influence on autogenous shrinkage. Fig. 2 gives the ratio (β) up to 90 days of autogenous shrinkage between mixtures having water–binder ratios of 0.3 and 0.5. It can be seen that, in the early days of hydration, the autogenous shrinkage of the low-water superplasticized pastes (w/b = 0.3) was always much higher than for the high-water pastes (w/b = 0.5), which is in agreement with data of the literature. This difference is probably not due to the superplasticizer (SP), since it has already been shown that SP has only a slight effect on autogenous shrinkage [35]. The increase of MK in the paste led to an increase of β: within the first week, β ranged from 1.5 for control mixtures to more than 3.3 for pastes with 20% MK. The ratio tended to decrease with time and reached a value between 1 and 1.5 at 3 months for all mixtures.

The efficiency of MK differed for the two w/b ratios. The reduction of autogenous shrinkage at 129 days is quantified on Fig. 3. This figure shows that the reduction was especially pronounced for pastes containing more water. MK was more efficient in reducing autogenous shrinkage for high-water contents, since the use of 20% MK led to 56%

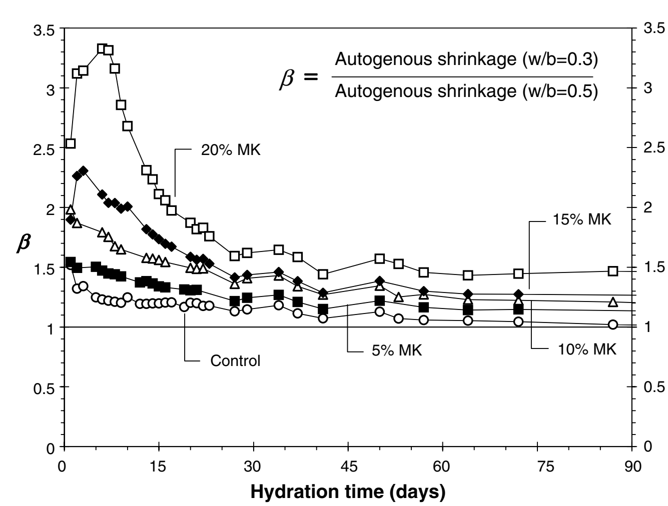

Fig. 2. Ratio of autogenous shrinkage between pastes at w/b of 0.3 and 0.5.

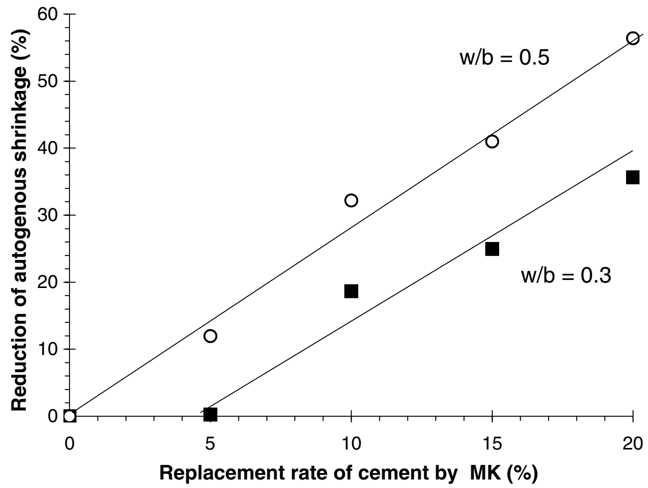

Fig. 3. Effect of MK on the long-term (129 day) reduction of autogenous shrinkage of cement pastes (w/b = 0.30 and 0.50).

