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HEAT EVOLUTION IN HYDRATED CEMENTITIOUS SYSTEMS ADMIXTURED WITH FLY ASH

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Abstract

In this study a calorimeter was applied to investigate the hydration of cements with fly ash (pulverised fuel ash – PFA) admixture. Four cements were used to produce the binders containing from 5 to 60% fly ash. The process of hydration in cementitious systems with fly ashes is slower than in reference pastes without admixtures. However, the calorimetric calculations and the shape of heat evolution curves seem to indicate a complex interaction between the components of cement and ash resulting in the increasing total heat evolved values per unit of cement. At higher fly ash content the accelerating effect of alkalis and alumina should be taken into account and discussed in terms of the composition of initial cement. The modifications of hydration kinetics and mechanism in this case is very well visualised by means of calorimetry.

Keywords: flay ash cement, heat of hydration, hvfa cements

Introduction

The kinetics and mechanism of hydration in cementitious systems with different admixtures can be investigated by use of calorimetry. The rate of heat evolution *vs*. time plots shows the occurrence of the two peaks with so-called induction period between them. In some cements there is also a third peak attributed to the transformation in aluminate hydrated phase. It can be generally attributed to some excess of tricalcium aluminate and replacement of tricalcium sulphoaluminate phase (AFt) by monosulphoaluminate (AFm) or renewed formation of this former one [1]. The length of this induction period and the height of peaks depend on the activity of cementitious material and reflect the accelerating or retarding effect of solid admixtures or additives present in solution. Sometimes an additional third effect can be observed.

Fly ash has been used as a standard component of cements and concrete for over forty years [2–4]. The following benefits are achieved when fly ash is added as cement replacement in concrete: reducing the cement content (reducing costs), reduced heat of hydration, improving workability, improving durability (particularly sulphate corrosion resistance). In spite of the slower strength development within the first days, the required levels of strength are attained at later ages.

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The glassy, aluminosilicate phase, being the main constituent of fly ash transforms into calcium silicate hydrate and ettringite on hydration, as a result of the so-called pozzolanic reaction with calcium ions [5]. These calcium ions are released to the solution from the calcium silicate clinker minerals. The process of hydration product formation and development of hardened matrix in cementitious systems with fly ashes is generally slower than in reference pastes without admixtures but the microstructure thus obtained shows better compactness and low permeability, due to the presence of higher C–S–H with low calcium hydroxide content. One should remember that the hydrolysis of clinker minerals is accelerated by alkalis, always present in fly ash. This effect is visible particularly at higher percentage of admixture – nowadays in European standards the fly ash content in cement could attain 55% by mass (pozzolanic cement) [6]. The effect of fly ash on the aluminate phase hydration is not explained in detail [3]. Both the acceleration and retardation are reported and this may be due to the complexity of reactions and products taking part in this process, where not only the alumina bearing components are involved but also sulphates and alkalis.

Experimental

Four different commercial cements were used in these investigations. These cements were produced in four cement plants in Poland. They show different chemical and phase composition, as well as standard properties (tested and denoted following the standards ENV 196 and 197). The short characteristics of cements is given below:

Cement CEM I 52.5 R

Cement of very high compressive strength, high content of silicate phases (alite – 60.6%; belite – 13.1%; tricalcium aluminate – 9.6%) and specific surface area of 4300 $cm^2 g^{-1}$.

Cement CEM I 42.5 R

Sulphate resistant cement of high compressive strength (low tricalcium aluminate content below 3%, low alkali content below 0.6%).

Cement CEM I 32.5 R

General-purpose cement with relatively high alkali content (Na_2O_{eq}>1%); further described as CEM I 32.5 R*.

Cement CEM I 32.5 R

General-purpose cement with moderate strength development as compared with the former one; further described as CEM I 32.5 R**.

The mixtures containing from 5 to 60% fly ash cement replacement were produced using the fly ash from one source, meeting the requirements of low calcium pozzolanic material to be potentially used in cement production (specific surface of 3430 $cm^2\ g^{-1}$).

The heat evolution on hydration of pastes prepared at water to solid ratio 0.5 was followed by microcalorimetry BMR, differential microcalorimeter constructed in the Institute of Physical Chemistry, Polish Academy of Science. The initial temperature was kept constant at 25%.

