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NANOMODIFIED PORTLAND CEMENT COMPOSITIONS WITH ALKALINE ACTIVATION

This paper deals with design of rapid hardening Portland cement compositions modified ultrafine mineral additives, polycarboxylate type superplasticizer, alkali-containing activator. Nanoparticles relating to microheterogeneous systems are characterized by high values of specific interfacial area and "excess surface energy" and promote more complete synergic effect of other components activity. The possibility of increasing of liquid phase alkalinity due to interaction of sodium sulphate and calcium hydroxide in the presence of such ultrafine aluminium containing additives as metakaolin was established.

Keywords: **nanomodification, rapid hardening Portland cement compositions, ultrafine supplementary cementitious materials, alkaline activation**

INTRODUCTION

Currently, there is a critical need for advanced building materials for new high-performance construction and to repair and enhance the performance of existing structures. These materials are required to be increasingly more energy-efficient, environmentally friendly and affordable [1-5].

Innovative methodology of development of monolithic and precast construction of optimized energy potential bases on nanomodification of Portland cement (manipulation of the structure at the nanoscale - less than 100 nm - to develop cement compositions with enhanced or novel properties and functions) by two ways - the adding of the material synthesized nanoscale modifiers and synthesis of nanoscale systems in the material during its manufacturing [6-8]. The unique technology of the new X-SEED hardening accelerator (Crystal Speed Hardening concept) based on adding of synthetically produced nanoparticles of CSH crystals [9]. The active CSH crystals can virtually grow without energy barrier in the pore solution between the cement grains.

Nanomodification of cement-based materials also can be achieved by adding of ultrafine mineral additives and alkaline activation of cementitious compositions [10-13]. Ultrafine particles of supplementary cementitious materials (SCMs) which are characterized by high values of specific interfacial area and surface energy provide optimization of particles size distribution by the criterion filling voids, more complete synergic effect of other components, directed formation of the micro-structure of the cement matrix due to its compaction and pozzolanic reactions in unclincker part [12]. In this study an attempt has been done for development of nanomodified alkaline activated rapid hardening Portland cement compositions with ultrafine mineral additives.

1. EXPERIMENTAL PART

Ordinary Portland cement (OPC) CEM I 42.5 JSC "Ivano-Frankivskcement" based on Portland cement clinker with mineralogical composition [mass.%]: C_3S - 64.20; C_2S - 12.88; C_3A - 5.65; C_4AF - 14.62 - was used in the investigations. Low calcium fly ash (FA), metakaolin (MK) and silica fume (SF) were used as supplementary cementitious materials.

The content 10.0; 50.0 and 90.0 vol.% of OPC particles is equal to 5.75; 19.42 and 56.29 μm correspondingly (Table 1). The values D_{10} for fly ash, metakaolin and silica fume are correspondingly 9.01, 2.2 and 0.07 μm. The particle size distribution roughly meets the requirements of the gap-graded particle size distribution in cementitious systems.

Table 1. **Chemical composition of Portland cement and mineral additives**

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	R_2O	SO_3
OPC	21.44	5.22	4.84	64.68	0.55	0.95	2.32
Fly ash	43.75	21.79	21.34	4.83	2.15	1.80	0.35
Silica fume	94.7	0.7	5.3	0.9	1.0	1.2	–
Metakaolin	54.21	44.59	0.75	0.45	–	–	–

GLENIUM ACE 430 (superplasticizer based on polycarboxylate ether polymers) and sodium sulphate Na_2SO_4 as alkaline hardening activator of cementitious systems were used in the investigations.

Physical and chemical analysis methods (X-ray phase, thermal, electron microscopy analysis a.o.) were used for investigation of hydration processes of nano-modified Portland cement compositions with alkaline activation. The particle size distribution of OPC and mineral additives was determined by a laser granulometer Mastersizer 2000. The blending of OPC with ultrafine additives (metakaolin, fly-ash, silica fume) was carried out in vibration mill.

