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Short communication

Influence of Portland cement composition on early age reactions with metakaolin

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Abstract

The reactivity of two metakaolins, which vary principally in their surface area, and Portland cements of varying composition were examined via isothermal calorimetry for pastes at water-to-cementitious materials ratio of 0.50 containing 8% cement replacement by weight of metakaolin. Both metakaolins examined appear to have a catalysing effect on cement hydration. Calorimetry showed accelerated hydration, a slight increase in cumulative heat evolved during early hydration, and – for some cements examined – apparently an increased intensity of the heat evolved, particularly during the period typically associated with hydration of calcium aluminates. The higher surface area metakaolin had a greater effect. It is proposed that the presence of metakaolin may enhance dissolution of cementitious phases and/or provide additional, well-dispersed sites for nucleation of hydration products, in addition to increasing the early age concentration of solubilized aluminium (due to metakaolin dissolution). The increased intensity of some of the calorimetry data also suggests that some additional exothermic reactions are occurring, which may be related to an increased reactivity of calcium aluminate phases in the cement as well as the reaction of the metakaolin. This effect is apparently increased as the cement equivalent alkali content increases.

Keywords: Alkalis (D); $Ca_3Al_2O_6$ (D); Calorimetry (A); Fineness (A); Hydration (A)

1. Introduction

Metakaolin (MK) is a supplementary cementitious material (SCM) derived from heat treatment of natural deposits of kaolin. Typically, metakaolins show high pozzolanic activity due to their amorphous structure and high surface area [1–3]. Because their reactivity derives from heat treatment, the influence of processing variables (e.g., calcining temperature, particle shape and size) influences MK reactivity [4].

In Portland cement concrete, MK reacts at normal temperatures with calcium hydroxide in cement paste to form mainly calcium silicate hydrates (C–S–H), C_2ASH_8 (gehlenite hydrate), and C_4AH_{13} (tetracalcium aluminate hydrate) [5]. The formation of secondary C–S–H by this reaction both reduces total porosity and refines the pore structure, improving the strength and impermeability of the cementitious matrix [4,6,7].

Metakaolin differs importantly, however, from most other SCMs, because of its rapid reaction rate, its high reactivity with calcium hydroxide (which is produced during the hydration of the calcium silicate phases in the cement), and its ability to accelerate cement hydration [8,9]. MK has been demonstrated to increase the rate of heat evolution during cement hydration [10]. This has been attributed both to the accelerating effect of MK on Portland cement hydration and the high reactivity of MK with CH.

For this reason, quantification of the heat of hydration in MK/Portland cement[1] systems can be used to examine the rates

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[1] Several studies have examined the reaction between MK and CH in isolation, i.e., in systems prepared with different MK:CH, subjected to different temperatures (see, for example, [5,11–14]) However, in an MK/PC system (containing up to 25% MK), the development of the hydrated phases occurs quite differently than in MK/CH systems [15]. Thus, examination of MK/PC systems is necessary to best understand the reaction of MK in cementitious materials.

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of reaction between MK and cement and MK and the CH produced by initial hydration. In addition, this type of information can improve understanding of the implications of the use of MK on strength development (see for example, the work of [16,17]) and also can be used to assess the suitability of metakaolin-containing binary, ternary, and quarternary blends for mass concrete, where exothermicity is a concern.

This research examines the early age heat of hydration developed in MK/PC pastes, using cement of different compositions to examine the influence of cement composition on reactivity with MK. To the authors' knowledge, the influence of the cement mineral composition and equivalent alkali content ($Na_2O_{eq} = Na_2O + 0.658 \cdot K_2O$) on the early age reaction of metakaolin/cement systems has not been addressed previously in published research.[2] In this investigation two different metakaolins (which vary principally in their fineness) were combined, at 8% replacement levels, with cements selected to vary primarily in their tricalcium aluminate (C_3A) and equivalent alkali contents.

