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Heat of hydration of high reactive pozzolans in blended cements: Isothermal conduction calorimetry

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Abstract

A study was carried out comparing silica fume (SF) and dealuminated kaolin (DK) as pozzolanic materials in blended cements. Ten, 20 or 30 wt% of SF or DK were substituted for Portland cement. The kinetics of hydration up to 45 h were studied using isothermal conduction calorimetry. Blends containing pozzolanic materials usually have decreased heats of hydration compared to pure cement during the period of C_3S hydration, i.e. during the main hydration peak. Depending on the chemical composition and the activity of the pozzolan, the reaction taking place with the lime typically contributes to the heat output after the main hydration peak.

The pozzolanic activity of DK is the principal factor and heat evolution increases with respect to pure PC mortar, during the first 15 h. The presence of hydrated silica (silanol groups) in DK increases the pozzolanic activity especially before and during induction period. The acidic silanol sites are capable of a fast acid–base reaction with the alkalis and with any $Ca(OH)_2$ present in cement during the induction period.

Keywords: Heat of hydration; Silica fume; Dealuminated kaolin; Cement; Conduction calorimetry

1. Introduction

The dominant role of pure PC is slowly decrease in the favor of substituted cements and composite cements. Now days all over the world there are specialized plants for marketing the mixing components of cements. The intensive academic and applied research well make the use of various industrial waste by-products as well as several natural materials more feasible and interesting in the future. The aim of utilization of by-products is not only to make the cements and concrete less expensive but also to give the concrete tailored properties suitable for certain purposes.

Ina previous study [1], we concluded that dealuminated kaolin (DK) is a good candidate to be used as additive in blended cements to give the concrete a certain desirable properties. Dealuminated kaolin has much higher pozzolanic activity than silica fume, especially at early hydration time. This higher activity of DK was a result of the higher surface area, of the structure of silica and of the presence of hydrated silica (silonal groups; Si–OH). It has been shown that silica in DK is present as sheets of large dimensions [2,3]. Silica with this structure tends not to agglomerate as severely as silica fume. However, there are two points must be taken in consideration for DK to be used in blended cement. The first is that DK contain about 9% amorphous Al_2O_3 in the bulk chemical composition. This may change the chemistry of DK–cement hydration reaction than those of silica fume (SF)–cement hydration or affect the long-term stability of concrete. The later effect may be caused by the potential formation of ettringite in sulfated media due to the high Al_2O_3 content. The second point is that DK-lime reaction (pozzolanic reaction) produces a large amount of heat than the corresponding SF–lime reaction. Hydration heat is an important factor affecting the setting and characteristic behavior of Portland cements. Temperature variation during hydration

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may cause thermal stresses that can results in crack formation [4]. Knowing the effect of substitution on the heat liberation became increasingly important especially in massive construction.

2. Materials and methods

Silica fume was obtained from Ferrosilicon Co. Edfo, Egypt. Dealuminated kaolin was obtained from Egyptian Shaba Co., Egypt. It is produced as a waste by-product of aluminum extraction from calcined kaolin by sulfuric acid. The detailed characterization of DK and SF is given in another paper [1]. The chemical composition of the Portland cement used is: CaO, 63.82; SiO_2, 20.88; Al_2O_3, 6.91; Fe_2O_3, 2.12; MgO, 2.31; SO_3, 1.89; K_2O, 0.21; Na_2O, 0.12 and L.O.I, 1.81 and the Blaine surface area is about 3500 cm^2/g. SF and DK used to replace 10, 20 and 30% of normal Portland cement to form mixes SF1, SF2 and SF3 for silica fume and DK1, DK2 and DK3 for dealuminated kaolin.

