Journal of Thermal Analysis and Calorimetry, Vol. 77 (2004) 151–158

STUDIES OF CEMENTITIOUS SYSTEMS WITH NEW GENERATION BY-PRODUCTS FROM FLUIDISED BED COMBUSTION

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Abstract

The rate of heat evolution as well as total heat output are strongly affected by other components of hydrating mixture, apart from neat portland cement, such as slag, fly ash and other industrial by-products; among them the wastes from fluidised bed combustion (FBC) has been taken into account recently. In this study the calorimeter was applied to follow the early hydration of cements produced with these materials. They interact with cement paste in a few ways: as set controlling agent and as active pozzolanic admixtures. Thus the rate of heat evolution/hydration is modified, depending on the composition of clinker and percentage of waste in the mixture. After the series of measurements for clinker–waste mixture hydrated systems also some 'model' mixtures were investigated to separate the effects from particular waste components.

Keywords: bottom ash, cement setting, FBC fly ash, FBC wastes, heat of hydration

Introduction

Calorimetry is the only method giving a general view on the course of hydration process in cementitious systems. The kinetics and mechanism of hydration in cementitious systems with admixtures can be thus followed continuously and directly. The role of particular factors affecting rate of reactions with water can be clearly visualised [1–4]. Slag, fly ash and other industrial by-products have been used as cement admixtures/components of cementitious materials for a long time; their effect for both early hydration reactions and the properties of hardened cement matrix is well known. Some new waste materials appeared recently in power industry and they must be implemented in some way for ecological reasons. In order to achieve this on a large scale, for example in building technologies, they should be thoroughly tested.

The wastes generated during the fluidised bed combustion are collected in de-dusting systems (very fine grained FBC fly ash; 70% of waste mass) or separated as so-called bottom ash (with coarse particles, higher sulphate content; sulphate phase in form of anhydrite). They are stable, as concerns the physical and chemical

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1388–6150/2004/ $ 20.00

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Kluwer Academic Publishers, Dordrecht

characteristics, when originating from one installation. They are composed mainly of the following materials, active in the presence of hydrating clinker minerals:

A) disordered alumina and silica containing substance, coming from inorganic components of coal, decomposed on heating at relatively low temperature in fluidised bed (800°C). Siliceous material transforms into calcium silicate hydrate (C–S–H) on hydration, as a result of the so-called pozzolanic reaction with calcium ions released to the solution from the calcium silicate clinker minerals. Alumina is incorporated to C–S–H or takes part in ettringite formation;

B) calcium sulphate (gypsum or anhydrite) acting as set controlling agent, reacting with the tricalcium aluminate from cement clinker giving ettringite;

C) lime more or less carbonated, playing the role of alkaline activator or nucleating agent.

Thus the multi-component FBC waste materials can be potentially used as both set controlling and pozzolanic admixture to cement. One should mention that their effect must be investigated not only from the setting and hardening point of view, but also in terms of durability.

The rate of heat evolution *vs*. time plots shows the occurrence of two peaks with a substantial heat evolution decrease (so-called dormant period) between them. This dormant period reflects very slowly occurring reactions leading to the transformation of plastic cement paste into hardened matrix (cement setting). Proper, moderate setting is achieved by use of set controlling admixtures (gypsum or anhydrite), reacting with the tricalcium aluminate from cement to form calcium sulphoaluminate phase (ettringite), instead of rapidly crystallized calcium aluminate hydrates. For this purpose the by-product gypsum/anhydrite generated in desulphurisation installations is used [5]. The reactions of tricalcium aluminate hydration are very exothermic, hence a delayed hydration or transformation between different forms of aluminate (or sulphoaluminate) products gives very often an additional third peak on the heat evolution curve [6].

While calcium sulphate acts as set controlling admixture, the other components of fluidised bed residue enter the hydration reaction, but after the initial hydrolysis of clinker minerals. In cement–admixture hydrating system not only the pozzolanic reaction affect the setting/hardening but also the physical processes, for example the intensive nucleation of hydration products on the surface of waste particles, due to their high fineness. The rate of hydration process/rate of heat evolution increases or decreases, depending on the reactivity and composition of cement – admixture system.

