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Heat of hydration of Portland Cement–Metakaolin–Fly ash (PC–MK–PFA) blends

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Abstract

In the present study two pozzolanic materials are used, Metakaolin (MK) and Fly Ash (PFA), as binary and ternary partial replacement binders with Portland cement (PC) to investigate their effect on the rate of heat evolution (dQ/dt in J/gh) during hydration, and the heat of hydration, (Q(t) in J/g). For binary PC–PFA blends PC hydration is enhanced in the very early stages of hydration, but at extended periods (up to 120 h) an increase in PFA replacement level causes a systematic reduction in heat output. For binary PC–MK blends the results suggest that the MK initially diminishes PC hydration but the subsequent pozzolanic reaction of MK increasingly contributes to the heat output causing some blends to exceed the heat output of the PC control. For both systems a principal controlling factor in the PC hydration rate (and the heat evolution rate) is the water requirement of the pozzolan, but for PC–MK blends the pozzolanic reaction of the MK makes a significant contribution to the heat output. However this reaction is controlled both by the availability of water and the supply of Ca^{2+} ions from the hydrating PC which introduces an increasing level of complexity to the heat output versus time profiles. When combining MK and PFA in ternary PC–MK–PFA blends the MK has a dominant influence on the heat output versus time profiles.

Keywords: Hydration; Calorimetry; Fly ash; Pozzolans

1. Introduction

The hydration of cementitious materials is exothermic, energy of up to 500 J/g of cement (120 cal/g) being liberated [1]. Because the thermal conductivity of concrete is relatively low, it acts as an insulator, and in the interior of a large concrete mass, hydration can result in a large temperature rise. The exterior of the concrete loses heat so that a steep temperature gradient may be established, and during cooling of the concrete surface cracking may result. Therefore knowledge of the heat-producing properties of different cementitious materials is required in order to choose a suitable cement for a given construction project. For example, although low activity pozzolans such as (fly ash) PFA result in an overall diminution in heat output of Portland cement (PC)–PFA blends relative to PC, in the short term PC–PFA blends can show enhancement of PC hydration and heat output. Kokubu [2] reported on a study that used water washed fly ash to investigate the influence of the soluble components (mostly calcium sulphate) of fly ash. It was found that with increase in the PC replacement level with fly ash, the time (approximately 8 h) at which the rate of heat evolution reached a second peak was slightly reduced and also a higher peak was produced in spite of decreasing cement content. It was suggested that the effect of fly ash on cement hydration at early ages is controlled by the finely divided property of the PFA or the increase of the cement hydration through the increase of available space for hydration products [2].

In a later paper Langan et al. [3] found that during the first minutes of hydration, the heat evolved tends to increase with the partial replacement of PC with FA as more water is available for the initial hydrolysis. Langan et al. suggested that FA removes calcium ions from the solution, depressing the concentration in the first few hours and delaying the CH and CSH nucleation and

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CH crystallization [3]. The effect of FA is more significant at higher w/c ratios mainly in the induction and immediate post induction periods [3]. In the immediate post induction period the increase in the availability of water may subsequently enhance the hydration process as more water can react with the newly exposed surfaces. During this stage, the main hydration component is C_3S [3] and its hydration is accompanied by the crystallization of CH from the supersaturated solution. An increase in the heat of hydration during this period may also be influenced by an increase in the number of nucleation sites provided by FA particles for deposition of cement hydrates.

Frias et al. [4] reported work relating to the difference in the heat evolved (relative heat output) from PC–PFA and PC–(MK) Metakaolin (and also PC–SF) mortars for up to 120 h hydration. A w/b ratio of 0.5 was used with a sand to cement ratio of 3:1. The PC replacement levels were 10% for MK and 10% and 30% for PFA. The authors found that the total heat evolved (up to 120 h hydration) decreased with increasing replacement levels of PC with PFA whereas increasing replacement levels of PC with MK showed no substantial changes. However the 10% PC–MK blended mortar produced a higher output than the original PC; this was attributed to the higher pozzolanic activity of the MK. When measuring relative temperature rise, i.e. relative to PC mortar, MK mortar showed two peaks, the first at about 8 h and the second at 18–20 h. The authors suggest that the peak at 8 h is due to the reaction of CH with SiO_2 to form C–S–H gel and that the second peak is due to the reaction of CH with Al_2O_3 (and SiO_2) to give C_4AH_{13} (and C_2ASH_8) [5]. This explanation is however not feasible as the alumina and silica are combined within the metakaolin structure and could not react independently. The drop in relative heat output of PC–PFA mortar was attributed to the reduced PC content (dilution effect) and the negligible contribution from pozzolanic activity by the PFA [4]. The work by Frias et al. [4] is supported by later work of Poon, et al. [5] who reported the results of research on the rate of pozzolanic reaction of metakaolin in blended cement pastes and made comparisons with pastes containing FA (and silica fume). Cement was replaced with 5%, 10% and 15% MK making a total of 30 g dry powder. Heat evolution and cumulative heat evolution were measured against time. The authors reported that the initial rate of pozzolanic reaction was higher for the PC–MK blended cements and the cumulative heat was slightly higher for 5% and 10%PC–MK blended cements when compared to the PC control [5].

Bai and Wild [6] carried out similar work to that of Frias et al. [4] on mortar cubes with a maximum PC replacement level of 40% and MK levels of up to 15%. The authors found replacement of PC with PFA in binary blends depressed temperature rise, due to dilution of the PC by PFA, but MK replacement of PC in binary blends enhanced temperature rise. The latter was attributed to the increased rates of heat evolution during the first few hours of hydration resulting from the combined effects of pozzolanic reaction and acceleration of PC hydration. In agreement with Frias et al. [4] the temperature rise of PC–MK mortars with respect to PC mortar showed two distinct peaks. However in contrast to Frias et al. [4], Bai and Wild [6] interpreted the first peak, occurring at 6–10 h, as being associated with the pozzolanic reaction of MK and acceleration of cement hydration which are subsequently thus retarded by reaction with sulphate and formation of ettringite on MK particle surfaces, and the second peak, occurring at about 24 h, as being associated with the break down of ettringite to monosulphate and renewed hydration of MK [6]. The MK and PFA in PC–MK–PFA ternary blends have a compensatory effect, thus a 10%MK–10%PFA–80%PC blend has a similar temperature rise versus time profile to that of the PC control.

