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THE HYDRAULIC ACTIVITY OF HIGH CALCIUM FLY ASH

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Cementitious mixtures with so-called high calcium fly ash show better strength parameters as compared to the ones with conventional siliceous fly ash. This practical feature is the consequence of improved hydraulic activity. Differential thermal analysis and thermogravimetry were used, together with the other methods, to evaluate the reactivity of high calcium fly ash in mixtures with cements. This type of fly ash exhibits hydraulic properties (setting and hardening on hydration) and durability, after hardening, in the presence of water. The so-called pozzolanic activity is the feature of high active silica containing fly ash while the hydraulic activity is related to the high calcium ones. However, the chemical and phase composition is variable and related to the particle size. The hydraulic/pozzolanic properties are strongly improved by additional grinding (specific surface increase).

Keywords: *calcium hydroxide determination, chemical composition, high calcium fly ash, hydraulic activity, phase composition*

Introduction

Fly ash is produced as a waste material in the combustion of pulverized coal in power plants. For many years it has been used as cement mineral addition or as a component in concrete production. Among the factors improving the fly ash reactivity the most important are: the type and quality of pulverized fuel, the conditions of the combustion process and last but not least the method of de-dusting and desulphurization of flue gases [1, 2]. There are many types of fly ash wastes and by-products generated nowadays, differing with chemical composition and properties. Following the criteria proposed by Jarrige [3], the three groups of fly ash can be distinguished: silicate–aluminate fly ash with SiO_2 as a main constituent, aluminate–silicate fly ash with Al_2O_3 as a main constituent and sulfate–calcium fly ash with calcium compounds as main constituents.

The siliceous fly ash is commonly used in cement and concrete production, because of its ability to react with calcium hydroxide evolved on hydrolysis of calcium silicates from cement clinker. The hydrated calcium silicates and aluminates are thus produced. This fly ash property being the base of practical implementation is known as pozzolanic activity. This fly ash is recommended by the European Community standard for cements EN 197-1 [4] (in standard described as ‘V’ fly ash), together with the other type of fly ash, namely the so-called high calcium fly ash (‘W’), used on lower scale. The latter is the subject of this work.

The high calcium fly ash is produced in the form of very fine powder, exhibiting not only the pozzolanic properties but also the setting behavior, originating from the presence of highly active constituents, such as reactive lime, reactive silica and alumina. The CaO content is within the range from 10 to 40% and therefore the so-called self-setting is observed, where CaO from fly ash plays a role of pozzolanic reaction activator or binding agent. For this reason this fly ash is determined as a pozzolanic and hydraulic material. Apart from the reactive CaO such components as reactive silica (SiO_2) and alumina Al_2O_3 are present. In the residue the iron oxide Fe_2O_3 and some other compounds can be found.

In this work the hydraulic/pozzolanic properties of lime fly ash are examined and discussed.

Chemical composition of high calcium fly ash

In Table 1 the chemical composition of high calcium fly ash produced as a result of coal combustion in conventional furnaces of different power stations is shown.

The phase composition of high calcium fly ash from conventional furnaces is more complex than the composition attributed to the siliceous fly ash. It relates both to the vitreous and crystalline part of this material. The vitreous phase is particularly differentiated and, in author’s opinion, seems to be similar to the granulated blast furnace slag vitreous component [5]. Apart from the silica and alumina rich glass there is also glassy domains attributed to the $CaO–Fe_2O_3–SiO_2$ system.

The chemical composition of the high calcium fly ash is different for particular grain size fractions [6], as it is shown in Table 2.

In finest fractions a higher content of calcium compounds was found, while in coarser particle fractions (40–60 μm, >60 μm) SiO_2 is a main component.