2. RESULTS AND DISCUSSION

The degree of additional interfacial active surface of OPC and SCMs could be obtained by the determination of the new coefficient of incremental surface activity K_{isa}, which shows the distribution of particle content in the total surface. Coefficient K_{isa} was calculated by the product of ratio specific surface particles to their volume (S/V) and incremental volume of each fraction [13]. The coefficient K_{isa} for fly ash is 2.6 times higher than the value of the same parameter for OPC. The incremental surface activity coefficient of such ultrafine mineral additives as MK and SF is 15.82 and 531.8 $\mu m^{-1}\cdot$vol.% respectively, while of OPC - only 3.81 $\mu m^{-1}\cdot$vol.%. This fact indicates the increasing of the surface activity of ultrafine particles.

The amount of ultrafine particles up to 1÷2 μm in ultrafine supplementary cementitious materials is 10÷15 vol.% but they have a significant influence in total specific interfacial area [2, 8]. The particles of nanostructure scale, which have defined a supply of free surface energy, increase the interface that can accelerate chemical reactions, detect catalytic activity and cause more substantial influence of superficial atoms on the synthesis of the cementitious systems strength.

The high flowed fine-grained concrete (cement:sand = 1:3, W/C = 0.39, F = 168 mm) based on nanomodified Portland cement compositions (NPC) characterized by high intensity of strength development in the early stages of hardening (Fig. 1). Thus, the strength of the modified fine-grained concrete increased 2.7 times after 10 hours and two times after 15 hours compared with concrete based on OPC. The compressive strength of modified fine-grained concretes based on NPC after 10 hours and 15 hours increases of 3.3 and 2.3 times respectively compared with the fine-grained concrete based on CEM I 42.5 due to significant water reducing effect (ΔW/C = 23%, F = 112 mm).

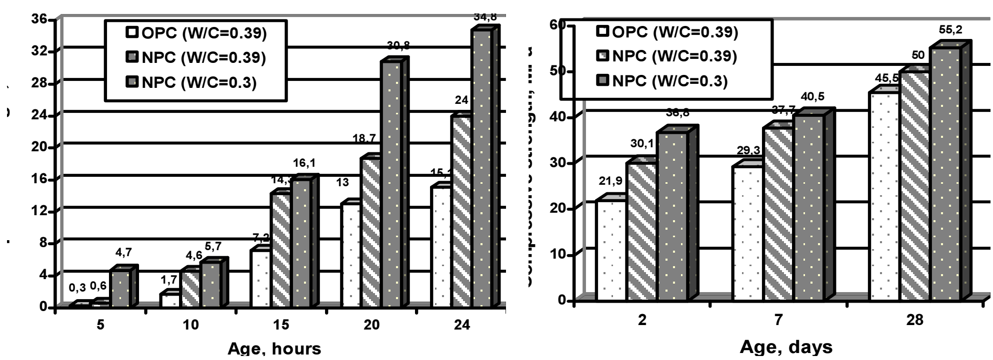

Fig. 1. Compressive strength of fine-grained concretes (C:S = 1:3) based on OPC and nanomodified Portland cement compositions

Test results showed that early strength of fine-grained concrete based on NPC (W/C = 0.39, F = 168 mm) increases on 37.4% compared to OPC, and standard strength is R_{28} = 50.0 MPa. Due to the significant water reducing effect (ΔW/C = = 23%, F = 112 mm) the strength of nanomodified Portland cement composite after 24 hours increases up to 34.8 MPa (technical effect ΔR_{c1} = 130.4%), after 2 days of hardening technical effect slightly decreases (ΔR_{c2} = 68%) and compressive strength after 28 days of hardening is 55.2 MPa. Herewith NPC characterized by significant increasing of early strength with index R_{c1}/R_{c28} = 63.0% and R_{c2}/R_{c28} = = 66.7%.

