

USE OF DTA IN THE INVESTIGATIONS OF FLY ASHES FROM FLUIDIZED BED BOILERS

K. Rajczyk^{1}, E. Giergiczny¹ and M. A. Glinicki²*

¹Institute of Mineral Building Materials, Opole, Poland

²Institute of Fundamental Technological Research, Polish Academy of Science, Warsaw, Poland

Abstract

DTA method was used to follow the hydration process of cement admixtures containing fluidized bed combustion by-product, formed on joined combustion and desulphurisation in some installations with fluidized bed. Based on endothermic peaks attributed to the dehydration of phases formed on hydration, the conditions leading to the formation of so-called 'delayed' ettringite were found. This calcium alumino-sulphate hydrate is responsible for lower durability of fluidized bed ash containing material. DTA method is also beneficial in the studies of fluidized bed combustion by-product itself, giving information about the un-burnt carbon content and pozzolanic properties.

Keywords: DTA, fluidized bed combustion fly ash, hydration

Introduction

The reduction of SO₂ emission to the atmosphere, as is required by ecological rules, led to the development of new combustion installations with simultaneous desulphurisation of flue gas. Thus the conventional power plant furnaces are being replaced frequently by the fluidized bed combustion chambers and the new by-products – fluidized bed combustion fly ashes (FBC ashes) different from the 'traditional' ones. Determination of their characteristics is necessary for appropriate applications (e.g. in cement and concrete production).

Differential thermal analysis (DTA), thermogravimetry (TG) and calorimetry have been extensively used to investigate the hydration process in cement system containing inorganic residue materials left after combustion of coal [1–3].

In this work, at first thermal methods appeared practical in the characterisation of fluidized bed combustion by-product itself, giving information about the un-burnt carbon content, important for the potential use of fly ash, because carbon content (as loss on ignition) it is limited in standards for conventional fly ash used as cement and concrete component.

Studies on the hydration process in cement systems with fluidized bed combustion fly ash are necessary for further proper disposal of this waste material. The

* Author for correspondence: E-mail: krajczyk@immb.opole.pl

prevention of durability decrease is particularly important. The current study has been carried out using Mettler Thermoanalyzer TA-1 from the first hours from processing with water until the full hardening. Special attention was paid to the formation of ettringite phase ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$), which is a potential source of expansion in cement-ash mixtures and collapse of hardened material, apart from the beneficial contribution in strengthening of structure [4]. This phase was also identified by XRD and SEM methods.

Experimental

The chemical composition of fluidized bed fly ash (determined by analytical methods according to European Standards) used in this work is given in Table 1. For the potential use of fly ash the determination of the un-burnt carbon residue is critical because of limitation in standards for fly ash implemented as cement and concrete component. Current standard requirements allow the maximum loss on ignition at 950°C to be 5%; this value may be greater when in the presence of materials other than carbon components. Our tests using of DTA and TG show that there is a high carbon content in fly ash from black coal combustion (exothermic peak with maximum at temperature 500°C), while in case of fly ash from brown coal combustion there is no residual coal. In both ashes a substantial amount of calcium carbonate is present; this sorbent residue decomposes at approximately 800°C .

Table 1 Chemical composition of fluidized bed combustion fly ash as compared to the composition of classic pulverized fuel ash from conventional combustion chambers [mass%]

| Component | Fly ash from the black coal combustion in fluidized bed | Fly ash from the brown coal combustion in fluidized bed | Fly ash from the black coal combustion in conventional furnace |
|--------------------------------|---|---|--|
| L.o.i. | 11.1 | 4.1 | 1.8 |
| SiO ₂ | 33.6 | 31.1 | 52.3 |
| CaO | 16.4 | 26.8 | 4.1 |
| Al ₂ O ₃ | 18.1 | 22.6 | 28.5 |
| Fe ₂ O ₃ | 6.9 | 3.1 | 6.4 |
| MgO | 2.7 | 1.8 | 2.4 |
| SO ₃ | 6.5 | 4.9 | 0.4 |

In Fig. 1 the XRD patterns showing the phase composition of fluidized bed fly ash are presented.

It is evident from Fig. 2 that the loss on ignition for brown coal combustion is totally attributable to the presence of calcium carbonate.

The mechanisms and kinetics of hydration process in cement – fly ash systems are not clearly understood and have become a topic of active research in many parts of the world. Practical experiments provide clues to the utilization of these materials.

