# Mechanochemical Activation of Coal Fly Ash for Production of High Strength Cement Conglomerates

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## Abstract

In this work the experimental results of the investigation carried out on the use of micronized fly ash as pozzolanic material for production of cement mortars are presented. The milling of fly ash was carried out in planetary ball mill; the size distribution of micronized material was similar to silica fume, normally used to produce high strength conglomerates due to its very high specific surface. Micronized material was also beneficiated reducing the unburned fraction by means of triboelectrostatic separation. The mechanical strength tests of mortars were performed through the substitution of cement or sand (between 10 and 25 % in mass) with Micronized Fly Ash (MFA), Beneficiated Micronized Fly Ash (BMFA) and Silica Fume (SF), respectively. The water/cement ratio (w/c) was regulated to obtain equal workability of the mixtures (from 0.35 to 0.4). The best value of compression strength at 28 days (more than 100 MPa) is obtained with BMFA (in substitution of sand): this value is 34 and 10 % higher than reference mortar with Ordinary Portland Cement (OPC) and mortar with SF, respectively. On the basis of these results a chemico-physico-mechanical improvement of the fly ash was achieved making reutilisation of this by-product in high strength cement conglomerates feasible.

**Keywords:** coal fly ash, cement conglomerates, mechanochemical activation, LOI reduction

## INTRODUCTION

Cement concrete is the most widely used construction material in the world. Silica fume, also known as microsilica, is a by-product of the reduction of high purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys. Silica fume consists of very fine vitreous particles with a surface area ranging from 13 000 to 30 000 $m^2/kg$ when measured by nitrogen absorption techniques, with particles approximately 100 times smaller than the average cement particle. Because of its extreme fineness and high silica content, silica fume is a highly effective pozzolanic material [1]. For this reason, although it was a waste of industrial materials, it became the most valuable by-product among the pozzolanic materials.

Fly ash (FA) is a waste material produced from combustion of coal in thermal power plants; it is mainly composed of vitrified (amorphous) alumina silicate melt in addition to a small amount of crystalline minerals. Most FA hydrates slowly and may contain high unburned carbon content.

Appa Rao [2] pointed out that mortars develop the highest compressive strength at a curing age of 28 days with silica fume content in the range 20–25 %; moreover his study showed that both initial and final setting times decrease with silica fume content increase.

A recent study [3] established that mortars with fine fly ash require less water than coarse fly ash mortars.

Another research [4] confirmed that cement substitution by fly ash increases compressive strength; moreover it showed that the compressive strength is affected by the mean particle diameter of fly ash, in fact the strength decreases as the particle size increases, especially at the age of 28, 56 and 120 days.

A later study [5] confirmed that the highest compressive strength of fly ash substituted mortars primarily depends on the fineness of fly ash incorporation. However, this study pointed out that increasing the fineness may result in higher mixing water demand due to the increase in surface area of fly ash particles.

In the present, research as-received fly ash was micronized in a planetary ball mill until the size distribution of micronized material was similar to silica fume; micronized FA was also beneficiated reducing the unburned fraction by means of triboelectrostatic separation. The purpose of the present research is to investigate how reutilisation of Micronized Fly Ash (MFA), Beneficiated Micronized Fly Ash (BMFA) and Silica Fume (SF) in mortar affects the properties of fresh and hardened mixes. Tests were carried out to indicate which of the industrial by-products was potentially suitable cement replacement. Mechanical strength tests of mortars with cement or sand substitution by the SF, MFA or BMFA (between 10 and 25 % in mass) were carried out to point out the mix design with higher compressive strength. Moreover, initial and final setting time, water demand and compressive strength development at different curing ages (2, 7 and 28 days) were evaluated as performance factors of the blended cements.

## MATERIALS AND METHODS

### *Materials*

Table 1 shows the chemical composition of the materials used in this study. After mechanochemical activation a variation in coal FA chemical composition was not observed, as it results in a structural change (crystalline to amorphous transition). As can be seen, the beneficiation of MFA decreased the LOI from 7 to 4 %.

### *Mechanochemical grinding of FA*

The activation technique of mechanochemical grinding to obtain MFA was employed in this study in order to increase pozzolanic activity of the materials. During mechanochemical activation, particles undergo a large number of direct impacts (because of milling mass) and the surface properties of the material modify in time; these impacts create microdefects and electrostatic charges on the particles increasing their surface energy and chemical reactivity. The mill used in the present experimentation is a Fritsch Pulverisette 6, adopting the following grinding parameters: milling-to-milled mass ratio 10 : 1; rotation speed 450 rpm; diameter of grinding balls 5 mm; grinding time 4 h; volumetric mill filling factor 30 %. The milling treatment was stopped for few minutes to avoid excess temperature increase during fly ash grinding.

