

Improvement of the modified heavy concrete properties based on the use of activated silica fume

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Abstract. This article deals with the use of silica fume and ways of its activation to modify the structure of cement stone and concrete on its basis. With regard to any type of filler, namely silica fume, questions that are relevant: how to enter and how many, what mechanisms are involved in the process of structure formation, how much it costs achieved by the effect of modifying the structure and others. Formation of the answers to these questions require a systematic approach to vision problems. Therefore the role of microdispersed fillers in the modification process of the cement stone and concrete structures based on it must be considered together with other sized inclusions at different scale levels. The technology of synthesis of the complex additive based on ultrafine microsilica and superplasticizer “Plastilit RK” with characteristics allowing to use it as an effective additive in concrete has been developed. Studies have confirmed the effect of micro-silica fume in an acid medium (pH=2.1), enriched with oxonium H_3O^+ ions, oxonium cations provide H^+ , and in an alkaline medium (pH=10-11), enriched with hydroxyl groups OH^- - anions OH^- , with obtaining dimers of orthosilicic acid $Si(OH)_4$. It was shown that orthosilicic acid particles formed during the chemical dispersion of silica fume are additional crystallization centers, which allows speeding up the process of cement hydration.

1 Introduction

The relevance of this work involves finding ways to improve the properties of concrete and quality characteristics of products on their basis. One simple and effective methods of modifying a cement matrix structure due to initiate activity mineral administered in concrete additives. In this work, the task was to reduce the silica fume consumption and increase its efficiency in cement concrete due to chemical activation. The aim of research is to develop a technology of concrete with improved physical and mechanical properties based on the use of chemically activated silica fume as a part of the complex organic-mineral additives. The methodological basis of the research was the basic provisions of building materials science in the field of structure formation of cement concretes, as well as

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the provisions of modern chemistry concerning the methods of converting silica fume particles to the active form.

The theoretical basis of the work was the research of domestic and foreign scientists dedicated to the structure of cement composites and the problems of modifying hydration systems hardening due to mineral and chemical additives. Based on the works of Korolev E.V., Kaprielov S.S.[1, 2] concerning the behavior of amorphous quartz in water, acidic and alkaline medium, and given information on the modification of concretes, where the most optimal are complex additives containing related to the crystal-chemical structure of the SiO_2 particles, it is believed that the chemical activation of silica fume is inexpensive and promising direction for modifying structure of cement stone and concrete on its basis. A special role belongs to the fillers, and particularly micro- and ultrafine fillers in the structure formation of cement stone and concrete on its basis, as they can participate not only in improving the packaging system, to reduce the amount of capillary-bound and free water, due to increased adsorption and chemisorption of water to bind them, can serve as crystallization centers and lower the energy threshold of this process, but also participate in heterogeneous phase formation processes of hydrate compounds [3,6,9]. To enhance the effect of the action of fillers, and a corresponding increase in the quality of the cement matrix and concrete on their basis, including the reduction of consumption, developed many ways to activate: regrinding, mechanical-chemical, vibroactivation, turbulent, acoustic, electromagnetic, thermal, atherothermal, electric pulse, and also activation with modified water [4-7]. Analysis of literature sources showed that one of the active effective pozzolanic mineral additive for cement and concrete matrices based on it, is silica fume - powdered waste of the ferroalloy production, containing SiO_2 at least 91% [10]. The effect of improving the quality of concretes with silica fume is greatly enhanced if silica fume is introduced in concrete mix as part of the complex with the superplasticizers or with additional organic-mineral additives that gives background chemical activation silica fume such additives [1,9]. In articles of chemistry and geology scientists have established experimentally that the amorphous silica may be dissolved in acid and converted into orthosilicic acid (H_4SiO_4 or $\text{Si}(\text{OH})_4$), and in an alkaline medium to transfer to the sodium salt or orthosilicic acid of potassium [9,11]. Established that silica containing nanomodifier role can perform sol solution (H_2SiO_3) met-silicic acid from soluble glass Na_2SiO_3 . One of the prerequisites for the selection of the activation of silica fume in this work was a chemical method, expressed in the treatment of concrete mixing water by the electrolysis method. It was found that the nature of the chemical activation action with regard to the silica containing fillers poorly understood, in this regard, the advanced leading scientific concept put forward is relevant.