In isothermal conduction calorimetry, the heat of hydration of cement is directly measured by monitoring the heat flow from the specimen when both the specimen and the surrounding environment are maintained at approximately isothermal conditions. Approximately 3 g of water were inoculated into an equivalent mass of a reactant powder that had been placed in a copper sample cup and placed within the calorimeter cavity. The cups were sealed with plastic film to minimize evaporation of water. Each reactant was allowed to equilibrate separately to 25 °C, prior to mixing. The water was equilibrated in a syringe and when equilibrium had been achieved the plastic film was penetrated and the water injected over the solids. The rates of heat evolution, dQ/dt in mW/g of pozzolana, were measured and recorded using a computer data acquisition system. Integration of the areas under the rate curves allowed calculation of the total heats evolved.

3. Hydration of pure PC

The rate of heat development versus hydration time curves up to 45 h for pure PC paste is illustrated in Fig. 1. The heat of hydration curve for pure PC shows the typical five stages of the hydration reaction as described in the literatures [5,6]:

(1) the initial reaction;
(2) the induction period;
(3) the acceleratory period;
(4) the deceleratory period;
(5) the period of slow continued reaction.

In the initial reaction, there is a rapid evolution of the heat culminating in a peak within the first 1–2 min. This was ascribed to the effects of heat of wetting of the cement and hydration of free lime.

$$CaO + H_2O \rightarrow Ca(OH)_2 + heat$$

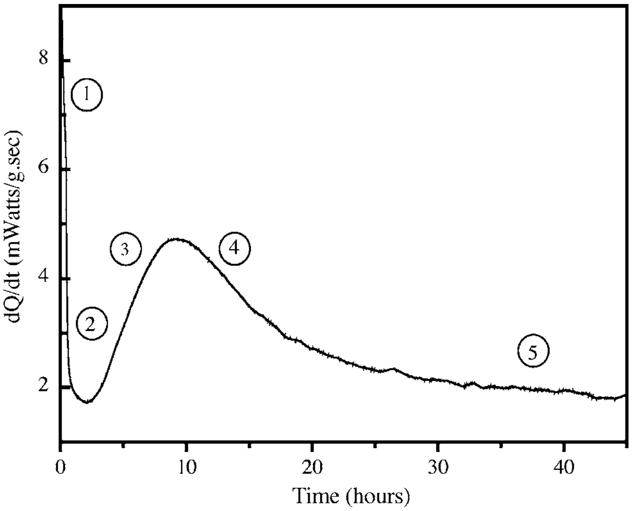

Fig. 1. The rate of heat evolution of cement hydration at 25 °C.

Some researchers [7] suggested that additional contributory factor to the first peak include heat of formation of ettringite $C_3(A,F){\cdot}3CS{\cdot}H_{31–32}$

$$C_3A + 3CSH_2 + 26H \rightarrow C_3A \cdot 3CS \cdot H_{31–32}$$

However, the current investigation seems to greatly agree with Bensted work [8], which indicated that the hydration of free lime makes only minor contribution to the first heat peak, and the main contribution to this peak appears to be from the hydration of calcium sulfate hemihydrate to the dihydrate gypsum. The hemihydrate is already present in the unhydrated cement, as seen in the XRD pattern in Fig. 2. This hemihydrate was formed from the dehydration of gypsum as a results of the heat generated during grinding of the clinker with gypsum.

$$CaSO_4{\cdot}0.5H_2O + 1.5H_2O \rightarrow CaSO_4{\cdot}2H_2O + heat$$

XRD investigation, conducted for samples hydrated at the same isothermal conditions, shows no ettringite up to 4 h, as shown in Fig. 2. During this period, the only sulfate-containing phase is gypsum.