The peculiarities of hydration mechanism of nanomodified cement compositions have been revealed by the investigations of interaction processes in the model systems $CaO+Na_2SO_4$+ultrafine mineral additive (metakaoline, fly ash or silica fume) with water. It was established that the pH of suspension of the model system $Ca(OH)_2+Na_2SO_4$, containing high aluminium fly ash, metakaoline increases (Fig. 2). At the same time, in the presence of microsilica the value pH of model system suspension decreases. The pH increasing leads to the destruction of the outer layer of mineral additives particles leaving more active cores exposed for reacting forming additional hydration products.

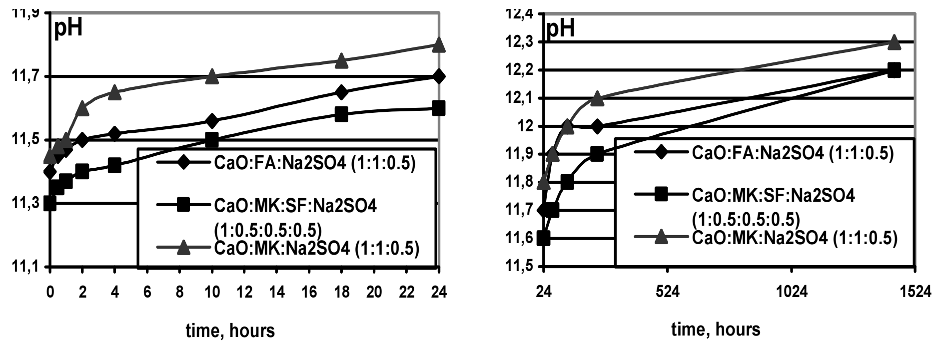

Fig. 2. Kinetics curves of pH of model system suspension

The slight lines of hexagonal calcium hydroaluminates type AF_m-phases (d/n = 0.810; 0.395; 0.288; 0.247 nm) appear in the system $Ca(OH)_2$:MK = 1:1 (Fig. 3a). But in the presence of aluminium-containing additives (metakaoline, fly ash) in this model system the lines of $Ca(OH)_2$ (d/n = 0.493; 0.263; 0.193 nm) significantly decrease and there are lines of ettringite (d/n = 0.971; 0.556 nm).

In the presence of high-aluminate metakaoline, fly ash the ion balance of the reaction between $Ca(OH)_2$ and Na_2SO_4 shifts to the side of $CaSO_4 \cdot 2H_2O$ and NaOH owing to the ettringite formation. Metakaoline additive is characterized by high value of Al_2O_3 (42 mass.%) in comparison to fly ash (21÷23 mass.%). This factor and high surface activity of metakaolin initiates the reaction between $Ca(OH)_2$ and Na_2SO_4 to form the gypsum dihydrate and sodium hydroxide in the process of hydration and alkalinity of the liquid phase of cement paste increase.

Controlling the ettringite formation can yield useful properties of cement compositions such as the early hardening, high strength and expansion. Increased amounts of the ettringite crystals in early stages of hydration (4÷12 hours) obtained as a result of reaction between calcium hydroxide, sodium sulfate and high aluminate containing additives are provided to acceleration of hardening process in Portland cement paste. The alkaline cation of sodium contributes to hydrolysis of the alite phase of the Portland cement clinker. The reactions connected with pozzolanic activity of the ultrafine additives are accelerated and new fibrous formations as the CSH-phases take place in unclinker part of cement matrix.