In chemical activation with acids or salts which reduce the pH of the medium, as is known, steel reinforcement of ferroconcrete products corrosion increases. For this reason, washing water recommended after the treatment of fillers and excipients with acids, which is economically disadvantageous. Thus, on the basis of the foregoing, in this work the decision was made to carry out a chemical fume activation in an alkaline medium. Based on these studies [12-18] on the behavior of amorphous silica in an alkaline medium, it can be assumed that the chemical activation of the silica fume is a promising direction for modifying cement stone and concrete on its basis in the complex supplements. This use of silica fume can solve several problems both to improve the ecology of the Russian Federation (silica fume - waste production) and private organizations (relatively low consumption of activated silica fume).

2 Materials and methods

In studies on the development of concrete mixtures compositions, materials with the following characteristics were used: Portland cement CEM I 42.5N produced by "EUROCEMENT group" JSC - as a binder, compliant with GOST 31108-2016 "General construction cement. Technical conditions" and GOST 30515-2013 "Cements. General technical conditions." The natural sand of the Kapyikha open pit, located in the village of Balakirevo, Vladimir region with a size module 2.5, was used as fine aggregate. The properties of sand were determined by methods in accordance with GOST 8735-88 "Sand concrete for construction quality. Test data methods". It was established that the proposed sand according to the content of clay, dust and organic impurities, the particle size distribution correspond to the standard requirements of GOST 8376-2014 "Sand for construction works. Technical conditions". Granite crushed stone (DorNerudResurs LLC, Saratov) of a fraction from 5 to 20 mm corresponding to the requirements of GOST 8267-93 "Crushed stone and gravel from dense rocks for construction works" was used as a large aggregate. Mixing water corresponds to GOST 23732-2011 "Water for concrete and mortars. Technical conditions". The content of sulfate does not exceed more than 2,700 mg /l (in terms of SO₄) and all salts more than 5,000 mg /l.

As a superplasticizer used superplasticizer "Plastilit RK", the product of "NPO SYNTHESIS" LLC. According to its consumer properties, the additive "Plastilit RK" meets the requirements for plasticizing and water-reducing additives GOST 24211-2008 "Additives for concrete and mortars. General technical conditions". As a chemical reactionary pozzolanic additive, powdered waste of silica fume MK-85 from ferroalloy production by "Kuznetsk Ferroalloys" OJSC with a particle size of 5-50 microns, which under the action of high temperature are converted into glassy amorphous dust, was used.

In this work we investigated the processes of physical and chemical activation of silica fume and studied hardening processes, structure formation of cement stone and concrete of various compositions based on it, modified by obtained additives. Experimentally determined the amount and size of silica fume dispersion products obtained by chemical activation by laser diffraction (Analyzette 22 particle size analyzer) and the phase composition of the resulting additive by X-ray phase analysis (ARL X'TRA diffractometer) and IR-spectroscopy (IR-spectrometer Varian 640-IR).

Efficacy plasticizing additives ability was evaluated by the change of workability of the concrete mix and the concrete strength of the proposed composition compared to the control composition. Treatment of the test results of concrete compressive strength was carried out according to GOST 10180-2012 "Concretes. Methods for determining the strength of the control samples".

3 Results

Effectiveness of the additives was evaluated to improve the mechanical and physical-chemical properties of the modified materials. To determine the optimum content of silica fume in concrete, intended for manufacturing of effective ferroconcrete high-speed lines sleepers, the range used in an amount of 5% by weight of cement. The optimum content of additive was determined by the change in the compressive strength of samples cubes measuring 15×15×15 cm after 28 days normal hardening.

The test results, presented in Table 1 and Figure 1, indicate that the optimum content of silica fume is 15%, the increase in strength relative to the control sample is 33.39%.