Experimental

Materials

In this study the calorimeter was applied to follow the early hydration of two different series of cement produced basing on the same cement clinkers, differing with the type of wastes. These admixtures were collected as a bottom residue in the fluidised bed combustion with simultaneous desulphurisation process or precipitated in de-dusting installations as FBC fly ash. To assess the role of FBC waste, different mixtures were produced (see tables) by co-grinding. Gypsum occurring in some mixtures is also a by-product from desulphurisation process. Finally, the model systems were prepared using microsilica as a perfect active pozzolanic material and/or limestone as a model of inert filler, originating from desulphurisation agent. Composition of particular components and cementitious mixtures are given in Tables 1–4.

Table 1 Mean chemical composition of FBC fly ash (FA) and bottom ash (BA)

	Component / mass%								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	Na_2O+K_2O	*l.o.i.*
FA	42.62	22.51	9.58	0.92	7.92	2.53	6.41	3.52	3.90
BA	32.82	14.27	4.20	0.55	25.86	2.06	17.06	1.68	1.34

Table 2 Mean phase composition of clinker

Phase content / mass%			
C_3S	C_2S	C_3A	C_4AF
55.4	16.0	13.0	8.9

Table 3 Composition of cements with FBC fly ash admixtures

Component	Percentage in sample			
	IFA (reference)	2FA	3FA	4FA
Clinker	89.5	63.0	60.0	60.0
FBC Fly ash	–	29.7	33.0	35.5
Limestone	4.5	4.5	4.5	4.5
Gypsum	6.0	2.8	2.5	–
SO_3 content	3.23	3.2	3.22	2.23

Table 4 Composition of cements with FBC bottom ash admixtures

Component	Percentage [mass%] in sample			
	1BA	2BA	3BA	4BA
Clinker	65.5	67.5	58.5	67.5
Gypsum	4.0	4.0	–	2.0
FBC fly ash	26.0	24.0	25.0	26.0
Limestone	4.5	4.5	4.5	–
FBC bottom ash	–	–	12.0	4.5

The crystalline components of wastes, such as quartz, anhydrite and lime/limestone or carbon, immersed in amorphous aluminosilicate product, were detected by XRD and DTA/TG.

In these cements FBC fly ash was implemented in cements 2FA–4FA in amount corresponding to fly ash from conventional combustion for cement type CEM II/B-V (that is those containing less than 80% Portland cement clinker and more than 20% mineral admixture) [7]. In cement 4FA there is no gypsum supplement; therefore an assumed constant SO_3 content is not achieved. A constant percentage of limestone is used as secondary component [7] to lower the clinker content.

In the next series with sample code ‘BA’ (Table 4), the bottom ash was used as a secondary cement constituent (in 4BA, instead of limestone), or as a set controlling admixture (in 3BA), to produce cement type CEM II/B-V without any other calcium sulphate. 1BA and 2BA are the references for them.

Finally the third series of samples was produced in which Portland cement was admixtured with limestone, as a fine-grained inactive filler or/and silica fume as pozzolanic component, at constant gypsum content 5%. Composition of these mixtures is given in Table 5.

Table 5 Composition of model cements with limestone and silica fume (constant gypsum content – 5 mass%)

Component	Percentage [mass%] in sample					
	1M	2M	3M	4M	5M	6M
Cement clinker	90	90	75	75	75	67
Limestone	5	–	20	12	15	20
Silica fume	–	5	–	8	5	8

Thus the cement with different proportion between active and less active components and even with lower clinker content were produced. In this case cements 1M and 2M can be considered as ‘references’. According to clinker content the samples 3M–6M can be classified as CEM II type ones [7].