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Table 1 Chemical composition of high calcium fly ash

Component	Content in mass/% power station		
	1	2	3
L.O.I.	2.1	0.2–1.4	2.5
SiO_2	42.8	22.8–70.0	50.8
Al_2O_3	17.5	2.3–4.9	3.5
Fe_2O_3	4.4	2.9–6.7	5.2
CaO_{total}	23.4	17.5–49.5	26.2
including CaO_{free}	4.1	0.5–12.4	5.3
MgO	0.9	1.8–9.4	4.4
SO_3	4.3	2.0–11.3	6.0
Na_2O	0.1	0.2–0.4	0.2
K_2O	0.2	0.1–0.3	0.3
rest	4.3	–	0.9

The differentiation of chemical composition may be taken into account in practice, by selective fly ash collection in particular sections of electrofilter on de-dusting (Fig. 1). In section III, far away from furnace, the finest particles rich in calcium and magnesium compounds and relatively poor in silica, while fly ash collected in section I is enriched in silica containing compounds (Table 3).

Hydraulic activity of the high calcium fly ash

Fly ash, as it has been mentioned above, exhibits hydraulic and pozzolanic properties characterized by the following factors [5–7]:

- modulus of basicity M_b=CaO [mass]/(SiO_2+Al_2O_3+ +Fe_2O_3) [mass]
- high free lime content resulting in pH=12–13,
- high specific surface,
- compressive strength of fly ash paste after 28-day hardening – minimum 1 MPa.

The very slow, complex processes occurring in the hydrating high calcium fly ash, include first of all the reactions between free lime and active silica, reactions of active minerals (e.g. anhydrite) with glassy phase constituents [8–14].

The rate and intensity of these processes depends upon the properties of fly ash, such as chemical and mineral composition, fineness as well as upon curing conditions, that is the temperature, humidity, use of special thermal treatment (low- or high-pressure steam curing).

In order to assess the hydraulic activity of fly ash the following studies were carried out:

- the studies of fly ash containing pastes hydration
- the studies of fly ash–cement mixtures.

Hydration of high calcium fly ash

The fly ash sample of chemical composition given in Table 2 (initial sample) was used in these studies (sample A). The X-ray diffractions pattern of this sample is shown in Fig. 2.

The main crystalline components detected in this sample are: quartz, anhydrite, free CaO, anorthite, gehlenite and hematite.

In the studies the three kinds of samples were used: raw fly ash with the Blaine specific surface of 233.0 $m^2\ kg^{-1}$, collected directly from electrofilter (sample A in Table 2) and ground fly ash samples: sample A_1 –to the specific surface 559.0 $m^2\ kg^{-1}$ and sample A_2 –to the specific surface of 744.0 $m^2\ kg^{-1}$ respectively. The pastes were mixed at water to solid ratio 0.4. The mortars were produced, stored and tested following the European standard EN 196-1 [15].

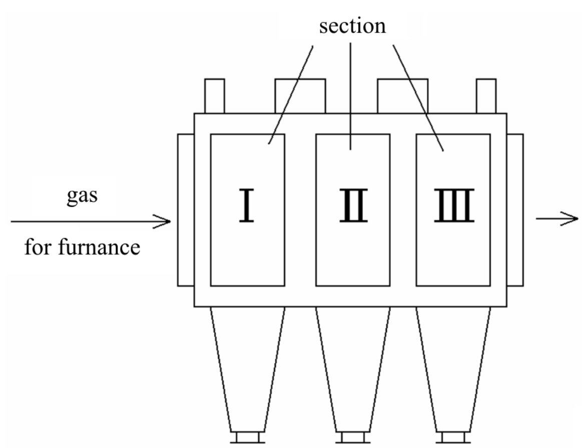

Fig. 1 Three sections electrofilter scheme

Table 2 Chemical composition of high calcium fly ash for particular grain size fractions

Grain size fraction/µm	Content of particular component/mass%									
	L.O.I.	SiO_2	Al_2O_3	Fe_2O_3	CaO	CaO_{free}	SO_3	MgO	Na_2O	K_2O
Initial sample (sample A)	3.9	44.4	16.4	6.6	22.1	2.4	4.6	1.0	0.1	0.5
0/20	3.7	19.2	11.5	6.6	43.0	7.2	12.8	0.8	0.2	0.6
20/40	4.2	35.2	16.1	7.4	31.2	5.6	4.9	1.4	0.1	0.4
40/60	2.6	45.4	17.7	7.6	22.6	3.4	2.3	1.5	0.1	0.4
>60	3.3	59.2	19.7	5.3	9.6	0.8	1.0	0.4	0.1	0.4

