

Mechanically activated fly ash as a high performance binder for civil engineering

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Abstract. This study is aimed for investigation of fly ash binder with suitable properties for civil engineering needs. The fly ash from Czech brown coal power plant Prunerov II was used and mechanically activated to achieve suitable particle size for alkaline activation of hardening process. This process is driven by dissolution of aluminosilicate content of fly ash and by subsequent development of inorganic polymeric network called geopolymer. Hardening kinetics at 25 and 30 °C were measured by strain controlled small amplitude oscillatory rheometry with strain of 0.01 % and microstructure of hardened binder was evaluated by scanning electron microscopy. Strength development of hardened binder was investigated according to compressional and flexural strength for a period of 180 days. Our investigation finds out, that mechanically activated fly ash can be comparable to metakaolin geopolymers, according to setting time and mechanical parameters even at room temperature curing. Moreover, on the bases of long time strength development, achieved compressional strength of 134.5 after 180 days is comparable to performance of high grade Portland cement concretes.

1. Introduction

The ashes are one of the main by-products of human activities arising from burning of coal for production of electricity and heat in power and heating plants. Today, the worldwide production of coal burning ashes are estimated somewhere around 700 million tons per year [1]. The ash arising mainly from mineral content of burned coal and principally are ashes divided to two categories, according to place of origin in combustion process. Bottom ash comprises approximately 20-25% of total coal burning ashes and takes place as a solid product in fire chamber. Remaining part of solid products are fly ashes, risen by stream of combustion products. Because of their origin, fly ash particles have very fine nature with diameters in range of 0.2 – 1000 µm [1]. In past century, the environmental and health risks associated with this fine nature of fly ash were recognized and today is fly ash mainly separated from combustion stream by electrostatic separators as a by-product.

Because of spherical shape, content of silica and aluminum oxide and mainly amorphous composition, fly ash has potential to be used as valuable industrial material. In last decades, fly ash is increasingly used in civil industry as a partial replacement of clinker in ordinary Portland cement (OPC) for their latent hydraulic properties when reacts with excess of calcium hydroxide in clinker-water mixture to precipitate of C-S-A-H gel and so on participates in final structure of hardened concrete [2]. However, despite to long term investigations, it is still only 53% of produced fly ash reused worldwide, mainly for environmental recultivations. It is because of replacement can be only partial and in many cases have blended concrete inferior mechanical performance.

Another possibility for reuse of fly ash in mass scale is process called geopolymerization [3,4]. This process consists of alkaline activation of a variety of materials including thermally activated clays



[5,6], coal fly ash and blast furnace slag to produce a solid material with mechanical and thermal properties potentially suitable for wide range of industrial applications. From a general point of view, the alkaline activation of an aluminosilicate material take place by blending with a highly concentrated alkaline solution of an alkali metal hydroxides or silicates [3,4]. In this case, the alkali solution control the disaggregation processes of the solid phase via dissolution of solid particles and cleavage of the Si-O and Al-O bonds [4]. The subsequent hardening of geopolymer binder takes place, by the polycondensation mechanism and gel precipitation [7]. These processes leads to solid phase formation and hardening of the binder. Unfortunately, in the case of fly ash, it is necessary to apply high temperatures and highly concentrated aggressive solutions for proper hardening [1,4].

In this paper, we are demonstrating possibility to use mechanical activation for improvement of fly ash reactivity in alkaline conditions. This process is composed of intensive milling and lies in high energy grinding which led to defects introduction and increase of surface area of individual grains of binder [6]. This process aid to better accessibility of reactive material and speeds up the hardening reaction of binder. The results indicate that fly ash can be converted to binder with excellent binding properties, comparable with high performance concretes. The time-resolved oscillatory rheometry was used to determination of setting time and reaction kinetics for better description of prepared binder.

2. Materials and binder preparation

In this study, the fly ash from coal power plant Prunerov II of CEZ a. s. was used. Table 1 summarizes chemical composition determined by X-ray fluorescence (XRF) spectrometer Bruker AXS S4 Explorer calibrated for aluminosilicate materials. The loss on ignition was determined by thermogravimetric measurement on TA Instruments Q500. According to result of chemical analysis, this fly ash can be classified as Class F with low amount of sulphates. The process of mechanical activation is composed of intensive milling process. The milling process was performed in laboratory vibrational mill BVM-2 for period of 150 minutes. Material after mechanical activation was investigated by static light scattering (SLS) instrument HORIBA LA-960 and consists of very fine particles, how can be seen in Figure 1 a). This result is consistent with scanning electron microscopy (SEM) observation in Figure 1 b), which was taken by microscope JEOL JCM-5000. SEM analysis reveal that particles are of irregular shape with considerable part of particles in submicrometer region. Tested binder was prepared as a mixture of mechanically activated fly ash and potassium silicate solution, with silicate module 1.61 and content of solids 35.03 %, in weight proportion of 10:8.

