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HEAT EVOLUTION IN HYDRATED CEMENTITIOUS SYSTEMS ADMIXTURED WITH DIFFERENT SET CONTROLLING COMPONENTS

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Abstract

Calorimetry has been used in the investigations of cementitious systems with different set controlling admixtures. The kinetics and mechanism of hydration process was thus characterized on two different cement clinkers mixed with calcium sulphate containing materials. These admixtures were collected as a residue in the fluidised bed combustion (FBC) of coals with simultaneous desulphurisation process – so-called bottom ash. Apart from anhydrite/gypsum, they were composed mainly of alumina and silica containing material of disordered structure, originating from the coal contaminations of clay character. Anhydrite/gypsum acts as set controlling admixture. The aluminosilicate component reacts with calcium ions released to the solution from the calcium silicate clinker minerals.

It has been found that fluidised bed combustion wastes can be successfully used as set controlling admixture. There is no other harmful effects; those could be easily detectable by calorimetry. However the effect is dependent upon the composition of cement clinker. At low calcium aluminate content a slight acceleration of hydration process can be easily observed, particularly at higher amount of admixture. In the mixtures with high calcium aluminate clinker the heat evolved is slightly reduced in the presence of admixture. The dominating role of aluminate phase in heat evolution process within the first hours of hydration process has been thus proved.

Keywords: cement setting, FBC wastes, heat of hydration

Introduction

The kinetics and mechanism of hydration in cementitious systems with different admixtures can be successfully investigated by use of calorimetry [1–4]. The rate of heat evolution *vs.* time plots show the occurrence of two peaks with the so-called dormant period between them. This dormant period means a substantial heat evolution decrease within some hours after mixing with water and reflects very slowly occurring reactions leading to transformation of plastic cement paste into hardened matrix. This process is known as cement setting. Proper, moderate setting is achieved with help of set controlling agents, usually calcium sulphate in form of gypsum or anhydrite. They act as set controlling admixture reacting with the

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tricalcium aluminate from cement clinker giving calcium sulphoaluminate phase known as ettringite, instead of rapidly crystallized calcium aluminate hydrates. The natural sulphate materials have been used for this purpose for a long time, until the by-product gypsum appeared. Recently there is a huge amount of gypsum containing wastes of different origin available, mainly the materials from different desulphurisation installations; among them those from fluidised bed combustion of coals with simultaneous desulphurisation process are produced [5].

Apart from gypsum, this new type wastes are composed of alumina and silica containing substance of disordered structure, coming from inorganic components present in coal (clay minerals), as well as of the residue of desulphurisation agent (usually lime). While gypsum acts as set controlling admixture, the aluminosilicate phase enters the hydration in the presence of calcium ions and other components of basic cement paste and transforms into calcium silicate hydrate, as a result of the so-called pozzolanic reaction. Lime residue also takes part in this process. The rate of hydration process/rate of heat evolution increases or decreases, depending on the reactivity of admixture. Very active, amorphous components take up calcium ions and promote the hydrolysis of calcium silicates from cement. However, one should remember about the significant contribution of calcium aluminate – calcium sulphate reaction in the heat evolution process on one side and the 'dissolution' of neat cement in the presence of even very active admixture on the other side. These preliminary studies followed by the other standard measurements, allowed to elucidate the scale of fluidised bed wastes disposal in cement, an important task from natural environment protection point of view.

Experimental

Materials

In this study the calorimeter was applied to follow the early hydration of cements produced basing on two different cement clinkers, differing with calcium aluminate content (cement phase responsible for initial quick setting) mixed with calcium sulphate containing admixtures. These admixtures were collected as a residue in the fluidised bed combustion with simultaneous desulphurisation process from installations fed up with brown or black coal (so-called bottom ashes). Chemical composition of cement clinkers and wastes, phase composition of clinker are given in Tables 1–3.