Table 3 Chemical composition of high calcium fly ash in particular sections of electrofilter

Component	Content/mass%		
	section I	section II	section III
SiO_2	57.8/82.0	34.8/44.5	30.4/33.3
Al_2O_3	1.5/2.6	3.7/5.1	4.4
Fe_2O_3	2.3/6.4	4.2/7.1	4.7/6.6
TiO_2	0.2/0.5	0.6/0.7	0.7/0.8
MgO	0.7/2.6	4.1/4.2	4.1/4.8
CaO_{total}	10.8/24.0	32.0/37.5	37.5/39.4
Mn_2O_3	0.1/0.2	0.2/0.3	0.3/0.4
SO_3	1.2/3.7	7.6/8.6	8.2/14.6
K_2O	0.06/0.08	0.08/0.13	0.11/0.19
Na_2O	0.08/0.09	0.20/0.39	0.26/0.56
C	0.43	0.61	1.74

In Fig. 3 the DTA curves of hydrated fly ash pastes are shown (the dried 180 mg samples thus produced were heated in TA-1 Mettler thermoanalyser in argon atmosphere, Pt crucibles, at heating rate 10°C min^{-1}). It can be easily seen that the ground fly ash sample (curves A_2) reveals significant chemical activity in reaction with water.

The ground fly ash sample is more hydrated as it can be derived from the deep endothermic peak with maximum temperature in the range 125/135ºC. This peak is attributed to the gel-like and crystalline hydration products–calcium silicate and calcium aluminate hydrates respectively. In case of raw fly ash sample (curves A) these peaks are negligible – it means that the hydration process goes very slowly. The heat evolved on hydration of finely ground fly ash (specific surface – 744 $m^2 kg^{-1}$), determined using calorimetric method, proves also the binding properties of this material (Fig. 4).

