Cementitious and pozzolanic behaviour of fly ash

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Abstract. Pozzolanic behaviour of fly ash was studied in mortars and pastes from lime-fly ash mixtures. Compressive strength increase of the mortar specimens that were cured in humid environment was a direct manifestation of a pozzolanic reaction of the fly ash with lime. Mineral composition of the reaction products was studied by X-ray diffraction analysis. Morphology of the samples was observed using SEM equipped with EDS detector. Analysis of a paste with the lime to fly ash ratio of 1:1 revealed that virtually all Ca(OH)$_2$ in the paste was consumed within 5 years. The crystalline products of the pozzolanic reaction included calcium hemicarboaluminate hydrate and monocarboaluminate hydrate and some ettringite.

1. Introduction
Siliceous fly ashes from high temperature coal combustion in power plant are materials that usually possess a satisfactory pozzolanic properties. Particles of the fly ashes with spherical shape are formed by the rapid cooling of molten ash particles and have an amorphous, glassy character. The proportion of the glass phase in the ash is usually 60-85%. Siliceous fly ashes contains high content of silica and alumina and also a smaller content of other compounds, e.g. Fe$_2$O$_3$. They can be used as inorganic reactive additions to concrete, as a component in some cements, in production or autoclaved aerated concrete, etc. When used, they must meet the required criteria. Their pozzolanic ability to react with calcium hydroxide in the presence of water at ambient temperature can be used also in lime-fly ash mixtures. The rate of the pozzolan reaction of ash with lime at normal temperatures is relatively slow. The reason is the relatively large size of the fly ash particles as well as their relatively small and "smooth" surface and hard and glassy nature. Contribution of fly ash to the strength in lime-ash or cement-ash materials develops only slowly. A limiting factor is moisture content in materials because reduction of the moisture content lowers the rate of the puzzolan reaction. After the moisture content drops below a certain threshold value, the fly ash in the mixture acts just as an inert filler. In the course of reaction between calcium hydroxide and fly ash different compounds can form, depending on the composition of ash and lime. The reaction product mainly include a nearly amorphous C-S-H or C-S-(A)-H phase [1]. Crystalline phases usually include mainly the Afm phases or some ettringite if sulphate anions are available in the system [1-3].

Metakaolin is much more reactive than the fly ash. Its main reaction products in the presence of small amounts of CaCO$_3$ in lime is C-S-H phase, calcium hemicarboaluminate hydrate 3CaO·Al$_2$O$_3$·0.5CaCO$_3$·0.5Ca(OH)$_2$·11.5H$_2$O, monocarboaluminate 3CaO·Al$_2$O$_3$·CaCO$_3$·11.5H$_2$O and also strätlingite 2CaO·Al$_2$O$_3$·2SiO$_2$·8H$_2$O that forms in the case when Ca(OH)$_2$ is consumed [1-7].

Our research was focused on the study of strength development and mineral composition changes in lime-fly ash mortars and pastes that were cured in moist conditions at relative humidity RH 100% in closed containers. These conditions enabled to monitor the development of strength in the samples as the result of the pozzolanic reaction.
2. Experimental

2.1. Materials

a) Natural standard silica sand with continuous grading according CEN EN 196-1.
b) Hydrated calcium lime powder designated CL90-S according to CEN EN 459-1 was produced by Calmit s.r.o. from the plants: (1) Tisovec, Slovakia and (2) Žírany, Slovakia.
c) Fly ash from high-temperature coal burning power plant Nováky (size fraction 0-0.25 mm). SEM images of particles in fly ash are given in figure 1 (a, b). Its composition is given in table 1.
d) Metakaolin produced by Keramost a.s. Czech Republic, designed as KM 60.
e) Plasticizing admixture (PA): A polycarboxylate based superplastificator was used. It was dosed in mass percentage of a lime-fly ash binder.
f) Tap water.

Table 1. Chemical composition of used materials: lime (L), Fly ash (FA) and metakaolin (MK).

| Material | Chemical composition in wt. % |
|----------|-------------------------------|
|          | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | TiO₂ | MnO  | K₂O  | Na₂O | P₂O₅ | SO₃ | LOI* |
| Lime (1) | 2.00 | 0.82  | 0.32  | 70.4 | 1.63 | -    | n    | 0.31 | 0.03 | n    | 0.17 | 24.20 |
| Lime (2) | 0.35 | 0.13  | 0.08  | 73.3 | 0.60 | -    | n    | 0.16 | < 0.2 | < 0.01 | 0.55 | 24.60 |
| Fly ash  | 53.50 | 17.8  | 11.7  | 8.0  | 2.13 | 0.56 | 0.20 | 1.60 | 0.90 | 0.40 | 0.98 | 1.98    |
| MK       | 52.61 | 40.5  | 1.2   | 0.1  | 0.34 | 0.52 | n    | 1.54 | < 0.2 | 0.10  | 0.02 | 2.78    |

* LOI – Loss of ignition

Figure 1 (a, b). SEM of particles in fly ash: (a) - the typical spherical shape of the fly-ash particles; (b) diatomite – typical silicate shells of algae (Diatomaceae) from the coal.