Results and discussion

The sets of calorimetric curves, where *W*(*t*) is the 'thermal power', that is the heat evolved per time unit, are shown in Figs 1–4. The calculations of heat evolved values were carried out for 1 g of cementitious material (cement+fly ash) as well as for 1 g of cement in 'initial' sample and the results are given in Tables 1–4.

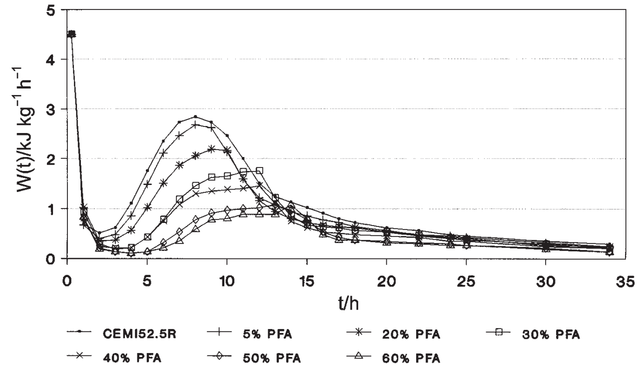

Fig. 1 Calorimetric curves of cement CEM I, 52.5 R samples mixed with PFA

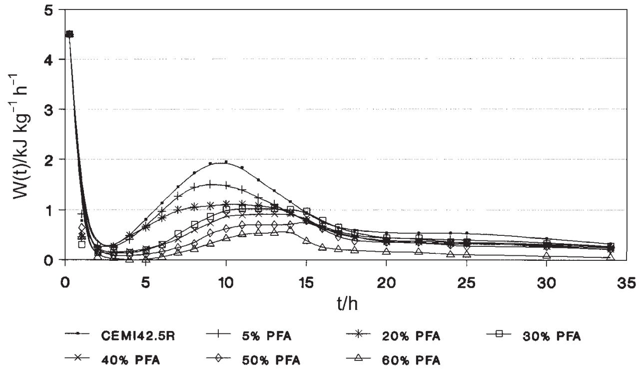

Fig. 2 Calorimetric curves of cement CEM I, 32.5 R samples mixed with PFA

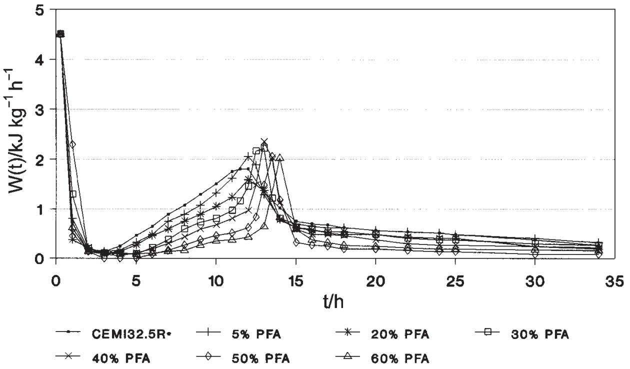

Fig. 3 Calorimetric curves of cement CEM I, 32.5 R* samples mixed with PFA

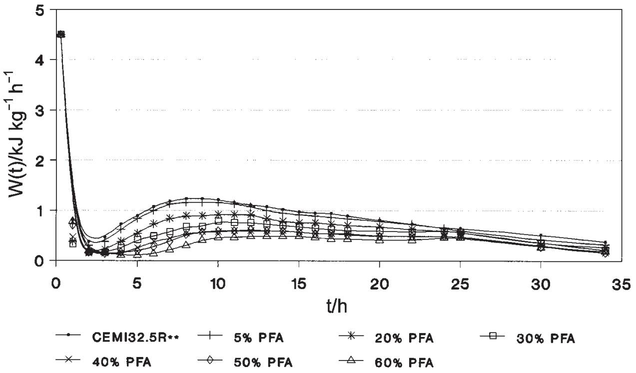

Fig. 4 Calorimetric curves of cement CEM I, 32.5 R** samples mixed with PFA

Table 1 Heat evolved during 24 and 72 h hydration of cement CEM I 52.5 R with fly ash

