Composite Materials Based on Cement Binders Modified with SiO₂ Nanoadditives

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Abstract. Development of nanotechnologies allows to solve a number of problems of construction materials science: increase in strength, durability, abrasion resistance and corrosion resistance that determines operational reliability of building constructions. Generally it is achieved due to nanoparticles that modify the structure and properties of the existing materials or products and are entered into their volume or on a surface layer. It’s theoretically and experimentally proved that the modified water has the bigger activity owing to the change of the ionic composition influencing the pH size and other parameters. As nanoparticles have a high level of surface energy, they show the increased tendency to agglomeration, meanwhile the size of agglomerates can reach several micrometers. In this regard an urgent task is to equally distribute and disaggregate the nanoparticles in the volume of tempering water. The experiments on studying of influence of the nanoparticles of silica distributed in volume of liquid by means of ultrasonic processing on characteristics of cement and sand solution and heavy concrete have been conducted. Nanoadditive influence on density, speed of strength development, final strength under compression of materials on the basis of cement depending on nanoadditive mass percent has been established.

Keywords: hydrothermal solution, modifiers, nanosilica, equal distribution, durability

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Introduction

According to GOST (State Standard) ISO/TS 80004-1–2014, nanotechnology is a set of the technological methods applied for studying, designing and producing of materials, devices and systems including the focused monitoring and construction management, and interaction of the separate elements of a nanodiapason (about less than 100 nanometers in one of the spatial directions). The application of nanoadditives is limited due to their increased cost and that leads to new approaches of their production. Hydrothermal solutions are raw sources for sols and SiO₂ nanopowders production.

Technology of nanosilica production from hydrothermal solutions

Mutnovsky field on the Southern Kamchatka is one of places where in the Russian Federation the hydrothermal resources (250–300 °C) are located. Due to the water phase discharge of the heat carrier of Mutnovsky geothermal power plants (1100–1200 t/h) and the SiO₂ content in the initial environment (650–800 mg/kg), the potential capacity of one field of SiO₂ production reaches up to 3–5 thousand tons per year. Hydrothermal solutions are a nonconventional source of mineral raw materials, including amorphous silicas. Silicon dioxide is formed in a natural solution of orthosilicic acids (OSA) molecules as a result of a chemical interaction of solution with aluminosilicate minerals of breeds in a subsoil of hydrothermal fields. When the solution rises to the surface through productive wells and its temperature decreases, the solution becomes supersaturated and there polycondensation and nucleation of molecules OSA leading to formation of spherical silica nanoparticles with diameters of 5–100 nanometers occur [1–9].

Silica sol has been received as follows: the water environment containing orthosilicic acid (H₂SiO₄) with concentration of 600–800 mg/dm³ is sent to from the separators of geothermal power plant (GeoPP) to the reinforced concrete tank (cooler) where polycondensation of H₂SiO₄ with formation of silica particles (SiO₂) is carried out at 63 °C. After the cooler, the separator is delivered to a baromembrane ultrafiltration installation (BMU) to concentrate and produce a stable aqueous silica sol. The technological scheme of installation is presented in the fig. 1.

Characteristics of an initial separator: salinity – 702 mg/dm³, pH = 9.73, the total content of SiO₂ Cₜ = 716 mg/dm³, concentration of dissolved silicic acid (at 20 °C) – Cᵣ = 160 mg/dm³. Pressure difference on a membrane layer is 0.14 MPa, a consumption of the solution passing through the installation – 1.2 m³/h. In the first concentration phase silica sol with a density of 1015–1022 g/dm³ and a SiO₂ content of Cᵣ = 28–40 g/dm³ is received. In the second phase sol density is 1070 g/dm³ and content of SiO₂ Cᵣ = 115 g/dm³.

Silica sol has been used for receiving the low-aggregated nanodisperse powder with cryochemical vacuum sublimation [10, 11] (fig. 2).

