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EFFECT OF SYNTHETIC NANODISPERSED SILICA ON THE PROPERTIES OF PORTLAND CEMENT BASED MORTARS

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Abstract. The work deals with the modification of mortars by small quantities of nanodispersed material. The effect of amorphous nanosilica on Portland cement hydration and hardening has been investigated. The amorphous nanosilica is compared with the known mineral additive – microsilica.

Keywords: nanosilica, microsilica, Portland cement.

1. Introduction

To date the development of composition building materials is mainly aimed at the usage of technogenic wastes. The modification of compositions properties is possible at different levels of matter structure. It is known that the mortar is a heterodispersed structure, where the solid phase consists of two parts: skeleton formed by coarsely dispersed particles with the size of more than 10 μm and porous substance formed by fine-dispersed ultramicroheterogeneous (1–100 nm) and microheterogeneous (0.1–10 μm) particles [1]. Just ultramicroheterogeneous and microheterogeneous (till 500 nm) particles are nanodispersed ones. The formation of heterodispersed system structure depends on adhesion strength, where specific adhesion is formed at nanolevel. Therefore the investigation of mortar properties modification using nanodispersed materials is an urgent question.

This work deals with the research of amorphous nanosilica effect on hydration process and Portland cement hardness compared with the known mineral additive – microsilica.

2. Experimental

We used CEM I 32.5R Portland cement in accordance with European standards PN-EN 197-1 and different modifications of ultradispersed amorphous silica: nanosilica (white soot – WS) [2] and microsilica (MS). The physico-chemical properties of the initial silica are represented in Table 1.

Table 1

Physico-chemical properties of ultradispersed amorphous silica

Silica type	SiO_2 content, %	Grains size nm, [4]	Specific surface, m^2/g, [4]	Absorption, cm^3/g
Microsilica	92	~200	~20	~0.5
Nanosilica	93.52	50	173	2.42

The pozzolanic activity was determined *via* reaction of additives with calcium hydroxide from its saturated solution. Then CaO mass was determined in mg reacted with 1 g of additive for 30 days. The more $Ca(OH)_2$ is absorbed for the definite time, the more active is an additive [3].

Differential-thermal analysis was carried out using Termoanalizator TA Instruments SDT 32960, with the heating rate of 10°/min till the maximum temperature of 1273 K. Thermal effects were determined for the grout samples with water/cement ratio W/C = 0.5, where the part of cement was exchanged for ultradispersed silica. After the definite time the hydration process was retarded by acetone and samples were dried at 333 K for 8 h. The thermal analysis was carried out after 3 h, 24 h and 28 days of grout hydration.

The compression strength was determined in accordance with the standard EN 196-1. Taking into account the high water absorption of the synthetic silica and microsilica, we added a plasticizer based on melamine-formaldehyde polycondensate (1 % from cement mass) to the mortars.

3. Results and Discussion

In accordance with the European standard EN 197-1 microsilica is used to produce Portland cement with pozzolane or composition Portland cement. The effect of microsilica at different stages of hydration is thoroughly investigated [4, 5]. It is known that microsilica is an industrial waste obtained during metallic silica production or alloying silica and iron at high temperatures (2273–2473 K) in arc furnaces. The microsilica particles are formed due to the oxidation and condensation of silica gas oxide deposited as a dust. MS is an amorphous material and may contain crystal phase – crystoballite. The other form of ultradispersed amorphous silica may be synthetic silica or as it is often called – white soot. It is obtained by precipitation of amorphous silicic acid from the solutions of liquid glass by acids. Depending on filtration and drying conditions different types of WS are obtained. It has a developed specific surface which is 9 times higher than that of microsilica.

It was found that the pozzolanic activities of synthetic silica and microsilica are 405 and 220 mg CO/g of additive, respectively, at the same content of amorphous SiO_2. The increase of activity is concerned with different modifications of amorphous SiO_2 and reduction of particles size by 4 times. The reaction rate of nanosilica with calcium hydroxide for 2 days is 1.4 times higher compared with MS and their activity is similar only after 4 days. Moreover, the degree of pozzolanic reaction for MS dynamically decreases by 4–10 % after 4 days. The activity of nanosilica is more stable for 30 days (Fig. 1).

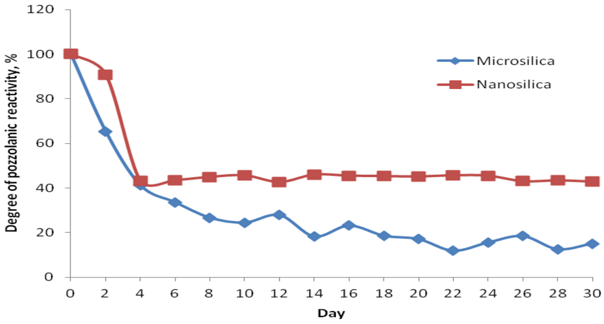


Fig. 1. Degree of pozzolanic activity *vs* time

Taking into account that nanosilica is a material with a high adsorption ability, the study of hydration process and cement grout hardness were carried out using the limited amount of nanosilica, 0.1 and 1 % of cement mass, in particular. The results were compared with 0.1 % of MS (Fig. 2).