### *Beneficiation of MFA*

Micronized material was also beneficiated reducing the unburned fraction by means of triboelectrostatic separation. A schematic of the laboratory-scale triboelectrostatic separator is shown in Fig. 1. The fly ash is placed in a vibratory feeder contained in a sealed tank. As the particles fall from the feeder, they are transported through a charging tube by gas conveyance at velocities up to 20 m/s. The flow of the $N_2$ conveyance gas is controlled by a rotameter. Particle−particle collisions and particle−wall collisions cause fly ash tribocharging, according to the work function of particles and wall. After the charging tube, the particle laden stream is injected into the top of a separation chamber or electric field cell

TABLE 1

Chemical composition of the investigated materials

| Material | Compound, mass % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | LOI | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ |
| OPC* | 1.67 | 17.6 | 5.05 | 3.75 | 56.2 | 14.7 | 0.35 | 0.68 |
| SF | 4.36 | 86.37 | 0.39 | 1.90 | 5.29 | 0.96 | 0.17 | 0.56 |
| MFA | 7.04 | 47.75 | 29.16 | 8.08 | 5.93 | 1.48 | 0.18 | 0.38 |
| BMFA | 3.97 | 49.33 | 30.12 | 8.35 | 6.13 | 1.53 | 0.19 | 0.39 |

* Ordinary Portland Cement.

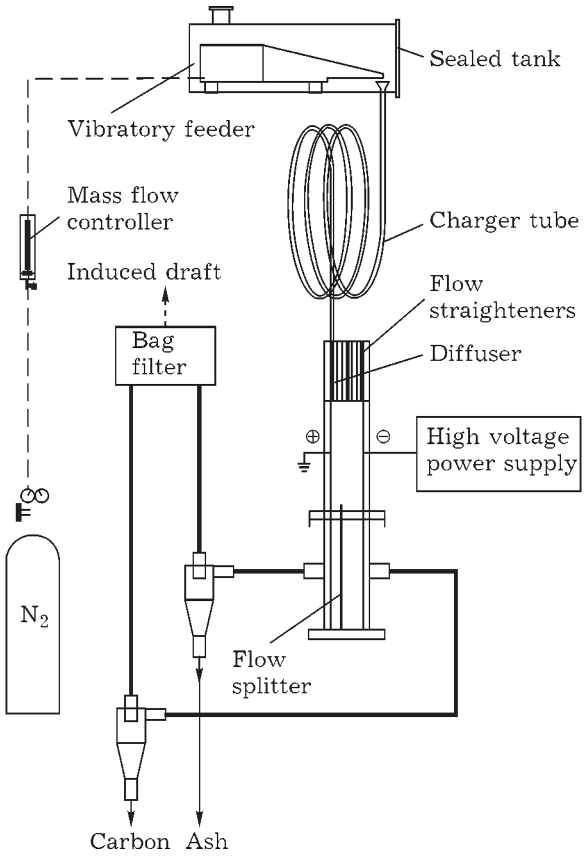


Fig. 1. Scheme of the triboelectrostatic separator used in the investigation.

containing two parallel plate, copper electrodes across which a DC voltage (0–20 kV) is applied; the value which provides the highest LOI reduction is 5 kV. The fly ash is injected close to the positive plate.

At the bottom of the electric field zone there is a flow splitter that divides the particle-laden gas into two streams, higher LOI product and beneficiated ash (BMFA); the transport of these products to the two cyclones is facilitated by an induced draft fan.

### Mix design

A first series of mortars (mixes A) was realised, made of three types of binary blends between OPC and, respectively, one of the by-products tested in this paper: MFA, BMFA and SF. In this series the ratio of cement substitution was between 10 and 25 % in mass. In the second series (mixes B), the by-products were used in substitution of sand, with the same ratios of the first series. Water-to-binder (w/b) ratio was respectively 0.4 and 0.35 (by mass), for a total of 26 mixes tested, comprising the reference one (Mix 1, with 100 % OPC and 0 % by-products).