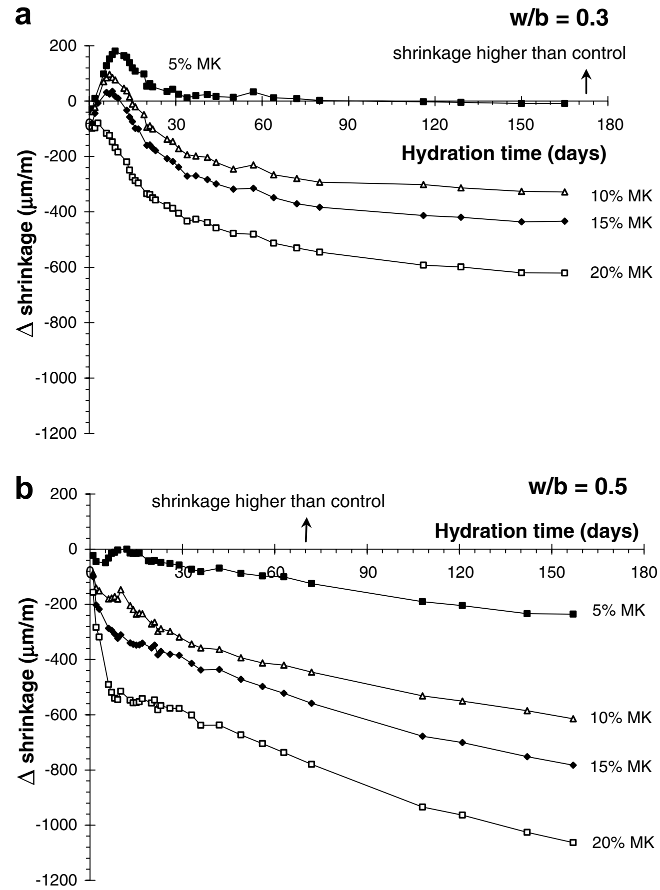

Fig. 4. Differences of autogenous shrinkage between pastes with MK and pastes with cement only (water/binder (a) 0.30 and (b) 0.50).

and 35% reduction for w/b ratios of 0.5 and 0.3 respectively. At low w/b ratio, 5% MK was not sufficient to modify the length change compared to the control mixture, so more MK is needed to reduce the autogenous shrinkage of plain cement pastes significantly. These modifications are related to various physical and chemical phenomena, as discussed later.

Fig. 1 reveals a few differences in the length change kinetics at young ages, depending on the water content of the paste. While all MK pastes with a w/b ratio of 0.5 showed decreased autogenous shrinkage from the start, it can be seen that this was not the case for the driest mixtures (w/b = 0.3), since the presence of MK increased the short-term shrinkage (this is especially evident for 5% MK). Fig. 4 highlights these differences of kinetics by showing curves obtained by subtracting the shrinkage of control mixtures from that of pastes containing MK. For low-water content, there is a clear acceleration of autogenous shrinkage at young ages, illustrated by the maximum in the curves of Fig. 4a, obtained for ages of 9, 7, 6 and 3 days for 5%, 10%, 15% and 20% MK, respectively. The phenomenon responsible for the short-term acceleration of autogenous shrinkage is probably related to heterogeneous nucleation of the hydration products on MK particle surfaces, which accelerates the formation of C–S–H and thus accelerates autogenous shrinkage. This effect is predominant compared to the effect of the reduction of autogenous shrinkage due to the dilution of the cement. This will be discussed later. For longer hydration times, there is a deceleration of the autogenous shrinkage relative to that of the control mixture, which may be related to the reaction of MK. In the case of high-water content (w/b of 0.5, Fig. 4b), the young-age acceleration is almost imperceptible and the overall tendency is rather a continuous decrease of autogenous shrinkage of MK pastes compared to control mixture.

There are only a few results available in literature concerning autogenous shrinkage of cement-based materials containing metakaolin. As reported in the introduction, some of these results are conflicting. The differences could be attributed to variations in the experimental conditions (pastes or concrete, testing apparatus), curing procedure and period, cement and MK types and contents, and specimen size and shape.