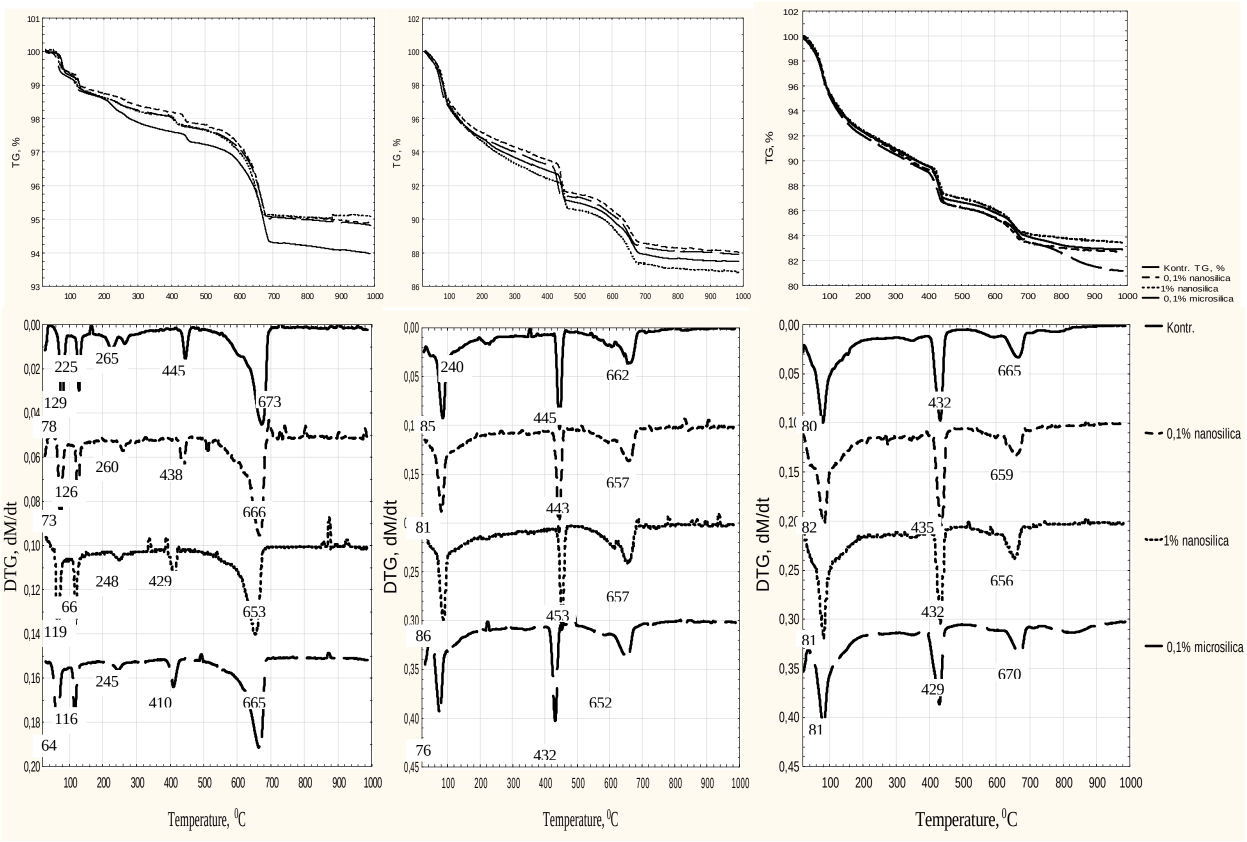
The curves form and mass losses within determined temperature range were analyzed. In the range to 673 K the endothermic effect is connected with the loss of physically bonded water dehydration of hydrate phases; within the range of 673–773 K – with calcium hydroxide decomposition and above 873 K – with carbonates decomposition. The exchange of cement for ultradispersed silica shifts endo-effects towards temperature decrease during hydration for 3 and 24 h, ***i.e.*** decreases activation energy. After 28 days it remains constant. The addition of MS (0.1 %) shifts endo-effects more greatly compared with nanosilica addition. It is connected with the presence of crystal phase in the microsilica.

Endo-effect connected with monosulphate $Ca_4[Al(OH)_6]SO_4*6H_2O$ dehydration at 498 K is not observed at DTG-curves for 3 h(Fig. 2). It means that etryngite crystals are formed at the initial stage and not recrystallized into low-basic hydroalluminates. Further this fact may influence the porosity and deformation growth [6] and decrease of strength, as a result.