### Sample preparation and testing procedure

Mixes containing the blends investigated were prepared according to UNI EN 197-1 and EN 196 [6, 7]. On the fresh mixes (pastes) 1, 3A, 5A and 7A (*i.e.*, with higher cement substitution ratio) setting time and water demand were evaluated. The hardened mix (mortars) for each sample was prepared using three 40×40×160 mm moulds filled and compacted using a vibrating table. The moulds were cured, taking samples at 2, 7 and 28 days for compressive strength measurements. The compressive strength was calculated as the average of three specimens.

## RESULTS AND DISCUSSION

### Water demand, initial and final setting time

As shown in Fig. 2, water demand is related to the fineness of the by-products, thus confirming that higher surface area particles of SF adsorb more water. The most satisfactory results were observed for mortar with 25 % of cement substitution by MFA (mix design 5A), characterised by only 150 ml of water demand, while mix design 3A (with 25 % of cement substitution by SF) showed an increase of 37 %, with a water demand of 205 mL.

Setting time of the pastes, which represents for industrial applications the time available for transportation and placement, was measured using a Vicat apparatus. The results, displayed

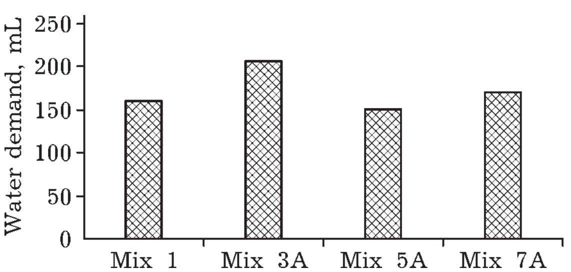


Fig. 2. Water demand in the investigated pastes.

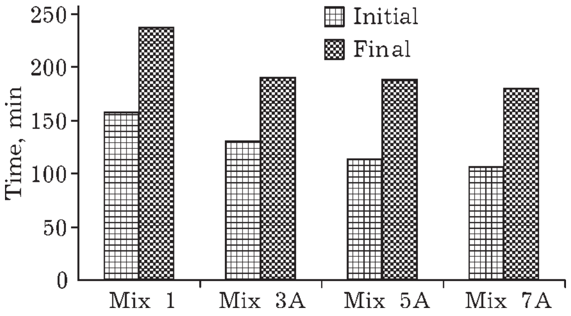


Fig. 3. Initial and final setting time in the investigated pastes.

in Fig. 3, show that both initial and final setting time of reference paste (Mix 1) are the largest measured. Mix design 7A (with 25 % cement substitution by BMFA) exhibited both the smallest initial and final setting times (106 and 180 min, respectively).

*Compressive strength*

Tables 2 shows the development of compressive strength up to 28 days for all mortars with water-to-binder ratio of 0.4 and 0.35, respectively.

Both minimum and maximum values of compressive strength for each w/b are developed by mortars with BMFA. In fact, the smallest values of compressive strength are shown by mix design 7A (with 25 % cement substitution by BMFA) at a curing age of 2 days (41.2 and 44.8 MPa at w/b of 0.4 and 0.35, respectively). Nevertheless, mix design 7B (with 25 % sand substitution of BMFA) after 28 days develops the highest compressive strengths of 93.4 and 106.6 MPa at the same w/b ratios. The latter value is 10 % higher than mortar with 25 % sand substitution by SF (mix design Mix 3B) and 34 % higher than reference mortar with 100 % OPC (mix design Mix 1). Using a w/b of 0.35, mortars with substitution of only 10 % of sand by BMFA (mix design Mix 6B) after 28 days develop the second highest value (98.6 MPa). With higher water amount (w/b = 0.4) the second highest value (92.8 MPa) is instead obtained replacing 25 % of sand with MFA (mix design Mix 5B). Furthermore, at the same curing age and for both w/b, all mix designs with sand substitution develop greater compressive strengths than reference mortar.