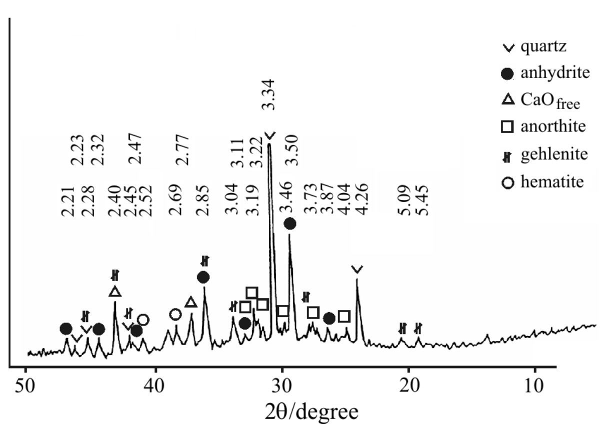

Fig. 2 XRD pattern of the high calcium fly ash

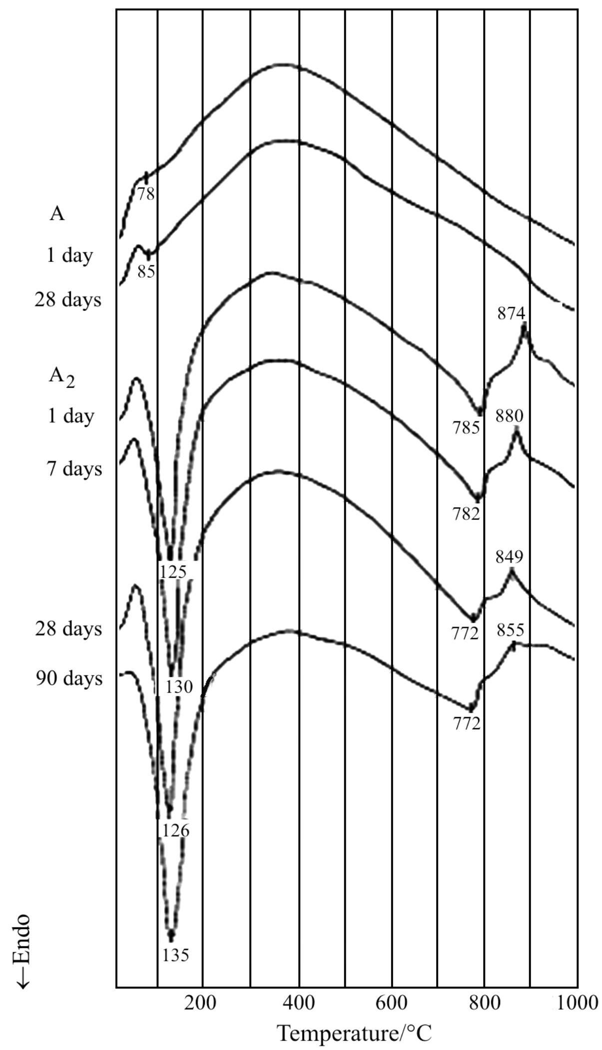

Fig. 3 DTA curves of hardened fly ash pastes. A – raw fly ash, A_2 – ground fly ash (specific surface – 744 $m^2 kg^{-1}$)

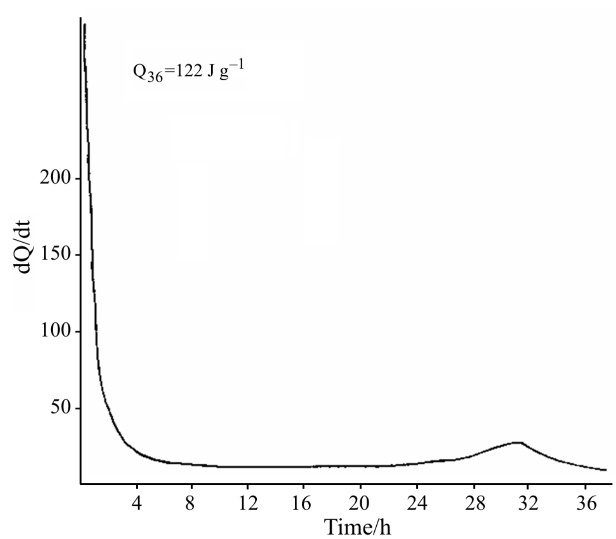

Fig. 4 Heat evolution on hydration of the ground high calcium fly ash (sample A_2)

Table 4 Compressive strength of hardened high calcium fly ash pastes

Specific surface of fly ash/$m^2\ kg^{-1}$	Compressive strength/ MPa at age			
	3 days	7 days	28 days	90 days
559.0	3.4	2.4	5.2	5.2
744.0	9.3	9.9	11.5	13.8

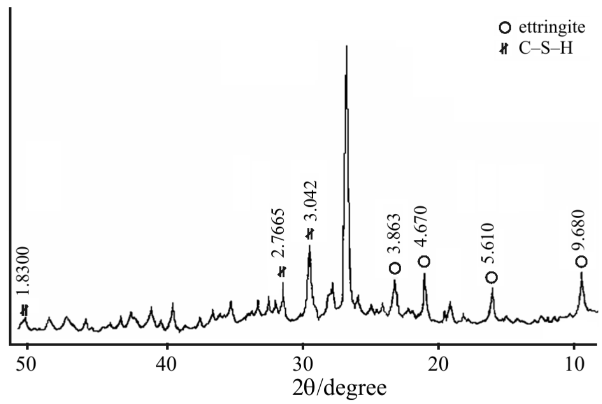

Fig. 5 XRD pattern of the hardened ground high calcium fly ash (A_2)

The X-ray diffraction studies of 28-day hardened fly ash sample (Fig. 5) exhibit the formation of ettringite $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$ (d=9.68, 5.61, 4.67 Å) and so-called C–S–H phase (d=3.04, 2.40 Å).

The hardened, finely ground high calcium fly ash containing paste, exhibits a significant strength development, growing with the specific surface (Table 4).

Effect of high calcium fly ash on the properties of cement–fly ash mixtures

Several samples were prepared with aim to evaluate the effect of high calcium fly ash on the properties of cement – fly ash mixtures. Their proportions are given in Table 5. The fly ash with chemical composition as an initial sample given in Table 2 (sample A) and typical siliceous fly ash type V, having pozzolanic properties, were used. The chemical composition of this latter sample (fly ash type V) was as follows [% by mass]: L.O.I. – 2.9, SiO_2 – 50.8, Al_2O_3 – 23.9, Fe_2O_3 – 8.6, CaO – 3.6, MgO – 2.8, SO_3 – 0.8, K_2O – 2.9, Na_2O – 0.8, specific surface – 295.0 $m^2\ kg^{-1}$. The standard portland cement type CEM I 32.5R was used. The compressive strength of mortars was determined after 2, 7, 28 and 90 days. The results are presented in Table 6.

