



# Effect of size fraction and glass structure of siliceous fly ashes on fly ash cement hydration



E. Tkaczewska\*

Department of Building Materials Technology, Faculty of Materials Science & Ceramics, AGH University of Science and Technology, Mickiewicz Ave. 30, 30-059, Krakow, Poland

## ARTICLE INFO

### Article history:

Received 3 October 2012

Accepted 28 March 2013

Available online 23 April 2013

### Keywords:

Cement hydration

Class F fly ashes

Size fraction

Glass structure

## ABSTRACT

Paper presents effect of size fraction and glass structure of fly ashes on cement hydration. Fly ashes below 16  $\mu\text{m}$  and 16–32  $\mu\text{m}$ , both from the 1st and 3rd section of electro-filter, were applied. Hydration heat, content of  $\text{Ca}(\text{OH})_2$  and unreacted  $\text{C}_3\text{S}$  were studied and compressive strength and microstructure were analysed. Results show that finer ashes have higher depolymerization degree of  $\text{SiO}_4$  units in glass what increases pozzolanic reactivity. Incorporation of fly ashes below 16  $\mu\text{m}$  from the 3rd section gives cement class 52.5 N. At 180 day,  $\text{Ca}(\text{OH})_2$  content decreases by 67% and  $\text{C}_3\text{S}$  hydration degree increases by 50% relative to control sample.

© 2013 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

## 1. Introduction

The siliceous fly ash (Class F according to ASTM C618-12) is one of the residues generated in bituminous coal combustion process, that are collected from the electro-filter. It has been used as component of blended Portland cement or as a mineral additive in concrete. The wide use of the siliceous fly ashes in the production of cement and concrete determines their pozzolanic activity, defined as the ability to react with calcium hydroxide, a by-product of the Portland cement hydration process, to form additional calcium silicate hydrate (the so-called C–S–H) and other cementitious compounds, that is, calcium aluminate hydrates ( $\text{C}_4\text{AH}_{13}$  and  $\text{C}_2\text{AH}_8$ ) and calcium aluminosilicate hydrates ( $\text{C}_2\text{ASH}_8$  and  $\text{C}_3\text{AS}_3\text{--C}_3\text{AH}$ ) [1]. As we know, the glassy phase is the reactive phase in the fly ashes and that their pozzolanic properties depends on the content of the active chemical component, that is, vitreous silica ( $\text{SiO}_2$ ) and vitreous alumina ( $\text{Al}_2\text{O}_3$ ). The content of glassy phase in siliceous fly ashes varies in the range 30–80 wt% and in some cases can even achieve even 90 wt% [1]. The pozzolanic reaction of the fly ashes starts with dissolution of vitreous coating on the surface of the fly ash grains and ions pass into solution, initially of Na and K, and than Al and Si. In liquid phases silica and alumina ions react with calcium ions to form hydrates both on the surface of the fly ash particles and in the pore solution.

Scientific literature clearly shows that rate of the pozzolanic reaction in cement matrix is attributed to many factors such as particle size distribution, specific surface area, chemical and mineral composition of the fly ashes [1–7], which should be taken into account for predicting the contribution of fly ashes in the final performance of pozzolanic cementitious systems. The results presented in works [8] show that the fineness of fly ashes is more important factor and give much effect on the pozzolanic properties of them. The finer fly ashes reveal greater amount of glass than their coarse fly ashes, what resulting from higher amount of grain with diameter below 45  $\mu\text{m}$ , especially below 10  $\mu\text{m}$  [1]. This very fine fly ashes, selected from the 1st section of electro-filter in electrostatic precipitator system, are rich in active chemical component, especially the great increase is observed for active  $\text{Al}_2\text{O}_3$  [5]. According to Tkaczewska [2], the summarized amount of active chemical components in fly ash fraction 0–16  $\mu\text{m}$  selected from the different section of electro-filter is higher than that in traditional siliceous fly ashes and the difference could be as much as 1.5 times. Of course, this is due to greater fineness fly ash fraction 0–16  $\mu\text{m}$ , but also can be resulted from different chemical composition and structure of the glassy phase. The glass former oxides in siliceous fly ash, independent on their fineness, are  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . The glass network is mostly composed of  $\text{SiO}_4$  tetrahedra each linked with bridging oxygens Si–O–Si. The aluminum ion also occupies middle of some of the tetrahedra. The negative charge created by the substitution of  $\text{AlO}_4$  tetrahedron for  $\text{SiO}_4$  tetrahedra is balanced by exchangeable cations, for example alkali metal ions ( $\text{Na}^+$  and  $\text{K}^+$ ). The consequence of that is increase in the depolymerization of Si–O–Si network [9]. The

\* Corresponding author. Tel.: +48 12 6172482; fax: +48 12 6172452.