From previous reports it is apparent that the influence of different pozzolans on the rate of heat evolution and the amount

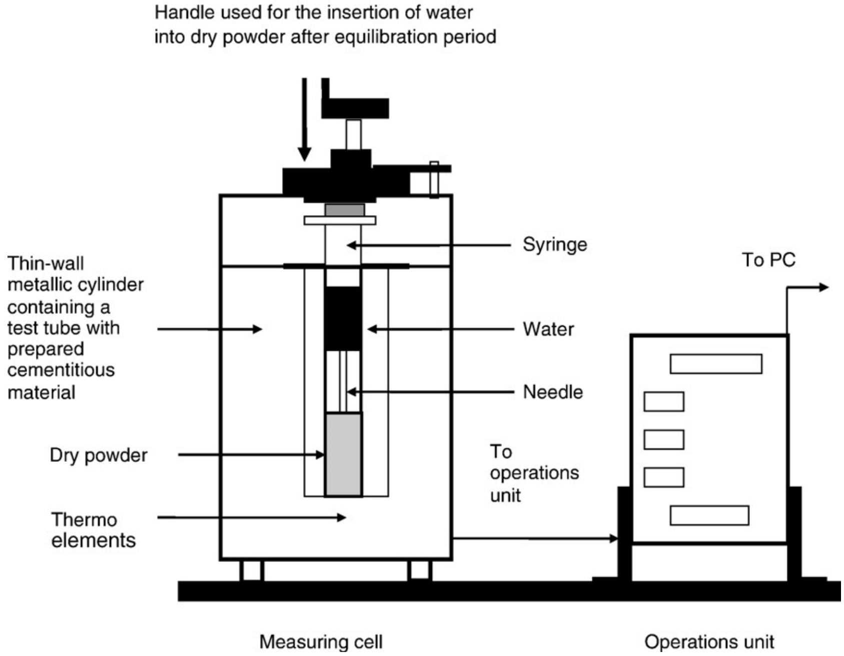

Fig. 1. Schematic diagram of Tonical Heat Flow Differential Calorimeter.

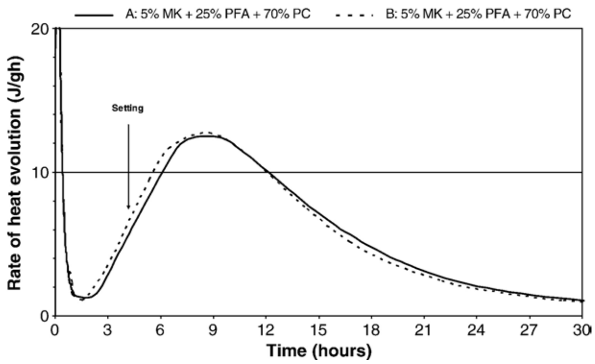

Fig. 2. A ternary MK–PFA–PC blend is used to show the repeatability of the Maximum heat evolution rate measured by the Tonical Heat Flow Differential Calorimeter.

of heat evolved in hydrating binary PC-pozzolanic blends is highly complex. It is also evident that in order to understand the processes that are occurring at each hydration stage the hydration period should be clearly specified, particularly whether it is pre-induction stage or post-induction stage. During the different stages of hydration a particular pozzolan may enhance or may diminish PC hydration, it may by pozzolanic activity contribute to the heat evolved and it may influence the amount of water available for PC hydration. The current work uses conduction calorimetry to compare the rates of heat evolution and the cumulative heat evolved from hydrating PC–PFA, PC–MK and PC–MK–PFA blends. Replacement levels of up to 20% MK and 40% PFA are employed with detailed monitoring of heat evolution rates over the first minutes of hydration in addition to more prolonged periods, with the objective of increasing understanding of these underlying processes.

2. Experimental procedure

A differential calorimeter (Tonical 7335 Heat Flow Differential Calorimeter) was used in this study (Fig. 1) to measure continually the quantity of heat evolved with time after the reactants were mixed together with water in the calorimeter specimen tube, and during the whole monitoring period. The calorimeter is calibrated by using a dedicated computer programme (5 calibration runs) and uses a hydrated reference sample and an un-hydrated sample. For each calibration run the voltage is increased, and the run is completed when thermal balance is achieved. As a result of the internal regression analysis the computer shows the device constant as a calibration factor in j/h × mV. The calibration factor must be determined for a fixed specimen volume and a particular operating temperature. In the current work a constant 5 g of sample was employed at an operating temperature of 25 °C.

The heat evolved during hydration of materials is detected as variation of the temperature by the thermo sensors and continually registered, evaluated and processed by an on-line computer. In a differential calorimeter the measuring cell is designed as a twin or differential measuring cell. This means that the thermo sensors between the thermoelements and the prepared cementitious materials are connected series-opposed (in difference). The heat evolved during a reaction (threshold of detection is 0.5 μW) is conducted across chains of thermoelements which surround the thin-wall metallic cylinder in the measuring cell. The heat output is converted to a voltage output (mVolts) which is recorded against time. Applying a known thermoelectric coefficient to the voltage output (variance ±10%) allows the rate of heat evolution (J/gh) to be determined. The recorded measurements from the differential calorimeter are shown in a graphical format. A duplicate run for a ternary MK–PFA–PC blend shown in Fig. 2 illustrates the reproducibility of the instrument.