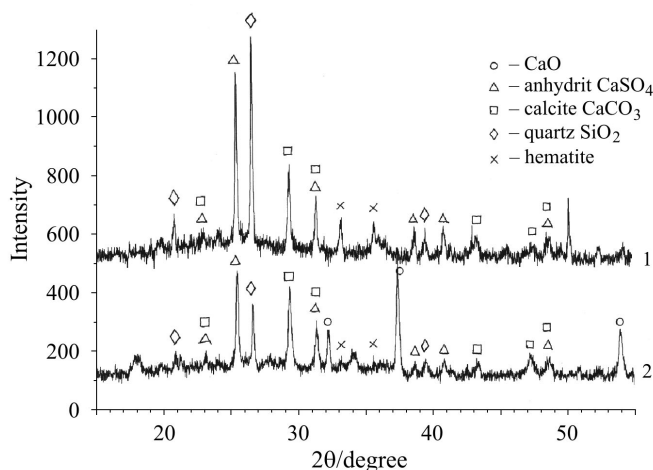


Fig. 1 XRD patterns of fluidized bed combustion fly ash. 1 – from the black coal combustion, 2 – from the brown coal combustion

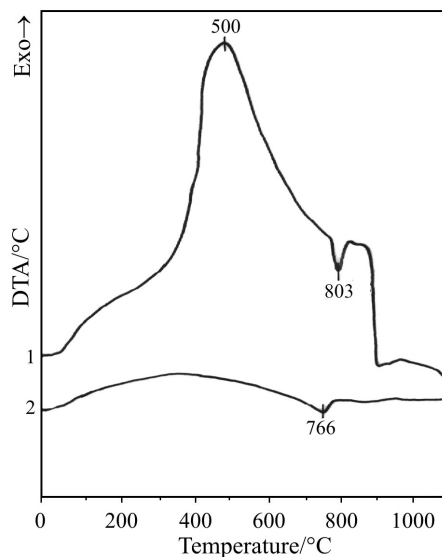


Fig. 2 DTA curves of fluidized bed combustion fly ash. 1 – from the black coal combustion, 2 – from black coal combustion

In the studies of hydration process by DTA-TG method the material from black coal combustion in fluidized bed installation was taken. The cement–fly ash mixtures with 20 and 40% fly ash (added as percent of cement mass) were produced. The hydrated cement pastes were mixed with water at water to (cement+FBC fly ash)=0.5, the hardened samples were examined after 1, 4, 8, 12, 24 h and 2, 3, 28 and 90 days. According to the data reported in [5, 6] the endothermic peak occurring on DTA curves

with maximum at 120°C is attributed to the calcium silicate hydrate (co-called C–S–H) decomposition. The shift of this peak toward the higher temperature (130–150°C) proves the formation of calcium sulpho-aluminate phase, so-called ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$). The endothermic peak at approximately 450°C is due to the decomposition of calcium hydroxide. The DTA of sample with 40% fly ash admixture after 3-day hydration shows splitting this maximum into two peaks; this indicates that within 3-day hydration in cement–fly ash paste there are two forms of calcium hydroxide. The calcium hydroxide content in cement paste is always a good estimation of the progress of pozzolanic reaction in hydrating cement–admixture systems [7]. Therefore based on DTA-TG results alone it is possible to assess the pozzolanic properties of FBC ash.

Analysis of DTA and DTG curves allows differentiation between the formation of hydration products in pastes without the FBC fly ash and with this admixture. In neat cement paste just after 1 h hydration the peaks attributed to the formation of C–S–H and ettringite are clearly visible (Fig. 3).

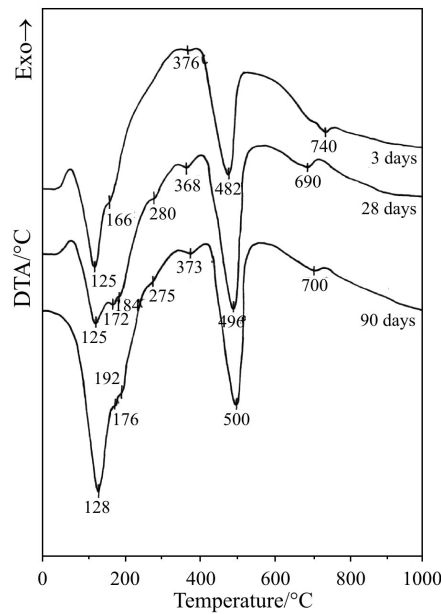


Fig. 3 DTA curves of hardened reference cement after 3-, 28- and 90-day hydration

Basic differences between the pastes without the FBC fly ash and with this admixture are clearly visible after 3, 28 and 90 days from the beginning of hydration. The first peak corresponding to overlapping decomposition of C–S–H and ettringite increases with time and shifts toward a higher temperature. In neat 3-day cement paste ettringite decomposes to the calcium monosulpho-aluminate, as is evident from the new small peak with its maximum at 166°C (Fig. 4a); in samples with 40% FBC ash this peak appears after 90 days (Fig. 4b).

