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Coal fly ash activation—Comparison of isothermal calorimetric data and mortar strength

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ABSTRACT

The aim of this study was to determine the effect of mechano-chemical activation of fly ash on the early strength of Portland cement fly ash blends. Triethanolamine (TEA) and alkalis (NaOH or Na_2SO_4) were used as chemical activators. The mechanical treatment was carried out with a vibratory disc mill. The effect of activation was determined by the combination of isothermal heat conduction calorimetry over 48 h in combination with measurements of compressive strength between 1 and 28 d. Direct comparison of the features of the heat flow curves with compressive strength evolution was enabled by applying a numerical quantification method to the calorimetric results. This procedure revealed a systematic increase in early strength produced by the combination of the fly ash activation methods (grinding, TEA, alkalis). In addition, the acceleration of the pozzolanic reaction by fly ash activation was verified by replacing the cement in a cement fly ash blend by the equivalent amount of portlandite.

1. Introduction

The use of coal fly ash as a concrete component is characterized by a number of improved concrete properties regarding workability, durability and carbon footprint owing to the reduction in the clinker content in the binder [1–5]. On the other hand, the late pozzolanic reaction of fly ash in cement fly ash blends lowers the early strength [5–7] which limits the use of fly ash. One possibility to improve strength is the activation of fly ash by mechanical [8–12], thermal [13,14], chemical [15–17] treatment or a combination thereof. The present study focuses primarily on the increase in early strength of blended cements by mechano-chemical activation of fly ash. It is well-known that mechanical activation results in an increase in the specific surface area of the fly ash particles and improves the mechanical properties of hydrated cement fly ash blends, as has been shown in [8,18,19]. At the same time, the higher specific surface provides additional area for chemical reactions. The addition of alkaline chemical activators leads to an increase of the basicity of the solution. Thus the combination of both activation methods is expected to result in higher dissolution rates of the amorphous fly ash glass and promotion of the early pozzolanic reaction.

One way to investigate the effectiveness of improving the properties of binders is by observing the hydration reaction by means of isothermal heat flow calorimetry [12,20,21]. The heat flow data at early hydration times reflect the four main cement hydration stages: rapid initial process (I), dormant period (II), acceleration period (III) and retardation period (IV) (Fig. 1). The early hydration is dominated by two main types of reaction: the silicate reaction (Eq. (1)) and aluminate reaction (Eq. (2)) as described, for example, by [22,23]:

$$C_3S + 3.9H \rightarrow C_{1.7}SH_{2.6} + 1.3\ CH \quad (1)$$

$$C_3A + 3\ Cs + 32H \rightarrow C_3A{\cdot}3Cs{\cdot}H_{32} \quad (2)$$

where C = CaO, S = SiO_2, A = Al_2O_3, s = SO_3 and H = H_2O.

During the retardation period some of the heat flow curves exhibit a shoulder [24] which is described by some authors as a “sulfate depletion peak” [23,25,26]. The peak is associated with the consumption of sulfate during the aluminate reaction and can be related to the formation of ettringite [27].

When plotted in one diagram for better comparison, heat conduction curves often overlap in the areas of interest making an accurate evaluation difficult or even impossible. Moreover, a purely qualitative comparison of the heat flow data restricts the information provided by the measurements. Thus this work also aims to improve the evaluation of such data. At first the reaction minima or maxima are determined, as shown by an example in Fig. 1. The slope of the tangent at the inflection point of the curve during the acceleration period corresponds to the rate of hydration. Evaluation of the heat flow data obtained in this way allows comparison with the corresponding compressive strengths

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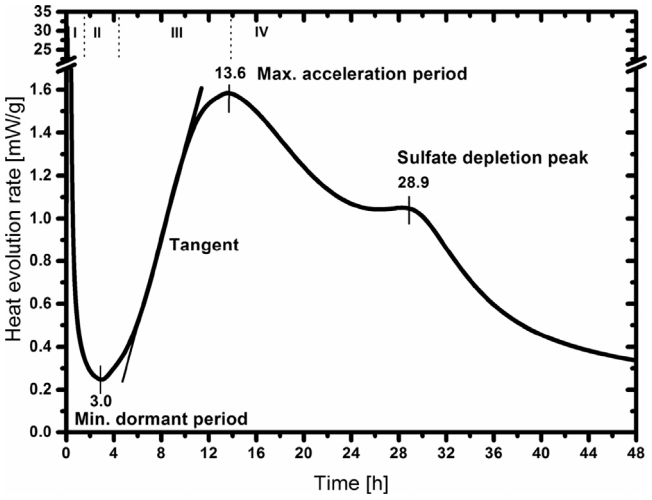

Fig. 1. Example of graphical evaluation of the heat flow curve. I: rapid initial process; II: dormant period; III: acceleration period; IV: retardation period.

thereby providing relationships between the thermochemical processes and physical properties of the hydration products.