2. Methods

2.1. Materials

To understand the effects of cement composition on the early age reactions with metakaolin, commercially available cements with varying composition were selected and were examined, both alone and with metakaolin. These cements were selected on the basis of their oxide analysis and Bogue potential compositions (Table 1). Because metakaolin is known to accelerate cement hydration, the cements were initially selected to allow for relative variations in composition:

(1) Variations in C_3A content, while the alkali equivalent remains nearly the same, may be examined by comparing Cements 1 (low C_3A), 2 (moderate C_3A), and 3 (high C_3A).
(2) Variations in the alkali equivalent content, while the C_3A content remains relatively the same, may be examined by comparing Cements 4 (low Na_2O_{eq}), 2 (moderate Na_2O_{eq}), and 5 (high Na_2O_{eq}).

However, after analysis of the results, it was determined that the variation in C_3S content likely also plays an important role. Thus, a third and fourth group of samples may be compared:

(3) Variation in C_3S content may be examined by comparing Cements 2 (low C_3S), 1 (moderate C_3S), and 3 (high C_3S), where the alkali content remains approximately the same,
(4) or by comparing Cements 5 (low C_3S), 2 (moderate C_3S) and 3 (high C_3S), where the C_3A content remains approximately the same.

Table 1
Chemical oxide analyses and Bogue potential compositions for five cements examined (% by weight)

Component	Cement				
	1	2	3	4	5
	Characteristic				
	Low C_3A	Mod C_3A/ Mod Na_2O_{eq}	High C_3A	Low Na_2O_{eq}	High Na_2O_{eq}
SiO_2	21.00	20.98	19.29	20.44	20.13
Al_2O_3	3.62	4.72	5.62	5.24	5.48
Fe_2O_3	3.47	2.99	2.82	3.99	3.26
CaO	62.52	63.56	64.21	63.22	60.93
MgO	4.29	2.24	0.86	1.05	2.45
SO_3	2.43	2.61	3.54	3.74	4.00
Na_2O	0.231	0.165	0.257	0.069	0.344
K_2O	0.404	0.523	0.464	0.343	0.866
Na_2O_{eq}	**0.50**	**0.509**	**0.562**	**0.295**	**0.91**
P_2O_5	0.054	0.335	0.256	0.092	0.157
TiO_2	0.172	0.241	0.614	0.318	0.214
SrO	0.050	0.035	0.231	0.065	0.194
Mn_2O_3	0.064	0.150	0.040	0.079	0.173
Cr_2O_3	0.005	0.008	0.014	0.012	0.025
LOI	1.69	1.44	1.79	1.33	1.78
C_3S	**59.0**	**55.9**	**62.9**	**50.4**	**42.0**
C_2S	**16.0**	**18.0**	**7.9**	**20.6**	**26.0**
C_3A	**4.0**	**7.5**	**10.1**	**7.1**	**9.0**
C_4AF	**11.0**	**9.1**	**8.6**	**12.2**	**10.0**

Bold data denotes key characteristic.

Of course, when using commercially available cements, it is difficult to examine the effect of one variable whilst attempting to maintain others approximately constant. However these five cements were selected for this research from a wide range of cements because the variation of the other parameters was considered sufficiently small. Also using commercially available cements, rather than laboratory-produced individual phases or blends, is more relevant to practical use.

With each of these cements, pastes were prepared at 0 and 8% replacement per mass with one of two MKs. Because of the known acceleration of PC hydration with finely divided supplementary cementing materials, two MKs of practically the same mineralogical composition, but with different surface areas, were used; the surface area of sample MK235 measured 11.1 m^2/g, while that of MK349 measured 25.4 m^2/g. Detailed chemical and physical analyses of these two materials are provided elsewhere [9,20,21].

2.2. Test methodologies

The heat of hydration for each sample type was evaluated via isothermal calorimetry, using a Thermometric 3114 TAM Air eight-channel heat conduction calorimeter, maintained at 25 °C. To obtain high quality data, each group of sample replicates was prepared in a precise and reproducible manner, while still

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[2] Most closely related to this investigation, Moulin et al. [18] examined the influence of sulfate and free lime content on rheological behaviour, setting time, and compressive strength of Portland cement/metakaolin mortars and Love et al. [19] characterized the extent of early reaction of a Portland cement/metakaolin combination, with and without alkali activation.

