

Processing and Application of Ultra disperse Wastes of Silicon Production in Construction

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Abstract. One of the promising applications of nanosilica is the modification of the properties of concretes and mortars to achieve improved performance characteristics and reduce construction time. This direction was called UHPC (Ultra High Performance Concrete). The global trend is to use of nanosized particles with a large surface area and high pozzolanic activity. Nanosilica is the modifier of "nanoconcretes" that is most accessible for mass use. The nano-dispersed silica dust, which is a product of a gas scrubbing in the ore-thermal production of silicon-containing alloys, contains about 75-85% of SiO₂ and a large amount of foreign impurities such as carbon, silicon carbide, iron, etc. Due to the low purity, crude gas scrubbing product finds wide use only in the construction industry as a mineral additive to cements. The cost of the initial gas scrubbing product is in the range from 5 to 20 thousand rubles per ton. Studies on the preliminary scrubbing of the crude product were carried out. A gas scrubbing product enriched to a silica content of 98% was obtained. Experiments to modify concrete with new enriched material in construction, in ferrous and non-ferrous metallurgy were carried out.

1. Introduction

Construction is an industrial sector that consumes a huge amount of materials of different nomenclature. Reducing the cost of construction works, reducing the cost of industrial and civil constructions without reducing the quality is one of the most important tasks, especially acute in the crisis periods of economic development. An attractive way to achieve these goals is to modify materials traditionally used in construction, such as concrete, as well as the development of new technologies, new competitive types of materials.).

2. Relevance and scientific significance of the issue with a brief literary review



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The use of concrete of various mineral additives, including those that are waste products, for example, of metallurgical production, in the production allows to solve several tasks, the most important of which is to increase the mechanical properties and performance characteristics of concrete while reducing the cost of the final product. However, another important task can be solved along the way - reducing the environmental load, as recycling of waste and their involvement in the further technological process will help unload sludge storages and waste storage sites, which are indispensable objects of large metallurgical productions. At the same time, costs of the respective productions for the maintenance of these facilities will be reduced. Studies, related to the processing of wastes, intensified in the second half of the twentieth century. Study of solid fraction of gases of metallurgical production produced after filtration made it possible to determine that it represents small particles of silicon dioxide. Since pozzolanic activity of this substance was already known, the first attempts to use this product for modifying concrete were made. This waste is condensed aerosols and, according to the generally accepted classification, belongs to the category of fumes. High efficiency distinguishes it among mineral additives for concretes. To date, there is a huge amount of publications about microsilica and microsilica concretes. In 1989, possibility of using ultradisperse wastes of ferroalloy production in combination with chemical additives as a microfiller for concretes was studied [1].

The possibility of using waste products of various metallurgical industries as secondary raw materials in the technology of obtaining concrete requires their detailed study with the object to make objective assessment of their effect on the properties of concrete, since the physicochemical properties of microsilica may differ significantly. Such factors as the composition of the melted alloys, technology of gas scrubbing of furnaces and the collection of waste fumes, have a decisive influence on the properties of the wastes. In further studies [2-5] it became clear that the use of silica-containing additives to modify concrete allows not only to save expensive cement, but also to improve important performance characteristics, for example, concrete placeability, frost resistance, corrosion resistance.

To study the modification of concrete with SiO₂ nanoparticles, a material prepared at the lab specifically for research was used [7]. The cost of such materials is much higher than the waste products.

3. Research objective

The purpose of this study is to determine the possibility of using pre-processed wastes of silicon for the modification of concretes.

4. Results of experimental studies

Dusts of gas scrubbing of electrothermal production of silicon and silicon ferroalloys belong to the group of sublimated dusts formed during evaporation in the high-temperature zone and subsequent condensation of sublimations.

Silicon-containing dust of electrothermal productions has an extremely low bulk density - 0.18-0.22 g/cm³, which makes it very difficult to transport and process it. Such dust contains a large number of spherical particles with a high content of amorphous silica.

However, dust composition of the silicon furnaces in the original form does not allow to use this waste as an additive to the concrete (in decreasing order): SiO₂ - 52.55%, C - 44.59%, SO₃ - 0.947%, CaO - 0.841%, Al₂O₃ - 0.295 %, K₂O - 0.255%, MgO - 0.165%, Fe₂O₃ - 0.157%, Na₂O - 0.086%, P₂O₅ - 0.059%, MnO - 0.0172%, TiO₂ - 0.01%.

In [6, 17-20], technology for processing wastes from silicon production was proposed.

The initial material of gas scrubbing of waste gases of electrothermal silicon production in ore-thermal furnaces is used in this work. According to electron microscopy, sludge consists mainly of spherical SiO₂ particles and carbon with an average size of 100 nanometers [11-14].

One of the effective ways of extracting carbon and amorphous microsilica from cyclone dust is flotation, during which separation of fine solid particles occurs due to the fact that their surface properties are significantly different.