Methods

The rate of heat evolution was followed in a differential BMR microcalorimeter, constructed in the Institute of Physical Chemistry, Polish Academy of Science (Warsaw) [8]. This is, among the other heat of cement hydration measuring systems [9–12] a very good one for small, model samples. Apart from cementitious mixtures, also the admixtures were subjected to heat evolution measurements. Hydrating pastes were prepared at water to solid ratio 0.5 on 5.00 g cement samples; the initial temperature was kept constant at 25°C.

Results and discussion

The heat evolved values were computed and they are given in Tables 6, 7; the heat evolution curves are shown in Figs 1–4. They are plotted in an extended scale for d*Q*/d*t* axis to visualise the differences.

Table 6 Heat evolved values in hydrated systems with FBC wastes

$Q(t)$/J g^{-1}	Sample code according to Tables 3 and 4								
	0BA*	1FA	2FA	3FA	4FA	1BA	2BA	3BA	4BA
24 h	147	220	205	181	189	182	211	217	218
72 h	227	277	245	228	248	312	346	355	362

*0BA – waste material – bottom ash

Table 7 Heat evolved values in hydrated model systems

$Q(t)$/J g^{-1}	Sample code according to Table 5					
	1M	2M	3M	4M	5M	6M
24 h	296	339	298	311	331	295
48 h	382	433	392	410	425	389

The heat evolved values which reflect the formation of hydration products for the series with fly ash show that the total heat is not reduced proportionally with cement clinker content but less decreases, owing to the activity of admixtures taking part in hydration reactions; in such a way the admixtures play a role of partial cement replacement.

As it results from the heat evolved values given in Table 6, so-called bottom ash gives fairly good heat effect, due to the reaction between the pozzolanic constituents,

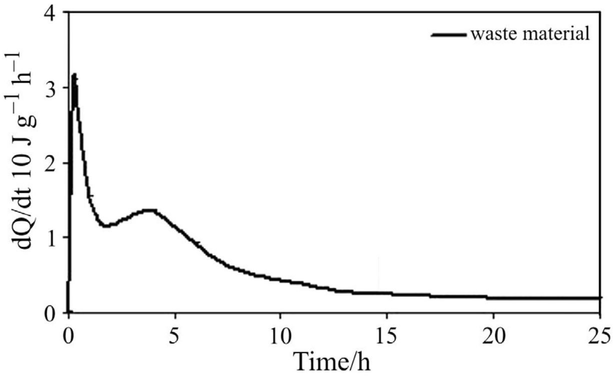

Fig. 1 Heat evolution on hydration of FBC waste material

lime and calcium sulphate. The heat evolution curve (Fig. 1) is of similar character that the one for cements with two peaks and an inflexion between them.

It has been found that fluidised bed combustion wastes can be successfully used as set controlling admixture; for cements corresponding to CEM II type there is no significant shortening or elongation of the so-called induction period – it means that initial setting time does not decline from the value for reference (Fig. 3). When cement of higher clinker content (CEMI) is used as reference, this induction period is obviously shorter (Fig. 2). A similar shape of heat evolution curves seems to point out further on that the FBC wastes act as cement+gypsum substitute. There is no other harmful effects; those could be easily detectable by calorimetry. Further on it seems that bottom ash in this case is better cement replacing material – it must be concluded from the similar shape of heat evolution for 1BA and 3BA samples (bottom ash used as 12% admixture).