Table 1 Chemical composition of clinker

Clinker sample	Component/wt%							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O+K_2O	1.o.i.*
1	20.3	6.8	2.9	65.6	1.4	0.7	1.0	0.4
2	22.4	4.3	5.3	66.4	0.7	0.2	0.4	0.2

* -loss on ignition

Table 2 Chemical composition of fluidised bed combustion wastes

Waste sample	Component/wt%								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	Na_2O+K_2O	1.o.i
FBCbr.	32.2	19.9	4.0	1.5	24.0	1.3	13.3	1.3	1.8
FBCbl.	43.4	14.7	4.4	0.6	16.3	2.0	14.6	2.7	1.3

FBC wastes from brown (br.) or black (bl) coal combustion

Table 3 Phase composition of clinkers

Clinker sample	Phase content/wt%			
	C_3S	C_2S	C_3A	C_4AF
1	55.4	16.0	13.0	8.9
2	62.2	17.3	2.5	16.1

The crystalline components of wastes, such as quartz, anhydrite and lime immersed in amorphous aluminosilicate product, were detected by XRD.

The cementitious mixtures produced further on by simultaneous grinding to the specific surface about 400 $m^2 kg^{-1}$ were characterised by assumed constant 3.50 wt.% SO_3 content, that is the maximum value for standard cements. Three types of mixtures were taken into account:

- reference samples composed of clinker (over 90 wt.%) and natural gypsum, corresponding approximately to the standard CEM I cements [6];
- cement samples composed of clinker (approximately 83–85%) and fluidised bed combustion waste (approximately 11–13%) to give the standard CEM II/A cement (having more than 80 wt.% Portland cement clinker); these cements were enriched in 3–4% natural gypsum to keep the constant SO_3 content;
- cement samples composed of clinker (approximately 74–78%) and fluidised bed combustion waste (approximately 22–26%) to give the standard CEM II/B cement (having less than 80 wt.% Portland cement clinker); there were cements without natural calcium sulphate material – cement and admixture contents were calculated to keep constant 3.50% wt. SO_3 content.

Composition of cementitious mixtures is given in Table 4.

One can notice that clinker 1, because of higher 'internal' sulphate content, needs less sulphate bearing admixtures and the cementitious mixtures show higher clinker contents. Simultaneously this clinker reveals significantly higher calcium aluminate content and its setting process should be therefore thoroughly controlled. For this reason the level of sulphur oxide in all cements was assumed as a standard limit value.

Methods

The rate of heat evolution was followed in a differential BMR microcalorimeter, constructed in the Institute of Physical Chemistry, Polish Academy of Science

Table 4 Composition of cements with fluidised bed combustion waste admixtures

Cement component	Content in wt.% in cement according to cement sample code*									
	1	2	1A	1B	2A	2B	1C	1D	2C	2D
Clinker 1	93.7		86.1	85.4			78.5	77.2		
Clinker 2		92.7			84.02	83.26			75.5	74.0
Gypsum	6.3	7.5	3.15	3.2	3.73	3.72				
FBCbrown				11.4		13.0		22.8		26.0
FBCblack			10.75		12.25		21.5		24.5	
SO_3	3.47	3.51	3.49	3.51	3.49	3.50	3.50	3.50	3.49	3.5
Type of sandard cement	CEM I		CEM II/A				CEM II/B			

*Sample code: 1,2 – type of clinker; A,C – admixtured with FBC waste from black coal; B,D – admixtured with FBC waste from brown coal

(Warsaw). 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 Table 5, as heat evolved after 24 and 72 h hydration; the heat evolution curves are shown in Figs 1 and 2. They are plotted in an extended scale for dQ/dt axis to visualise the differences. It has been found that fluidised bed combustion wastes can be successfully used as set controlling admixture; there is no significant shortening or elongation of the so-called induction period – it means that initial setting does not decline from the value for reference.