2.1. Materials and mixing

Data on the oxide compositions, and properties of the cementitious materials used in this research including the phase composition of Portland cement calculated using Bogue's equations, are shown in Table 1. A single batch of South Ferriby Portland cement, in accordance with BS EN 197-1 [7] supplied by Rugby Cement was used. Imerys supplied the MetaStar 501 MK and its composition is given in Table 1. Ash Resources Ltd supplied the class F, low lime, PFA and its composition is given in Table 1. The reactive silica content (determined by Associate Cement Cos. Ltd, India as per BS EN 196-2 [8]) is 34.3%, thus approximately 69% of the silica content in the PFA is reactive. The PC, PFA and MK were blended by hand until a uniform colour was achieved and 5 g of the mixture was placed in the calorimeter specimen tube and agitated, to allow the water, when

Table 1
Compositions and physical properties of PC and PFA, MK

Oxide	Composition (%)		
	PC[a]	MK[b]	PFA[c]
SiO_2	20.80	52.10	49.80
Al_2O_3	4.80	41.00	26.40
Fe_2O_3	3.60	4.32	9.30
CaO	63.40	0.07	1.40
MgO	1.10	0.19	1.40
SO_3	3.10	–	0.80
Na_2O	0.13	0.26	1.50
K_2O	0.84	0.63	3.50
TiO_2	0.30	0.81	1.00
Cl	–	–	0.01
Freelime	1.40	–	–
Bogue's compositions (%)	PC	MK	PFA
Tricalcium aluminate (C_3A)	6.63	–	–
Tricalcium silicate (C_3S)	53.70	–	–
Dicalcium silicate (C_2S)	19.21	–	–
Tetra-calcium alumino ferrite (C_4AF)	10.95	–	–
Properties	PC[a]	MK[b]	PFA[c]
Loss on ignition	1.90	0.60	4.90
Fineness (m^2/g)	0.44[d]	12.00[d]	0.53[d]
Initial setting time (min)	130[e]	–	–
Final setting time (min)	165[e]	–	–
Standard consistency (%)	27[e]	–	–
True material density (g/cm^3)	3.07[f]	2.34[f]	2.47[f]

Data supplied by: [a]Rugby Cement Ltd; [b]Imerys; [c]Ash Resources Ltd: Experimentally determined: [d]Malvern Particle Size Analyser (Mastersizer 2000); [e]Vicat apparatus; [f]Density bottle method.

added, to be distributed evenly throughout the powder. A syringe, holding 2.5 g of water, with an attached needle was incorporated in the tube such that the needle penetrated the dry powder ready for mixing. Thus all the thermal measurements were made at a fixed w/b ratio of 0.5. The compositions of the different blends investigated are given in Table 2.

2.2. Thermal measurements

The calorimeter specimen tube containing the prepared cementitious materials, as detailed in Tables 1 and 2, was placed into a Tonical 7335 Heat Flow Differential Calorimeter. The lid was placed on top of the measuring cell and the temperature was allowed to equilibrate to [25 ± 1] °C for approximately 1 h in the chamber. When equilibration had been achieved, the PC measuring programme was started and the water was injected into the dry hydraulic cementitious material. An immediate exothermic reaction took place, producing heat, which was measured relative to the initial equilibrated temperature of [25 ± 1] °C in the measuring cell. Although the initial hydration rate (primarily as a result of C_3A but with some contribution from C_3S) is very rapid and is normally completed within the first 10 min or so, the sensitivity of the response time of the calorimeter is such that this first heat evolution peak is resolved clearly by the calorimeter data. Thus the relative influence of the different pozzolans and their PC replacement levels on the very early rates of hydration can be established unequivocally. Their relative influence can also be established with respect to the second heat evolution peak following the induction period.

The rate of heat evolution, dQ/dt in J/gh, and the heat of hydration, Q(t) in J/g, were recorded for approximately 60 and 120 h respectively. By 30 h however heat evolution rates had dropped to very low levels and continued to decline gradually. The data gained from the PC, PC–PFA, PC–MK and PC–MK–PFA pastes were then used to assess the influence of binder composition on the hydration process during the different stages of hydration over the 120 hour period.

In addition standard consistence measurements were carried out on PC, PC–PFA and PC–MK pastes using a Vicat apparatus in accordance with BS EN 196-3 [9]. These tests were carried out in order to establish the initial change in water demand when PC was combined with PFA and with metakaolin. The Vicat tests were started 4 min from the addition of water. The standard consistence is that recorded for the test in which the plunger of the Vicat apparatus penetrates the paste to a depth of 34 mm (i.e. [6 ± 1] mm from the plunger to the mould base plate) in 30 s. The value recorded was an average of two equivalent tests.

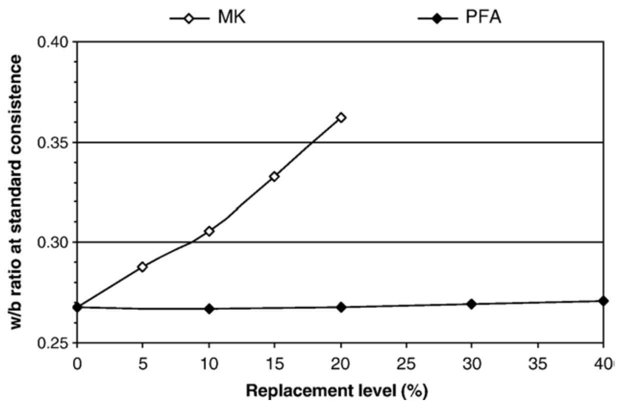

Fig. 3. w/b ratios at standard consistence for binary PC–PFA and PC–MK pastes.

Table 2
Mix proportions for heat of hydration

	(wt.%)			Total replacement (%)		(g)			
	PK	MK	PFA			PC	MK	PFA	Water
1	100	0	0	0	Control	5.00	0	0	2.50
2	95	5	0	5	MK only	4.75	0.25	0	2.50
3	90	10	0	10		4.50	0.50	0	2.50
4	85	15	0	15		4.25	0.75	0	2.50
5	80	20	0	20		4.00	1.00	0	2.50
6	90	0	10	10	PFA only	4.50	0	0.50	2.50
7	80	0	20	20		4.00	0	1.00	2.50
8	70	0	30	30		3.50	0	1.50	2.50
9	60	0	40	40		3.00	0	2.00	2.50
10	80	5	15	20	20	4.00	0.25	0.75	2.50
11	80	10	10	20		4.00	0.50	0.50	2.50
12	80	15	5	20		4.00	0.75	0.25	2.50

3. Results

The rate of heat evolution (J/gh) and the heat of hydration (J/g) data are given as per gramme of binder (i.e. PC plus pozzolan).

