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INFLUENCE OF ULTRAFINE GROUND FLY ASH ON THE MICROSTRUCTURE AND PROPERTIES OF CEMENTITIOUS MATERIALS

The influence of the process of mechanical activation in electromagnetic mill on the properties of fly ash are shown. The effect of ultrafine fly ash and chemical admixtures of polyfunctional action on the properties of cementitious materials was investigated. It was observed that combination of such complex chemical admixtures and ultrafine fly ash provides the reaching of technological, technical and economical effects in concretes. The using of fly ash ultrafine particles gives the possibility of manipulation and control of properties of cementitious materials and design of High Performance Concretes new generation on their base.

Keywords: **ultrafine fly ash, microstructure, cementitious system, flowability, mechanical strength**

INTRODUCTION

Nowadays building with using High Performance Concretes (HPC) has become increasingly popular in world practice. However, the production of these types of concrete involves using high-quality binders and microfillers. The theoretical principles of strength synthesis and durability of High Performance Concretes are based on creating optimal microstructure of cement matrix, reducing porosity by using chemical admixtures of polyfunctional action together with ultrafine supplementary cementitious materials and improving their production technology [1, 2].

Supplementary Cementitious Materials (SCM) - are widely used today in the technology of binding materials production. In most SCMs are represented by industry waste products, such as fly ash, slag, silica fume or other natural materials such as quartz sand and limestone. The idea of creating High Performance Concretes involves optimization of micro- and mesostructure due to the high packing density of fine particles (physical optimization), hydraulic and pozzolanic reactions in supplementary cementitious materials (chemical optimization) and also to improving the transition zone between the cement matrix and aggregate (optimization of coupling) [2].

According to Collepardi, Aïtcin, Jasiczak, Zaychenko e. a., construction building with using High Performance Concretes continues to increase. The main difference between traditional and High Performance Concrete is lower water-cement ratio, reduced amount of coarse aggregate, the optimal grain structure and availability of using modern superplasticizer and fine supplementary cementitious materials (microsilica, fly ash, etc.) [1-5].

Fine ground supplementary cementitious materials could significantly influence the building and technical properties of materials, the kinetics of hydration and hardening properties of binders. Considerable interest for the future investigations study is a by-product of coal burning - fly ash [6]. Different studies have demonstrated technical and economic possibility of using fly ash as supplementary cementitious material in the manufacture of Portland cement. By increasing the amount of fly ash to 30% the decreasing of cements activity was observed. For obtaining cements with fly ash without decreasing of strength and technical properties of concrete it is appropriate to use activated ash. Investigations show that the most effective and economical way is mechanical activation [7, 8].

During the process of mechanical activation energy which influences directly the crystal and molecular substructure of solids is the most effective way catalytic effect. This leads to an increasing of dislocations, the disclosure of the active surface amorphization of structural elements. Amorphization in its turn contributes to a significant increasing of active centers. Last decades of the century milling process was mainly improved by the increasing in the size of mills and their power. However, the use of modern mills today allows to reduce the cost of metal, grinding and to reduce energy consumption by 50÷60% and to get ultrafine materials. They eliminate overheating of the material, reliable and easy in operating [7].

Ultrafine product - "superpucolana" consisting of spherical silica-alumina grains which contain large amounts of alkali metals was proposed [9]. This material is obtained from fly ash by the process of mechanical activation. The dispersion of "superpucolana" expressed through the residue 45 μm sieve is 1÷2%, and the content of fractions ≤ 20 μm is more than 90%, and large amount of particles smaller than 1 μm. The additive has high pozzolanic activity, more than 120% after 90 days. Using "superpucolana" even after replacing 25 mass. % of the cement significantly influences the reduction of early strength, but increases strength after 28 days. The basic properties of "superpucolana" is low water demand, which increases the rheological parameters of concrete mix and by reducing water-cement ratio influence on the increasing of concrete strength characteristics. Due to its properties "superpucolana" can be used in the manufacture of binders and concrete as high pozzolanic supplementary cementitious material. The use of ultrafine fly ash with more high specific surface than cement creates different opportunities for the production of new types of concrete [2, 8].

