Production and characteristics of hydrothermal SiO_2 nanoparticles and applications for cement composites

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ABSTRACT

Technology of production of new type of amorphous SiO_2 sols, gels, and nanopowders with precursor based on hydrothermal solution was developed. The processes of orthosilicic acid polycondensation (OSA), ultrafiltration membrane concentration, sol-gel transition, and cryochemical vacuum sublimation were studied. The technological scheme can to regulate average nanoparticles diameter, specific surface area, density, diameters, and pore's volume of nanopowders, density of surface silanol groups, sizes of fractal agglomerates. SiO_2 nanoparticles in combination with microfiber were used for acceleration kinetics of portland cement hydration and modification the nanostructure of concrete for rising its compressive and flexural strength, water inpermeability, frost resistance and impact viscosity of destruction. Untoxic hydrothermal SiO_2 nanoparticles with high biochemical activity stimulated the growth and development of agriculural plants improved crop yields.

Keywords: Hydrothermal SiO_2 nanoparticles, orthosilicic acid polycondensation, ultrafiltration, concrete' nanostrcuture, agriculture, medicine.

1 HYDROTHERMAL NANO-SiO_2 IS A NEW TYPE OF AMORPHOUS SILICA

Amorphous nanodispersed silicon dioxide SiO_2 is currently one of the most common nanomaterials. The relatively low cost of production and its physical and chemical properties make it possible to obtain and use nanosilica in large quantities. In various forms of nanopowders, gels, xerogels, aerogels, sols and sol-gel synthesis products, nanosilica is used as an independent product or one of the components of the final product. A new renewable source for the production of nanosilica is a hydrothermal solution exists in the depths of deposits as a result of the interaction of water with rock minerals at elevated temperatures and pressures. Silica come in the hydrothermal solution as orthosilicic acid molecules.

2 TECHNOLOGY OF NANOSILICA PRODUCTION

A reagent-free technology for the production of a new type of amorphous nanosilica in the form of stable aqueous sols, gels and nanopowders has been developed (Fig. 1) [1, 2, 3]. Its physical and chemical characteristics are studied and directions of application in industry are proposed: first of all, in the production of Portland cement concrete, growth stimulators of agricultural plants and medical preparations.

The production technological scheme includes the processes of polycondensation of orthosilicic acid OSA molecules in a hydrothermal solution and the assembly of SiO_2 nanoparticles with an adjustable size [1, 2, 3]. By the selection of the pore diameter at the stage of ultrafiltration membrane concentration [3], SiO_2 nanoparticles and ions of dissolved salts are separated in such a way that the degree of concentration of SiO_2 nanoparticles becomes many times higher than that of ions. As a result, the thickness of the double electric layer and the zeta potential of the surface of the nanoparticles ensure the stability of concentrated aqueous sol with a SiO_2 content of up to 40 wt. % and higher. By the process of sol-gel transition with a decrease in pH values in the range of 5-6, SiO_2 gels are obtained. Using the processes of coagulation and vacuum sublimation, SiO_2 nanopowders are extracted from sols. The technology allows you to adjust the structural and morphological characteristics of nanopowders and gels. Three forms of hydrothermal nanosilica – sols, gels, nanopowders - have physical and chemical properties that allow us to find a number of applications. Hydrothermal nanosilica has a high specific surface area of up to 500 m^2/g, high density of surface silanol groups up to 4.9 nm^{-2}, low degree of crystallinity, small size of fractal agglomerate about 30 nm, high sorption ability and chemical activity of the surface, non-toxicity [2]. The exclusion from the technological scheme of traditional chemical reagents such as sodium silicate, acids, alkalis, ion exchange resins and low specific consumption of electrical energy lead to a low production cost of hydrothermal nanosilica. The final particle sizes of silica depend primarily on the temperature and pH at which the polycondensation of the OSA molecules takes place. An increase in the polycondensation temperature and a decrease in pH slow down the reaction and increase the final particle size. At the polycondensation stage, the temperature ranged from 20 to 90°C (pre-cooling in heat exchangers), pH - from 9.2 to 4.0 (solution acidification). The range of silica concentrations in the initial solution is C_t= 400-800 mg/kg (the sum of the concentrations of the colloidal phase and dissolved silica). The exclusion from the technological scheme of traditional chemical reagents such as sodium silicate, acids, alkalis, ion exchange resins and low specific consumption of electrical