In the case of low-water content materials, our results at a w/b ratio of 0.3 on cement pastes are in contradiction with those of Brooks and Megat Johari [30], who studied autogenous shrinkage of concrete having a w/b ratio of 0.28. Their measurements were performed in two stages, the first one covering the time of initial set to approximately 24 h, while the second one began at 24 h and ended at 200 days. The measurement method used in the second stage was similar to the one used in the present paper. Their results depended on the initial time from which they started the shrinkage measurements. They found that MK reduced the early autogenous shrinkage (up to 24 h), the highest reduction being obtained at high replacement levels. However, the long-term shrinkage measured from 24 h led to opposite results, since the use of MK significantly increased the autogenous shrinkage of concrete, the highest values being obtained for the lowest replacement level (5%). When the two stages of measurements (from initial set up to 200 days) were combined, it was found that the concrete with

5% MK exhibited the maximum long-term autogenous shrinkage, while those with 10% and 15% MK showed lower autogenous shrinkage than the control concrete.

For high-water content, our results can be compared with those given by Wild et al. [31] and Kinuthia et al. [32], both papers coming from the same research team. The former [31] worked on cement pastes having a water–binder ratio of 0.55 and containing up to 25% of MK. For the short term (up to 14 days), all compositions except 10% MK exhibited an overall expansion, which was imputed to the excess of water within the moist-cured bars (due to high w/b ratio). Above 14 days, pastes with MK were in the shrinkage zone and the autogenous shrinkage showed a well-defined maximum at 10% MK. This maximum was attributed to a synergetic effect of cement hydration and pozzolanic reaction in removing water from the system to produce self desiccation. The pastes containing more than 10% MK presented a marked reduction in autogenous shrinkage, the reduction being much greater at longer curing times. This reduction was attributed in part to the formation of increased amounts of C_2ASH_8 and reduced amounts of C_4AH_{13}. This hypothesis was not verified by experiments. The latter [32], who also worked on cement pastes (w/b of 0.5), came to similar conclusions, the behavior of pastes changing at around 10% of MK: at 5% and 10% MK, the autogenous shrinkage started slowly at young ages but reached higher long-term values, the maximum being obtained for 10% replacement; the use of 15% and 20% MK significantly reduced autogenous shrinkage, the latter even leading to an overall expansion. According to the authors, the maximum at 10% MK was attributable to acceleration of the early hydration of cement, while the expansive process due to MK was related to the nature of the reaction products formed as a result of the MK pozzolanic reaction.

Most of our results at the w/b ratio of 0.5 are significantly different from those of the above-mentioned authors, the only apparent similarity being the reduction of autogenous shrinkage at higher MK replacement levels (15% and 20%). These differences are probably due the variations of composition and reactivity of cement and MK, which can affect the CH/MK ratio and consequently the kind and proportion of phases formed by the CH–MK pozzolanic reaction [7,31]. The main contradictions between the literature and our study were that the overall length changes were not positive (expansion) and a pessimum at 10% MK was not observed in the present study, since the reduction of autogenous shrinkage was proportional to the amount of MK in the mixture. Concerning the pessimum effect observed in the literature, it should be noted that it was not systematically found for all pastes. Kinuthia et al. [32] showed that it depended on the composition of the cement used and they highlighted a clear relationship with the C_3A content of their cements, the amount of shrinkage recorded in MK pastes decreasing systematically with increasing C_3A content (Fig. 5). This phenomenon only concerned pastes with MK, since neat pastes with all their three cements presented almost the same autogenous shrinkage. According to the authors, the way in which MK controlled the autogenous shrinkage could be attributed to changes in the rate of cement hydration. When comparing autogenous shrinkage of this study (10% MK) with the results obtained by Kinuthia et al. [32], it can be seen (Fig. 5) that:

– the shrinkage behavior obtained with our cement (10% of C_3A) is not incompatible with the results of these authors;
– the absence of expansion, and so the apparent contradiction between the different results, might be partly explained by the differences in cement compositions.