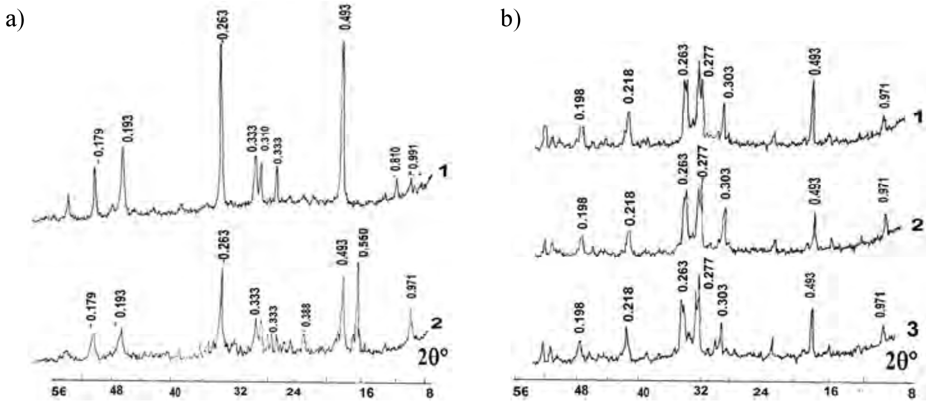

Fig. 3. XRD of the interaction products in the model systems with water after 2 days: 1 - $Ca(OH)_2$:MK (1:1); 2 - $Ca(OH)_2$:MK:Na_2SO_4 (1:1:0,5) (a) and XRD of cement pastes after 24 h of hydration: 1 - OPC; 2 - NPC; 3 - NPC* (b)

There are main lines of ettringite (d/n = 0.973; 0.561; 0.388; 0.348 nm) and $Ca(OH)_2$ (d/n = 0.493; 0.263; 0.193 nm) on the diffractograms of OPC paste after 24 h of hydration (Fig. 3b). At the same time NPC paste diffraction peak of ettringite is higher, but the intensity of $Ca(OH)_2$ line is lower, that indicates the accelerating of hydration and structure formation processes. Thus, the early strength of NPC paste increases by 2.5 times compared to OPC. The strength of nanomodified Portland cement compositions with alkaline activation (NPC*) after 24 h increases in 3 time due to maximum volume concentration of solids and maximum packing density of cement pastes.

CONCLUSIONS

The nanomodified rapid hardening cement compositions with alkaline activation based on ordinary Portland cement with ultrafine mineral additives characterized by high mechanical properties. Optimization of particle packing system by ultrafine mineral additives, which determines the initial density system, availability energy active ultrafine particles in supplementary cementitious materials based on metakaolin that interact with $Ca(OH)_2$ (early pozzolanic reaction) with additional formation of hydrosilicates, AF_m- and AF_t-phases in unclincer part of cement matrix creates the possibility of obtaining of monolithic and precast construction of optimized energy potential.

The nanomodified cement compositions with alkaline activation allowed realize the crystal speed concept based on formation crystals of ettringite and ultrafine CSH crystals at early stage of structure formation due to reaction between sodium sulphate with Al-containing metakaoline and fly ash additives and achieved sustainable production of rapid hardening concrete.

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NANOMODYFIKOWANE KOMPOZYTY Z CEMENTU PORTLANDZKIEGO CEMENTOWE Z AKTYWACJĄ ALKALICZNĄ

W artykule przedstawiono szybkotwardniejące kompozyty z cementu portlandzkiego modyfikowane ultradrobnymi dodatkami mineralnymi oraz domieszkami superplastyfikatora polikarboksylanowego i aktywatora alkalicznego. Nanocząstki systemów mikroheterogenicznych charakteryzują się wysokimi wartościami powierzchni właściwej międzyfazowej oraz "nadmiarem energii powierzchniowej", co powoduje bardziej kompletny synergiczny efekt działania innych składników. Uzyskano możliwość zwiększenia aktywności alkalicznej fazy ciekłej ze względu na interakcje siarczanu sodu i wodorotlenku wapnia w obecności ultradrobnych cząstek aluminium zawierających takie dodatki, jak metakaolin.

Słowa kluczowe: **nanomodyfikacja, szybkotwardniejące kompozyty z cementu portlandzkiego, ultradrobne dodatki do cementów, aktywacja alkaliczna**