1. MATERIALS AND METHODS

Ordinary Portland cement (OPC) CEM I - 42,5 R JSC "Ivano-Frankivskcement" with specific surface of 380 m^2/kg was used in the investigations. Fly ash (FA) was used as supplementary cementitious material. Polycarboxylate type superplasticizer

(PC) was included in cementitious systems as modifier. The samples of mineral additives were ground in laboratory electromagnetic mill to obtain the samples of different specific surface area.

Physico-mechanical tests of cements and concretes were carried out according to usual procedures. The evaluation of the properties of plasticized cementitious systems was carried out through flowing and compressive strength tests. The physico-chemical analysis (methods of X-ray diffractometry, electron microscopy, differential calorimetry) were used for investigation of cementitious systems hydration processes. The particle size distribution of fine ground SCMs was determined by a laser granulometer Mastersizer 2000.

2. RESULTS AND DISCUSSION

According to particle size distribution analysis CEM I - 42,5 R contains 10, 50 and 90 vol. % of particles smaller than 5.75, 19.42 and 56.29 μm respectively. Chemical and phase composition of fly ash quality is determined by its dispersion, form of particles surface, its activation should provide the destruction of the surface of spherical particles of ash and dispersion of large particles with increasing its share of the total surface. Curves with particle size distribution of materials are shown in Figure 1. It is observed that ultrafine fly ash is characterized by 34 vol. % of particles smaller than 1 μm, which is in 3.1 times higher compared with ash.

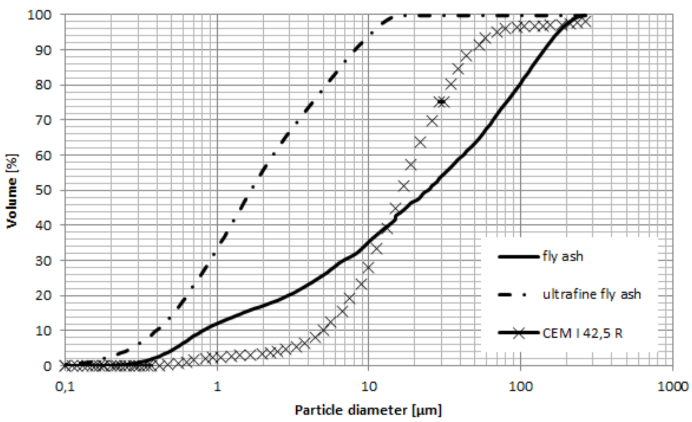

Fig. 1. Characteristics of partical size distribution of materials

According to the electron microscopy data (Fig. 2), the main component of ultrafine fly ash is crushed silica-alumina phase and grains in the form of balls with average diameter of 10 μm. According to EDAX analysis of the composition of particles activated fly ash is presented in oxides, mass. %: Al_2O_3 - 26.96, SiO_2 - 40.27, CaO - 2.58, K_2O - 2.19, FeO - 4.79.

The pozzolan activity of fly ash was investigated by the quantity of bounded $Ca(OH)_2$ after 30 days. There is a formation of calcium silicates and aluminosilicates (C-S-H and C-S-A-H phases) with low CaO/SiO_2 ratio during the reaction process of fly ash with $Ca(OH)_2$ The interaction of ultrafine fly ash with $Ca(OH)_2$ increases, it is higher on 31.8% comparatively with fly ash (Fig. 3). The SEM images of these samples are shown in Figure 4 (a, b).

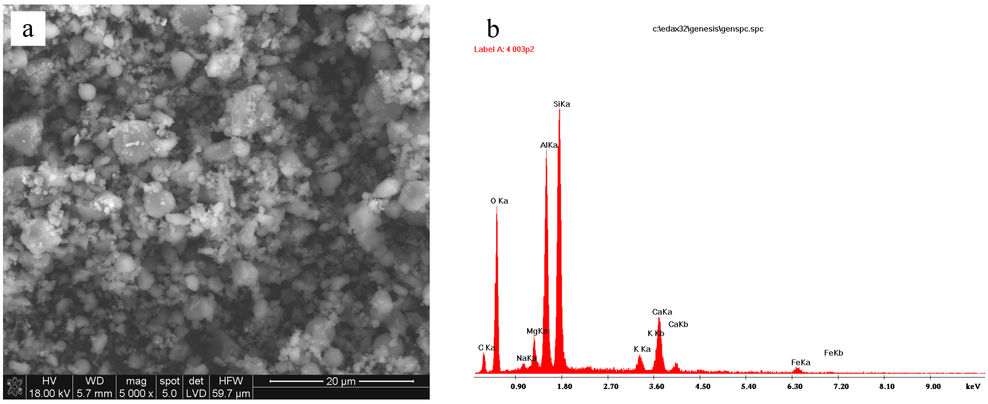

Fig. 2. Microstructure (a) and EDAX spectrum in spot EDX3 (b) of ultrafine fly ash