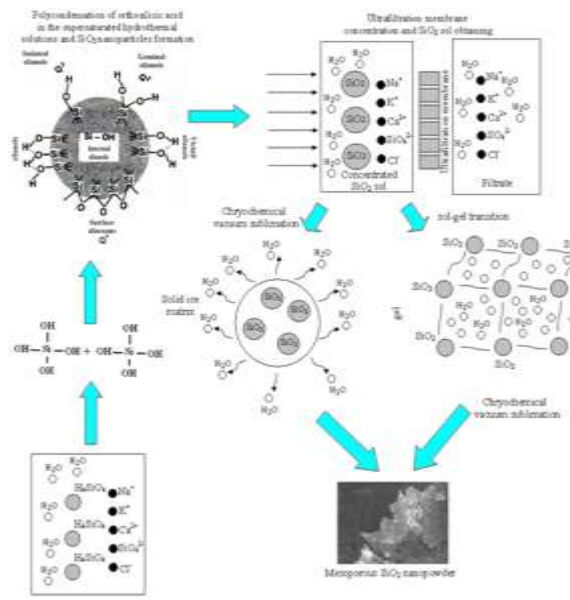

Figure 1. Technological scheme of hydrothermal nanosilica production.

energy lead to a low production cost of hydrothermal nanosilica.

The final particle sizes of silica depend primarily on the temperature and pH at which the polycondensation of the OSA molecules takes place (Fig. 2). An increase in the polycondensation temperature and a decrease in pH slow down the reaction and increase the final particle size. At the polycondensation stage, the temperature ranged from 20 to 90°C (pre-cooling in heat exchangers), pH - from 9.2 to 4.0 (solution acidification). The range of silica concentrations in the initial solution is C_t= 400-800 mg/kg (the sum of the concentrations of the colloid phase and dissolved silica).

Concentrated silica sols were obtained from the liquid phase of hydrothermal solutions after OSA polycondensation by 3-step ultrafiltration membrane concentration: at the first step, the SiO_2 content in sol was increased from 0.05 to 0.3-0.4 wt. %, at the 2nd step- up to 10 wt. %, on the 3rd - up to 20-30 wt. % and higher. The capillary type ultrafiltration membrane cartridge had an inner diameter of capillaries of 0.8 mm, a filtering surface area of 55 m^2, and a minimum mass weight cut off parameter MWCO = 10-100 kD.

Gel samples were obtained from concentrated sols by acidification and lowering the pH from 8-9 to 5-6.

SiO_2 nanopowders were obtained by cryochemical vacuum sublimation of sols and gels. Before sublimation in a vacuum chamber, the sols and silica gels were dispersed using a nozzle, the droplets were solidified in liquid nitrogen at a temperature of 77 K, and cryogranules were obtained. After dispersion, the droplet size was 30–100 μm, the corresponding average droplet cooling rate was about 125 K/s, and the crystallization rate was 0.26 mm/s.