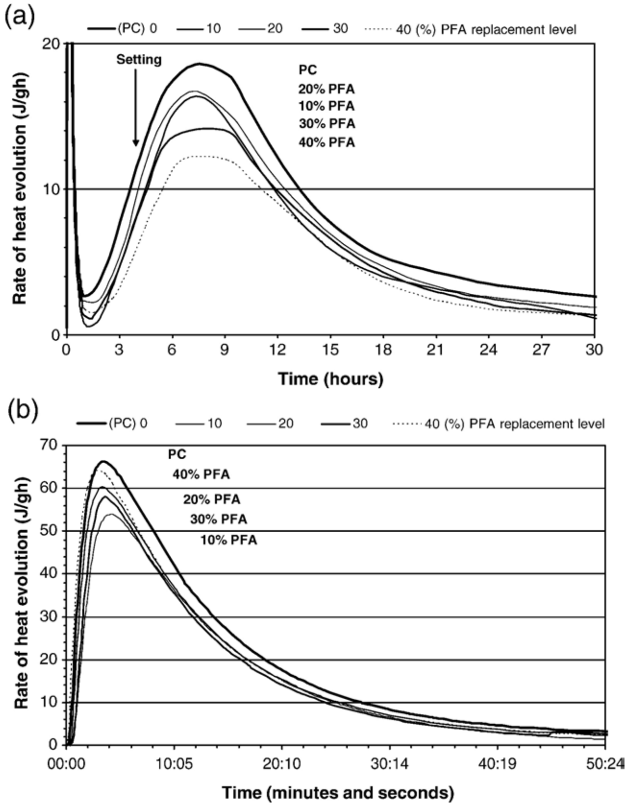

Fig. 4. Maximum heat evolution rate (first and second peaks) versus PC replacement level for binary PC–PFA blends.

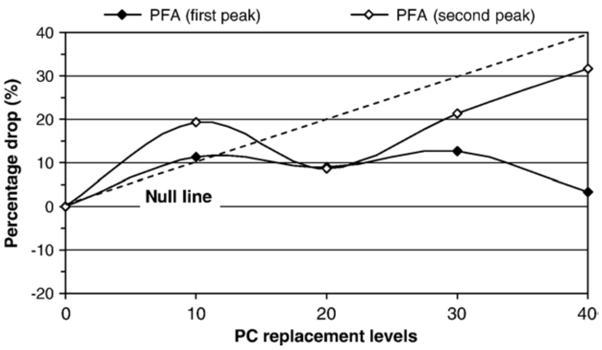

Fig. 5. Percentage drop in the maximum heat evolution rate (first and second peaks) versus PC replacement level for binary PC–PFA blends.

The binary and ternary blended pastes results are presented in Figs. 3–15.

3.1. Standard consistence

Fig. 3 shows the w/b ratio at standard consistence versus percentage replacement level of PC by PFA and by MK. It is clear from the graph that PFA has a negligible effect on the water demand of PC–PFA blends whereas for PC–MK blends increasing MK levels produce an increasing water demand.

3.2. Binary PC–PFA pastes

Fig. 4(a) shows the rate of heat evolution (J/gh) versus time (up to 30 h) for PC and the PC–PFA blends. In this graph the first heat evolution peak that occurs prior to the induction period is not distinguished clearly due to the scale employed. Fig. 4(b) shows this peak on a much expanded time scale (0–0.5 h) and a much contracted heat evolution rate scale (0–70 J/gh), where it is well defined. Although for this first peak all PFA levels produce a reduction in the maximum heat evolution rate relative to PC, interestingly this reduction generally decreases as the PFA level increases (apart from the 20% replacement level). In fact for the 40% PFA blend the rate of heat evolution prior to the maximum appears slightly greater than for PC alone. For the second peak, although again all PFA levels produce a reduction in the maximum rate of heat evolution relative to PC the order is reversed in that this reduction generally increases as the PFA level increases(again apart from the 20% replacement level).

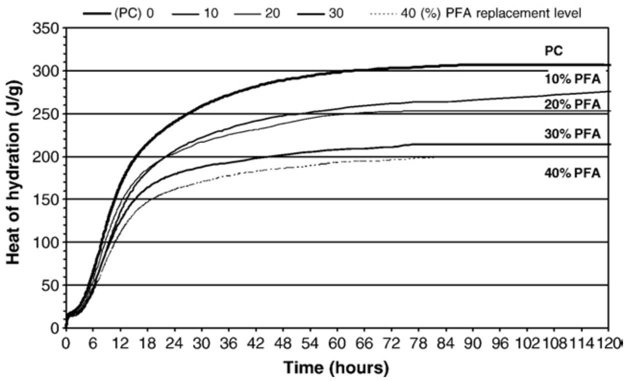

Fig. 6. Cumulative heat of hydration of PC–PFA blends at 120 h relative to PC.

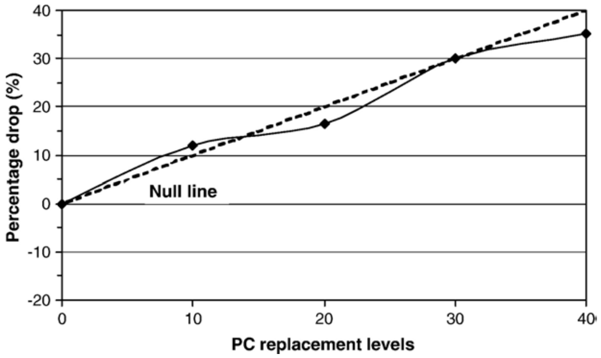

Fig. 7. Percentage drop in cumulative heat of hydration of PC–PFA blends at 120 h relative to PC.