The induction period associated with pure OPC paste hydration is about 2.5 h. There are many hypotheses regarding to the cause of the induction period and its termination [9,10]. Many researchers favor the hypotheses that the induction period cause by the formation of a protective layer on the C_3S particles [9,11]. The induction period ends when this layer destroyed or rendered more permeable by aging or phase transformation [5]. Damidot et al. [12] showed that the initial period of congruent C_3S dissolution ends when the critical concentrations of 5.5 mM of CaO and 1.7 mM SiO_2 in solution are reached, irrespective of the W/C ratio. Thereafter, the concentration of silica fall while that of lime remains constant for a period before starting to rise again. This indicates the precipitation of C–S–H with low C/S ratio (1.0) at a critical level of supersaturation. One this protective layer of C–S–H formed the concentration of lime and silica controlled by the C–S–H/solution equilibrium [13]. There are many experimental evidence proved the occurrence of a structure change in C–S–H, at the end of the induction period. The NMR evidence [13,14] indicated that the hydration products formed up to the end of the induction period contains only monomeric silicate and the dimers and larger ions start to form at the beginning of the acceleratory period. Setting takes place during the acceleratory period [7]. At that time, the silicate begins to hydrate rapidly, reaching a maximum rate at the end of the acceleration period, which correspond with the maximum rate of heat evolution. It is generally accepted that the rate of hydration in the acceleratory period is controlled by the rate of C–S–H formation [13].

There is a fairly general agreement that, during the deceleratory period, the reaction makes transition from the chemical control to the diffusional control. Knudsen [15] and Bezjak [16], consider the diminishing in the reaction rate to be attributable, at least in part to, to the depletion of small particles, which have completely hydrated. Thus, the switch from the acceleratory period to the deceleratory one depends on the particle size distortion of the cement [17,18]. In an analysis of the hydration kinetics of two C_3S preparations with different fineness, Brown [19] observed that early hydration was controlled by the fineness to which the C_3S had been ground. Both the rate of hydration and the extent of hydration achieved were dependent on surface area. Kinetics in the deceleratory period was independent of the fineness.

The hydration occurs during the slow continuing reaction period is responsible for much of the reduction in the porosity and increase in the strength, in pastes mortars and concerts. Despite this there has been little study of the mechanisms operating during this period. Brown et al. [9] point out the difficulty in developing kinetic models during this period due to the lack of accurate data of hydration available in the literature.

In the calorimetry carves the rate of heat evolution levels off, showing a distinct change of slope. Microstructural studies indicate that, during this period, a portion of the C–S–H forms within the boundaries of the original grains as inner product. This product has a homogenous appearance and in TEM studies is seen to be quite distinct from outer products [20]. Taylor has purposed that this inner-product may be formed by a solid state mechanism [21], in which Ca^{2+} and Si^{4+} move outwards and H^+ inwards. The rate controlling process for this mechanism would be the migration of silicon. Alongside the formation of inner product, outer products C–S–H and calcium hydroxide must continue to form in the remaining pore space. Bezjak [22] suggested that the reaction rate is limited by the growth of the outer product, i.e. the rate-limiting factor is the amount of available space in which the outer product can grow.

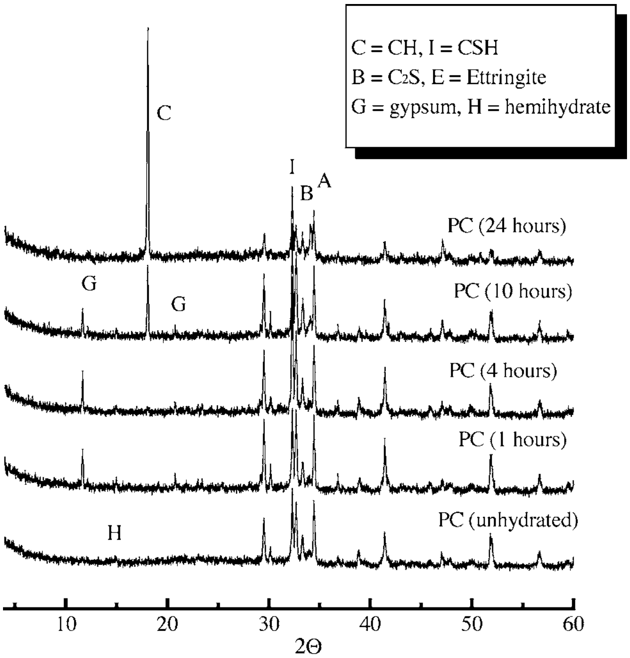

Fig. 2. XRD patterns of PC hydrated for different times under isothermal conditions at 25 °C.