3.2. Role of MK in the reduction of autogenous shrinkage

The use of mineral admixture to replace a fraction of the cement could lead to many effects on autogenous shrinkage of cement pastes, the main ones being:

- A dilution effect, related to the decrease in the amount of cement. On the one hand, knowing that less cement implies less hydrated cement, the dilution should lead to a decrease in autogenous shrinkage, at least in the short term. On the other hand, for a given volume, pastes with mineral admixtures have higher water–cement ratios than the control mixture. This could sometimes improve the degree of hydration of the cement [36,37], and consequently produce more hydrated cement and maybe more autogenous shrinkage.
- Heterogeneous nucleation, which is a physical process leading to a chemical activation of the hydration of cement. It is related to the nucleation of hydrates on foreign mineral particles, and it mostly depends on the

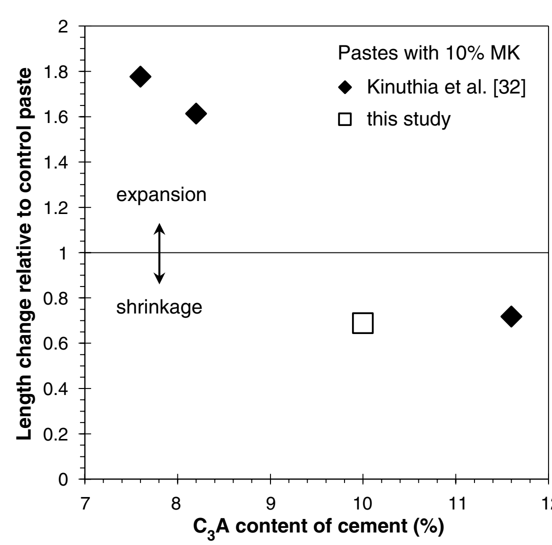

Fig. 5. Effect of C_3A content of cement on length change behavior relative to control of pastes containing 10% MK.

fineness of the mineral admixture particles. For a given age, heterogeneous nucleation involves more hydrated cement, so more autogenous shrinkage.

- The reactivity of mineral admixtures, which leads to the production of hydrates responsible for various phenomena having opposite effects:
  - self desiccation, which tends to cause an increase in the autogenous shrinkage, particularly affects pastes containing silica fume;
  - strengthening of the paste, which could reduce its deformability;
  - pozzolanic reaction itself, which produces hydrates involving volume changes. However, not all authors agree on the overall change of volume (shrinkage or swelling) associated with the reactions.

In order to highlight the effect due to MK on autogenous shrinkage of cement pastes, it was decided to dissociate the dilution from the other effects. So the dilution effect was evaluated from pastes containing an inert mineral admixture composed of particles large enough for it to be assumed that heterogeneous nucleation was not significant (quartz Q_{ref}). It has already been shown elsewhere [33] that the quartz Q_{ref} characterizes only the dilution effect associated with the use of mineral admixture in cement based materials. The autogenous shrinkage of cement pastes containing 10% and 20% of Q_{ref} is given in Fig. 6, in comparison with 10% and 20% MK pastes. Although the pastes with Q_{ref} and MK (10% or 20%) have the same amount of cement, it can be seen that the kinetic and long-term values of autogenous shrinkage are quite different. The autogenous shrinkage of MK pastes occurs earlier but slows down after 20 days. It also reaches values significantly under those of Q_{ref} pastes. So these results tend to show that the activity of MK helped to counteract the increase of autogenous shrinkage due to cement alone.

Over the three main properties which differentiate Q_{ref} and MK (particle form, fineness and reactivity), two of them surely have a significant effect on autogenous shrinkage: the particles of MK are probably small enough to serve as nucleation sites for cement hydrates, enhancing hydration and consequently increasing autogenous shrinkage; moreover, the reactivity of MK might greatly influence the overall length changes. Fig. 7 gives the differences of autogenous shrinkage (Δ *shrinkage*) between pastes with MK and pastes with Q_{ref}, obtained from Fig. 6 by subtracting Q_{ref} curves from MK curves. The resulting curves should characterize the heterogeneous nucleation and pozzolanic effects of MK on autogenous shrinkage.