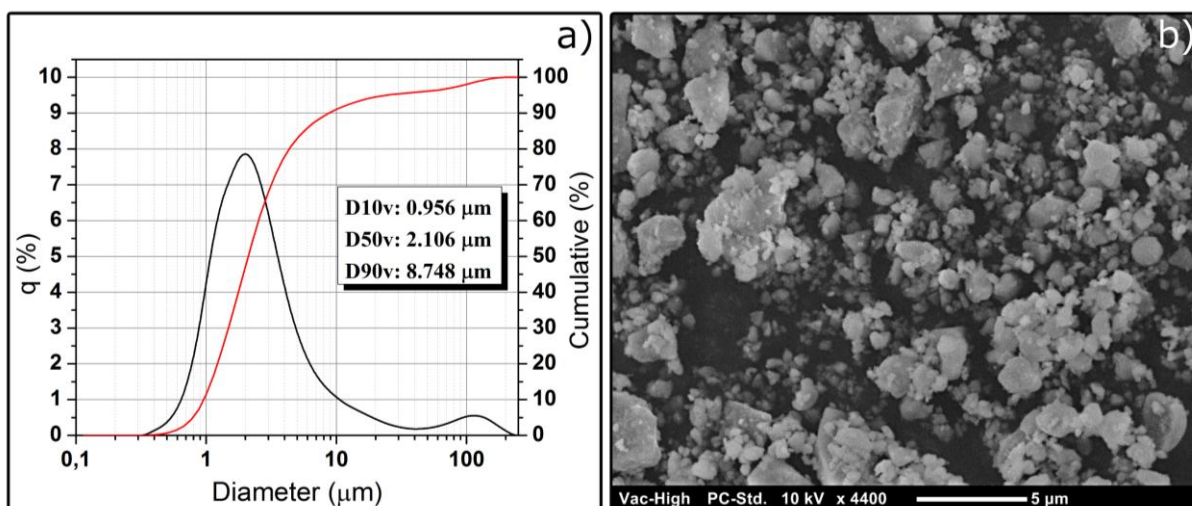


Figure 1. Fly ash after mechanical activation (a) particle size distribution, (b) SEM image of fly ash

Table 1. Chemical composition of fly ash [mass %].

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	Others	LoI	Total
53.00	29.22	8.37	2.43	1.67	1.11	0.63	0.29	1.59	1.63	100.00

3. Measurements and results

3.1. Determination of setting time

The setting time and reaction kinetics were determined by time-resolved oscillatory rheometry measurements with small amplitude on a strain controlled rheometer Ares G2 from TA Instruments in plane-plate geometry according to the references [8] and according to our procedure described earlier [9]. The procedure is as follows. Mechanically activated fly ash in accurate amount of 50 g was poured into 40 g of potassium silicate solution and then were mixed in laboratory vacuum mixer for 5 minutes and immediately transferred into the rheometer. The mixture in an amount of approximately 500 μ l was placed into the middle of plane plates and the gap was set to a working distance 0.8 mm. The edges of mixture were protected by a thin layer of silicone oil to avoid evaporation of water. Isothermal heating was initiated after 12 minutes for a period of time necessary for mixture hardening. The measurements were performed at radial velocity 10 rad/sec and strain 0.01% to ensure a minimal influence on the hardening process. Subsequently, the maximum of loss tangent was traced and the point of maximum value can be considered as transition of inner structure from pseudoliquid solution to inorganic polymer network. Figure 2 shows time dependences of storage (G') and loss (G'') modules and of tangent delta for the alkali activated fly ash binder. Results indicate that reached setting time is comparable with metakaolin and calcined shale binders. Moreover, application of elevated temperatures was not necessary, as it is usually needed by fly ash binders.

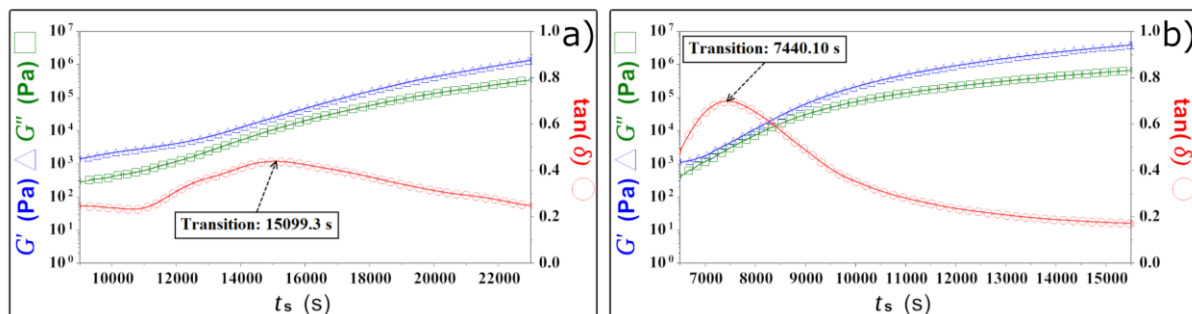


Figure 2. Results of hardening process measurements at isotherms (a) 25°C and (b) 30°C