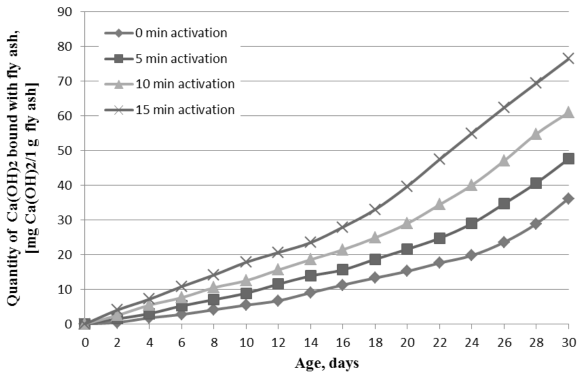

Fig. 3. The influence of ultra-fine grinding on the pozzolan activity of fly ash

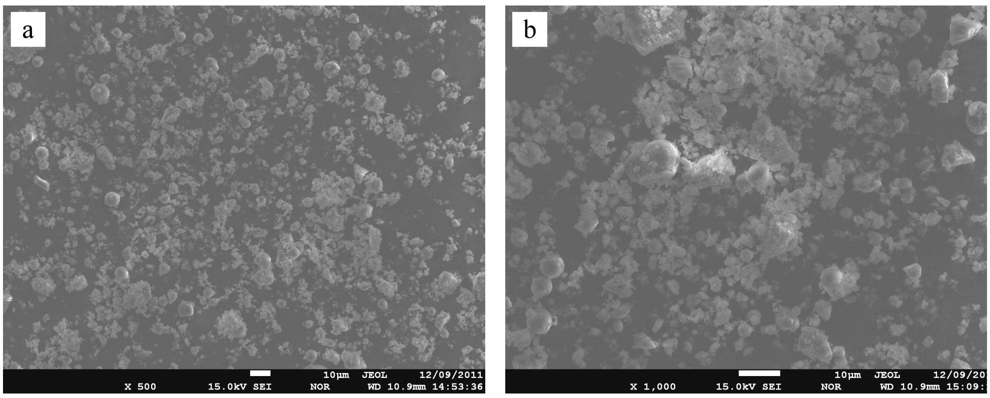

Fig. 4. SEM images of fly ash pozzolan reaction with solution $Ca(OH)_2$ after 30 days:
a) fly ash; b) ultrafine ground fly ash

Addition of ultrafine fly ash may improve the structure of the interfacial transition zone (ITZ) between additive and cement matrix (Fig. 5a, b) further; the ultrafine fly ash acting first as a fine filler and later reacting with the portlandite in the ITZ to form C-S-H. Mechanical activation of fly ash can significantly improve its structure-forming properties by increasing the active surface in 2-3 times.

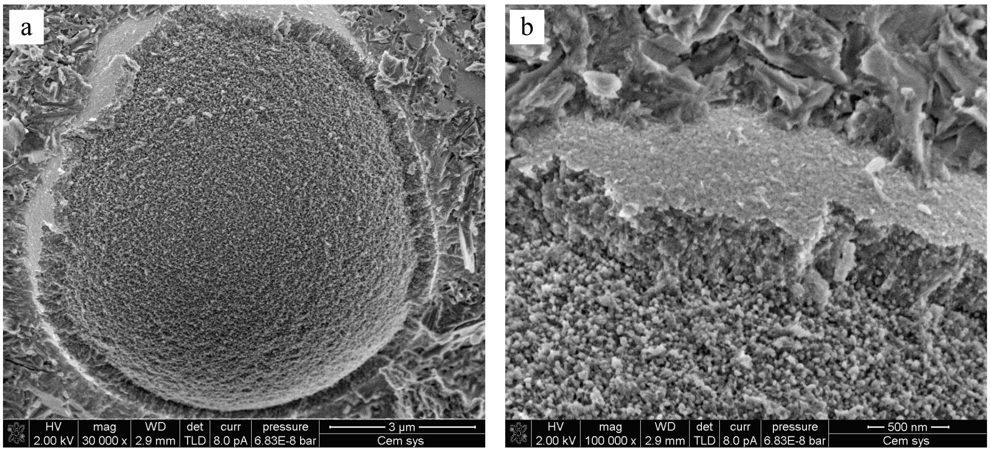

Fig. 5. Microstructure of cementitious system with ultrafine ground fly ash after 28 days of hardening