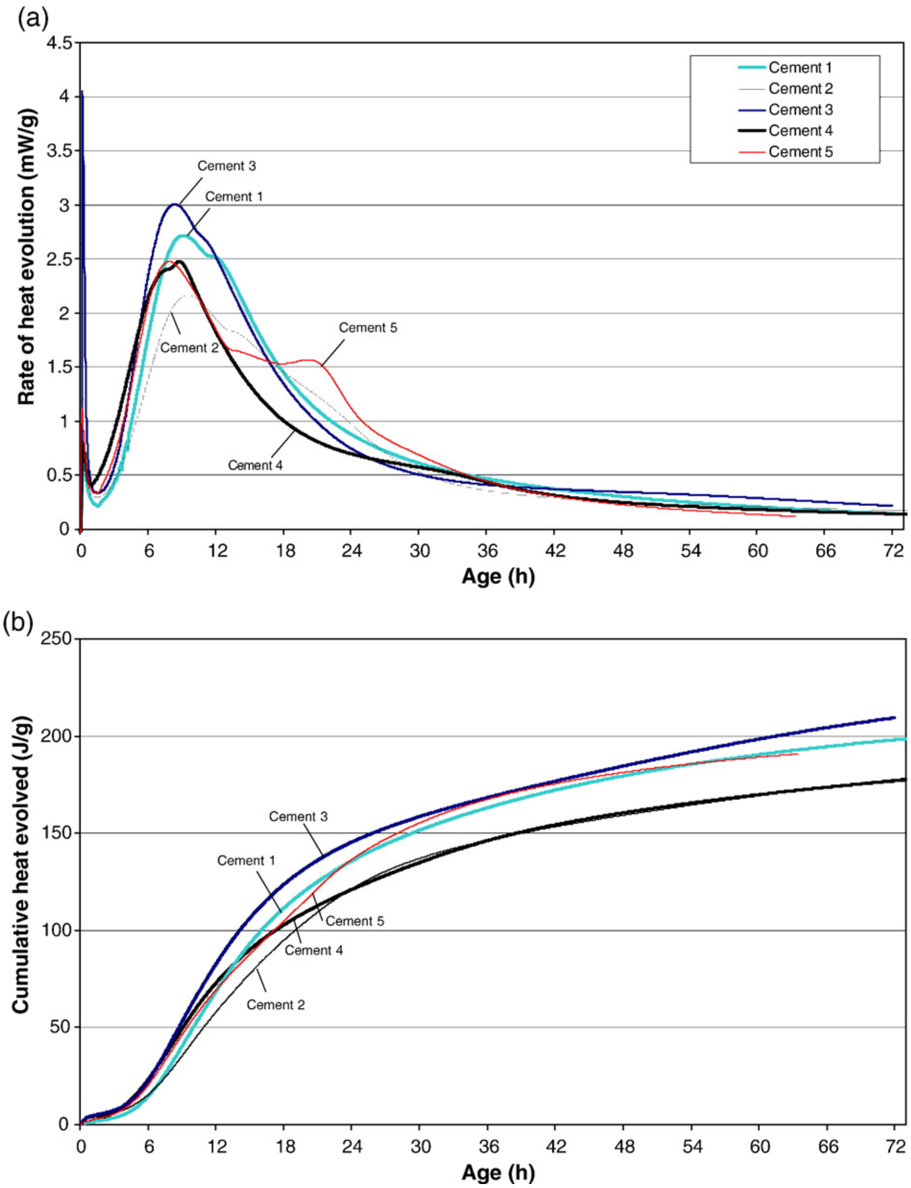

Fig. 1. Comparison of the (a) rate of heat evolution and (b) cumulative heat evolved for the five different cements examined.

maintaining a rapid rate of preparation (∼4 min.) such that the very early hydration data may be recorded. After acclimatizing all materials and mixing implements in a 25 °C environmental chamber, the PC and MK were blended manually for 30 s. After the addition of water, to produce a w/cm of 0.50,[3] the paste was blended 10 s by hand and then an additional 50 s mechanically. Polyethylene ampoules were filled with approximately 10 g of each paste.

All experiments were conducted in replicates of three, and data were collected for at least 72 h. When running multiple mixtures concurrently, the calorimeter and data collection process were started upon addition of water to the first mixture. As subsequent mixtures were produced, the time that water was added was recorded so that the curves could be offset when analysing the data.

