Modified heavy concrete based on activated micro-silica for sleepers of high-speed highways

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Abstract. A method has been developed for the synthesis of a complex additive based on ultrafine silica and superplasticizer "Plasticite RK", which allows to obtain modified concrete with a given set of operational properties. The problem of reducing the consumption of micro-silica and increasing its efficiency in cement concretes due to chemical activation is solved. The effect of activation of microcosm in an acidic medium (pH = 2.1) enriched with oxonium \( \text{H}_3\text{O}^+ \) ions and \( \text{h}^+ \) cations is experimentally confirmed, and in an alkaline medium (pH = 10-11) enriched with hydroxyl groups of \( \text{OH}^- \) anions of \( \text{OH}^- \), with the production of dimers of orthosilicic acid \( \text{Si(OH)}_4 \), formed during chemical dispersion of microcosm are additional centers of crystallization, which concentrate new formations around themselves, forming a stable colloidal system. It has self-reinforcing processes associated with the recrystallization of colloidal size neoplasm particles into larger ones that participate in the construction of a spatial framework, which is compacted and strengthened due to prolonged hydration, contributing to an increase in the strength characteristics of cement stone and, accordingly, concrete. The use of chemical activation of micro-silica with water treated by electrolysis and enriched with hydroxyl ions \( \text{OH}^- \) with pH = 10-11, introduced into the matrix of the concrete mixture, in a comparative analysis showed an increase in strength by 58.8 % in comparison with the control sample of the factory composition without the use of micro-silica as part of a complex additive.

1. Introduction
The methodological basis of the study was the main provisions of construction materials science in the field of structure formation of cement concretes, as well as the provisions of modern chemistry concerning the ways of transferring micro-silica particles to the active form. In this paper, the goal was to reduce the consumption of micro-silica and increase its efficiency in cement concretes due to chemical activation. The aim of the study is to develop a concrete technology with improved physical and mechanical properties based on the use of chemically activated silica as part of a complex organomineral additive for sleepers of high-speed highways.

Based on the work [1,2] concerning the behavior of amorphous quartz in water, acidic and alkaline media, as well as taking into account information on the modification of concrete, where the most...
optimal are complex additives containing SiO₂ particles related to the crystal chemical structure, it can be assumed that chemical activation of microsilicon is an inexpensive and promising direction for modifying the structure of cement stone and concrete based on it. A special role belongs to fillers and especially micro-and ultrafine fillers in the structure formation of cement stone and concrete based on it, since they can participate not only in increasing the packing of the system, reduce the volume of capillary-bound and free water, by increasing the volume of adsorption and chemisorption-bound water, act as centers of crystallization and lower the energy threshold of this process, but also participate in heterogeneous processes of phase formation of hydrate compounds [3-9]. To enhance the effect of fillers and improve the quality of cement matrices and concretes based on them, including reducing their consumption, many activation methods have been developed: domol, mechanochemical, vibration activation, turbulent, acoustic, electromagnetic, thermal, aerothermal, electric pulse, as well as activation with modified water [4,5,7]. Analysis of literature sources has shown that one of the effective pozzolanic active mineral additives for cement matrices and concretes based on it is microsilicon—a dust-like waste of Ferroalloy production containing at least 91% SiO₂ [10-20].

The effect of improving the quality of concrete is significantly enhanced if micro-silica is introduced into the concrete mix in combination with superplasticizers or with additional organomimneral additives, which gives the prerequisites for chemical activation of micro-silica with such additives [1,9]. In the works of scientists of chemistry and Geology, it was experimentally established that amorphous silica can be dissolved in acid and converted to orthosilic acid (H₄SiO₄ or Si(OH)₄), and in an alkaline environment converted to the sodium or potassium salt of orthosilic acid [1,9,19]. It was found that the role of a silica-containing nanomodifier can be performed by a Sol (H₄SiO₄) solution of metacremic acid from a soluble Na₂SiO₃ glass. One of the prerequisites for choosing the activation of micro-silica in this work was a chemical method, expressed in the treatment of the water of concretes by electrolysis. It is established that the nature of the chemical activation action in relation to silica-containing fillers is insufficiently studied, and therefore the leading scientific concept put forward is relevant.

2. Materials and methods
In this work, we investigated the processes of physical and chemical activation of microsilicon, as well as studied the processes of hardening, structure formation of cement stone and various concrete compositions based on it, modified with the obtained additives. The amount and size of microsilicon dispersion products obtained during chemical activation by laser diffraction (particle size analyzer "Anlyzette 22") and the phase composition of the resulting additive were determined experimentally using x-ray phase analysis ("ARL XTRA" diffractometer) and IR spectroscopy (Varian 640-IR IR spectrometer).