Table 5 Composition of fly ash–cement samples

Sample number	Type of fly ash	Composition/mass%	
		Cement CEM I 32.5R	Fly ash
I	–	100	–
II	Siliceous fly ash V	70	30
III	High calcium fly ash (sample A)	70	30
II/A	Ground siliceous fly ash (V_1); specific surface 543.0 $m^2\ kg^{-1}$	70	30
III/A	Ground high calcium fly ash (sample A_1); specific surface 559.0 $m^2\ kg^{-1}$	70	30
IV	Ground siliceous fly ash (V_1); specific surface 543.0 $m^2\ kg^{-1}$	30	70
V	Ground high calcium fly ash (sample A_1); specific surface 559.0 $m^2\ kg^{-1}$	30	70

The 30% cement replacement by raw fly ash (V or A) brings about the compressive strength decrease as compared to compressive strength of cement after 2/90 days maturing. The reduction of strength is similar for both types of fly ash; it seems a little higher for the high calcium material (Table 6). Grinding operation resulted in activation of both types of fly ash. In case of siliceous fly ash (V_1) the pozzolanic activity increase is typical – the substantial changes are visi-

Table 6 Compressive strength of cement–fly ash pastes

Sample number	Fly ash type and content in cementitious mixture	Compressive strength/MPa at age			
		2 days	7 days	28 days	90 days
I	Cement	16.4	24.1	40.5	49.3
II	30% fly ash (V)	10.2	16.2	24.9	41.2
III	30% fly ash (A)	9.7	14.6	20.4	37.6
II/A	30% fly ash (V_1)	11.2	16.5	31.0	49.9
III/A	30% fly ash (A_1)	13.1	23.1	38.7	48.5
IV	70% fly ash (V_1)	1.2	3.8	9.7	25.2
V	70% fly ash (A_1)	3.9	16.5	32.4	37.5

ble at longer maturing, after 28 and 90 days respectively; the compressive strength is higher than for samples with raw material (Table 6).

Grinding appeared particularly effective as the way of high calcium fly ash (A_1) activation. The compressive strength of cementitious mixture with 30%

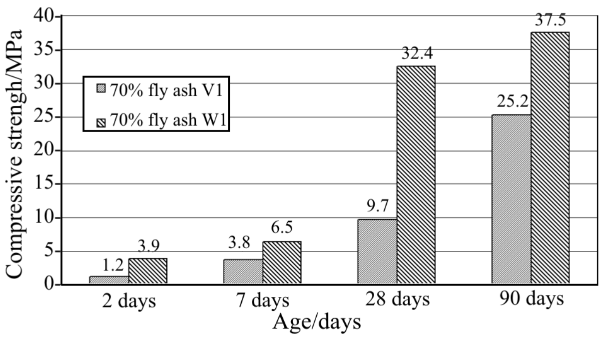

Fig. 6 Compressive strength of mortars with ground fly ash addend as 70% cement replacement

cement replacement by ground high calcium fly ash cement (A_1) is very similar to the values for standard neat portland cement CEM I (Table 6).

The difference is strongly pronounced in case of 70% ground fly ash containing mixtures. These differences are shown in Fig. 6. The modified hydraulic activity gives higher compressive strength of hardened mortars (Fig. 6).

The DTA curves for cementitious mixtures with 70% ground fly ash are presented in Fig. 7.

The following three DTA peaks can be distinguished:

- endothermic, in temperature range 100–300°C attributed to the dehydration of some crystalline and gel-like hydration products,
- endothermic, in the temperature range 400–500°C attributed to the $Ca(OH)_2$ decomposition,
- endothermic, in the temperature range 700–800°C attributed to the decomposition of carbonates.