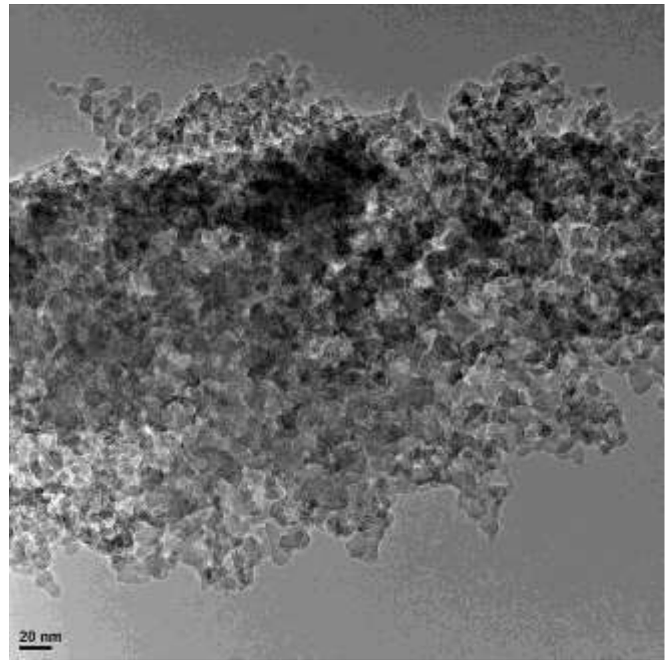

Fig. 2. TEM-image of hydrothermal SiO_2 nanoparticles extracted from the sol's sample. The specific surface area of the nanoparticles, determined by the method of low-temperature nitrogen adsorption, S_{BET} = 410 m^2/g, the average surface particle diameter d_{BET} = 6.65 nm.

The small size of the sol droplets, as well as the high heat transfer surface made it possible to achieve a quick hardening of the droplets, and the absence of particle coagulation. The particle sizes in the powders did not exceed the particle sizes in the sols. Vacuum sublimation took place at pressures of 0.02 - 0.05 mmHg without fragments of droplet moisture and particles sticking together. To accelerate sublimation, the heating was used. The temperature range of the heating surfaces in different parts of the vacuum chamber as it was heated during sublimation was from -80 to +25ºC.

The results of a series of experiments to study the effect on the kinetics of polycondensation of the pH of an aqueous solution at 20ºC were obtained. Before starting measurements, water samples were heated at 96-98 ° C to dissolve colloidal silica, then quickly cooled to 20°C and acidified to a predetermined pH value. Time τ_p of decreasing of supersaturation degree in 2.71 times for different pH values was as follows: pH = 8.0 - τ_p = 9.2 h; pH = 7.0 - τ_p = 14.2 h; pH = 6.0 - τ_p = 225 h; pH = 6.0 - τ_p = 225 h; pH = 5 - τ_p = 377.5 h, pH = 4.0 - τ_p = 3240 h. A decrease in pH to 5.0-4.0 was lead to an almost complete inhibition of the polycondensation of OSA.

With a decrease in the polycondensation temperature and an increase in the initial supersaturation S_m the nucleation rate increased and, accordingly, the final average diameter d_m of SiO_2 nanoparticles decreased, the polycondensation of OSA passed faster. At pH = 8.5–9.3 and temperatures of 65–90°C, the d_m values were 59–90 nm, at 40–65°C, d_m = 40–60 nm, and at 20–40°C, d_m = 5–40 nm.

3 HYDROTHERMAL NANOSILICA IN CONCRETE

In Portland cement concretes, hydrothermal SiO_2 nanoparticles, due to their high and chemically active surface, accelerate the kinetics of the formation of calcium hydrosilicates gel, reduce capillary porosity, regularize the gel structure, increasing the volume packing density of the gel nanogranules and increasing its modulus of elasticity and modulus of shear [4, 5, 6]. Nanomodification of concrete with hydrothermal SiO_2 leads to an acceleration of compressive strength gain: by 2 times at the age of 1-3 days and by 40-60 % at the age of 28 days. An increase in flexural strength and axial tension strength is achieved. The mechanism of material destruction changes and the fracture toughness and fracture energy coefficients increases. The most powerful effect of the influence of nanoparticles on the structure of concrete is expressed in an increase in the ability to dissipate the impact energy of destruction and an increase in the impact viscosity. Modification with nanosilica increases the durability of concrete: water resistance, frost resistance and abrasive resistance. The modification of concrete at different scale levels has a significant prospect. When modifying concrete with a combination of hydrothermal nanoparticles SiO_2 – basalt microfiber, a synergistic effect is manifested: the flexural strength increases by 3.4 times, the specific energy of impact destruction - by 22.2 times (Fig. 3, 4), the impact viscosity coefficient - by 2.7 times. Nanomodification with hydrothermal SiO_2 nanoparticles is used in heavy weight concrete, and also has broad prospects for use in concrete with cement-substituting materials – silica, fly ash, slag, aluminosilicate additives, in monolithic and block construction, construction of transport bridges, 3D-printing.