A similar shape of heat evolution curves seems to point out that the FBC wastes either at lower or higher amount act as cement + gypsum substitute. In spite of many other components occurring in waste material there is no other harmful effects; those could be easily detectable by calorimetry.

However the effect is dependent upon the composition of initial cement clinker and it relates both to the rate of heat evolution and total heat evolved after a time. At low calcium aluminate content (cement 2 and 2A – D) a slight acceleration of

Table 5 Heat evolved values in hydrated systems

Q(t)/J g^{-1}	Sample code according to Table 4									
	1	1A	1B	1C	1D	2	2A	2B	2C	2D
24 h	302	285	289	285	301	192	192	207	198	233
72 h	488	475	497	493	505	426	422	418	384	413

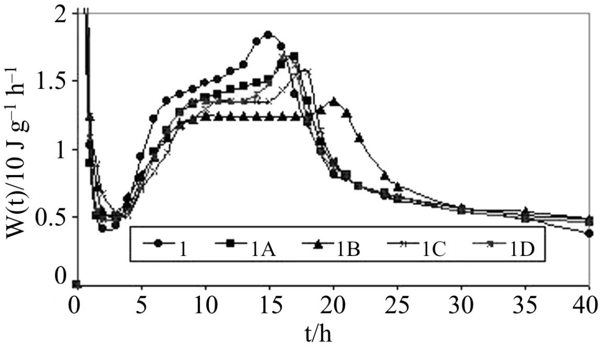

Fig. 1 Heat evolution on hydration of high C_3A cements with FBC wastes

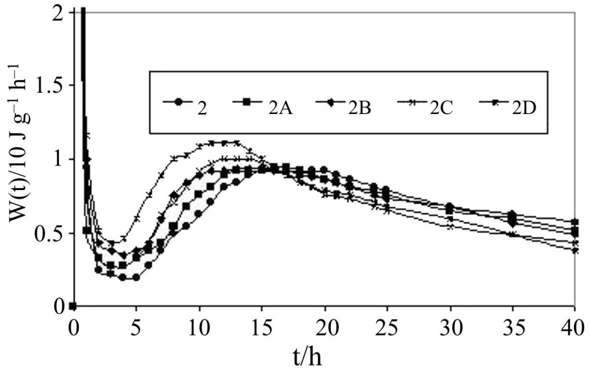

Fig. 2 Heat evolution on hydration of low C_3A cements with FBC wastes

hydration process can be easily observed, particularly at higher amount of admixture. In this case the pozzolanic reaction and dissolution of lime from waste gives more heat than the clinker thus replaced. In the mixtures with high calcium aluminate clinker the heat evolved is slightly reduced in the presence of admixture. Heat evolved on pozzolanic reaction is not equivalent to the 'loss' with aluminate phase. However, the lowest heat evolution rates for 1B sample as compared to the others (1A, 1D, 1C) as well as the highest heat evolution for 2D prove the increasing role of pozzolanic substance with growing percentage. Simultaneously it seems that the FBC material from the brown coal is a little more active. One should notice that the differences between the heat evolved values for two series of cement samples are rather small, within a few percent. It proves the substituting action of FBC wastes as cement admixtures.

These preliminary studies were followed by the other standard measurements, which allowed to elucidate the scale of fluidised bed wastes disposal in cement, an important task from natural environment protection point of view, in terms of standard requirements.

Conclusions

- Waste material from fluidised bed combustion can be successfully used as set controlling admixture as it results from the shape of heat evolution curves – initial setting does not decline from the value for reference.
- Calorimetric data indicate the substituting role of FBC waste in cementitious mixtures.
- The rate of heat evolution and heat evolved is dependent upon the composition of cement clinker. At low calcium aluminate content a slight acceleration of hydration process can be easily observed, particularly at higher amount of admixture. In the mixtures with high calcium aluminate clinker the heat evolved is slightly reduced in the presence of admixture.
- The tricalcium aluminate phase plays a dominating role in heat evolution process within the first hours of hydration.

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