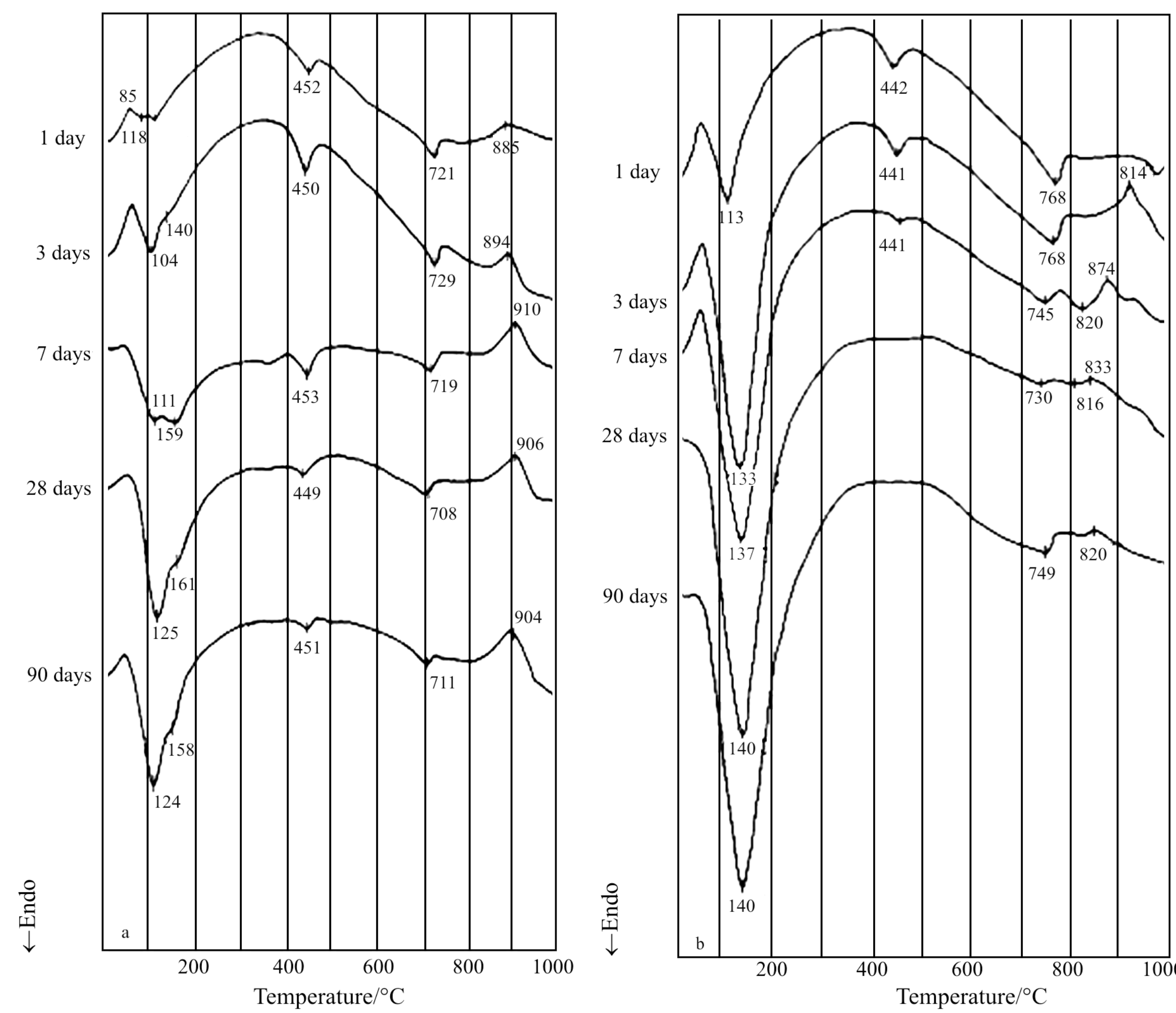

Fig. 7 DTA curves of hardened cement – fly ash samples; a – for 70% fly ash V_1 containing mixture, b – for 70% fly ash A_1 containing mixture