TABLE 2

Compressive strength at different curing age

| Mix | Mix design, % | | | Compressive strength, MPa | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | SF | MFA | BMFA | 2 days | | 7 days | | 28 days | |
| | | | | Mix A | Mix B | Mix A | Mix B | Mix A | Mix B |
| | | | | *w/b of* 0.4 | | | | | |
| Mix 1 | 0 | 0 | 0 | 48.8 | | 53.6 | | 77.0 | |
| Mix 2 | 10 | 0 | 0 | 46.0 | 49.3 | 56.5 | 58.9 | 80.0 | 79.9 |
| Mix 3 | 25 | 0 | 0 | 45.8 | 51.0 | 54.1 | 64.4 | 77.0 | 91.0 |
| Mix 4 | 0 | 10 | 0 | 42.8 | 49.9 | 55.3 | 58.7 | 81.0 | 81.0 |
| Mix 5 | 0 | 25 | 0 | 41.6 | 51.0 | 52.0 | 59.4 | 75.8 | 92.8 |
| Mix 6 | 0 | 0 | 10 | 44.0 | 50.0 | 56.5 | 61.9 | 83.0 | 83.0 |
| Mix 7 | 0 | 0 | 25 | 41.2 | 51.2 | 53.7 | 62.7 | 76.5 | 93.4 |
| | | | | *w/b of* 0.35 | | | | | |
| Mix 1 | 0 | 0 | 0 | 49.5 | | 58.9 | | 79.5 | |
| Mix 2 | 10 | 0 | 0 | 47.9 | 51.7 | 57.9 | 64.9 | 86.8 | 81.0 |
| Mix 3 | 25 | 0 | 0 | 47.0 | 57.9 | 55.6 | 68.2 | 84.1 | 97.0 |
| Mix 4 | 0 | 10 | 0 | 47.0 | 51.9 | 56.9 | 60.9 | 87.0 | 95.4 |
| Mix 5 | 0 | 25 | 0 | 45.2 | 54.9 | 54.3 | 69.5 | 81.7 | 97.3 |
| Mix 6 | 0 | 0 | 10 | 48.0 | 52.3 | 57.7 | 63.7 | 89.2 | 98.6 |
| Mix 7 | 0 | 0 | 25 | 44.8 | 57.9 | 54.8 | 70.3 | 84.3 | 106.6 |

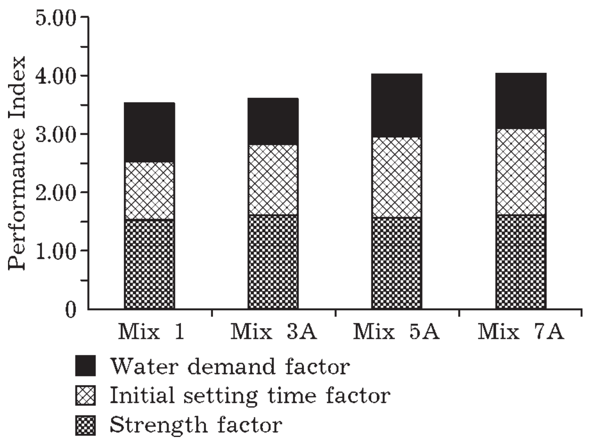


Fig. 4. Performance Index for some investigated mix design (water/binder of 0.35).

### *Performance Index*

With the aim of evaluating a comprehensive performance of the mix series compared to the reference one, a cumulative index (Performance Index $I_p$) taking into account all the parameters measured during the work was introduced and defined as follows:

$$I_p = F_s + F_t + F_w$$

where the parameters $F$ are, respectively, the factor of compressive strength ($F_s$), initial setting time ($F_t$) and water demand ($F_w$). The first factor is the ratio between the compressive strength developed after 28 days by each mix and the nominal strength of the cement used (52.5 MPa), while the last two factors represent the parameters obtained by each mix, normalised to the values obtained by Mix 1 (100 % OPC). In Fig. 4 the conformity index results obtained with w/b of 0.35 are shown. Mix design Mix 7A (with 25 % cement substitution by BMFA) and Mix 5A (with 25 % cement substitution by MFA) show quite the same highest value, 10 and 12 % larger than mix design Mix 3A (with 25% cement substitution by SF) and reference mortar (100 % OPC), respectively.

## CONCLUSIONS

The following conclusions can be drawn from the present experimental study:

1. Substitution of sand with Micronized FA enables one to reduce water demand, initial and final setting times, although lower setting times are achieved using Beneficiated Micronized FA.

2. Best mechanical performances in terms of compressive strength are obtained by mortar with the highest substitution (25 %) of sand by BMFA: the strength value at 28 days of curing is 10 and 34 % higher than mortar with 25 % sand substitution by SF and reference mortar, respectively.

3. Almost the same highest values of the conformity index are obtained for mortars containing MFA and BMFA. In particular, beneficiation of MFA increases mechanical strength and decreases initial setting time but affects water demand negatively.

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