4. Hydration of DK-blended cements

The rate of heat development curves for different DK-blended cements in comparison with pure PC cement are shown in Fig. 3. Dealuminated kaolin mixes (DK1 and DK2) show the occurrence of shoulders after the first heat peak and before the induction period, which became a distinct peak at mix DK3. Bensted [8] refer to this peak as an indication of false or flash set, i.e. the set regulation by calcium sulfate is not proceeding smoothly [23]. In the current investigation, the XRD analysis on samples hydrated at the same isothermal conditions, indicated that in all mixes no or at least small amount of ettringite formed up to 4 h and must of the sulfate remain as dihydrate, see Figs. 2–4. So that this peak can be accounted due to the reaction of the surface silanol groups of DK with calcium hydroxide and/or alkali present in cement.

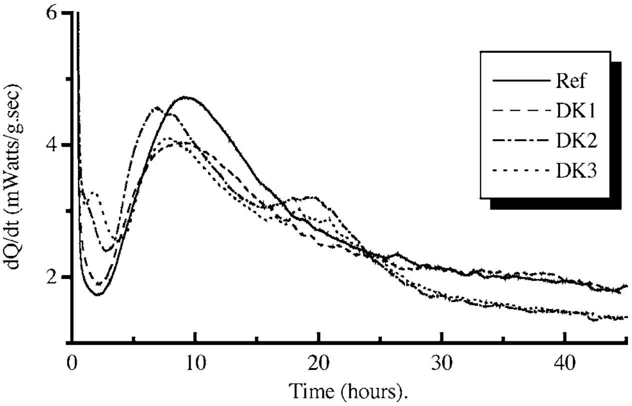

Fig. 3. The rate of heat evolution of DK-blended cements hydrated at 25 °C.

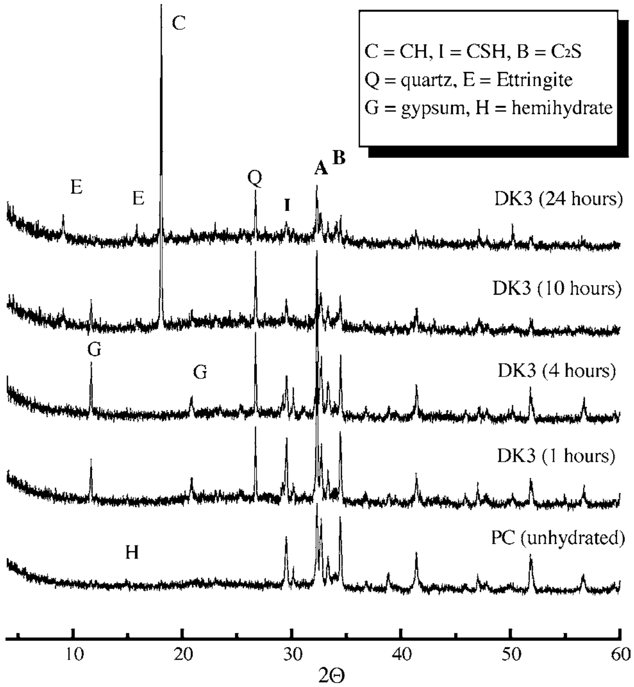

Fig. 4. XRD patterns of mix DK3 hydrated for different times under isothermal conditions at 25 °C.