3.2. Mechanical properties

For compression strength investigation, binder was prepared according to procedure described in section 2 in amount of 18 weight parts and mixed with 30 weight parts of calcined chamotte with granularity range of 0-0.5 mm. The mixing was performed in planetary mixer for a period of 10 minutes. Subsequently, the mixtures were cast in moulds with dimensions of 20×20×20 mm for compressional strength determination. Samples were cured at ambient temperature in polypropylene bags to prevent humidity loss. Mechanical properties were determined on LABTEST 6.100 SP1.

Results in figure 3 (a) indicate that mechanical strength suitable for civil engineering was reached after 3 days. After 28 days, compressional strength reached values, comparable to superior grades of OPC and geopolymer binders. But even after this period the hardening reaction is not complete and after 180 days mechanical parameters reached values comparable to so called “Ultra high performance concretes” used for demanding applications in civil engineering [2, 10].

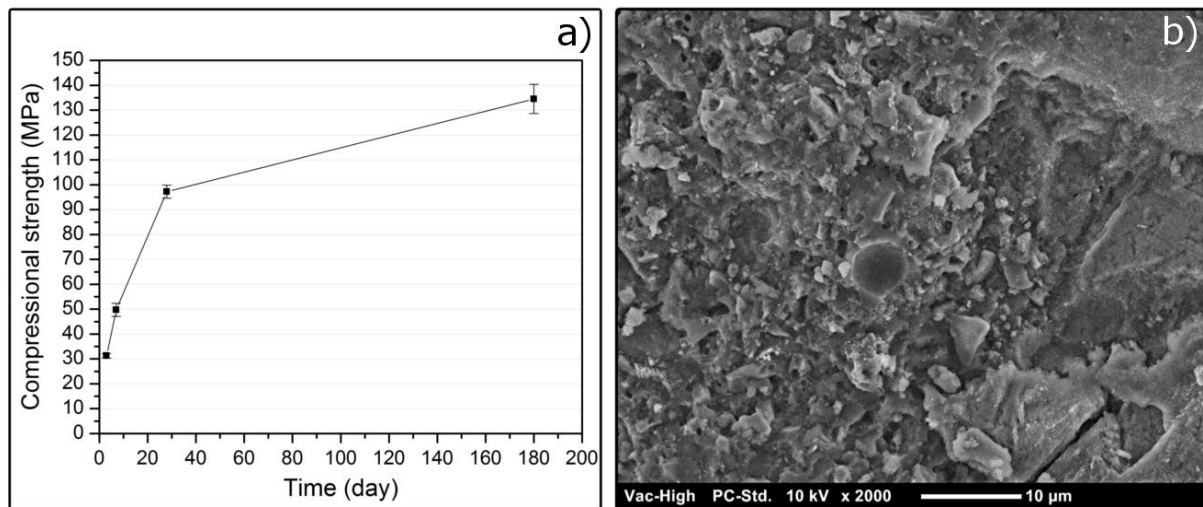


Figure 3. Evolution of compressional strength (a) and microstructure of binder after 180 days (b)

These results correspond to SEM observations. In figure 3 (b) the magnified structure of binder after 180 days and homogeneous structure of dense geopolymer binder is observable. This structure with minimum of cracks is leading to such high mechanical performance.

4. Conclusions

This study demonstrates, that fly ash can be used as suitable binder for demanding civil engineering needs and with proper treatment can outperform even high grades of cement binders. Moreover, setting time of presented binder is shorter even as metakaoline geopolymer binders. This behaviour is caused mainly by fineness of milled fly ash particles and by low porosity of particles as well. This properties leads to low demand of admixture water, rapid dissolution of fly ash particles and to fast construction of geopolymeric binding structure. How it was demonstrated, this binder have long term strength development and with 134.5 MPa in compression after 180 days can be compared with Ultra high performance grades of concrete.

Acknowledgments

The result was developed within the CENTEM project, reg. no. CZ.1.05/2.1.00/03.0088, cofunded by the ERDF as part of the Ministry of Education, Youth and Sports OP RDI programme and, in the follow-up sustainability stage, supported through CENTEM PLUS (LO1402) by financial means from the Ministry of Education, Youth and Sports under the National Sustainability Programme I.

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