Investigations of fine concretes properties with the addition of ultrafine fly ash showed that the replacement of 10 and 20 mass. % Portland cement increases concrete strength during all period of hardening (Table 1). Using 20 mass. % of ultrafine fly ash provides increasing of strength on 17% compared to concrete without additives. It should be noted that due to the high pozzolanic activity of ultrafine fly ash fine-grained concrete strength increases to 57.5 MPa after 90 days of hardening.

Table 1. **The properties of fine-grained concretes (cement : sand = 1:2)**

Cement	W/C	Flowability [mm]	Compressive strength [MPa] after days			
			2	7	28	90
cement (100%)	0.39	110	15.9	24.8	37.1	39.5
cement (90%) ultrafine fly ash (10%)	0.39	112	16.2	25.0	38.5	53.1
cement (80%) ultrafine fly ash (20%)	0.39	114	20.7	29.2	43.5	57.5
cement (70%) ultrafine fly ash (30%)	0.39	115	14.8	20.5	35.5	53.2

Testing of fine concrete containing 20 mass. % of ultrafine fly ash and chemical admixture PC (polycarboxylate superplasticizer) showed (Table 2) that the flowability of fine-grained concrete mixtures increases to 240 mm (technological effect ΔF = 114%). In the same time concrete strength increased from 37.4 to 60.7 MPa (ΔR_{28} = 62%).

Table 2. **The properties of fine-grained concretes (cement : sand = 1:2)**

Concrete	W/C	Flowability [mm]	Compressive strength [MPa] after days			
			2	7	28	90
cement (100%)	0.39	112	17.9	25.5	37.4	39.3
cement (80%) ultrafine fly ash (20%)	0.39	118	22.7	27.4	42.7	59.4
cement (80%) ultrafine fly ash (20%)+1,2 mass.% PC	0.39	240	14.3	40.1	60.7	65.7

It should be noted that the use of ultrafine ground fly ash with polycarboxylate type superplasticizer gives a possibility to obtain High Performance Concretes with high building and technical properties. Thus, increasing the energy content of ultrafine active fractions in ultrafine fly ash provides the increasing efficiency of superplasticizers action in the mixture, density and strength of concrete.

CONCLUSIONS

Ultrafine ground fly ash due to the big amount of active fractions more intensively reacts with calcium hydroxide during hydration process. The use of ultrafine supplementary cementitious systems improves the efficiency of chemical admixtures based on polycarboxylates and their combination is characterized by synergetic action. This gives the possibility to obtain High Performance Concretes which can be used for repair and renovation of reinforced concrete constructions with providing next effects: technological effect - the flowability of the concrete mix increases to 240 mm without strength loss (ΔF = 114%), technical effect - compressive strength is higher (ΔR_{28} = 62%), the economic effect - gives the possibility to reduce costs by reducing the cement content (ΔC = 20%). The new challenges in construction materials mean that such sustainable, efficient, High Performance Concretes will have even more benefits in the future.

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WPŁYW BARDZO DROBNOZIARNISTYCH POPIOŁÓW NA MIKROSTRUKTURĘ I WŁAŚCIWOŚCI MATERIAŁÓW CEMENTOWYCH

Przeprowadzono badania wpływu ultradrobnego popiołu lotnego i domieszek chemicznych na właściwości materiałów cementowych. Stwierdzono, że kombinacja domieszek chemicznych i najdrobniejszych cząsteczek popiołów lotnych w betonie zapewnia osiągnięcie doskonałych efektów technicznych i ekonomicznych. Stosowanie bardzo drobno mielonych cząsteczek popiołu daje możliwości modyfikacji i kontroli właściwości materiałów cementowych oraz możliwość projektowania na ich podstawie wysokowartościowych betonów nowej generacji.

Słowa kluczowe: **popiół bardzo drobno mielony, mikrostruktura, materiały cementowe, urabialność, wytrzymałość mechaniczna**