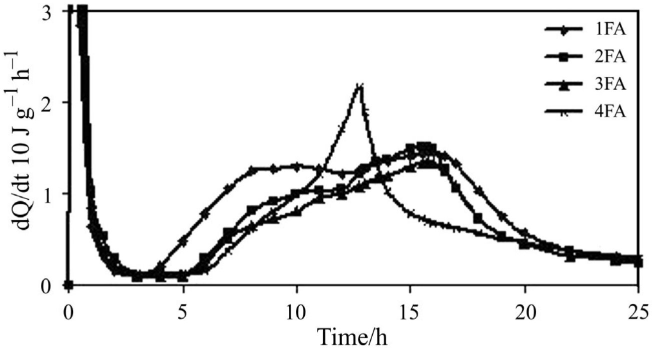

Fig. 2 Heat evolution on hydration of high C_3A cements with FBC wastes

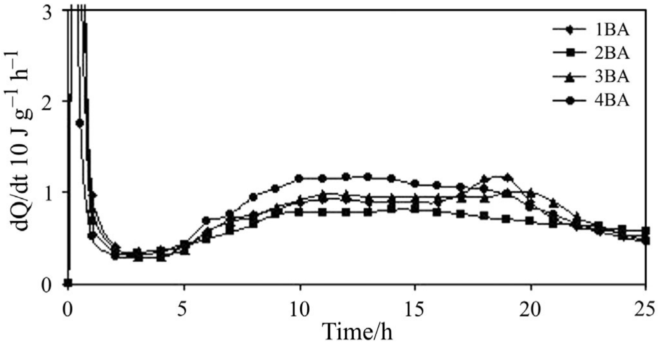

Fig. 3 Heat evolution on hydration of low C_3A cements with FBC wastes

However, the effect in every case is dependent upon the composition of hydrating mixture and the competition between the particular components should be discussed. At first the SO_3 content must match exactly with aluminate and active alumina content.

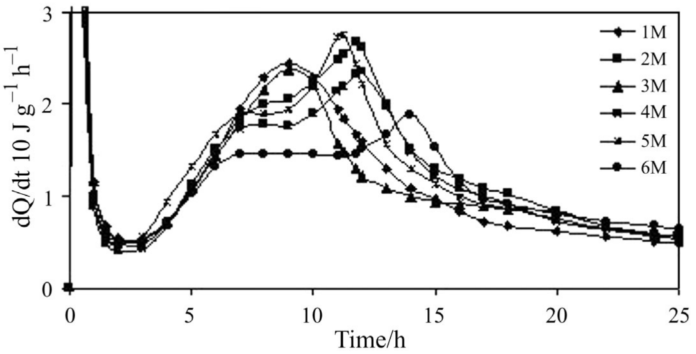

Fig. 4 Heat evolution on hydration of model cements

In Fig. 2 there is a plot for FA4 with lowered SO_3 to slightly above 2%; a sharp third peak indicates that the sulphate content is not sufficient to transform calcium aluminate into ettringite but also the calcium aluminate hydrates appear. This third peak, occurring in case of other samples with or without FBC wastes, is reduced in samples 2BA and 4BA, that is in the presence of a little lowered amount of fly ash or bottom ash used as secondary component instead of limestone. It seems that the reasons for this are more complex, the equilibrium in the liquid phase must be involved.

The studies in the model system put some light on this problem. At constant gypsum content, changeable tricalcium aluminate and at the presence of pozzolanic admixture with fine-grained filler this third peak appears when Ca ions are taken up from the solution by active pozzolana. Apart from this it is clearly visible that high percentage of fine grained filler does not lower the heat evolved value. On the other hand, every active pozzolanic admixture on the level 5–8%, mixed together with active filler (12–20%) gives the material type CEM II, having the heat of hydration not lower than reference CEM I with limestone secondary component (Table 7). Microsilica gives a substantial heat evolved increase when added at 75% clinker content. In one case, at 67% clinker content the heat evolution rates are lower; the Ca ions concentration becomes not sufficient to transform pozzolana quickly into hydration product.

These studies were followed by the other standard measurements, which allowed to prove very good compatibility between the calorimetric results and strength or setting time data.

Conclusions

- Waste material from fluidised bed combustion in form of fly ash or bottom ash can be successfully used as set controlling admixture; initial setting does not decline significantly from the value for reference type CEM II cement.
- Calorimetric data indicate the substituting role of FBC waste in many cementitious mixtures; bottom ash in some cases is better cement replacing material than the fly ash.

- The SO_3 content in cement/cement admixture must match exactly with calcium aluminate (in cement) and with active alumina content (in admixture).
- Fine grained limestone filler does not lower the heat evolved value when added as 20% cement replacement – it proves a significant role of nucleation step in hydration.
- The third peak on the heat evolution curve reflecting cement hydration appears when Ca ions are taken up from the solution by active pozzolana.

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