3. Results and discussion

Fig. 1 shows data for both the rate of heat evolution (mW/g) and the cumulative heat evolved for each of the five cements. Rate data and the cumulative heat evolved (J/g) for the cements alone and in combination with each of the two metakaolins (MK235 and MK349) examined are shown in Fig. 2. All results are normalized per gram of paste. The curves presented in Figs. 1 and 2 represent the average of data of three replicates for each sample type, although for each sample type the results for the different replicates were approximately the same.

The results for the blended pastes are quite interesting because the rates of heat evolution vary significantly with the addition of metakaolin and also with the variation in MK

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[3] This w/cm was selected to ensure good workability and to follow the previous work with metakaolin by Justice and co-workers [9,20,21].

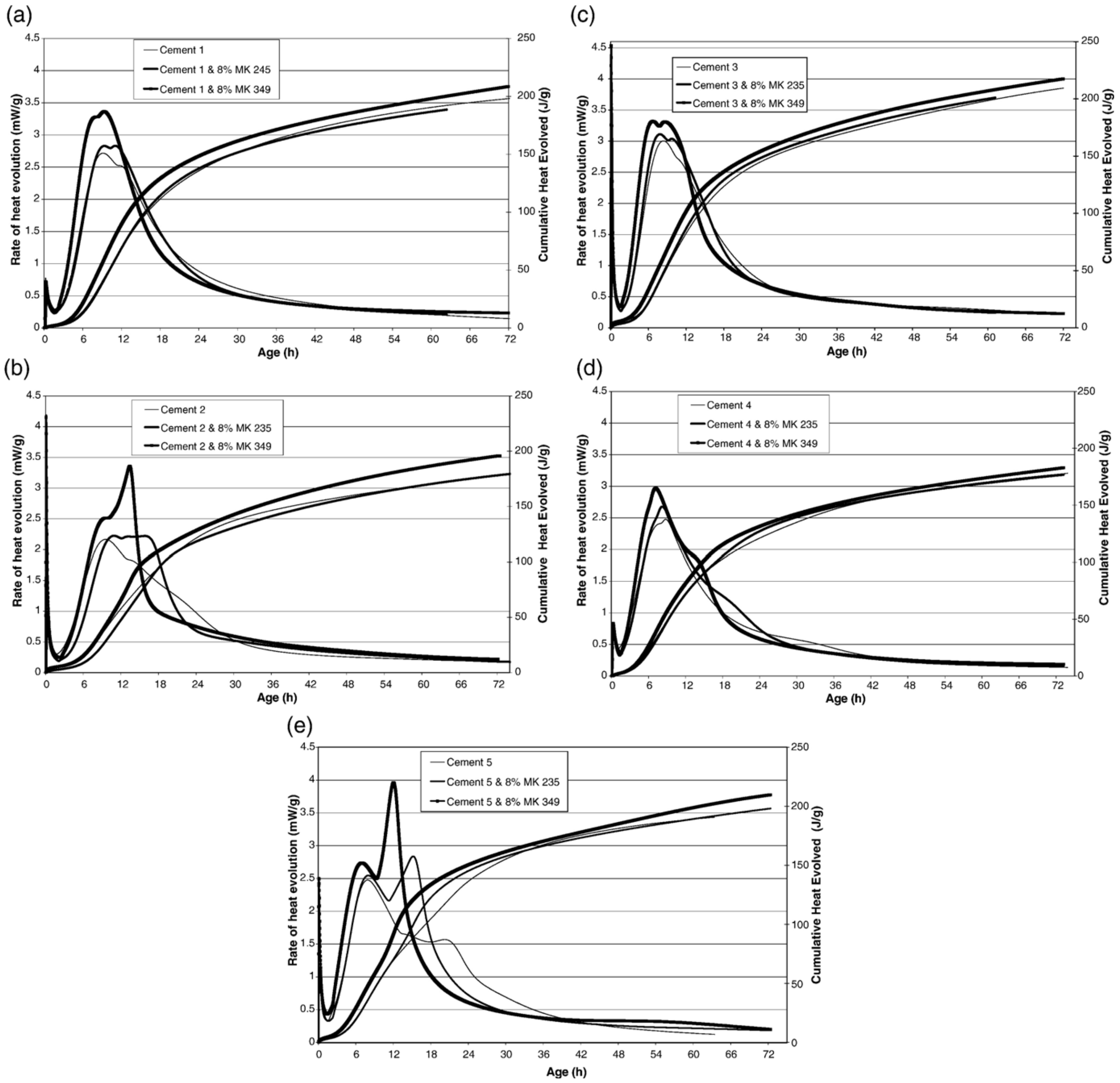

Fig. 2. Calorimetry data, including rate of heat evolution and cumulative heat evolved, for each cement alone and in 92/8 blends with each metakaolin. Data for low-C_3A Cement 1 is shown in (a), moderate-C_3A/moderate-alkali Cement 2 in (b), high-C_3A Cement 3 in (c), low-alkali Cement 4 in (d), and high-alkali Cement 5 in (e).