There is no CH appear in the XRD patterns of the hydration of pure cement up to 4 h, see Fig. 2. This mean the amount of CH formed my be beyond the detection limit of XRD analysis, since the dissolution of C_3S is immediate after the contact with water [24] and that at the end of the induction period, the silicate undergo hydration to the extent of about 2% [25]. In DK mixes also, DK may induce the formation of CH by acting like a sink for calcium and hydroxyl ions. Weakly acidic silanol groups are capable of a fast acid–base reaction with $Ca(OH)_2$, and total heat evolved will be the heat of reaction plus the heat of neutralization:

$$2\mathrm{Si_S{-}OH} + \mathrm{Ca(OH)_2} \rightarrow (\mathrm{Si_S{-}O})_2\mathrm{Ca} + 2\mathrm{H_2O}$$

Fig. 5 represents the evolution of the hydration heat of mortars made with the different percent of DK substitution relative to 100% PC mortar, with a reference point of zero being assigned to the hydration heat developed by the 100% PC mortar. This representation of the data shows clearly the two effects of substitution of the pozzolanic materials on the heat development. These effects can be summarized as the pozzolanic activity and the dilution effect. The pozzolanic effect is expected to increase the heat output due to the reaction of pozzolans with calcium hydroxide. The dilution effect expected to decrease the heat output due to the dilution in the main cement compounds (C_3S). The acceleration effect of DK on C_3S hydration appears as the shift of beginning of the onset climbing of the acceleratory period. This effect clearly appears in Fig. 5 for mixes DK2 and DK3, as the heat difference with respect to the pure cement paste is positive for these mixes after the induction period. This was further confirmed by the plotting the total heat evolved with time in Fig. 6. The total heat evolved at the first 9 h increased with increasing DK contents.

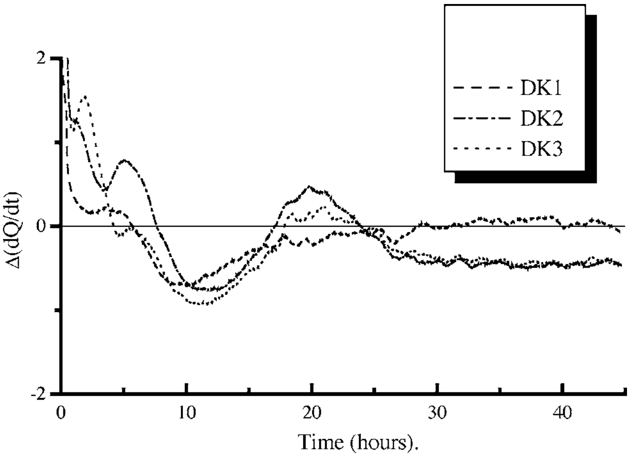

Fig. 5. The difference in the rate of heat evolution of DK-blended cement and pure PC.

The dilution effect appears as a reduction in the main hydration peak. The reduction in this peak increases as the percentage of DK substitution increases, see Fig. 3. This clearly appears as a decrease in the heat difference between the DK-blends and the pure PC pastes, in Fig. 4. In mixes DK2 and DK3, after the main hydration peak, a shoulder appears before the end of the deceleration period. These shoulders appear as clear peaks in Fig. 4. In general, a similar, but less distinct, shoulder appears in some Portland cements due to the conversion of ettringite to monosulfate [7]. However, this peak did not appear in the pure PC paste in the current study, therefore it cannot account for such transformation although it does coincide with it. This peak can be accounted due to the pozzolanic reaction of DK with the relatively high concentration of CH produced after the main hydration peak. At the final stage, after 25 h, the dilution effect appears again in the high DK substituted mixes (DK2 and DK3) as a lower heat output in the slow, continuing, diffusionally controlled reaction region.

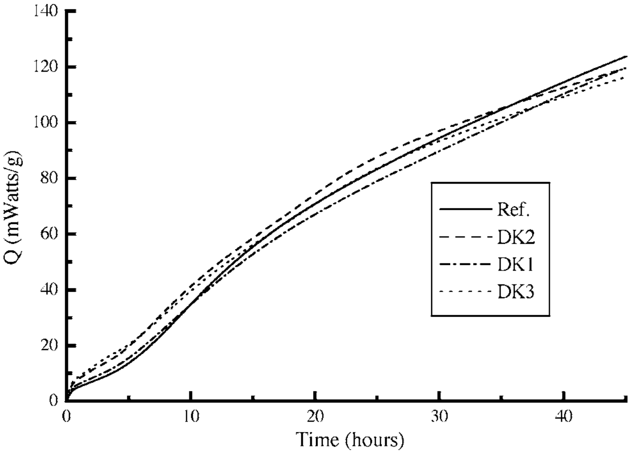

Fig. 6. Total heat of hydration of DK-blended cements at 25 °C.