SEM images of the cement matrice structure can be used to judge about changes due to modification by hydrothermal SiO_2 nanoparticles. The modified cement paste has a denser structure. The modified cement paste structure includes a greater amount of low-base hydrosilicates of calcium, while there are more high-base hydrosilicates in the non-additive cement matrice and hexagonal plates of portlandite are present. These differences in structure can be explained by: 1) the contribution of the pozzolanic reaction between SiO_2 nanoparticles and portlandite with a transition to low-basic calcium hydrosilicates; 2) the appearance of additional crystallization centers of calcium hydrosilicate particles due to the high specific surface area of SiO_2 nanoparticles and, accordingly, a decrease in the final size of calcium hydrosilicate particles and an increase in the degree of their polymerization and the volume density of their packing. An additional factor may be the role of a micro-filler with SiO_2 nanoparticles in the structure, meso- and macropores of the cement matrice. An increase in the compressive strength of concrete, a decrease in the volume, average pore diameter and an increase in the uniformity of the pore diameter distribution occurs due to a change in the structure.

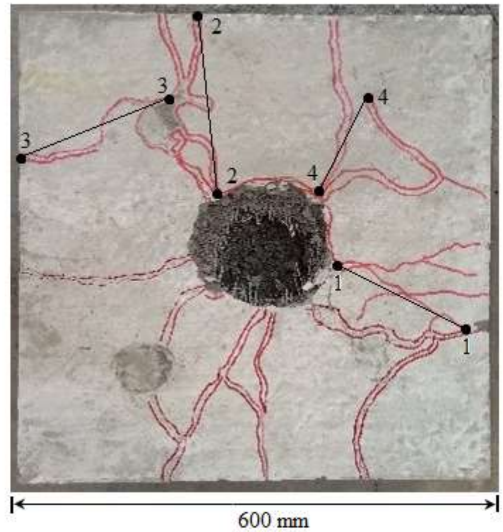

Figure 3. The surface of the concrete after complete impact destruction (maximum number of blows N_{cd}).

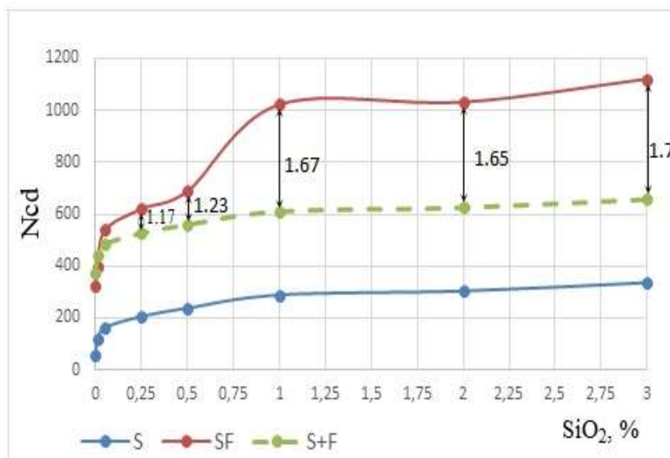

Figure 4. Number of blows N_{cd} of complete destruction of concrete samples modified with SiO_2 sol (S) and with combination SiO_2 nanoparticles-basalt microfiber (SF) depending on the dose of SiO_2 nanoparticles.

The possibility of obtaining cement composites based on different-scale modifiers is shown: hydrothermal SiO_2 nanoparticles 0.01-3.0 wt. % in the form of sol and nanopowder and basalt microfiber 1.5 wt. %. The developed series had high rheological characteristics, increased mechanical characteristics of compressive strength in 28 days age F^{28}_{com} - up to 51.1 MPa, flexural strength F^{28}_{flex} - up to 13.2 MPa, early strength development, impact viscisity of destruction N_{iv} up to 26-30, specific energy of impact destruction E_{im}/S_c up to

199.94 kJ/m^2. The largest increment during modification with a combination of SiO_2 nanoparticles - microfiber was observed in impact destruction viscosity. Cement composites have shown an increase in durability indicators: water resistance, frost resistance, abrasiveness. Cement composites have different areas of application: in monolithic construction, block prefabricated structures that require increased flexural strength and crack resistance, increased ability of impact energy dissipation, in compositions with cement substitute and supplementary materials, microsilica, fly ash, in and road surfaces.