The results of mass loss within the temperature range till 673 K and 673–773 K, as well as the content of adhesive water and $Ca(OH)_2$ in cement grout are represented in Fig. 3. Relative to the mentioned indexes the effect of 0.1 % nanosilica and microsilica is the same. The introduction of additives (0.1 %) increases $Ca(OH)_2$ content in all periods of cement hardening as a result of nucleation effect of ultradispersed silica particles [4] and only 1 % of soot decreases calcium hydroxide content. If we compare the investigated sample with the control cement grout, the introduction of 0.1 % of additive decreases adhesive water content for 3 and 24 h by 1 % and the increase is observed only after 28 days.

In connection with small amounts of ultradispersed additives which affect the strength, they are used as aqueous suspensions for well mixing cement-sand solutions. The estimation of strength change is represented as the index of active strength (IAS) – ratio between compression strengths of mortar + silica and control mortar (Fig. 4).

It should be noted that introduction of 0.1 and 1 % of nanosilica and 1 % of microsilica significantly increases compression strength at the earlier stages of hardening. Moreover, the effect of WS (1 %) on the strength is by 10 % higher compared with MC (1 %). The effect of 0.1 % of amorphous silica is also important. Just such amount guarantees strong structure that is connected [1] with hydrosilicates and silica gel formation which intensively bound Portland at the initial stage of cement hydration. The excess of formed gel may form loose coagulation structure incapable of hardening. Therefore, the strength decreases.



a) b) c)

Fig. 2. Derivatogramms of cement grout: for 3 h (a); for 24 h (b) and for 28 days (c) of hydration

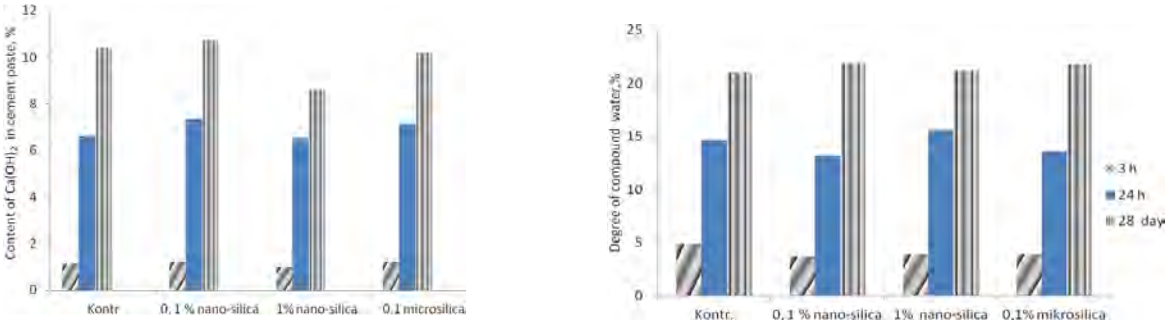


Fig. 3. Content of calcium hydroxide and mass loss of cement grout with ultradispersed additives

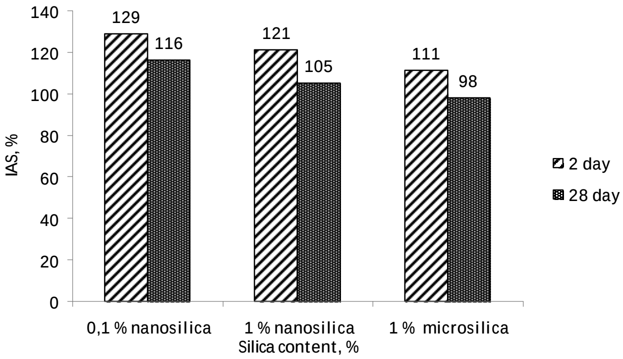


Fig. 4. Index of active strength *vs* content of ultradispersed additives

4. Conclusions

Pozzolane activity of ultradispersed silica depends on obtaining method of amorphous silica and particles size. The double increase of nanosilica activity compared with that of microsilica is connected with 4-fold decrease of particles size. The optimum content of synthetic nanosilica in mortars was confirmed by the experiments. 0.1 % of nanosilica ensures the increase of strength by 29 % for 2 days and by 16 % – for 28 days. We may assert that nanodispersed silica additive in small amounts is the most effective one at the initial stage of mortar hardening.

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ВПЛИВ СИНТЕТИЧНОГО НАНОДИСПЕРСНОГО КРЕМНЕЗЕМУ НА ВЛАСТИВОСТІ БУДІВЕЛЬНИХ РОЗЧИНІВ НА ОСНОВІ ПОРТЛАНДЦЕМЕНТУ

Анотація. *В роботі запропоновано модифікувати властивості цементного розчину з використанням малих кількостей нанодисперсного матеріалу. Досліджено вплив аморфного нано-кремнезему на процеси гідратації і твердіння портландцементу у порівнянні з відомим мінеральним додатком – мікрокремнеземом.*

Ключові слова: *нано-кремнезем, мікрокремнезем, портландцемент.*