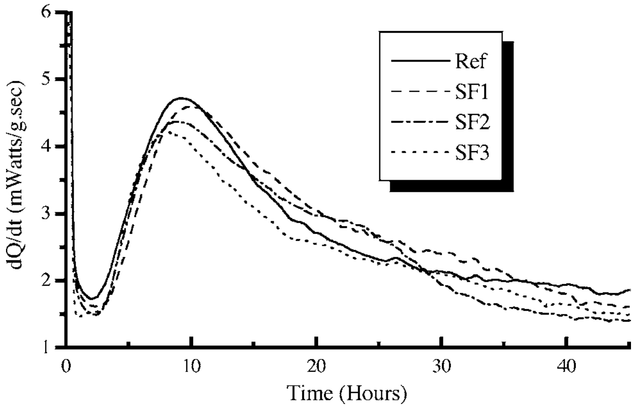

Fig. 7. The rate of heat evolution of SF-blended cements hydrated at 25 °C.

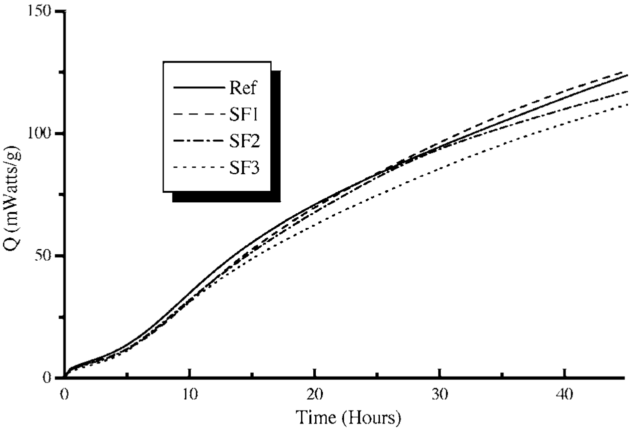

Fig. 9. Total heat of hydration of SF-blended cements at 25 °C.

5. Hydration of SF-blended cements

In SF mixes, the first peak (initial reaction) decreased as the SF content in the mix increased. Where this is not clearly shown in Fig. 7, Fig. 8 shows SF mixes give much lower heat in the first few minutes than pure PC paste. This effect of SF continues through the induction period; as the base line of heat evolution during the induction period decreases as the SF content increases, see Fig. 7.

In the acceleratory period, mix SF3 shows a clear acceleration [26,27] effect on C_3S. This appears in Fig. 8 as a small peak (at 5–7 h) over the reference line. As in DK mixes, the main hydration peak decreases as the degree of PC substitution by SF increases.

In the deceleratory period, mixes SF1 and SF2 show very broad shoulders. As the case of DK blends, this shoulder cannot be accounted for by ettringite formation, but are due to the pozzolanic reaction. These shoulders differ from that of those of the DK blends in that they are spread over broad time intervals, this is likely due to the slower pozzolanic reaction with SF. Thus, SF mixes reach the period of the slow, continuous reaction at a longer time (about 36 h). During this period, then the heat output of SF mixes decrease below that of the pure PC paste due to the dilution effect. Pastes made with SF evolve less heat than the base mortar during the first 10 h of the hydration. It appears that SF starts to contribute to the heat evolution (pozzolanic reaction) almost 16 h after mixing as indicated by the diffuse shoulder after the main hydration peak.