Table 7 Mass loss of hardened cement–fly ash samples

Age/days	Mass loss in the 100–400°C range/%	
	Mixture IV (70% V_1 fly ash)	Mixture V (70% A_1 fly ash)
1	1.38	4.79
3	3.49	10.89
7	5.06	13.17
28	7.74	16.04
90	7.67	15.44

In case of 70% ground high calcium fly ash containing samples, calcium hydroxide from cement calcium silicate phases hydrolysis enters the hydration with fly ash components within 7 days. An improved hydraulic activity of ground material can be derived also from the depth of DTA endothermic peak in the temperature range of 100–400°C. This peak, attributed to the dehydration of hydrates formed between fly ash and cement components is significantly greater than in case of 'parallel' 70% pozzolanic, siliceous fly ash (V) sample. It can be also derived from the calculations based on TG mass loss in the same temperature range (Table 7).

Conclusions

- High calcium fly ash from conventional installations show variable chemical and mineral composition, strongly affected by the size of fly ash particles. High calcium fly ash constituents, such as free CaO, anhydrite $CaSO_4$, active glassy phase improve the hydraulic properties of this material.
- High calcium fly ash can be characterized by hydraulic activity i.e. after mixing with water it exhibits setting and hardening. Additional grinding gives a significant increase of hydraulic activity in case of high calcium fly ash. The structure of fly ash particles is collapsed, thus the exposure of fly ash substance to water becomes better. As a consequence, higher quantity of hydration product and higher strength of hardened mortar is observed.
- The main hydration products formed as a result of reaction between fly ash and water are calcium silicate hydrates (C–S–H) and hydrated calcium aluminates or sulfoaluminates (as ettringite $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$). Their amount in hydrating mixture grows significantly when ground high calcium fly ash is used.
- The cements with the ground high calcium fly ash mixtures exhibit better strength parameters than the mixtures with standard pozzolanic siliceous fly ash.

References

1 S. Bastian, Structural concrete with fly ash, Arkady, Warszawa 1980 (in Polish).
2 M. Bukowska, B. Pacewska and T. Wilińska, J. Therm. Anal. Cal., 74 (2003) 931.
3 A. Jarrige, Use of ash in cement and concrete manufacture, IInd Conference on the use of fly; United Nations Economical Committee (European Sections of Experts), Prague 1969.
4 PN-EN 197-1-Cement, Part 1. Composition, requirements, conformity assessment.
5 V. S. Ramachandran, R. F. Feldman and Y. Y. Beaudoin, Concrete Science; Treatise on Current Research, Heyden & Son Ltd., 1981.
6 Z. Giergiczny and A. Weryńska, Influence of fineness of fly ashes on their hydraulic activity. Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete; Proceedings Third International Conference Trondheim, Norway 1989.
7 E. Giergiczny, Z. Giergiczny and E. Michniewicz, The properties and use of fly ashes from the brown coal combustion, 4th International Symposium on the Reclamation, Treatment and Utilization of Coal Mining Wastes, Cracow 1993.
8 L. K. A. Sear, Properties and use of coal fly ash, Thomas Telford, London 2001.
9 A. E. Galabina, Autoclaved building materials from wastes generated in power plant. Edited by Strojizdat, Leningrad 1986 (in Russian).
10 S. Antiohos, V. G. Papadakis, K. Maganari and S. Tsimas, The development of blended supplementary cementing materials consisting of high and low calcium fly ashes, Proceedings of the 11th International Congress on the Chemistry, Durban, South Africa, 2003, Vol. 2, pp. 747–756.
11 T. R. Naik and S. S. Singh, Use of high calcium fly ash in cement based construction materials. Fifth CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Milwaukee, USA, Supplementary Papers, 1995, pp. 1–44.
12 X. Wang, W. Zimmermann, K. C. Ng, A. Chakraboty and U. Keller, J. Therm. Anal. Cal., 76 (2004) 659.
13 R. B. Freeman and R. L.Carrasquillo, Production of sulfate resistant concrete containing high calcium fly ash and sodium admixture, Fifth CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Milwaukee, USA 1995, Vol. 1, pp. 153–176.
14 Z. Giergiczny, J. Therm. Anal. Cal., 76 (2004) 747.
15 EN 196-1 'Methods of testing cement – Part 1: Determination of strength'.

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