Fig. 5 shows the percentage drop in the maximum rate of heat evolution relative to PC for both the first peak (prior to the induction period) and the second peak (immediately after the induction period). Included on the graph is what is termed the 'null line'. This is the line representing the expected fall in the rate of heat evolution if the component partially replacing the PC has no influence whatsoever on the hydration process. Any point above this line effectively represents a decrease in heat evolution rate relative to that expected (i.e. a diminished reaction) and any point below this line an increase (i.e. an enhanced reaction). For the first peak, above 10% PFA there is a marked enhancement in reaction which increases significantly

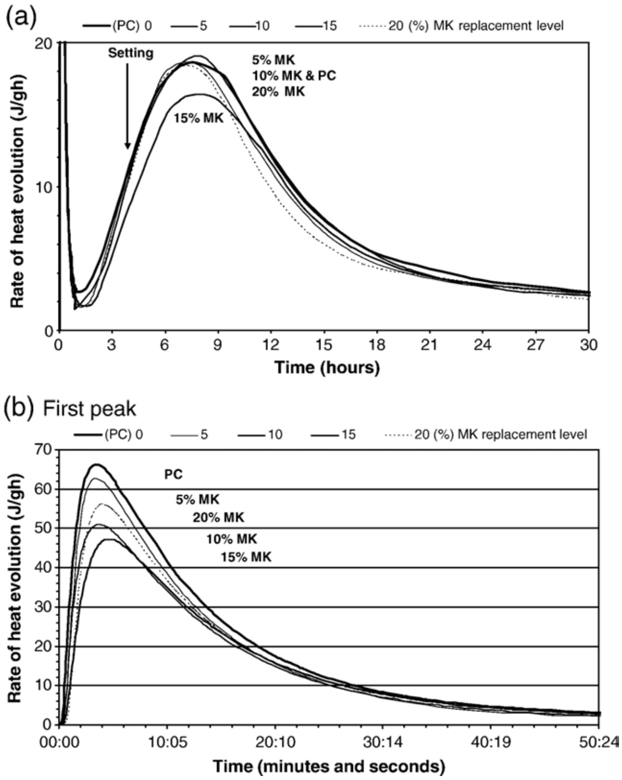

Fig. 8. Maximum heat evolution rate (first and second peaks) versus PC replacement level for binary PC–MK blends.

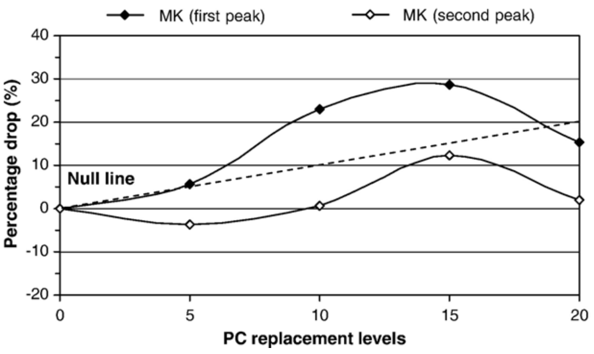

Fig. 9. Percentage drop in the maximum heat evolution rate (first and second peaks) versus PC replacement level for binary PC–MK blends.

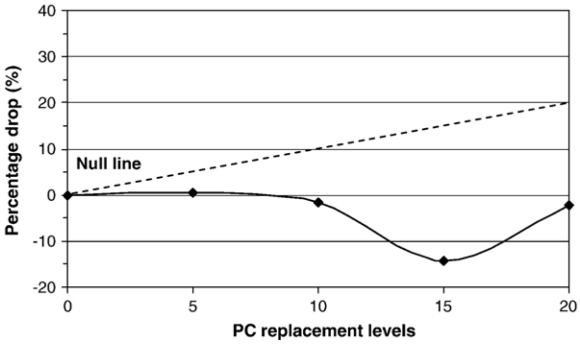

Fig. 11. Percentage drop in cumulative heat of hydration of binary PC–MK blends at 120 h relative to PC.

with increase in PFA content. For the second peak the degree of enhancement is much less, particularly at high PFA contents.

Fig. 6 shows the cumulative heat of hydration (J/g) for PC–PFA blends up to 120 h. It is interesting to note that although as expected at early ages the PC–10%PFA blend shows a lower cumulative heat of hydration than the more highly substituted PC–PFA blends (corresponding to much lower heat evolution rates), by 120 h, where the heats of hydration are beginning to level off the PC–10% PFA blend has developed a heat of hydration value in excess of all the other blends. Fig. 7 shows the percentage drop (relative to PC) in the cumulative heat of hydration versus PFA content. It is significant that at this stage the points follow the null line quite closely. This confirms that the PFA is effectively acting as an inert cement substitute and simply diluting the PC and proportionally reducing the total heat evolved. The fact that this effect is not apparent at the early stages of hydration, where increasing PFA content results in increasing enhancement of heat evolution rates (presumably as a consequence of increased cement hydration) is due to the effective increase in w/c ratio as the PFA content increases.

3.3. Binary PC–MK pastes

Fig. 8(a) shows the rate of heat evolution versus time for PC–MK blends and Fig. 8(b) shows the first heat evolution rate peak on a much expanded time scale. Surprisingly, for the first peak, MK produces much greater reductions in heat evolution rate than do equivalent levels of PFA. This is apparent from Fig. 9 which shows the percentage drop in heat evolution rate versus MK level for both the first and second peaks. For the first peak 10%MK and particularly 15%MK blends show substantial diminution of heat evolution rates whereas the 5%MK and 20% MK blends are close to the null line. For the second peak all compositions are below the null line indicating relative enhancement of heat evolution rates, but interestingly the same pattern of changes is apparent as for the first peak, in that the

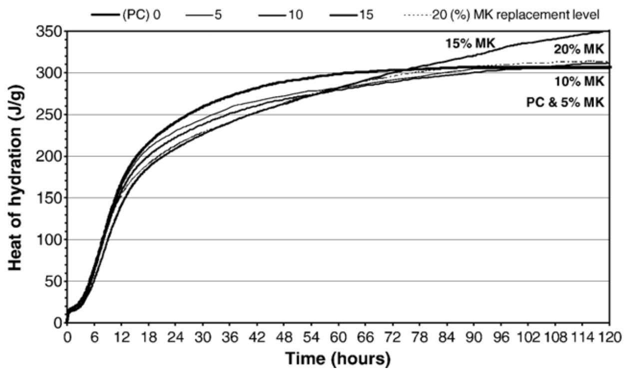

Fig. 10. Cumulative heat of hydration of binary PC–MK blends at 120 h relative to PC.