E-mail address: [tkaczews@agh.edu.pl](mailto:tkaczews@agh.edu.pl)

works [2,10,11] show that the same fly ash fraction, but selected from the 3rd last section of electro-filter, reveals higher depolymerization degree of glassy network as a result of higher content of Na and K ions in it.

Due to the amphoteric properties, aluminium ions in the glass are network formers (coordination 4) and also modifiers (coordination 6). According to Bumrongjaroen et al. [12] the function of the aluminum ions in glass depends on the aluminum saturation index (parameter ASI), defined as the charge ratio  $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O} + 2\text{CaO})$ . In glass with ASI value less than 1, the aluminum ion is only network former ( $\text{AlO}_4$ ). However the amount of tetrahedral aluminum ions in fly ash glass is limited by content of Na and K ions [13,14]. In glass with ASI value greater than 1, the aluminum ion is network former and network modifier ( $\text{AlO}_6$ ) [7]. The increase in content of the active  $\text{Al}_2\text{O}_3$  in fine grains of fly ashes is directly connected with greater amount of  $\text{AlO}_4$  units in their glass structure, which in turn results in greater amount of alkali metal ions [11]. If the fly ashes have greater increase in content of aluminum oxide in relative to content of sodium and potassium oxides, it can be concluded that the residual Al ions can act in the form of  $\text{AlO}_6$  octahedra. The results presented in [15] indicate that pozzolanic activity of the siliceous fly ashes increases with content of  $\text{AlO}_6$  units in glass structure (Al ions in coordination 6 easily go into solution than Al ions in coordination 4).

The rate of the pozzolanic reaction of the fly ashes is also determined by other factors. According to Ref. [16] dissolution rate of the fly ash glass increases with pH above 9 in liquid phase in cement paste. The increases in alkalinity of the solution are connected with passing  $\text{Na}^+$  and  $\text{K}^+$  ions from the fly ash and cement [17]. The significant influence has also temperature (influence on hydroxide ions concentration in the pore solution) and water/cementitious material ratio (influence on alkalinity of the pore solution) [18].

As we know, the siliceous fly ashes are inert addition not showing hydraulic properties as cementitious materials. The introduction of fly ashes reduces the content of the Portland cement in the mixture and consequently reduces the amount of alite ( $\text{C}_3\text{S}$ ) in the mixture (dilution effect). The fly ash-Portland cement mixture has lower hydraulic activity in comparison to that of Portland cement, that is, reveals lower intensity of hydration process and differ properties. The lower rate of heat evolution of hydrating fly ash-Portland cement mixture is confirmed by longer induction period and lower intensity of the main peak on the microcalorimetric curve [2,3,18–22]. The fly ashes also delay initial and final setting times of the cement pastes and decreases early strength of the cement mortars, mainly due to dilution effect as well as slow rate of the pozzolanic reaction at initial stage, to about 28 days. With time of hydration, after about several weeks of hydration, the progress of pozzolanic reaction is significant, what improves properties of fly ash cement, especially its compressive strength, which is comparable to or even higher than that of Portland cement. The process of hydration product formation and development of hardened matrix in cementitious system with fly ashes is generally slower than in reference paste, but microstructure thus obtained shows better compactness due to the presence of higher content of C–S–H, both from the hydration of Portland cement and from pozzolanic reaction, with low content of  $\text{Ca}(\text{OH})_2$ ,

which partially is fixed by fly ashes in pozzolanic reaction. The greater reduction in calcium hydroxide content, the greater increase in  $\text{C}_3\text{S}$  hydration degree. The content of  $\text{Ca}(\text{OH})_2$  is reduced, although the hydration process of fly ash-Portland cement mixture is still continued [23].