Sample PFA content/%	Heat calculated for 1 g of hydrated sample (cement+fly ash)/kJ kg^{-1}		Heat calculated for 1 g of cement in hydrated sample/kJ kg^{-1}	
	after 24 h	after 72 h	after 24 h	after 72 h
Reference	322	400	322	400
5	301	387	317	407
10	295	376	328	418
20	265	294	330	441
30	229	298	327	425
40	203	261	339	436
50	163	206	324	409
60	149	191	374	477

Table 2 Heat evolved during 24 and 72 h hydration of cement CEM I 42.5 R with fly ash

Sample PFA content/%	Heat calculated for 1 g of hydrated sample (cement+fly ash)/kJ kg^{-1}		Heat calculated for 1 g of cement in hydrated sample/kJ kg^{-1}	
	after 24 h	after 72 h	after 24 h	after 72 h
Reference	261	364	261	364
5	221	329	233	325
10	203	305	226	339
20	190	279	237	349
30	169	258	241	368
40	156	233	260	387
50	124	195	247	389
60	90	106	221	263

Table 3 Heat evolved during 24 and 72 h hydration of cement CEM I 32.5 R[*] with fly ash

Sample PFA content/%	Heat calculated for 1 g of hydrated sample (cement+fly ash)/kJ kg^{-1}		Heat calculated for 1 g of cement in hydrated sample/kJ kg^{-1}	
	after 24 h	after 72 h	after 24 h	after 72 h
Reference	222	321	222	321
5	210	311	221	326
10	221	323	245	358
20	184	281	249	370
30	177	268	253	383
40	152	225	258	391
50	127	200	272	406
60	114	167	286	420

Table 4 Heat evolved during 24 and 72 h hydration of cement CEM I 32.5 R[**] with fly ash

Sample PFA content/%	Heat calculated for 1 g of hydrated sample (cement+fly ash)/kJ kg^{-1}		Heat calculated for 1 g of cement in hydrated sample/kJ kg^{-1}	
	after 24 h	after 72 h	after 24 h	after 72 h
Reference	261	364	261	364
5	221	329	233	325
10	203	305	226	339
20	190	279	237	349
30	169	258	241	368
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As one can notice the fly ash content increase is accompanied with lowering and broadening of heat evolution main peak and the elongation of the induction period. More or less pronounced shift of maximum heat evolution rate toward later ages of hydration is also found. These effects are the consequence of slower hydration process in cementitious systems with fly ash. The cement sample CEM I 32.5 R** (Fig. 4), showing the lowest heat of hydration and moderate heat evolution, seems to be not so retarded by the fly ash addition. In one case a significant growth of 'aluminate' third peak growing with the content of fly ash is observed (plots for mixtures in Fig. 3).

The heat-evolved values are, of course, proportionally lowered with cement content in the samples. However, the drop of heat evolved is not proportional to the reduction of 'pure' cement in the paste. Thus, the calculation of total heat evolved for 1 g of cement in the produced cement+fly ash mixtures has been done. These results are presented in the tables. The heat evolution changes thus observed reflect the complex modification of hydration kinetics. Based upon the theoretical knowledge dealing with cement hydration one can find some details in cement – fly ash interaction on the hydration process at early age and show the active role of pozzolanic component. The strong relationship between the initial cement properties and kinetics of heat evolution in admixtured cement pastes is clearly visible as well.

Conclusions

In spite of the complexity of problem some more general conclusions can be drawn:

– cements show different 'sensitivity' to fly ash admixture on hydration; it depends on phase composition, alkali content and fineness,

– with increasing fly ash admixture the heat evolution process is generally slowed down because of the lower rate of pozzolanic reaction though the decrease of total heat evolved on hydration of neat cement is in most cases higher than the expected value, resulting from 'dilution' of cement,

– at 5% fly ash admixture the heat evolution curve and heat output remain almost unchanged; the fly ash particles presumably play a role of nucleating agent for the hydration products,

– at fly ash admixture >30% the hydration process is severely retarded (elongated induction period),

– at high alkali content in cement the contribution of aluminate component to the heat evolution/hydration of cement+fly ash paste is evidenced.

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