Table 1. Composition and results of concrete tests

| № | Materials | Composition, kg / m ³ | | | | |
|---|--|----------------------------------|----------------|----------------|--------------------|-------------------|
| | | Control | №1 (10% MC) | №2 (15% MC) | № 3 (20% MC) | №4 (25% MC) |
| 1 | CEM I 42,5N | 420 | 378 | 357 | 336 | 315 |
| 2 | Water | 147 | 147 | 147 | 147 | 147 |
| 3 | Granite rubble | 950 | 950 | 950 | 950 | 950 |
| 4 | Sand | 845 | 845 | 845 | 845 | 845 |
| 5 | Superplasticizer "Plastilit RK" | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 |
| 6 | Silica fume MK-85 | - | 42 | 63 | 84 | 105 |
| 7 | W/S (C + SF) (Water-Solid relationship – Cement + Silica fume) | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 |
| 8 | The compressive strength at 28 days, MPa | 47.04 | 53.17 | 62.76 | 45.03 | 30.81 |

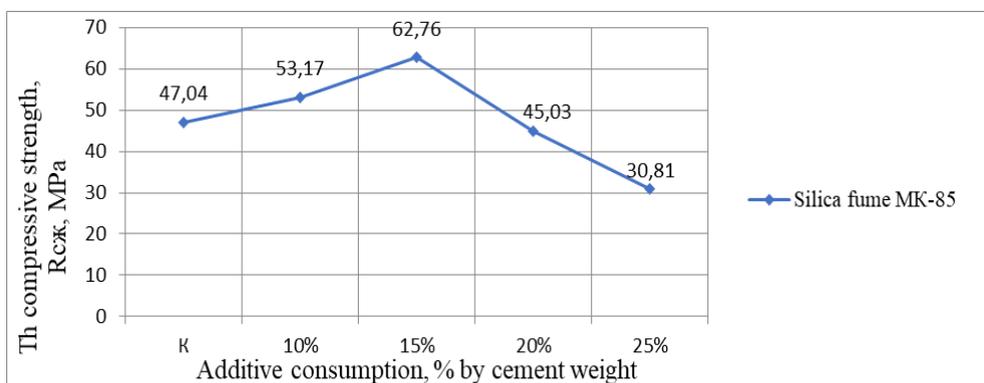


Fig. 1. The dependence of the compressive strength of concrete the additive consumption

Using spectroscopy, shown in Figure 2, shows the infrared (IR) spectra of the silica fume (MK): in the dry condition and treated by activated waters of "acidic water (AcW)" and "alkaline water (AlW)" types and the IR spectrum of the quartz glass, which was taken as a reference sample.

From the IR spectra it can be seen (Fig. 2) that the oscillation region of quartz glass coincided with silica fume mixed with water treated by electrolysis with pH = 2.1-3,0 enriched with oxonium ions H₃O⁺ (type AcW) and with water treated by the method of electrolysis with pH = 10-11, enriched with OH⁻ hydroxyl ions (type AlW).

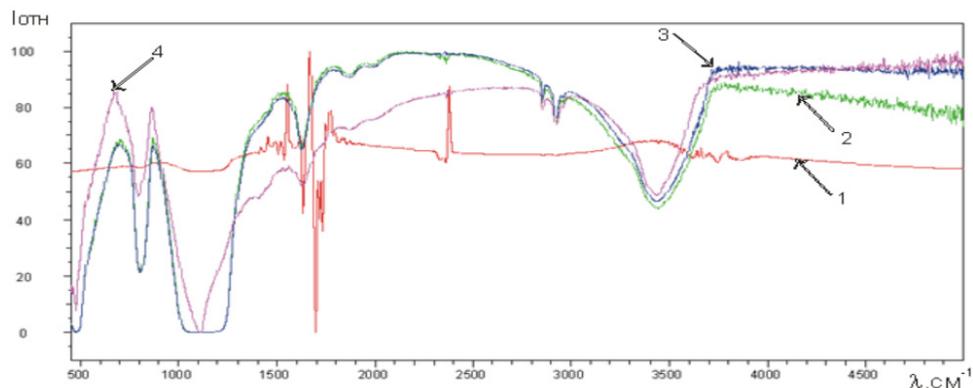


Fig. 2. IR spectra of samples: 1 - MK; 2 - MK treated by AcW; 3 - MK treated by AIW type; 4 - Quartz glass