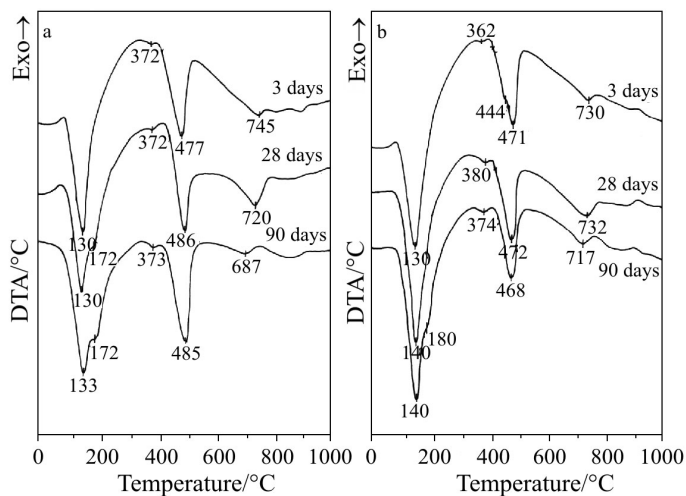


Fig. 4 DTA curves of hardened cement–fly ash material after 3-, 28- and 90-day hydration. a – paste with 20% fluidized bed fly ash, b – paste with 40% fluidized bed fly ash

XRD analysis was also carried out in addition to DTA. It is apparent that the FBC admixture modified substantially the course of hydration process, particularly in relation to the ettringite phase. In cement pastes without admixture the ettringite appeared just after 1 h from processing with water. The intensity of ettringite peak was highest after 1 and 2 days beyond which this peak reduced in intensity. After 28 days the ettringite peak disappeared with simultaneous growth of calcium monosulpho-aluminate peak.

The ettringite formation is quite different in FBC fly ash containing paste. A small ettringite peak is visible at the beginning and increases steadily with time reaching the highest intensity after 28 days.

The change of ettringite peak intensity within 90-day hydration is shown in Fig. 5, and is compatible with DTA results. The XRD data also indicate the so-called

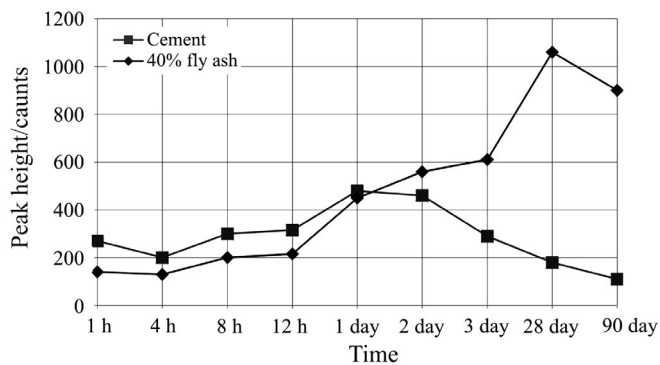


Fig. 5 Intensity of ettringite peak vs. time

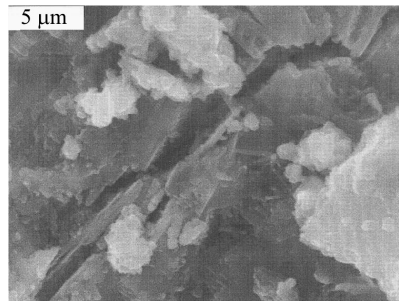


Fig. 6 Microstructure of paste with 20% FBC fly ash after 90-day hardening

delayed formation and crystallization of ettringite in the samples admixed with fluidized bed fly ash. However, a direct correlation is not possible because the peaks attributed to calcium silicate hydrate (C–S–H) and ettringite decomposition overlap and cannot be separated.

The formation of delayed ettringite may be accompanied by expansion of paste and further on the microcracks leading to the durability decrease [8]. The presence of sulphate in form of anhydrite in FBC material may provide a plausible explanation of this behaviour.

The pastes observed under SEM reveal the presence of cracks in hydrated silicate area. The ettringite phase, crystallized after hardening of the other paste components may be the source of these structural imperfections (Fig. 6).

Conclusions

This experimental study has shown:

- the DTA-TG method is an appropriate technique for the studies of fluidized bed combustion by-products and mechanism of their role in hydrating cement systems.
- the anhydrite component present in hydrating cement–fluidized bed combustion mixture can be the source of the so-called ‘delayed’ ettringite formation, reducing the durability of hardened cement–ash material.

References

- 1 T. Zaremba, A. Dutkiewicz, J. Hehlmann, W. Mokrosz and E. Kujawska, *J. Therm. Anal. Cal.*, 74 (2003) 503.
- 2 J. Zelic, D. Rušić and R. Krstulovic, *J. Therm. Anal. Cal.*, 67 (2002) 613.
- 3 J. Dweck, P. F. Ferreira da Silva, P. M. Büchler and F. K. Cartledge, *J. Therm. Anal. Cal.*, 69 (2002) 179.
- 4 P. Claster and M. Murat, *Cem. Concr. Res.*, 14 (1984).
- 5 R. Cioffi, M. Marroccoli, L. Santoro and G. L. Valenti, *J. Thermal Anal.*, 38 (1992) 761.
- 6 E. T. Stepkowska, J. L. Perez-Rodriguez, M. C. Jimenez de Haro and M. J. Sayagues, *J. Therm. Anal. Cal.*, 69 (2002) 187.
- 7 K. Rajczyk and E. Giergiczny, 8th Conference on Calorimetry and Thermal Analysis, Zakopane, Poland 2000.
- 8 W. Kurdowski, Kurdowski Symposium Science of Cement and Concrete, Cracow 2001.