surface area (Fig. 2). In general, the metakaolin/cement pastes showed higher cumulative heats of hydration and faster rates of reaction than companion plain cement pastes, especially at ages <6–10 h. Using a semi-adiabatic method, other researchers [10] found that the addition of 10% and 30% metakaolin increased heating over time in Portland cement mortars, particularly in the range of ~20 h; unfortunately because the cement composition in this previous study was not provided and because of the relatively low resolution of the early heat generation data, direct comparisons with the results presented herein are not possible.

With the five cements examined here, generally greater reaction acceleration (apparent from a couple of hours of age) and greater cumulative heat (particularly at 12+h) were observed with the finer metakaolin (MK349). Similar results have been reported in the literature [9,20,21]. The metakaolin also clearly influenced the intensity of the second and third (and, perhaps, fourth) peaks. The influence of the cement composition on the metakaolin reaction, as well as the influence of the metakaolin fineness, is considered in more detail in the following discussions.

3.1. Variation in cement composition

Three "peaks" in heat evolved with type are typically associated with cement hydration and are apparent in all of the calorimetry data for the cement pastes (Fig. 1) and PC/MK blends (Fig. 2). An initial peak occurs immediately after mixing the water with the cement, which occurs due to dissolution and initial formation of ettringite (Aft) phases. However, it is difficult to carry out a rigorous analysis of the first temperature peak, as the samples have just been introduced to the calorimeter. A second and third peak occur some hours later, and in some samples, a smaller fourth peak may also be apparent.

In the hydrating cement paste, at the end of the induction period, the pore solution becomes supersaturated in Ca^{2+} and OH^-, and $Ca(OH)_2$ products begin to nucleate [6]. The second peak, then, typically corresponds to the hydration of the C_3S, which forms the first C–S–H and portlandite ($Ca(OH)_2$). After the induction period, the second peak typically occurs in these samples between 8.5 and 9.5 h of age. Here, the highest second peak level is noted for the cement with highest amount of C_3S — Cement 3 with 62.9% C_3S. Moreover, it is noticed that the greater the amount of C_3S, the earlier this second peak occurs, when comparing Cements 2 (low C_3S), 1 (moderate C_3S), and 3 (high C_3S), which have approximately the same alkali content. In comparing the relatively low-C_3S Cement 5 with the others, this trend is not apparent, likely due to the relatively higher (0.91%) alkali content. From the cumulative heat of hydration data (presented for each cement in Fig. 1b), the quantity of C_3S in the cement also appears to influence the rate at which hydration continues. The slope of the cumulative heat curve at ages ~12–24 h is generally steeper when greater amounts of C_3S are present, as expected.

The third peak observed in the rate of heat evolution data for cement pastes is typically associated with the reaction of C_3A and it is suggested that this corresponds to the renewed formation of ettringite [22,23]. In most of the cements and blends examined, the third peak occurs approximately 1 to 5 h after the second peak. The duration between the second and third peak, however, is somewhat longer for Cement 5 (Fig. 1e), where the third peak is not observed until perhaps ~14 h, although a more pronounced peak is found at ~20–21 h.

At ~30 h, it is possible to see another or fourth peak in some cementitious systems. This peak has been associated with hydration of the ferrite phase or with the conversion of Aft to AFm phase [22,23]. For these data, a fourth peak is only slightly apparent at ~28–36 h in Cement 4 (Fig. 1), which is, interestingly, the cement with the highest C_4AF content. In addition, for Cement 5, it is possible that the peak apparent some hours earlier – at 20–21 h – may also indicate a reaction of the ferrite phase or a conversion from Aft to AFm; further analysis is necessary to better understand the relationship between these calorimetry data and the products present at these early ages in the hydrating Cement 5.