Thus it can be concluded that the treatment of silica fume by water AcW and AIW types, we obtained dimers of orthosilicic acid $\text{Si}(\text{OH})_4$, which is a proof of chemical activation of silica fume. After that, when it was found that the process of dispersing the silica fume to the condition of orthosilicic acid $\text{Si}(\text{OH})_4$ and its dimers (oscillation range is interval from 1027 to 1195 cm^{-1}) is influenced by: oxonium ions H_3O^+ in an acidic medium, hydroxyl ions OH^- in an alkaline medium.

Based on the obtained experimental data can be offered theoretical scheme of the chemical activation of silica fume with water, treated by electrolysis with a pH = 10-11, enriched with hydroxyls ions OH^- (type AIW). Subsequently it was decided to carry out treatment of silica fume by water obtained by electrolysis with pH = 10-11.

It is known that for cement stone modifying the most optimal are complex additives containing related to the crystal-chemical structure of inorganic particles, for example the SiO_2 particles. However, use of dispersed silica-based modifier can be technologically complicated, since it is necessary to provide a preliminary dispersion of particles and their uniform distribution over the volume of the material. This problem can be solved if the additive is prepared in an aqueous medium, which is the mixing water in the presence of superplasticizer (SP). Thus SP inputted into the complex additive has a dual function: firstly, it stabilizes the growth of colloidal silica aggregates, and, secondly, further solves the technological problem of uniform distribution of the complex additive in the cement system. In our experiments, the complex additive was obtained by initially mixing the silica fume with water treated by electrolysis with pH = 10-11 and holding for 10 minutes, then superplasticizer was added, the quantitative ratios of the components are shown in Table 1. To activate the silica fume, we used the following: pretreated water by the electrolysis method with pH = 10-11, superplasticizer "PLASTILIT RK" and silica fume MK-85.

The number and size of the colloidal silica particles obtained by chemical activation of the MK was determined by laser diffraction method (particle size analyzer "Analyzette 22"). The phase composition was determined by addition of the resulting X-ray diffraction (diffractometer "ARL X'TRA") and IR spectra were recorded on a Fourier-spectrometer of "FSM 1201" brand with resolution of 4 cm^{-1} . Complex additive, which showed that the additive is X-ray amorphous and consists of colloidal aggregates of spherical shape.

To improve the quality of the matrix, obtained from the developed optimal concrete mixture composition (Table 1), samples were constructed and tested for strength. Experimental compositions were prepared by dosing by weight of the components, followed by mixing all the components, but the silica fume was mixed with water treated by electrolysis and enriched with OH^- hydroxyl ions with pH = 10-11 before the test,

followed by aging for 10 minutes. Table 2 shows the ratio of binder components (matrix) with the amount of the activator and the test results (Fig. 3).

Table 2. Developed matrix compositions using activated silica fume (water treated by electrolysis and enriched with hydroxyl ions OH⁻ with pH = 10-11)

| № p / p | Materials | Composition, kg / m ³ | | | | |
|---------|---|----------------------------------|----------------|----------------|----------------|----------------|
| | | Control | №5 (10% MC) | №6 (15% MC) | №7 (20% MC) | №8 (25% MC) |
| 1 | CEM I 42,5N | 357 | 378 | 357 | 336 | 315 |
| 2 | Water with a pH = 10-11, enriched with ions OH ⁻ | - | 147 | 147 | 147 | 147 |
| 3 | Water | 147 | - | - | - | - |
| 4 | Granite rubble | 950 | 950 | 950 | 950 | 950 |
| 5 | Sand | 845 | 845 | 845 | 845 | 845 |
| 6 | Superplasticizer "Plastilit RK" | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 |
| 7 | Silica fume MK-85 | 63 | 42 | 63 | 84 | 105 |
| 8 | W/S (C + SF) | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 |
| 9 | The compressive strength at 28 days, MPa | 62.76 | 59.11 | 69.98 | 50.39 | 34.78 |