2. Materials and methods

A siliceous hard coal fly ash and a Portland cement CEM I 42.5 R according to DIN EN 450 and DIN EN 197, respectively, were chosen for the investigations. Both materials were analysed by ICP-OES and XRD; their chemical and mineralogical compositions are listed in Table 1 and Table 2.

The mechano-chemical activation of the fly ash was carried out according to the following procedure. Chemically pure NaOH and Na_2SO_4 were used as alkali additives (Table 3). Triethanolamine was added to some of the samples as an organic activator. Usually this alkanolamine is used as a cement grinding aid in cement manufacture. In certain dosages it shows a positive effect on early strength as published by [28–30].

The additives were dissolved in deionized water at the proportions shown in Table 3 and added to the fly ash. This procedure allows more effective dosage as well as the creation of a reaction medium at the boundary surfaces during the later grinding process.

The blended fly ash was homogenized in a 3D-shaker mixer for 2 h, then ground for 12 s in a vibratory disc mill and mixed with the OPC at the ratio 1:1. The median of the particle size distribution (d_{50}) of the activated fly ash is shown in Table 3. The final blends were homogenized in the 3D-shaker mixer for another 0.5 h and stored in a N_2 atmosphere until further processing.

With fly ash cement blends only indirect evidence of the activation of fly ash is obtained because a reaction of the additives with the cement cannot be completely excluded. In order to exclude this during the hydration reaction, the cement was replaced by portlandite in accordance with [15]. Thus a blend of portlandite and activated fly ash (PFTN12) as well as a reference sample with portlandite and untreated fly ash (PF) were prepared at a ratio of 1:5 (Table 3), i.e. based on a portlandite content of 20 wt.% typical for fully hydrated Portland cement.

Mortar bars (4 cm × 4 cm × 16 cm) were produced according to DIN EN 196-1 with cement, quartz sand and water at 1:3:0.5 by weight where the cement was replaced by 50 wt.% activated fly ash. A reference sample with untreated fly ash was also prepared. After filling, the moulds were stored at nominally 98 % RH and 20 °C (± 2 °C) for 24 h before demoulding the specimens and measuring the compressive strength at 1 d. The bars were then stored in water and the compressive strength measured at ages of 2 d, 7 d and 28 d.

The portlandite fly ash mortar blends (PF Ref and PFTN12) were mixed at a w/b ratio of 0.5 with 0.7 M KOH solution instead of water in order to produce a high pH as in hydrated cement. The compressive strength of these blends was measured after seven days. It was not possible to determine early compressive strength owing to the absence of clinker phases in these samples.

The eight channel conduction calorimeter TAM Air by TA Instruments was used to measure the heat flow. The binder mixtures were weighed out into 20 ml glass ampoules. Admix ampoules were used to enable water addition (w/b ratio of 0.6) and mixing at 20 °C inside the device. Measurements were performed over 48 h to track exothermal processes during the early stage of hydration. In the case of the portlandite fly ash blends, the hydration process was induced by the addition of 0.7 M KOH solution instead of water. The heat flow was recorded for more than 84 h.

Table 1
Mineralogical and chemical composition of CEM I 42.5 R.

Mineralogical composition [wt.%]										
Alite	Belite	Tricalcium-aluminate	Brownmillerite	Anhydrite	Hemihydrate	Calcite	CaO	MgO	K_2SO_4	Quartz
65.0	3.8	7.5	10.9	2.5	3.1	1.9	0.5	1.4	2.8	0.5

Chemical composition [wt.%]										
LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	SO_3	K_2O	Na_2O	P_2O_5
2.6	19.5	4.7	3.0	64.0	2.2	0.2	0.2	2.6	0.8	0.1	0.1

Table 2
Mineralogical and chemical composition of fly ash.

Mineralogical composition [wt.%]							
Amorphous	CaO	Maghemite	Hematite	Mullite	Quartz	Calcite	Anhydrite
68.0	0.2	0.4	1.1	20.5	9.1	0.2	0.4

Chemical composition [wt.%]										
LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	SO_3	K_2O	Na_2O	P_2O_5
4.5	53.0	24.3	8.1	4.6	1.3	1.2	0.1	0.4	1.9	0.4	0.1