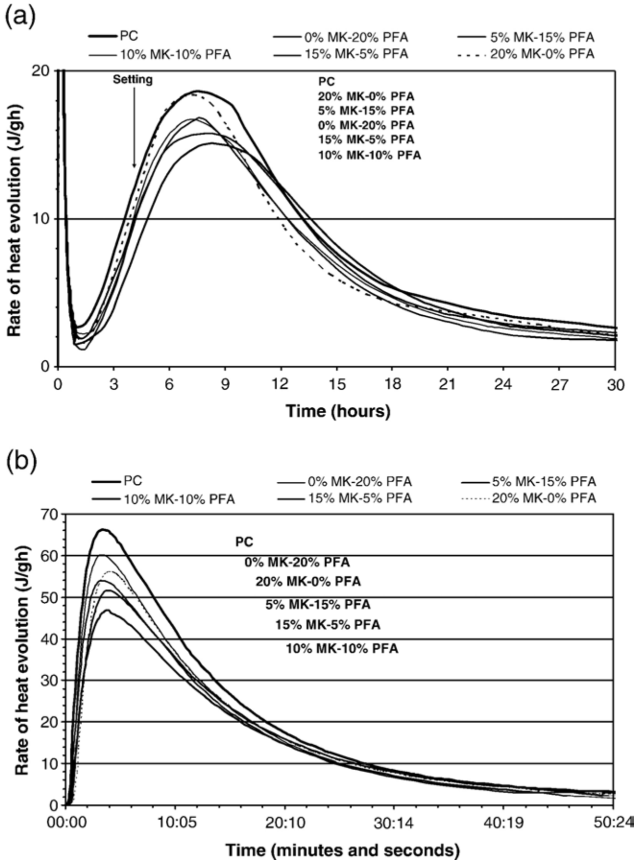

Fig. 12. Maximum heat evolution rate (first and second peaks) versus PC replacement level for ternary PC–MK–PFA blends.

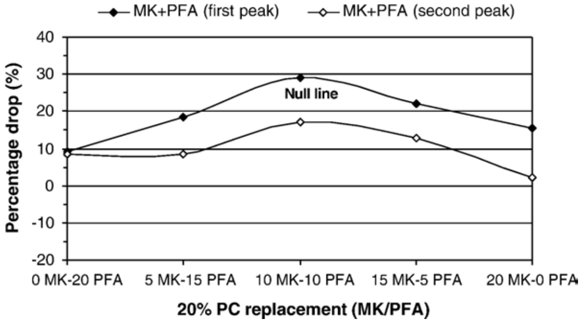

Fig. 13. Percentage drop in the maximum heat evolution rate (first and second peak) versus MK/PFA replacement for ternary PC–MK–PFA blends at 20% total replacement.

15%MK blend shows only minimal enhancement of the heat evolution rate relative to the other compositions.

Fig. 10 shows the cumulative heat of hydration for the PC–MK blends up to 120 h. At short hydration times (2–8 h) the cumulative heats of hydration reflect the different and non systematic heat evolution rates, with the 15%MK blend in particular showing a much lower cumulative heat of hydration than the other blends which themselves show lower cumulative heats of hydration than PC. However by 120 h the cumulative heats of hydration of the 5%MK, 10%MK and 20%MK blends are all similar to that of PC and are still increasing relative to PC. In addition the 15%MK blend shows a substantially greater cumulative heat of hydration than that of the PC. In fact it is clear from Fig. 11 that all the PC–MK compositions (unlike the PC–PFA compositions) are significantly below the null line indicating that the MK–CH–H hydration reaction contributes significantly to the heat of hydration. What is not clear, is why compositions at around 15%MK behave in a somewhat irregular manner (showing a contribution to the cumulative heat of hydration even greater than the 20%MK blend) and whether this is a real effect. However as PFA behaves principally as a dilutant and contributes little to the heat of hydration, then ternary blends containing MK together with PFA and PC might (if the effect is real) be expected to show a similar pattern of changes. The composition selected (20% total replacement of PC) enables a symmetrical set of compositions to be followed.

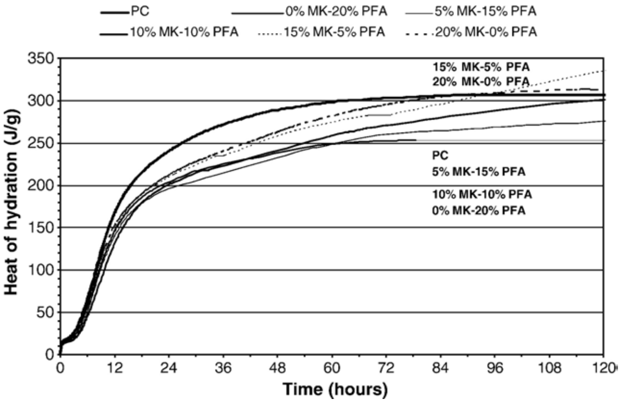

Fig. 14. Cumulative heat of hydration of ternary PC–MK–PFA blends at 20% replacement and at 120 h relative to PC.

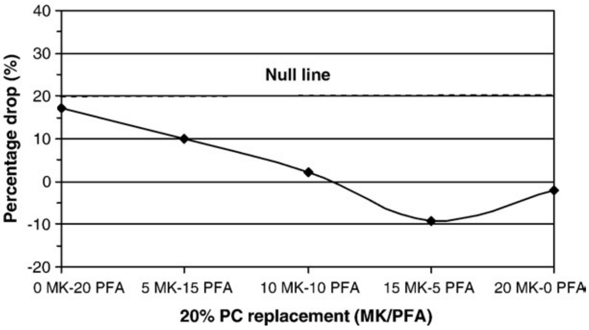

Fig. 15. Percentage drop in cumulative heat hydration of ternary PC–MK–PFA blends at 20% replacement and at 120 h relative to PC.