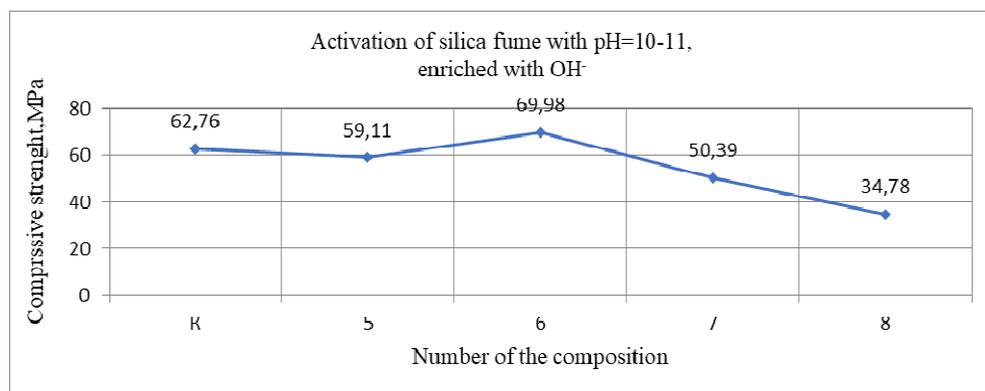


Fig. 3. Diagram of the concrete strength change at the age of 28 days, depending on the composition

A comparative analysis of the quantitative composition of the control matrix and experienced, using pre-activation of silica fume with the same qualitative composition, we can conclude:

- pre-activation of silica fume in alkaline medium can increase the strength of the matrix (composition №6) in relation to the composition without the use of activated silica fume (control) by 19.09%;

- increase the strength of the developed matrix composition was realized due to additional activation silica fume by water treated by electrolysis with a pH = 10-11, enriched with hydroxyls ions OH⁻ in combination with the superplasticizer "Plastilit RK". Using the optimal composition of the developed matrix with strength of 57.5 MPa, effective concrete with enhanced performance characteristics was obtained.

4 Discussions

1. The essence of the physicochemical activation of the inorganic microfiller is revealed and the positive effect of the proposed preliminary preparation on the structure formation of the hydration hardening system is established.

2. Scientific and practical ways of effective use of the obtained complex additive in cement concretes are substantiated.

The methodological basis of the research was the basic provisions of building materials science in the field of structure formation of cement concretes, as well as the provisions of modern chemistry concerning the methods of converting silica fume particles to the active form.

The decrease in cement consumption, by replacement its silica fume, a positive effect on physical and mechanical properties of concrete.

5 Conclusion

By IR-spectroscopy confirmed the effect of activation of silica fume in an acid medium (pH=2.1) supplemented with H₃O⁺ ions, oxonium cations provide H⁺, and in an alkaline medium (pH=10-11) supplemented with hydroxyl groups of OH⁻ - anions OH⁻; to produce dimers of orthosilicic acid, Si(OH)₄.

The use of chemical activation of silica fume by water treated by electrolysis and hydroxyl ions OH⁻ enriched with pH = 10-11, introduced into the concrete matrix, with the comparative analysis showed an increase strength by 58.8% compared with the control plant composition (without the use of silica fume in the complex additive).

Studies have confirmed the effect of micro-silica fume in an acid medium (pH = 2.1), enriched with oxonium H₃O⁺ ions, oxonium cations provide H⁺, and in an alkaline medium (pH = 10-11), enriched with hydroxyl groups OH⁻ - anions OH⁻, with obtaining dimers of orthosilicic acid Si (OH)₄.

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