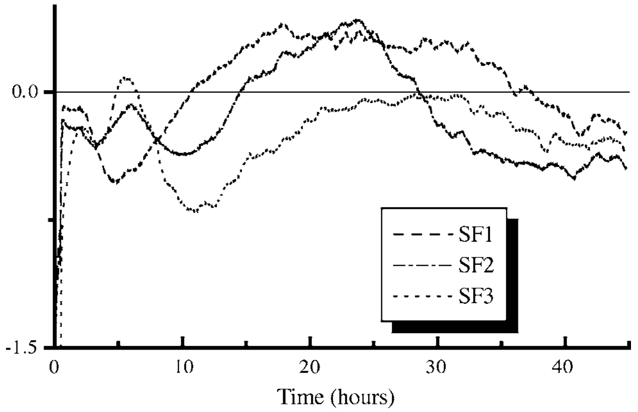

Fig. 8. The difference in the rate of heat evolution of SF-blended cement and pure PC.

Fig. 9 shows the total heat liberated during the first 45 h of different SF-blended cement with comparison to that of pure PC pastes. After 25 h of hydration, the total heat of mix SF1 (10% SF) was greater than that of pure PC. However, the mixes with higher silica fume contents (20 and 30% SF) diminish the total heat liberated over the time range studied (45 h). This result is in agreement with previous study by Ma et al. [28] that reported the substitution level of 7.5% of silica fume increased the heat liberation.

6. Conclusions

There is a difference in literature about the time at which different pozzolainc materials like silica fume and fly ash start to participate in the heat of hydration (pozzolanic activity). These results indicate that there are two different effects to be considered regarding the behavior of materials. These are: the pozzolanic activity and the influence of substituting PC by additions. The later may simply dilute the effects of PC hydration (effect of dilution) and/or may accelerate PC hydration.

The pastes containing pozzolanic materials or slag usually have decreased heat of hydration compared to cement during the period of C_3S hydration, i.e. the main hydration peak. Depending on the chemical composition and the pozzolanic activity of the material, the reaction taking place with the lime contributes to the total heat output, but generally after the main hydration peak.

In the case of DK, pozzolanic activity is the principal factor and heat evolution increases with respect to the 100% PC mortar, during the first 15 h. The presence of hydrated silica (silanol groups) in DK play a great role in the pozzolanic activity especially during this period. The silanol groups, as showed in the calorimetric study act like a weak acid ($K_1 = 10^{-9.8}$) [29]. These acidic sites are capable of a fast acid–base reaction with the alkalis and any $Ca(OH)_2$ present in cement before the induction period. The total heat evolved will be the heat of reaction plus the heat of neutralization:

$$2Si_S\text{–}OH + Ca(OH)_2 \rightarrow (Si_S\text{–}O)_2Ca + 2H_2O$$

This fast removal of the alkalis and $Ca(OH)_2$ from the reaction media induces the hydration reaction of the C_3S. It is important to indicate that both DK contents (20 and 30%) produced a slight increase of the hydration heat between 18 and 25 h. This behavior of the DK is in agreement with the behavior, of metakoalin (MK) [30]. Frias et al. [30] reported that the maximum pozzolanic activity of the MK occurred between 18 and 30 h. Taking in account the difference between metakoalin and the dealuminated kaolin in the present investigation.

SF-blended cements exhibited behavior different from that of DK-blends. Due to its relatively slow pozzolanic activity, the limited heat released during this reaction could not compensate for the decrease in heat caused by dilution. Silica fume did not add to the hydration heat except after 12 h. SF was found to accelerate cement hydration only at high substitution levels. The dilution effect appears in the main hydration peak and in the slow continuous reaction period. Mortar containing a 10% SF produced the highest hydration heat, followed by the 100% PC mortar. The reduced level of the hydration heat relative to the 100% PC at an early age may be due to a lack of availability of CH. It was shown in [1], that the rate of the SF–CH reaction is dependent on the CH concentration.

Acknowledgement

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