The evolution of Δ *shrinkage* presents two phases (as indicated in Fig. 7):

- a first phase characterized by an increase in Δ *shrinkage*, which means that the paste with MK showed more autogenous shrinkage than the one with Q_{ref}. Knowing that the two mixtures had the same amount of cement

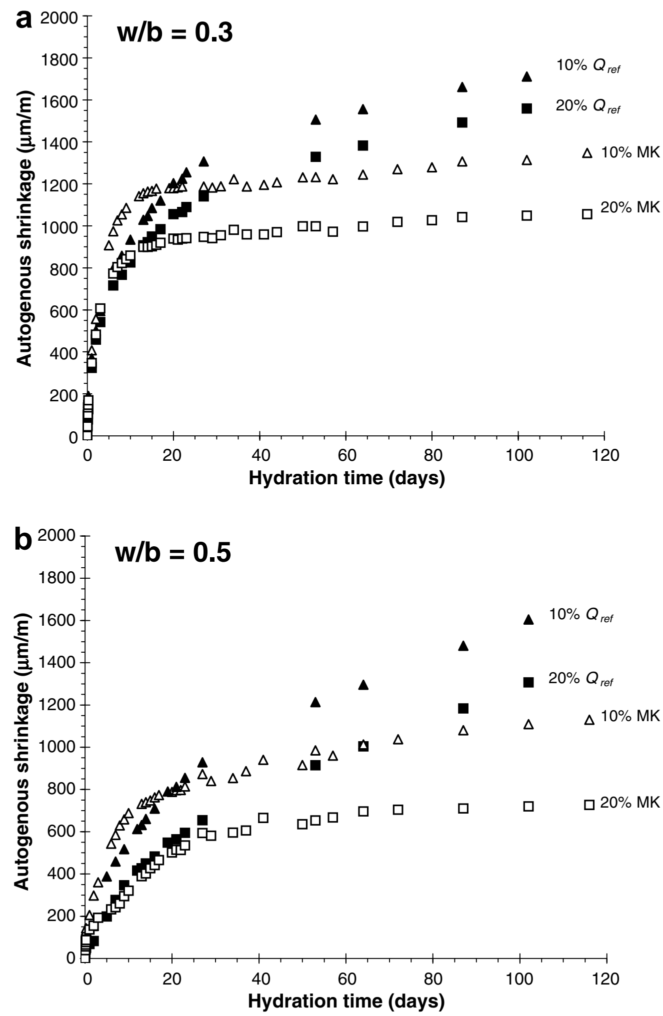

Fig. 6. Comparison of autogenous shrinkage between pastes containing 10% and 20% of MK and Q_{ref}, for water/binder ratios of (a) 0.30 and (b) 0.50.

and that Q_{ref} was coarse enough to be considered as having no effect on cement hydration, this increase of autogenous shrinkage was probably due to a heterogeneous nucleation effect. Metakaolin is known to accelerate C_3S hydration in the very early stages of curing [7].

- a second phase with a rapid and large decrease in Δ *shrinkage*, leading to a lower shrinkage of MK pastes in the long-term. This decrease was probably due to the pozzolanic activity of MK, which became predominant after a few days compared to the heterogeneous nucleation effect. DTA analysis showed that MK could react in the first few days of cement hydration (Table 2).

3.3. General comments

There is a consensus in the literature that the pozzolanic reaction between MK and CH contributes to the refining of the binder capillary porosity [2–7] as in the case of silica fume (SF) [38–42]. However, for cement–SF blends, the refinement of pore size distribution leads to an increase