This mode provides the process of receiving the powders having a specific surface up to 500 m²/g, the volume of a time is 0.20–0.30 cm³/g, the average diameter of a powder time is from 2 to 15 nm, average diameters of particles are from 5 to 100 nm, density of superficial silanol groups is up to 4.9 nm², residual humidity is up to 0.2 wt%, temped density is 0.035–0.300 kg/dm³. The chemical composition of the powder received with cryochemical vacuum sublimation in % in weight: SiO₂ – 99.700; Al₂O₃ – 0.173; CaO – 0.034; Na₂O – 0.034; K₂O – 0.069 [12, 13].
Fig. 1. Apparatus for producing a stable aqueous silica sol by ultrafiltration: 1 – hydrothermal cooling separators in heat exchangers; 2 – polycondensation of orthosilicic acid and the growth of silica particles under certain temperature and pH of the water; 3 – 3-stage ultrafiltration concentration of silica nanoparticles in hydrothermal environment (membrane filters)

Fig. 2. The scheme of cryochemical equipment for receiving nanodisperse silica: 1 – device for water sol preparation; 2 – dosing pump; 3 – cryogranulator; 4 – tanker with fluid nitrogen; 5 – container for storage of cryogranules; 6 – industrial cold-storage plant; 7 – sublimation dryer; 8 – storage cabinet for finished stock

Materials. Prototypes

The portland cement (PC) which is classified as the CEM-I type in accordance with GOST (State Standard) 31108–2003 was applied as a binder of a class 42.5R. Diorite crushed stone of fraction from 5 to 20 mm in accordance with GOST (State Standard) 8267 (tempered density is 1300 kg/m³, true density – 2.73 g/cm³) and quartz feldspar sand according to GOST (State Standard) 8736 (fineness modulus (MF = 3.4 and MF = 2.9), true density – 2.62 g/cm³) mixed with standard quartz monofractional sand have been used as fillers. Nano-silica powder with a specific surface of $S_{BET} = 156$ m²/g, the average diameter of a time of $d_p = 7$ nm, the total volume of a time of $V_p = 0.298$ cm³/g and silica sol being an opalescent liquid $\rho = 1072$ g/dm³, $pH = 9.1$, with a mass fraction of $SiO_2 = 115$ g/dm³ have been used as modifiers. The additives have also been used for the improvement of mix characteristics: solution of a superplasticizer (SP) with a density of 1099 g/dm³ with the content of a solid phase of 219.8 g/dm³; complex additive “Relamiks T2” (technical conditions 5870-002-14153664–04); additive – superplasticizer of polycarboxylates series having highly effective abilities on the water reducing in the form of water solution with a density of 1082 g/dm³ and content of solid of 412 mg/g.

Silica powder was injected into a water phase until equal distribution of its powder particles in the volume of liquid using the ultrasonic processing. Then it was added to cement and sand mix, preparing the solution. The solution was poured into the prisms of standard square section ($40\times40\times160$ mm) and then put on a vibrating table and condensed. When the samples were prepared, they were released from the forms and were stored in bathtubs filled with water before reaching the certain age. The durability tests of samples at compression were carried out on the 3rd, the 7th and the 28th day.
Analysis of experimental researches results

The injection of the silica nanopowder (SN) into cement-sand-water system in the amount from 0.001 to 0.200 wt% in cement (tab. 1) leads to substantial increase in durability of the cement samples at compression up to 30–40 % in comparison with the control samples without a nanoadditive at the same age. Thus the injection of silica nanoparticles facilitates not only the increase in final durability at compression, but also in speed of strength development of samples with nanoadditives (fig. 3, 4).

Generally the density of solid cement samples changed as well as the compressive strength: it increased with the strength increase. The exception was a sample with additive of 0.04 wt%. Compressive strength with such mass additive was increasing, and density was decreasing: 0 wt% − ρ = 1970 kg/m³; 0.0075 wt% − ρ = 2000 kg/m³; 0.04 wt% − ρ = 1920 kg/m³; 0.18 wt% − ρ = 1990 kg/m³.