3.4. Ternary PC–MK–PFA pastes

Fig. 12 shows the first (b) and the second (a) peaks for the rates of heat evolution for the ternary PC–MK–PFA blends at 20% total replacement and Fig. 13 shows the percentage drop in the maximum heat evolution rate versus MK/PFA replacement for these peaks. Comparison of Fig. 13 with Fig. 9 shows a remarkable degree of similarity in the form of the curves although, as would be expected, relative to the null line the curves for the ternary blend tend to be lower at low MK levels due to increasing levels of PFA releasing increasing amounts of water for PC hydration. Fig. 14 shows the cumulative heat of hydration versus time for the ternary PC–MK–PFA blends at 20% replacement and Fig. 15 shows the percentage drop in the cumulative heat of hydration relative to PC. Comparison of Fig. 15 with Fig. 11 also shows a remarkable degree of similarity, both curves showing the same form relative to the null line. As might be expected, for the ternary blends compositions with high PFA contents show much higher percentage drops in cumulative heats of hydration relative to PC, again reflecting the diluting effect of PFA. The ternary blends, in common with the binary blends, also confirm that compositions containing MK levels around 15% show heat of hydration values considerably in excess of those for PC alone, again confirming that not only does the MK–CH–H hydration reaction contribute a significant amount to the overall heat evolution, but that certain compositions appear to contribute a greater amount of heat than the equivalent amount of hydrating PC.

4. Discussion

The behaviour of hydrating binary PC–PFA blends with respect to hydration rates, rates of heat evolution and cumulative heats of hydration appear to be relatively straightforward and can be explained with simple reference to basic reaction kinetics. The PFA–CH–H hydration reaction is a very slow reaction both as a result of the relatively low specific surface of PFA and also the low solubility of the alumino-silicate glass in the alkaline environment created by the hydrating PC. Thus during the period of rapid PC hydration the PFA effectively acts as an inert supplement to the PC, and the water associated with the PFA is made available as additional water for PC hydration. It has been observed [10–13] that the rate of heat evolution in the early stages of PC hydration is very sensitive to w/c ratio, increasing significantly as the w/c ratio increases up to a particular level. Therefore the drop in the rate of heat evolution relative to 100% PC (given by the null line) as a result of the diluting effect of the PFA is smaller than expected due to the effective increase in w/c ratio, which produces increasing PC hydration rates as the PFA content increases. This effect is very evident for the first heat evolution peak prior to the induction period (Figs. 4 and 5). By 120 hours a substantial proportion of the PC has hydrated and therefore the increases in the cumulative heats of hydration with time have levelled off (Fig. 6). As the PFA pozzolanic reaction has at this stage made a negligible contribution to the heat evolved, and has simply acted as a dilutant to the PC, the percentage drop in cumulative heat evolved is directly proportional to the PFA content (Fig. 7).

In contrast, the manner in which the MK influences the rate of heat evolution and the cumulative heat of hydration of PC–MK blends is much more complex and is less easily understood. MK is known to be highly reactive [6] and increasing MK levels produce an increasing water requirement (Fig. 3). The high water requirement of PC–MK blends initially results from the very large specific surface of the MK (12 m^2/g) which rapidly adsorbs water. The marked increase in the percentage drop in heat evolution rate (Fig. 9) for the first peak, indicating significant diminution of PC hydration as the MK level increases up to 15%, can be attributed to the increasing water demand by the MK. However, more difficult to explain is the reduction in the value of the percentage drop, to below the null line at 20%MK. A similar profile is apparent for the second peak (Fig. 9) although in this case the curve is below the null line, indicating an increase in the rate of heat evolution relative to PC alone. This non-systematic behaviour in the rate of heat evolution with MK level, is also apparent for the ternary blends (Fig. 13) but as might be expected the presence of PFA tends to reduce the percentage drop values relative to the null line, particularly at high PFA and low MK levels. With regard to the cumulative heat of hydration for the binary blends at 120 hours, increasing levels of MK produce increasing reductions in the percentage drop values relative to the null line as the MK level increases (Fig. 11), confirming that the reaction of MK with CH and H contributes to the cumulative heat evolved. This is particularly so at 15%MK although at 20%MK the effect is reduced. This anomalous behaviour of MK is further confirmed by the behaviour of the ternary blends (Fig. 15) although at high PFA levels the reduction in the percentage drop values relative to the null line is much reduced, because the PFA is acting principally as an inert dilutant. The reversed trend in the cumulative heat evolved in going from 15%MK to 20%MK is again clearly apparent.

It is suggested that the non-systematic behaviour of both the rates of heat evolution (first and second peaks) and the cumulative heat evolved (at 120 h) when MK is in combination with PC, is a function of the reaction of MK with Ca^{+2} at the different compositions and times investigated. The rate of PC hydration influences the supply of Ca^{+2} available for reaction with MK and the rate of the MK reaction influences the supply of water available for PC hydration. As the MK level increases there is an increase in water demand due to the huge specific surface of the MK and there is also less PC available to hydrate due to the dilution effect, thus the rate of heat evolution decreases. However it is proposed that the MK will also interact with Ca^{2+} ions in the pore solution provided by the hydrating cement. As the proportion of MK increases the rate at which Ca^{2+} ions are removed from the pore solution will increase and will tend to exceed the rate at which a diminishing proportion of PC is producing those ions, thus driving the PC hydration reaction forward at an increasing rate. This provides a possible explanation for the reversal in heat evolution rates (from decrease to increase) in going from 15% MK to 20% MK.

The influence of these initial interactions is superimposed on the post-induction-period second peak (Figs. 9 and 13), but after about 8 h the pozzolanic reaction of the MK with Ca^{2+} is beginning to contribute significantly to the heat evolution rate and thus the points for the second peak in Figs. 9 and 13 are below the null line. This is reflected in the cumulative heat of hydration versus time curves (Figs. 10 and 14) in that compositions with high levels of MK begin to evolve heat more rapidly than those with low MK levels. However as stated previously the reaction of MK is governed not only by the available moisture but also by the supply of Ca^{2+} ions from the hydrating PC and as the MK to PC ratio increases the supply of Ca^{2+} ions will also diminish such that a limiting composition will be reached at which the MK reaction is curtailed by an insufficient supply of Ca^{2+} ions. It would appear that the limiting composition, for both binary PC–MK and ternary PC–MK–PFA (20% replacement) compositions is between 15 and 20%MK (Figs. 9 and 13).