3.2. Influence of cement C_3A content

The influence of metakaolin addition on cements with varying C_3A content may be examined by comparing the data for Cements 1, 2, and 3 (Fig. 2a, b, and c). With each of these cements, both MKs generally accelerate the rate of hydration, which is apparent as a shift to the left in Fig. 2. Although MK influences the rates of heat evolution from both C_3S and C_3A hydration, it has an apparently lesser accelerating effect on C_3S hydration (peak 2) and a greater effect on C_3A hydration (peak 3).

In addition, while the third peak is generally lower than the second for the ordinary cement pastes, when MK is used at 8% replacement, the magnitude of third peak becomes greater (i.e., more exothermic) than in the ordinary paste. For the Cement 2/MK349 blend (Fig. 2b), for example, the third peak is much greater than the second. While the height of the third peak in the cement pastes tended to increase with increasing C_3A content, in the presence of MK 349, the maximum rate of heat evolution is just under 3.5 mW/g for the Cements 1, 2, and 3 blends.

The dramatic increase in the magnitude of energy release associated with the third peak is also apparent in Cement 5 (Fig. 2e), which is the cement with the highest alkali content, as well as the highest SO_3 content. With Cement 5, the increased third peak is apparent for blends of the cement with both metakaolins. This suggests that some additional exothermic reactions, likely related to the reaction of calcium aluminate phases, are occurring due to the presence of the metakaolin.

According to Frías and Cabrera [24], at 1 day, the calcium hydroxide contents of MK/PC blends containing 5–20% MK at w/cm of 0.55 are higher than in Portland cement paste alone. Data obtained by [9,20] on the same two metakaolins examined here at an 8% addition rate, but at a w/cm of 0.40, also showed that the CH content in the MK/cement blends was greater than in the cement paste alone, but only up to 8 h. However, both data – with the acceleration noted in the rate of heat evolution curves for the blended pastes – suggest that MK accelerates very early cement hydration reactions, perhaps by enhancing dissolution and/or by providing additional, well-dispersed sites of nucleation.

Justice and Kurtis [9,20] also report that after ~24 h, the CH content in the MK/cement blends is less than in the cement paste alone. Taken together, these observations suggest that in 8% MK/cement blends the rate of CH consumption, by a combination of cement hydration and pozzolanic reactions, at ages beyond 24 h is greater than the rate of CH production during that same period. This provides additional support for observations made by Wild and Khatib [17] in similar systems at 3–14 days of age.

Data in Fig. 2 also suggests that the MK with the greater surface area (i.e., MK349) has a greater accelerating effect than the coarser MK235. The MK349/cement blends showed the fastest rate of heat evolution, for the cements and addition rate examined. This agrees with prior results with the same metakaolins [20]. Also, the use of MK349 consistently resulted in greater cumulative heat generated at 72 h, with the greatest heat evolution observed in the blend with the highest C_3A content cement (Cement 3, Fig. 2c). However, the influence of the C_3A content was not clearly apparent when comparing the cumulative heat curves for the MK349/cement blends for low-C_3A Cement 1 with the moderate-C_3A Cement 2 (Fig. 2a and b). For the MK 235/cement blends, the cumulative heat evolved curves are approximately the same as plain cement *after ~30 h*, in general agreement with [10].

However, at earlier ages, the MK235/cement blend actually lags behind the plain Cement 2, but some acceleration in cumulative heat evolution is noted in the Cement 1 and 3 blends with MK235 at earlier ages. This agrees with results from [10] which showed an increase in heat of hydration between 18 and 30 h in mortars containing 10 and 30% metakaolin and with results from [25] which similarly showed an increase in heat of hydration in mortars containing 10 and 15% metakaolin. These observations suggest that strongly exothermic reactions occur between the cement and metakaolin, particularly in the first 24 h, and that the rates of these reactions are accelerated particularly by the increased surface area of MK349.