2.2. Manufacture of test samples

Two types of samples were prepared:
a) Lime-fly ash pastes were prepared by mixing lime (1), fly ash and water. The ratio of lime and ash was 1: 1. Thin plates of about 15 mm thick were prepared from the paste that were stored in a closed plastic container in a humid environment at RH about 100%. Fragments of the sample were used for X-ray diffraction analysis and electron microscopy scanning (SEM).
b) Lime-fly ash mortars, lime-fly ash-metakaolin mortar and lime-fly ash paste were mixed in a laboratory mixer. The composition of the mixes is given in table 2. Cylindrical test specimens of diameter and length of 30 mm were prepared in cylindrical forms from the prepared mixes. Their consistency was measured by flow table test. A carboxylate based plasticizing admixture (PA) was
used to prepare the MFA-2P-700 mortar. The produced mortar extremely fluid during the consistency test. All the samples were demoulded after 4 days and subsequently stored in a humid environment with RH 95-100%. The samples were used for compressive strength testing. Small fragments were used for electron microscopy.

Table 2. Composition of a paste (P) and mortars (M) and their consistency determined by a flow table. Under the term binder we mean the common content of lime (L), fly ash (FA) and metakaolin (MK).

| Sample    | L (g) | FA (g) | MK (g) | Binder (g) | Sand (g) | Water (ml) | W/B (-) | PA (%) | Flow (mm) |
|-----------|-------|--------|--------|------------|----------|------------|---------|-------|-----------|
| MFA-1-700 | 350   | 350    | -      | 700        | 1350     | 400        | 0.57    | -     | 147       |
| MFA-2P-700| 350   | 350    | -      | 700        | 1350     | 340        | 0.49    | 2     | >180      |
| MFA-50-350| 175   | 175    | -      | 350        | 1350     | 260        | 0.74    | -     | 148       |
| P-FA-3    | 300   | 300    | -      | 600        | -        | 320        | 0.53    | -     | -         |
| M-MK-FA-50| 175   | 125    | 50     | 350        | 1350     | 290        | 0.83    | -     | 160       |
| M-MK-FA-30| 245   | 75     | 30     | 350        | 1350     | 290        | 0.83    | -     | 148       |

2.3. Methods
Compressive strength of mortar and paste specimens was determined by using universal testing machine. Moist pastes were tested. Mineralogical composition of the pulverized lime-fly-ash pastes was determined by X-ray diffraction analysis on a Bruker D2 PHASER powder diffractometer using CuKα radiation (λ = 1.5418 Å) at step 0.02 2-theta and time per step 0.5 sec. Scanning electron microscope (SEM) Vega 3, Tescan was used for observation of samples. Acceleration voltage used was 30 kV. The SEM was equipped with EDS detector by Oxford Instruments.

2.4. Results
2.4.1 Results of X-ray diffraction analysis (XRD) of the lime-fly-ash paste. The results X-ray diffraction analysis (XRD) are shown in figure 2 and figure 3 shows changes in the mineralogical composition of the lime-ash paste that occurred during its deposition at RV 100% over time. Samples were analysed in the wet state. The reason was the high sensitivity of calcium alumina hydrates to water loss during drying at elevated temperatures shown in figure 3. For example, the calcium hemicarboaluminate hydrate 3CaO·Al₂O₃·0.5CaCO₃·0.5Ca(OH)₂·11.5H₂O (He) loses part of its crystal water already at drying at 40 °C. Due to these changes the intensity of its dominant basal line with d₆₆ 8.2 Å decreases (figure 3). At drying temperature above 100 °C total disappearance of the peak was observed, but also disappearance of the dominant line of ettringite at about 9° 2 theta was observed.