MK containing cementitious systems are also made more complex by the nature of the MK reaction, the direction of which is strongly influenced by the composition of the blend. At low MK to PC ratios the abundant supply of Ca^{2+} ions leads to the formation of C_4AH_{13} and C–S–H gel (see Wild et al. [14]) whereas at high MK to PC ratios the MK reaction products are C_2ASH_8 and C–S–H gel. The water demand of the former reaction [14] is higher than for the latter reaction, thus contributing to the water demand of the MK, particularly at low MK to PC ratios. Interestingly Wild et al. [14] reported a minimum in chemical shrinkage for PC–MK pastes at 15%MK and attributed this minimum to reduced formation of C_4AH_{13} and increased formation of C_2ASH_8. In addition, the reaction of MK with CH is likely to be influenced by the presence of sulphate in the PC. De Silva and Glasser [15] have shown that the presence of sulphate in hydrating MK–CH systems significantly modifies the heat evolution profile due to ettringite formation and its subsequent transformation to monosulphate. Clearly the complexity of the MK reaction means that in order to fully explain the heat evolution profiles of MK-containing PC-based systems a very detailed study is required of the reaction products formed, particularly at the early stages of hydration, for a wide range of PC–MK compositions. Although Love et al. [16] have recently reported such a detailed study, the investigation was restricted to white Portland cement at only one composition (20%MK) and at two ages (1 day and 28 days), whereas the current study involves ordinary Portland cement blended with a range of MK contents, from a period of a few minutes to 5 days. However their work does demonstrate that for their particular system the hydration rate of both the MK and the PC and the reaction products formed are influenced significantly by the presence of alkali.

5. Conclusion

The main conclusions that can be drawn from this experimental study may be summarised as follows:

- The results clearly demonstrate that the two pozzolans MK and PFA have different effects on heat evolution of binary pastes and must therefore influence hydration in different ways:
  i. The heat evolution results within the first hour of hydration suggest that MK diminishes PC hydration possibly due to MK's high water demand, whereas PFA appears to enhance PC hydration by making more water available for hydration of the PC. During the principal hydration period (between 1 h and 18 h) the converse appears to be the case in that PFA provides significant diminution in hydration possibly because it shows little pozzolanic activity at this stage and the dilution effect is beginning to predominate. In contrast MK produces minimal diminution in hydration and at certain levels enhances the overall hydration process due to the onset of rapid pozzolanic action.
  ii. Although MK initially (within the first hour) diminishes hydration, heat evolution data indicate that at extended periods (up to 120 h) the pozzolanic reaction further contributes to the heat output causing the binary blends to 'catch-up' with and in some cases exceed (15% MK) the PC control. As the MK replacement levels increase the amount of PC decreases and so does the supply of Ca^{2+} ions available to react with the MK. Thus at high replacement levels the rate of pozzolanic reactivity will be controlled not by the availability of the MK but by the availability of Ca^{2+}. In contrast, for binary PFA–PC blends at extended periods (up to 120 h) an increase in PFA replacement level causes a systematic reduction in heat output. This is due to the PFA's low pozzolanic activity at this stage of PFA–PC paste hydration and the reduction in PC content (dilution effect) of the PFA–PC paste.

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References

[1] A. M., Neville, Properties of Concrete, Pearson Educational Limited, Harlow, Fourth Edition, 1995, pp. 16, 17 and 37.
[2] M. Kokubu, Fly ash and fly ash cement. Proceedings of the Fifth International Symposium on the Chemistry of Cement (1968), Cement Association of Japan, Tokyo, 1969, pp. 75–105, Part IV.
[3] B.W. Langan, K. Weng, M.A. Ward, Effect of silica fume and fly ash on heat of hydration of Portland cement, Cem. Concr. Res. 32 (7) (2002) 1045–1051.
[4] M. Frias, M.I. Sanchez de Rojas, J. Cabrera, The effect that the pozzolanic reaction of metakaolin has on the heat evolution in metakaolin-cement mortars, Cem. Concr. Res. 30 (2) (2000) 209–216.
[5] C.S. Poon, L. Lam, S.C. Kou, Y.L. Wong, R. Wong, Rate of pozzolanic reaction of metakaolin in high performance-cement cement pastes, Cem. Concr. Res. 31 (9) (2001) 1301–1306.
[6] J. Bai, S. Wild, Investigation of the temperature change and heat evolution of mortars incorporating PFA and Metakaolin, Cem. Concr. Compos. 24 (2) (2002) 201–209.
[7] British Standards Institute, Cement – Part 1: Composition, Specification and Conforming Criteria for Common Cements. BS EN 197-1, 2000.
[8] British Standards Institute, Methods of Testing Cement, Chemical analysis of cement. BS EN 196-2, 1995.
[9] British Standards Institute, Methods of Testing Cement, Part 3. Determination of setting times and soundness. BS EN 196-3, 1995.
[10] K.B. Park, N. Takafumi, J. Plawsky, Modeling of hydration reactions using neural networks to predict the average properties of cement pastes, Cem. Concr. Res. 35 (9) (2005) 1676–1684.
[11] E.H. Kadri, R. Duval, Effect of silica fume on the heat of hydration of high performance concrete, Seventh Canmet / ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, vol. 2, 2001, pp. 635–644.
[12] Y. Zhang, W. Sun, S. Liv, Study on the hydration heat of binder paste in high-performance concrete, Cem. Concr. Res. 32 (9) (2002) 1483–1488.
[13] Portland Cement Association, Heat of Hydration of Portland Cements Concrete Technology Today, July 1997, pp. 2–4.
[14] S. Wild, J.M. Khatib, J. Roose, Chemical shrinkage and autogenous shrinkage of Portland cement–Metakaolin pastes, Adv. Cem. Res. 10 (3) (1998) 109–119.
[15] P.S. De Silva, F.P. Glasser, Hydration of cements based on metakaolin thermochemistry, Adv. Cem. Res. 3 (12) (1990) 167–177.
[16] C.A. Love, I.G. Richardson, A.R. Brough, Composition and structure of C–S–H in white Portland cement − 20% metakaolin pastes hydrated at 25 °C, Cem. Concr. Res. 37 (2) (2007) 109–117.