3.3. Influence of cement alkali content

The effect of cement alkali content on metakaolin reaction in a cement paste may be examined by comparing data for Cements 4 (low alkali), 2 (moderate alkali), and 5 (high alkali) in Fig. 2d, b, and e, respectively. Comparing the neat cement pastes (Fig. 1) shows that the second peak (due mainly to the hydration of C_3S) is slightly affected by the alkali content. However, the main effect of alkalis appears to occur during the hydration of C_3A. Comparison of the data for Cements 2, 4, and 5 (Fig. 1) shows that when the alkali content in the cement increases, the hydration of C_3A seems to be suppressed. These results are in agreement with [26], where it is reported that the degree of hydration of C_3A may be decreased as the quantity of Na_2O in solution is increased.

As in the previous discussion of Cements 1, 2, and 3, after the induction period, the presence of both metakaolins slightly accelerated the C_3S and C_3A reactions (i.e., the second and third peaks were shifted to the left) in Cements 2, 4, and 5. In addition, for the high-alkali (Cement 5) and moderate-alkali (Cement 2) cases, the intensity of the third peak is particularly heightened in the presence of metakaolin, with the finer MK 349 producing a greater increase. It is proposed that the abundance of alkalis may have promoted dissolution of the metakaolin, and consequently the cement hydration is accelerated and the intensity of the reactions associated with the third peak is increased as compared to the neat pastes. Similar trends (i.e., an acceleration in reaction rate and an increase in the magnitude of energy release) were reported by de Silva and Glasser [27] during the alkali-activated reaction of metakaolin with water. In addition, Love et al. [19] recently reported that alkali activation, using a 5 M KOH solution, substantially increased in the extent of metakaolin reaction at early ages in metakaolin/cement paste.

Because the availability of solubilized aluminium often limits the rate of formation of calcium sulfoaluminate hydration products in early age cementitious systems, it is proposed that an increase in metakaolin dissolution rate (presumably due to higher alkali contents) would accelerate C_3A hydration. It is also possible that the metakaolin reaction itself could contribute to the height of the third peak, by dissolution as well as the formation of intermediate or metastable products, particularly if the alkali concentration was substantial enough to produce effects such as those reported in [19]. Further investigation is necessary to better understand these reactions associated with the third peak in the presence of metakaolin.

This concept of increased metakaolin dissolution is supported, however, by the data which show that the finer metakaolin, which would be expected to have a faster rate of dissolution, produces greater acceleration and greater heat increase associated with the third peak. While this analysis presumes that the C_3A content in these three cements was approximately the same while the alkali content varied, in actuality, Cement 5 with the high-alkali content also contains 1.5–2% more C_3A than Cements 2 or 4. Consequently, the higher C_3A content could have also contributed to the height of the third peak of the blends of MK235 and MK349 with Cement 5.

4. Conclusions

From the results presented and discussed above, the following preliminary conclusions can be made:

- The metakaolins examined appear to have a catalysing effect on cement hydration, leading to an acceleration in the reaction rates, an increase in cumulative heat evolved during early hydration, and – for some cements – apparently an increased intensity in heat evolved during certain periods of early hydration. The surface area of the metakaolin also seems to influence this early hydration behaviour, with the higher surface area material producing a greater rate of heat evolution, greater cumulative heat, and greater intensities during early hydration. It is proposed that the metakaolins, then, may act to enhance dissolution of cementitious phases and/or by providing additional, well-dispersed sites of nucleation, in addition to increasing the solubilized aluminium in the system at early ages.
- Strongly exothermic reactions appear to occur between the cements and metakaolins examined, particularly in the first 24 h, and these reactions seem to be most closely associated with the “third peak” observed in calorimetry — that which is most often related to the reaction of calcium aluminate phases. It is proposed that some additional exothermic reactions are occurring, which are likely related to the reaction of calcium aluminate phases and the reaction of the metakaolin.
- The reaction of metakaolin appears to be quite sensitive to variations in total alkali content in the cement. In particular, when comparing cements of similar composition, when the alkali content increases, the introduction of metakaolin appears to result in exaggeration of the third peak observed during calorimetry. It is proposed that an increasing rate of metakaolin dissolution with increasing cement alkali content may accelerate or intensify the reaction of the C_3A phase.

These preliminary results demonstrate that the reaction of metakaolins during early hydration does vary with cement composition. However, further research is necessary to better understand the reactions and the products formed over time. Further investigation should also determine if these observations result in behaviour of practical significance (e.g., admixture compatibility, setting time, thermal issues, durability).

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