1. Introduction

Fly ashes (pulverised fuel ashes – pfa) are waste materials produced as a result of coal combustion. In this process the pulverised coal is fed to the combustion chamber and burnt at high temperature. The incombustible mineral substances are then subjected to the phase and chemical transformations. Over 80 wt. % of this material is transported with the flue gas and collected in electrical or mechanical precipitators. The residue is deposited as a bottom ash in a furnace.

Fly ashes are composed mainly of glass with some amount of crystalline phases. An unburned coal residue can be also present. The type and properties of fly ash are affected by the following factors [1], [2]:

– type of coal (anthracitic, black, bituminous, subbituminous, brown),
– fineness of coal before combustion,
– type of furnace, temperature and other conditions of the process,
– method of flue gas de-dusting,
– transport and storage of fly ash.

There are many of fly ash classification systems. According to the ASTM C 618 89 [3] the high calcium class C fly ashes and low calcium class F ones can be distinguished. This classification is based on the total SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ as well as CaO content.

It is generally known that the fly ashes from the black coal combustion exhibit low CaO content while those originating from the brown coal are the high calcium materials, with CaO content attaining 40 wt. % [4].

The fly ash particles are composed of glass and crystalline phases. The glass content is usually about 80 % by mass, in some cases attains 90 %. In the high calcium fly ash it is low, about 60 % by mass. In the low calcium fly ash the following crystalline phases can be present: quartz (SiO$_2$), mullite (3Al$_2$O$_3$ · 2SiO$_2$), magnetite Fe$_3$O$_4$) and haematite (Fe$_2$O$_3$). On the surface of low calcium fly ashes, a film of metallic iron is often observed on the magnetite or haematite crystals.

In the high-calcium fly ash, apart from the phases mentioned above, the following ones can be found: calcium silicates and aluminates (2CaO · SiO$_2$, CaO · Al$_2$O$_3$, 5CaO · Al$_2$O$_3$), calcium aluminosilicates (2CaO · Al$_2$O$_3$ · SiO$_2$) and calcium sulphates (CaSO$_4$, CaSO$_4$ · 2H$_2$O), calcium ferrites (2CaO · Fe$_2$O$_3$), calcium oxide (CaO and periclase (MgO)).

The hydration of fly ash should be considered separately for the low and high-calcium materials, because of the substantial difference in chemical and mineral composition [5], [6], [7]. Reactions occurring between cement and fly ashes in an early stage of hydration influence the rheological properties of cement pastes. The hydration of cement with fly ashes is a complex process because of the mutual interactions between the hydrating cement and fly ash components. Introduction to cement higher amounts of the fly ashes (also high-calcium fly ashes) require investigation of their impacts on the rheological properties of cement pastes dependent on their type and type of cement [8], [9], [10].

Stefania Grzeszczyk – Grzegorz Lipowski *

* Prof. Stefania Grzeszczyk, Dr. Ing. Grzegorz Lipowski
Department of Building Materials Engineering, Faculty of Civil Engineering, Technical University of Opole, ul. Katowicka 48, 45-061 Opole, Poland, Tel. ++48-77-4536645, E-mail stf@po.opole.pl
2. Experimental

2.1. Materials

The portland cements with differed content of C₃A (7.6 and 3.8 % wt.) and similar Blain’s specific surface — 340 m²/kg were used. The high-calcium fly ashes from the brown coal combustion and low-calcium fly ashes also with similar Blain’s specific surface — 320 m²/kg were taken. The chemical composition of the cements and fly ashes used in experiments is given in Table 1 phase composition of cement is presented in Table 2.

Chemical composition of cements and fly ashes.

| Component composition | Cement I | Cement II | Fly ash I | Fly ash II |
|-----------------------|----------|-----------|-----------|------------|
| Loss on ignition      | 0.8      | 0.6       | 1.0       | 1.9        |
| SiO₂                  | 22.7     | 20.1      | 50.4      | 30.0       |
| Fe₂O₃                 | 3.0      | 5.0       | 8.6       | 6.0        |
| Al₂O₃                 | 4.6      | 2.8       | 26.8      | 18.0       |
| CaO                   | 66.5     | 69.2      | 4.3       | 30.1       |
| MgO                   | 1.4      | 1.0       | 2.6       | 2.1        |
| SO₃                   | 0.6      | 0.5       | 1.2       | 10.8       |
| Na₂O                  | 0.2      | 0.1       | 1.6       | 0.2        |
| K₂O                   | 0.7      | 0.2       | 1.4       | 0.2        |
| CaO free              | 0.8      | 0.5       | 0.2       | 3.0        |

Mineralogical composition of cements. Table 2

| Phase composition | Cement I | Cement II |
|-------------------|----------|-----------|
| Content in % wt.  | 64.7     | 73.2      |
| C₃S               | 17.0     | 12.0      |
| C₃A               | 7.6      | 3.8       |
| C₄AF              | 7.8      | 11.0      |

The phase composition of fly ashes was characterized by XRD. The following crystalline phases have been detected: quartz, mullite in fly ash I and in fly ash II together also free CaO, anhydrite, calcium sulphate dihydrate - gypsum, hematite and gehlenite in fly ash II.