Hydrophobic poorly water-wettable particles (particularly carbon) are selectively attached to the interphase boundary (usually of gas and water) and rise up to the surface to form a foam product. Thus, they are separated from the hydrophilic well water-wettable particles, which precipitate to form a flotation tail. As flotation agents were used: foaming agents - diesel fuel, kerosene; collectors - pine oil, dimethylate.

As a result of flotation, a flotation tail in an amount of 31% was obtained, a foam product - in an amount of 40%, remainder - sand fraction.

Analysis of the flotation tail made with the use of Pioneer S-4 spectrometer showed that, compared to the initial dust, flotation tail is enriched in microsilica - the SiO_2 content was 75.12%, carbon content was 22.04%.

Slurry of flotation tail was coagulated, wherefore solution of aluminum sulfate of concentration 10 g/l was used as the coagulant, and flocculated. Flocculant was a solution of magnafloka concentration of 0.1 g/l. After this, centrifugation was carried out, as a result of which a thick suspension (precipitate) formed at the bottom of the vessel. The carbon content in the suspension is reduced to 5.36%, which was determined by a tubular laboratory electric resistance furnace SOUL-0,25.1/12.5-II UHL 4.2 in accordance with GOST 23581.9-79, clause 3. The rest part of the solution is drained. The suspension contains silica in the form of marbles, most of which are less than 0.5 μm in diameter.

Proposed technology makes it possible to isolate microsilica as a product-suspension with a moisture content up to 42%, which differs in chemical and granulometric composition from products of similar type given in [2, 3, 4]. Average particle size of silica allows us to apply the term "nanosilica" to this product.

Obtained product was used as a modifier of concrete. The results of the studies [2,3,4,7] helped to determine the approximate values of the concentration of the modifier for comparative tests.

To carry out experiments on the effect of the modifier on the strength, 2 series of samples with different concentration of the modifier, obtained by the described technology, were prepared.

Both series of samples were produced with the use of cement of the brand PC M400 D20 of the Angarsk cement plant. Value of water-cement ratio was 0.4, coefficient of grain separation was $\alpha = 1.1$. The concrete components were taken in the following ratio: cement/sand/gravel/water - 1: 1.2: 3.5: 0.4, so 1 m³ of concrete included cement - 375 kg, sand - 470 kg, gravel - 1300 kg and 150 liters of water.

Samples had standard for testing geometric shape and parameters - cubes with an edge of 10 cm. Experiments to determine the compressive strength were carried out on the test press IP-1000 M-auto equipped with an automated digital measurement and control system ASTM-Digital, which allows to visualize the loading process in form of diagrams "load-deformation", "load-time", "deformation-time" with an indication of current values of load and deformation. The test was carried out in automatic mode in accordance with GOST 10180 [9].

Samples of the first series were hardened under normal conditions for 15 days, after which they passed the strength tests. Concretes with the content of 5%, 10%, 15%, 20% of the modifier from the mass of cement were prepared. Also, for comparison, reference samples without additives were prepared

The results of the first series of tests testify that with the increase in the content of the modifier up to certain values, the strength of the samples from the modified concrete increases in comparison with the reference unmodified samples. The highest hardening was shown by samples with a modifier concentration of 10% of the mass of the cement. To destroy the reference sample, an effort of 63.5 kN was required, whereas the destruction of the sample with a ten percent concentration - an effort of 99.3 kN. Diagrams of loading of the samples are shown in Figure 1.

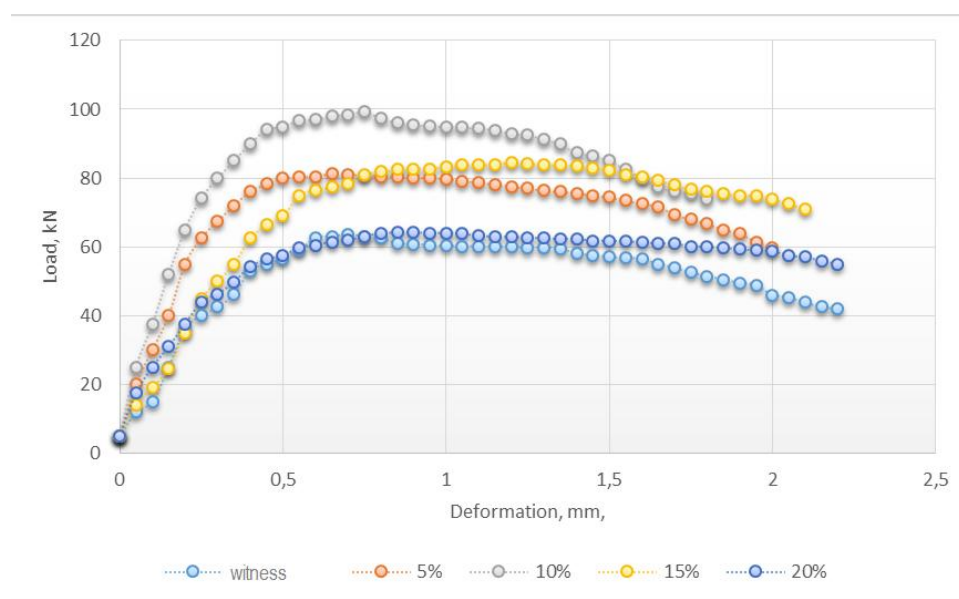


Figure 1. Diagram of loading of concrete samples (first series).