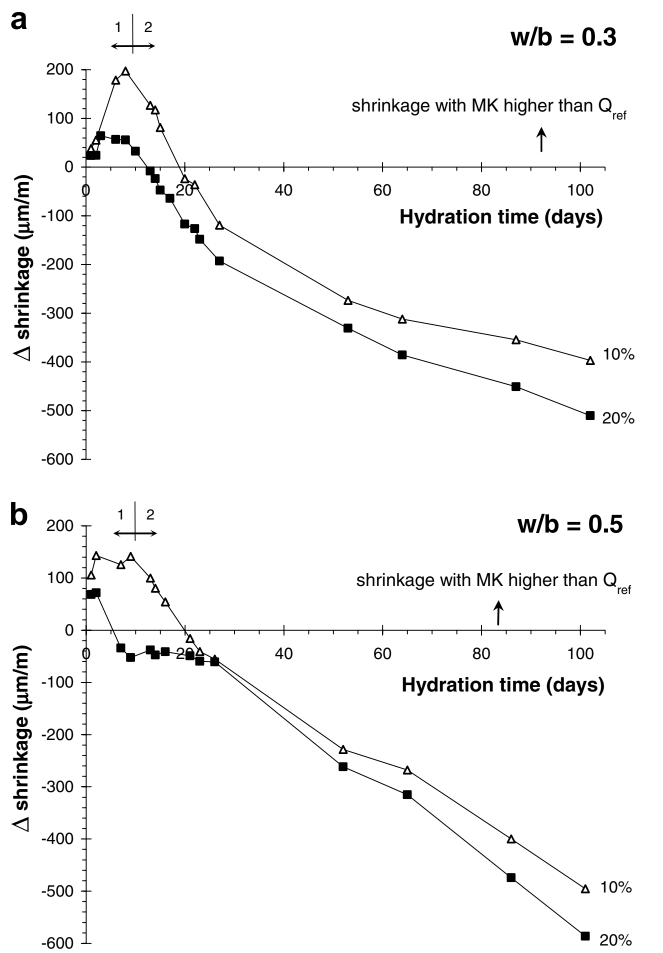

Fig. 7. Differences of autogenous shrinkage between pastes with MK and pastes with Q_{ref} (water/binder (a) 0.30 and (b) 0.50).

in capillary tension and, therefore, to an increase in autogenous shrinkage [35,43,44].

It was expected that a similar phenomenon would occur with cement–MK blends but it was not observed in this work. It seems that another phenomenon occurred, which counteracted the increase of pore capillary tension. Moreover, the separation of the effect of heterogeneous nucleation and pozzolanic activity from the dilution effect by using a coarse powder in the place of MK showed that a significant part of the reduction of long-term autogenous shrinkage in cement–MK pastes is due to the MK pozzolanic activity. Wild et al. [31] calculated the volume variation generated by MK–CH pozzolanic reaction by assuming ideal compositions for both gel and crystalline phases (Eq. (1)) and taking into account the compound densities. They found that this reaction produced a volume reduction of 4.56% i.e. increasing autogenous shrinkage. So it cannot explain our results.

$$3.5CH + AS_2 + 6H \rightarrow C_2ASH_8 + 0.5C_3S_2H_3 \quad (1)$$

In order to explain part of the autogenous shrinkage reduction of cement–MK for high replacement levels of cement by MK, Wild et al. [31] stated that this phenomenon could be due to the substitution of tetracalcium aluminate hydrate (C_4AH_{13}) by a lower density gehlenite hydrate (C_2ASH_8). However the fact that, according to our DTA results (Table 2), C_4AH_{13} was not detected does not support this explanation. It seems that this compound is produced only in MK–CH mixes [34].

More research is still needed to understand the effect of MK on autogenous shrinkage of cement–MK blends, especially to find whether the decrease is due to a swelling behavior or to a sudden increase in the paste rigidity, both of which are related to the pozzolanic reaction.

4. Conclusion

This work intended to clarify the part of the autogenous shrinkage involving cement and metakaolin. The following conclusions can be drawn from this study:

- Long-term autogenous shrinkage of cement–MK paste, with w/b ratios of 0.3 and 0.5, decreased as the cement replacement level by MK increased (5%, 10%, 15% and 20%). No overall expansion of pastes was observed at early ages. The apparent contradiction between the results of this study and other found in literature might be partly explained by the differences in cement and MK compositions.
- By separating the effect of heterogeneous nucleation and pozzolanic activity from the dilution effect by using a coarse powder in place of the MK, it was shown that a significant part of the reduction of long-term autogenous shrinkage in cement–MK pastes is due to the MK pozzolanic activity.
- It is well known that the pozzolanic reactions MK–CH and SF–CH contribute to the refinement of the binder capillary porosity, with its direct consequences on the improvement of the mechanical and durability characteristics. However, SF increases autogenous shrinkage while MK reduces it. This behavior needs to be explained by further research.

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