### Table 1

| Cement, g | Sand, g | Water, ml | SN g | % | f_c, MPa |
|-----------|---------|-----------|------|---|----------|
| Three days |         |           |      |   |          |
| 500.00    | 1500    | 200       | –    | – | 21.5     |
| 499.96    | 1500    | 200       | 0.0375 | 0.0075 | 32.7     |
| 499.80    | 1500    | 200       | 0.2000 | 0.0400 | 27.5     |
| 499.10    | 1500    | 200       | 0.9000 | 0.1800 | 35.6     |
| Seven days |         |           |      |   |          |
| 500.00    | 1500    | 200       | –    | – | 30.8     |
| 499.96    | 1500    | 200       | 0.0375 | 0.0075 | 46.6     |
| 499.80    | 1500    | 200       | 0.2000 | 0.0400 | 43.8     |
| 499.10    | 1500    | 200       | 0.9000 | 0.1800 | 47.8     |
| 28 days   |         |           |      |   |          |
| 500.00    | 1500    | 200       | –    | – | 42.7     |
| 499.96    | 1500    | 200       | 0.0375 | 0.0075 | 59.1     |
| 499.80    | 1500    | 200       | 0.2000 | 0.0400 | 50.4     |
| 499.10    | 1500    | 200       | 0.9000 | 0.1800 | 59.0     |

**Fig. 3.** Compressive strength of cement samples, depending on amount of the nanodisperse silica added

**Fig. 4.** Kinetics of strength development of cement samples in relation to the age of 28 days
Effects of silica sol additive were estimated according to the compressive strength increase of M200 mortar. The experiments on equable mixtures were carried out: the W/C of control samples without SiO₂ additive was equal to the W/C in solutions into which the silica sol was injected. Silica sol and superplasticizer solution were added to the tempered water and mechanically mixed. However at the equal W/C and equal amount of the added superplasticizer, the level of slump was lower in the solutions into which SiO₂ sol had been injected, i.e. that the liquid nanoadditive increased the viscosity and stiffness of a batch (fig. 5).

Fig. 5. Kinetics of strength development at compression of M200 mortar (W/C = 0.45):
1 – 1 % SP; 2 – 1 % SP + 0.5 % SiO₂

Gain of compressive strength with the different amounts of nanosilica additive at W/C = 0.45 on the 3rd day was ΔR₃ and on the 28th day – ΔR₂₈ (fig. 6).

Nanosilica sol increases the speed of strength development, i.e. influences the hydration processes, therefore the relation of R₂₈/R₃ becomes lower in comparison with control samples without a nanoadditive. At 3-days age the effect of the additive becomes significant: when SiO₂ increases from 0.05 to 0.50 wt% – R₃ strength monotonously increases as well. At 28-day age R₂₈ strength at W/C water/cement ratio = 0.45, at the SiO₂ flow rate = 0.05 wt% R₂₈ gain is insignificant.

The assessment of efficiency influence of SiO₂ sol on concrete strength characteristics was estimated separately and with superplasticizer. The results of samples experiments have shown that compressive strength gain at a SiO₂ dose of 0.01 wt% in cement was + 14.76 %, and at SiO₂ dose of 0.10 wt% in cement was + 21.86 %. The concrete experiments on compressive strength with injection of large amounts of SiO₂ sol nanoadditive (in amount of 0.3 %), have been carried out with superplasticizer “Relamiks T2”, which 1.0 wt% in cement had been injected at the different W/C from 0.50 to 0.38. They have shown that the effect of SiO₂ nanoadditive on concrete strength indicators is stronger that at low W/C (fig. 7).

Thus, gain of compressive strength in comparison with a control sample for 72 %, at the decrease of W/C from 0.50 to 0.39 compressive concrete strength increased almost for 85 %, bending strength – for 31 %, concrete density has increased for 7 %. At W/C = 0.38 and the given doses of nanosilica and superplasticizer the batch had the increased level of viscosity, could be barely fit in the prisms and there was a decrease in compressive strength gain to 71.8 % and in bending strength to 17.2 %. Generally the results have shown the regular decrease in compressive and bending strengths with the increase in W/C.
The effect of the sol addition on equable mixtures \((W/C = 0.61–0.71)\) was determined by testing samples of concrete of the following composition: cement (SC 550) – (345 ± 5); quartz feldspar sand – 400; standard quartz sand – 400; stone of fraction 5–20 mm – 1060.

Silica sol was injected in the amount of 2 % of cement weight. Sol dosage was calculated by the formula:

\[
V_{sol} = \left[ C \cdot \text{SiO}_2 / 100 \right] \times K_x, \tag{1}
\]

where \(V_{sol}\) – sol volume; \(C\) – cement consumption, g; \(\text{SiO}_2\) – given silica concentration, %; \(K_x\) – SiO2 content in the sol, g/dm3.