The use of basalt microfiber without SiO_2 nanoparticles, leading to the manifestation of shear stress between the lateral surface of the microfiber and hydrates of calcim silicates CSH-gel, led to a significant increase in the flexural strength: at the age of 1 day - 1.1 MPa (+ 22.2%), 7 days - 4.3 MPa (95.45 %), 28 days - 8.6 MPa (+120.5%). The increase in the effect of F_{flex} increment with the age of the cement composite is associated with an increase in the volume of CSH-gel during cement hydration. The effect of increasing the flexural strength F_{flex} of cement composites modified with SiO_2 nanoparticles and basalt microfiber at the age of 1 day was significantly higher than the effect of the increase in compressive strength - (63.6 - 236.3)%, at the age of 7 days - (2.3 - 46.5)%, 28 days - (4.6 - 38.3)%. The absolute F^{28}_{flex} value for the 3 wt. % SiO_2 composition reached 11.9 MPa, which is 3.05 times higher than in the control sample without nanoparticles and microfiber. The $F^{28}_{flex}/F^{28}_{com}$ ratio for the series SF (SiO_2 – microfiber) more than doubled from 0.11-0.12 to 0.25 compared to the series S (SiO_2). The synergistic effect of two different-scale modifiers at a dose of SiO_2 nanoparticles of 3 wt. % compared to the simple sum of the absolute increments in flexural strength due to the independent action of SiO_2 and microfiber nanoparticles at the age of 1 day was 2.33 times higher, at the age of 7 and 28 days it was 1.26-1.29 times higher. The synergistic effect for F_{flex} was achieved by increasing the volume fraction of the HD phase of the CSH gel with an high volume packing density of nanogranules and increased modulus of elasticity, within the volume of which the shear stress of the CSH gel increased relative to the lateral surface of the microfiber. The contribution of nanoparticles to the synergistic effect was higher at an early age of 1 day due to a relatively larger increase in the volume of CSH gel at this stage of alite C_3S hydration and a relatively larger contribution of the pozzolanic reaction.

3 PROSPECTS OF APPLICATIONS OF HYDROTHERMAL NANOSILICA IN AGRICULTURE AND MEDICINE

A sufficiently developed application of hydrothermal SiO_2 nanoparticles is the intensification of photosynthesis in chloroplasts of plant cells due to the photoluminescent radiation of SiO_2 nanoparticles. SiO_2 nanoparticles due their optical properties can absorb solar radiation in ultraviolet region with wave length of 200-360 nm and emit of luminescent radiation in visible region with wave length of 400-500 nm in which efficiency to absorbe radiation by photosynthetic pigments and caratinoids is high. An increase in the proportion of photosynthetic pigments of chlorophylls a (62 %) and b (79.3 %) [2], as a result, an increase in the growth rate, biochemical and biometric indicators at all stages of plant growth and development, a significant increase crop yields of agricultural plants from 9 to 60 %, increase of contents of caratinoids - 14.5 %, B_2 - 130 %, B_5 – 60 %, B_6 – 230 %, B_9 - 230 % and C – 14.4 % vitamins [2] and rising biological activity of raw plant's mass with respect to cultures of Daphnia magna – 352 % and Paramecium caudatum – 90.5 % [2]. Hydrothermal SiO_2 nanoparticles have great inhibition ability on microflora [2].

Hydrothermal nanosilica used as a feed additive that increases the productivity of farm animals (8-10 %), rate of mass growth (10-40 %), bone's strength (17 %), blood characteristics (Ca/P relation) and immunity (25 % rising of the proportion of big forms of lymphocytes) [2].

Non-toxic [2] hydrothermal SiO_2 nanopowders can be the basis for the creation of medical preparations:

- enterosorbents,
- drugs that improve the structure of bone, strength and plasticity of the articular-bone tissue and reduce Ca leaking.

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