The cement-fly ash mixtures used in the rheological investigations were prepared and homogenised in a laboratory mill. The fly ash content in cement was 20%, 40%, 60% and 80% wt.

2.2. Rheological measurements

The rheological measurements were carried out using the rotative viscosimeter type Rheotest RV - 2.1, with the modified surfaces of both cylinders. The rheological properties of pastes with fly ashes were determined from the flow curves, at growing and reduced rates of shearing in the range from 0 to 146 s⁻¹. The yield value and plastic viscosity were determined from the descending part of the flow curve, according to the Bingham's model.

3. Results and discussion

Figures 1 and 2 show examples of the obtained flow curves for cement-fly ash pastes with low content of C₃A in cement. Table 3 presents calculated yield values τ₀ and plastic viscosities ηₚ, cement-fly ash pastes.

Fig. 1. Flow curves of cement pastes with cement (C II) containing 3.8 % wt. C₃A and addition of low-calcium fly ashes (FA I).

The results obtained shown that the addition of low-calcium fly ashes (FA I) to high content C₃A cement (C I), demonstrated by big yield values and plastic viscosity, resulted in significant
improvement of rheological properties of cement pastes. A decrease of yield values and plastic viscosities with increasing fly ash content in cement is illustrated in Tab 3. The biggest improvement occurred (two times slope in plastic viscosity and yield value) with addition of 20% of fly ashes in cement. A further growth of percentage of fly ashes in cement doesn’t result in fluidity of cement pastes.

The addition of low-calcium fly ashes (FA I) in the mixtures with low amount of C₃A phase (C II), good fluidized by calcium sulphur, results in insignificant changes of rheological properties Fig 1. Cement II paste with low amount C₃A phase (3.8% wt.) is better fluidized than cement I pastes (C I) 7.6% wt. of C₃A. The yield value of pure cement paste with cement (C II) is a few times lower compared to the pure cement paste with cement (C I), this is also observed for plastic viscosity.

In case of high-calcium fly ashes from lignite coal combustion its unfavourable influence on rheological properties is significantly lower for cement (C II) with lower content of C₃A phase (Fig. 2). It was stated that rheological measurement is impossible to carry out when the addition of fly ashes exceeds 40% wt. in cement (C II), but for cement (C I) measurements were possible with 60% wt. fly ashes content in cement.

4. Conclusions

- Generally, content of low-calcium fly ash in cement-fly ash mixture results in an increase of the cement paste fluidity, on the contrary to the high-calcium ash when the addition results in decrease of the fluidity for both type of cement.
- An increase fluidity cement paste effect developed by the addition of low-calcium fly ash depends on C₃A phase content in cement. In case of cement paste with low C₃A amount good fluidized by calcium sulphur, influence of fly ashes on rheological properties is insignificant. A considerable increase of fluidity is observed in cement pastes reaches in C₃A which are characterized in low fluidity comparing to cement pastes poor in C₃A.
- Unfavourable impact of high-calcium fly ash in cement pastes on rheological properties of cement pastes occurs in a lower degree for cement pastes with low content of C₃A.

References

[1] ALONSO, J. L., WESCHE, K.: Characterization of Fly Ash, in Fly Ash in Concrete, Ed.: K. Wesche, E & FN SPON, London, 1991, pp. 3-23.
[2] BASTIAN, S.: Construction Concretes with Addition of Fly Ashes, (in Polish). Arkady, Warsaw, 1980.
[3] AIMIN, X., SARKAR, S. L.: Hydration and Properties of Fly Ash Concrete, in Mineral Admixtures in Cement and Concrete, Ed.: Ghosh S. N., ABI Books Pvt. Ltd., New Delhi, 1995, pp. 175-225.
[4] JOSHI, R. C., LOHTIA, R. P.: Types and Properties of Fly Ash, in: Mineral Admixtures in Cement and Concrete, Ed.: S. N. Ghosh, ABI Books Pvt. Ltd., New Delhi, 1995, pp. 119–157.

[5] UCHIKAWA, H., UCHIDA, S., OGAWA K.: Influence of Fly Ash Characteristics on the Rheological Properties of Fresh Fly Ash Cement Paste. Proceedings Annual Meeting of Material Research Society, M4.4, Boston 1982, Concrete Rheology, pp. 203-214.

[6] KURDOWSKI, W.: Chemistry of Cement, (in polish). PWN, Warsow, 1991.

[7] UCHIKAWA, H.: Effect of blending component on hydration and structure formation. Journal of Research of the Onoda Cement Company, 1986, vol. XXXVIII, no. 115, pp. 77.

[8] GRZESZCZYK, S., LIPOWSKI, G.: Rheological Properties of Cement Pastes Containing Fly Ash. International Conference on Engineering Rheology ICER '99, Zielona Góra 1999. Applied Mechanics and Engineering, vol. 4., pp. 215-220.

[9] GRZESZCZYK, S., LIPOWSKI, G.: Effects of Low-Calcium Fly Ash on The Rheology of Fresh Cement Pastes. Applied Mechanics and Engineering, vol. 3, no. 4, 1998, pp. 589-600.

[10] GRZESZCZYK, S.: Rheology of cement pastes. Monograph no. 47, KILiW Polish Science Academy, Warsaw, 1999.