XRD diffraction patterns in figure 2 revealed a decrease in portlandite content with time. The rate of reaction was relatively slow and the portlandite lines were observed even after 200 days of the paste curing. Later the lines of portlandite were only hardly observable and after 2000 days they were not present. The major crystalline products of the pozzolan reaction were calcium hemi-carboaluminate hydrate (Hc) and monocarboaluminate hydrate 3CaO·Al₂O₃·CaCO₃·11H₂O. These phases formed early as the result reaction of alumina with lime in the presence of carbonate ions (CaCO₃ in lime). The presence of carbonate ions eliminates the formation of Ca₂Al₃O₇. Over time, the intensity of the He lines decreased due to the conversion of hemi-carboaluminate to monocarboaluminate in the presence of CaCO₃. The results correspond to finding of [1-3]. The presence of amorphous C-S-H phases is virtually undetectable by diffraction analysis. (Their rise was mainly due to the increase in the strength of wet slurries and mortars).

Small amount of ettringite was also identified in the pastes throughout all curing period. Ettringite was probably formed as a result of the reaction of Al₂O₃ from the fly ash with a small amount of
sulphate ions present in the mixture and calcium hydroxide. Ettringite presence in the paste was most probably stabilized by the presence of carbonate anions in the system. Presence of carbonate ions supports preferential formation of Hc and Mc phases instead of monosulphate and "stabilization" of ettringite, because the monocarboaluminate is a more stable phase than the monosulfate. However, a certain amount of hexagonal AFm phases containing some SO$_4^{2-}$ ions cannot be excluded [1].

The presence of amorphous C-S-H phases was not identified by XRD analysis as these phase is virtually undetectable by diffraction analysis. However, its formation by the pozzolanic reaction probably mostly contributed to the compressive strength increase of lime-fly-ash mixtures.

Figure 2. Changes in mineralogical composition of the lime-fly ash paste cured at RH 100% over time. Symbols used: (P) portlandite, (E) ettringite, (Hc) hemicarboaluminate, (Mc) monocarboaluminate and (C) calcite, (Q) quartz.

Figure 3. Effect of drying of the lime-fly ash paste cured 29 days on the basal XRD lines of aluminate phases.

2.4.2 Compressive strength results. The compressive strength of the lime-ash mortars slowly but gradually increased during the whole testing period (figure 4). The highest values of compressive strengths were achieved by MFA-2P-700 mortars with the lowest water/binder ratio (table 2) where plasticizing admixture was used. Compressive strength of this mortar stored in water for about 700 days was even slightly higher.

Compressive strength of mortars with lower binder content was lower. The lowest values of compressive strength were obtained in mortars where some part of the fly ash was replaced by metakaolin. These mixtures contained an increased content of Al$_2$O$_3$ at the expense of SiO$_2$ and therefore less C-S-H phase is formed. This might suggest that the crystalline AFm phases contribute less to the compressive strength development than does the C-S-H phase. However, the lower strength development at later ages in the mixtures could also be affected by a partial loss of moisture content.
All the results underline the bonding potential of the fly ash. This potential is only exploited when there is a sufficient amount of water available for the pozzolanic reaction. Decrease in the compressive strength of lime-fly ash paste at later times in figure 4 also can be explained as the result of partial drying of the samples during its storage.

![Compressive strength development of specimens cured in humid environment.](image)

**Figure 4.** Compressive strength development of specimens cured in humid environment.

2.4.3 *Scanning electron microscopy of samples.* Appearance of the microstructure by SEM of FAM-2P-700 mortar and the X-ray microanalysis (EDS) of large hexagonal crystals that is visible in a cavity is shown in figure 5. The analysis of the hexagonal phase (spectrum 8) revealed that it probably corresponds an AFm phase containing sulphate ions, possibly monosulfate, or its solid solution with carbonate AFm.

![SEM image of lime-ash mortar FAM-2P-700 after 2 years of storage in water (left) with EDS spectra of the elemental analysis in selected points (right).](image)

**Figure 5.** SEM image of lime-ash mortar FAM-2P-700 after 2 years of storage in water (left) with EDS spectra of the elemental analysis in selected points (right).

Figures 6 (a, b) show spherical fly ash particles in mortars that are covered with reaction products and a surrounding distinct edge zone. figure 6 (c) shows hexagonal AFm phases in a lime-fly ash mortar and figures (d-f) show products of pozzolanic reaction in vicinity of fly ash particles in mortars.
3. Conclusion
High-temperature siliceous fly ash has a great pozzolanic bonding potential. The increase in compressive strength of lime-fly ash composites in a humid environment enabled to estimate the contribution of the puzzolanic reaction to the compressive strength of the composites. At a 1:1 ratio of lime-fly ash practically all calcium hydroxide reacted to produce the puzzolanic reaction products. The most important strength giving product of the pozzolanic reaction was C-S-H. The crystalline products were carboaluminate phases of AFm type. At higher content of sulphate ions in lime or fly ash some ettringite also formed. Its stability was likely to increase in the presence of CaCO₃ in lime.

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