Samples of the second series at the age of 6 days were subjected to wet steaming for 3 days and drying for 4.5 hours, after which they also underwent compressive strength tests. The purpose of steaming is an accelerated getting of concrete strength. This type of processing allowed to "artificially" age the concrete, up to the required "project" age of 28 days [8, 13, 15, 16]. Concentrations of additives in the concrete of the second series were 7%, 9%, 11%, and in this case also reference samples were prepared for comparison. In this case, such concentrations were chosen in order to determine the concentration, at which the greatest strength is achieved. The test loading of the samples of the second series is shown in Figure 2.

Tests of the second series revealed the best concentration, which provides the maximum strength - 9% of the nanomodifier from the mass of cement.

To destroy the reference sample of the second series, an effort of 68.5 kN was required. The most durable one of the modified samples required an effort of 143.2 kN (concentration of the modifier in this case was 9% of the mass of the cement). Great efforts, that were required to destroy the samples of the second series, are explained by the fact that the samples of the first series were not fully sustained, therefore the maximum values of the efforts expended for their destruction are much smaller.

In work [3], basic mechanisms of the structure formation of a mixed system when a modifier was introduced into concrete were determined. Two factors were singled out. The first factor associated with the size and high surface energy of the particles of ultradispersed material is expressed in the filling of the volume between the coarsely dispersed particles of cement and the formation of numerous coagulation contacts, and in filling the space between the crystalline hydrates in the resulting structure. The second factor associated with the chemical-mineralogical composition of ultradispersed material is expressed in a change in the balance between hydrate neoplasms in the structure toward an increase in the content of stronger and more stable secondary hydrates.

Our investigation on the Shimadzu XRD-7000S diffractometer made it possible to determine that a large number of crystalline neoplasms are present in the reference samples of concrete. At the same time, traces of the amorphous phase can be clearly traced in the modified sample.

From the point of view of the structural composition, content of Portlandite $\text{Ca}(\text{OH})_2$ has changed as follows - in the reference sample, content of this phase is 2.55%, while in the modified sample it is 14%. At the same time, a decrease in the SiO_2 content in the modified sample was observed - from 12.29% to 6.34% compared to the reference one.

This is explained by the fact that amorphous microsilica forms complex complexes with crystalline Ca (OH) ₂, and only the crystalline part of the complex compound is detected by the diffractometer. In the modified sample, proportion of the amorphous component responsible for the strength is 7% larger. In this connection, it can be assumed that the resulting complex compound leads to significant changes in the structure of concrete. These changes, both in terms of structural compacting and in terms of composition changes, lead to an increase in strength in modified samples [21].

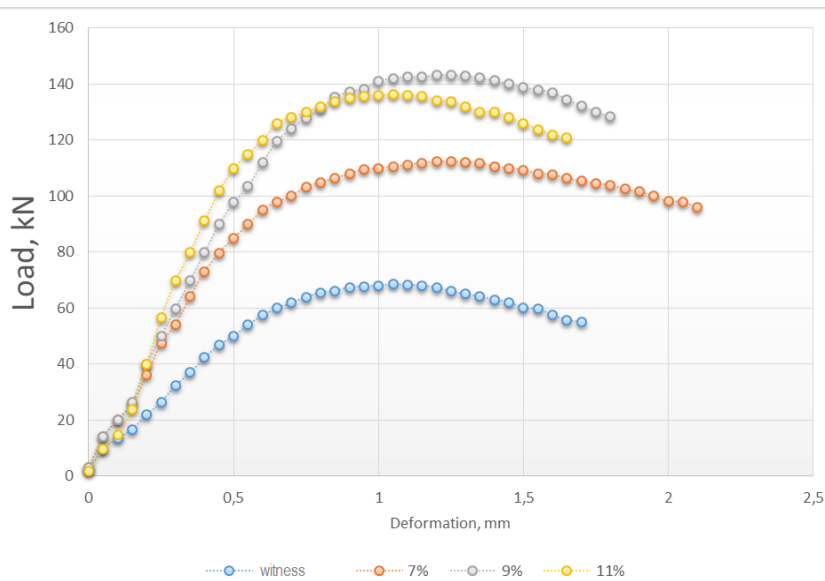


Figure 2. Diagram of loading of samples of "aged" concrete (second series).

5. Conclusions

1. Technology of processing of silicon production wastes with the purpose to obtain a product with a high content of ultradisperse silica is proposed.
2. Prospects of using this product as a modifier of concrete are demonstrated.
3. Possibility of increasing the strength characteristics of concretes more than twofold when modifiers are introduced into them is shown.
4. Optimal concentration of the additive for the most effective hardening was determined.
5. Assumption of a possible mechanism of hardening was proposed.

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