Equability of the concrete mixtures was achieved with the appropriate dosage of the polycarboxylate. The compositions of concrete mixtures are presented in tab. 2.

Analysis of experimental data leads to the conclusion that the additive of silica sol at a dose of 2 wt% SiO2 in cement in combination with the superplasticizer on the basis of polycarboxylate (PCX = 2.2–2.6 % from cement mass) results in the strength increase up to the maturity interval (1 day), this indicator reached 90–128 % (tab. 3).

Data of researches determine the use of cement systems of nanopowders and sols as modifiers, received from the hydrothermal solutions. Therefore, the mechanism of nanosilica action is complex due to the fact that nanosilica can be a filler and promote portlandite binding, form the additional centers of crystallization. Nanosilica takes part in binding of the forming lime, increases the density of system particles packing and is the center of crystallization of hydrate new growths.

The nanosilica presence influences the concentration of \(\text{Ca}^{2+}\) and \(\text{OH}^-\) ions in the liquid phase of portland cement pastes in the very first minutes of hydration in such a way that this leads to the reduction of duration of the induction period or the induction period does not occur at all. The formation of hydration products during the early period takes place with the participation of a surface of nanodisperse particles \(\text{SiO}_2\), and the surface of cement grains is blocked in a less degree with new growths that intensifies the hydration process of cement phases [5].

Thus, hydrothermal nanosilica makes triple impact on cement – it strengthens hydration, blocks times, i. e. reduces water penetration, increases the adhesion ability. The injection of silica sol makes allows to increase in compressive and bending strength, and therefore in durability of the products.

### Table 2

| Series | Composition No | Cement | Quartz feldspar sand | Standard quartz sand | Water | SiO2, % of cement | SVC 5New, % of cement |
|--------|----------------|--------|----------------------|---------------------|-------|------------------|-----------------------|
| 1      | 66             | 350    | 400                  | 400                 | 225.00| –                | –                     |
|        | 67             | 343    | 400                  | 400                 | 245.25| 2                | 2.33                  |
|        | 68             | 343    | 400                  | 400                 | 220.55| 2                | 2.58                  |
|        | 69             | 350    | 400                  | 400                 | 217.00| –                | –                     |
| 2      | 70             | 343    | 400                  | 400                 | 209.23| 2                | 2.23                  |

### Table 3

| Series | Composition No | SiO2, % of cement | SVC 5New, % of cement | W/C | Slump, cm | Mixture density, kg/m3 | Compressive strength, MPa | “Initial” strength, % \((R_1/R_{35})\) | Steam curing | Normal storage | Steam |
|--------|----------------|-------------------|-----------------------|-----|----------|------------------------|--------------------------|---------------------------|--------------|---------------|--------|
| 1      | 66*            | –                 | –                     | 0.643| 13       | 2345                  | 6.8                      | 12.0                      | 26           | –             | –      |
|        | 67             | 2                 | –                     | 2.33 | 0.715    | 10                    | 2322                     | 12.7 (+86 %)              | 19.8 (+65 %)              | 33.6 (+26 %) | –             | 38     |
|        | 68             | 2                 | –                     | 2.58 | 1.29     | 18–20                 | 2320                     | 15.5 (+128 %)             | –             | 36.4 (+37 %) | –      | 43     |
| 2      | 69*            | –                 | –                     | 0.620| 16       | 2322                  | 10.1                     | –                         | 28.5                      | 19.7                      | 35     |
|        | 70             | 2                 | –                     | 2.23 | 0.610    | 18                    | 2335                     | 19.2 (+90 %)              | –                         | 39.9 (+40 %)              | 26.6 (+35 %) | 48    |

* Compositions No 66 and No 69 – control, in brackets – the performance criteria.
CONCLUSIONS

1. The nanosilica extracted from hydrothermal solution actively influences on compressive and bending strength.

2. Due to the high specific surface of nanosilica powder the nanoparticles have high chemical activity, and acting as nanofillers – fill micropores of a cement stone that leads to the reduction increase in density and strength.

3. Silica nanoparticles influence on the hydration process, increase the speed of strength development in early terms in comparison with the control samples.

4. The effect of silica sol additive is stronger with a superplasticizer.

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