The aim of this study is investigation the relationship between structure of the glassy phase in siliceous fly ashes and pozzolanic activity of these materials. Because of the pozzolanic properties of the fly ashes are associated with the presence of the glassy phase in them, which content is greater for fine grinding fly ashes, the research will be carried out for the fly ash samples of the varying fineness. In order to verify the existence of the relationship glass structure–fly ash activity, the research will be also conducted for the same fly ash fraction selected from the initial ash samples.

## 2. Materials and testing procedures

### 2.1. Characterization of raw materials

The siliceous fly ashes came from 1st and 3rd section of electro-filter. Two fractions of fly ashes were studied: fraction A (particles below  $16\ \mu\text{m}$ ) and fraction B ( $16\text{--}32\ \mu\text{m}$ ). The ashes from 1st section were designed F1A and F1B, the ashes from 3rd F3A and F3B. The properties of ashes are shown in Table 1.

The fly ashes show changeable amount of alkalis with comparable amount of remaining main components. For the F1A and F3A the difference in alkalis content is 30%, for the F1B and F3B – 41%. The increase of Blaine surface of ashes from 3rd section, especially for F3A is connected with the greatest content of particles below  $10\ \mu\text{m}$ . The X-ray analysis confirms presence of two crystalline phases in ashes: quartz  $\beta$  and mullite (Fig. 1). The F3A gives the lowest diffraction peak of quartz ( $26.6^\circ 2\theta$ ) which suggests its very low content (Fig. 2a). The highest increase of broad diffraction effect in the range  $18\text{--}28^\circ 2\theta$  confirms the highest glass content in FA3 (Fig. 2b).

In the spectra IR of fly ashes (Fig. 3) the main band, linked with asymmetrical stretching vibrations of bridging bond of Si–O–Si, is located at lower waves number than in siliceous glass. It confirms the further polymerization of  $[\text{SiO}_4]^{4-}$  and the presence of bonds Si–O–Al in glass. The doublet of bands in the range  $780\text{--}800\ \text{cm}^{-1}$ , caused by symmetrical stretching vibrations of bond Si–O–Si, indicates the presence of quartz  $\beta$  in the ashes. The maximum located at  $730\ \text{cm}^{-1}$  is linked with bond Si–O–Al. The band at  $555\ \text{cm}^{-1}$  indicates existing rings of silica–aluminum tetrahedral in the glass, at  $465\ \text{cm}^{-1}$  – bending vibrations of bridge Si–O–Si.

In the  $^{27}\text{Al}$  MAS-NMR spectra of fly ashes (Fig. 4) the band at 60 ppm is linked with the presence of tetrahedra  $[\text{AlO}_4]^{5-}$  in glass. The F3A gives the highest intensity of this band, resulting from high content of  $[\text{AlO}_4]^{5-}$  replacing  $[\text{SiO}_4]^{4-}$  in glass. The F3A glass network reveals the highest depolymerization degree of anions  $[\text{SiO}_4]^{4-}$ . In the  $^{29}\text{Si}$  MAS-NMR spectra of ashes (Fig. 5) band in the region  $-108$  to  $-103$  ppm indicates presence of the elements of three-dimensional network of glass ( $Q^4$  structure) and bridging tetrahedra in the silicate ribbon ( $Q^3$  structure). For F3A this band is shifted to higher value of ppm as a result of ribbon network formation, with small content of remaining

**Table 1**  
Chemical analysis of fly ashes (wt%).

Sample	LO1	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	CaO	MgO	$\text{Na}_2\text{O} + \text{K}_2\text{O}$	$\text{SO}_3$	Blaine surface, $\text{m}_2/\text{kg}$
F1A	0.9	51.6	29.0	6.7	4.2	2.1	4.7	0.8	570
F1B	0.4	53.8	28.3	6.5	4.5	2.5	3.3	0.7	270
F3A	1.6	48.8	29.8	7.1	3.7	1.8	6.0	1.2	750
F3B	1.0	51.2	29.3	6.8	3.9	2.1	4.7	1.0	360

Download English Version:

<https://daneshyari.com/en/article/227860>

Download Persian Version:

<https://daneshyari.com/article/227860>

[Daneshyari.com](https://daneshyari.com)