The effectiveness of the plasticizing capacity of additives was evaluated by changing the workability of the concrete mix and the strength of the concrete of the proposed composition compared to the control composition. Processing of the results of the concrete compressive strength test was performed in accordance with GOST 10180-2012 "Concretes. Methods for determining the strength of control samples."

The following materials were used for the experimental part of the study: Portland cement GOST CEM I 42.5 N produced by EUROCEMENT group JSC, corresponding to GOST 31108-2016 "General construction Cements. Technical conditions" and GOST 30515-2013 "Cements. General technical conditions"; natural sand with a size modulus of up to 2.5 corresponding to the requirements of GOST 8735-88 "Concrete Sand for construction works. Test data methods". It is established that the proposed sand is used for the content of clay, all pulverized and organic impurities, and the granulometric composition of the radicals correspond to the additive standard requirements of GOST 8376-2014 "Sand for construction works. Technical conditions". As a large water-cement filler, granite rock rubble of a fraction from 5 to 20 mm was used that meets the requirements of GOST 8267-93 "Rubble and gravel from dense rocks for construction works". The water of concrete
closures corresponds to GOST 23732-2011 "water for concrete beginning and solutions" Technical conditions. The content of sulphate powder does not exceed more than 2700 mg/l (in terms of SO$_4^{2-}$) and all added salts more than 5000 mg/l.

The products of LLC "NPO SINTEZ" superplasticizer "Plasticine RK" were used as a superplasticizer. According to its consumer properties, the additive "PLASTICINE RK" meets the requirements for plasticizing and water-reducing additives of GOST 24211-2008 "Additives for concrete and building solutions. General technical conditions". As a reaction-chemical pozzolanic additive, a dust-like waste of micro-silica MK-85 of the Ferroalloy production of JSC "Kuznetsk Ferroalloy mixtures" with a particle size of 5-50 microns was used, which under the influence of a high temperature form turn the additive into a vitreous amorphous white dust.

3. Results and Discussion

In the course of research, it was noted that the strength of cement stone and concrete is higher in samples in which a stabilized suspension of microsiliicon prepared on the basis of water treated with electrolysis was used as the closing water. An electric current was passed through tap water, which mainly contains calcium and magnesium bicarbonates, so as a result of hydrolysis of water, calcium and magnesium hydroxides and carbon dioxide were obtained.

The total equation for electrolysis of tap water is as follows:

\[
\text{Ca(HCO}_3\text{)}_2 + 4\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{O}_2 + 2\text{H}_2 + 2\text{H}_2\text{CO}_3 \quad (1)
\]

\[
\text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2 \quad (2)
\]

\[
\text{Mg(HCO}_3\text{)}_2 + 4\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{O}_2 + 2\text{H}_2 + 2\text{H}_2\text{CO}_3 \quad (3)
\]

\[
\text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2 \quad (4)
\]

After treatment of tap water by electrolysis, low-soluble Ca(OH)$_2$, insoluble Mg(OH)$_2$, and weak carbonic acid are formed, which immediately breaks down into carbon dioxide and water. As a result of studies, the pH of water treated by electrolysis was 10. Therefore, after electric shock treatment, tap water mainly contains a strong base Ca(OH)$_2$ – a source of the OH-group that determines the alkaline medium of the solution.

As a result, microsiliicon introduced into water treated by electrolysis (pH=10) acquires increased chemical activity due to alkaline excitation by the reaction:

\[
\text{Ca(OH)}_2 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{H}_2\text{O} \quad (5)
\]

This is evidenced by a decrease in pH from 10 to 7.5. Then the calcium silicate is hydrolyzed to form calcium hydrolysilicate and calcium hydroxide:

\[
2\text{CaSiO}_3 + 2\text{H}_2\text{O} \rightarrow \text{Ca(HSiO}_3\text{)}_2 + \text{Ca(OH)}_2 \quad (6)
\]

This confirms an increase in the pH of the medium from 7.5 to 8.1 (after 3 hours) and to 8.7 (after 24 hours). When the "electrolysis water - micro-silica" stabilizer is introduced into the system, the pH of the medium is reduced from 7.5 to 6.8. Since the stabilizer contains sodium lignosulfonate, which is an anionic surfactant, some of the calcium ions interact with the plasticizer molecules, thereby reducing the pH of the suspension medium.

It was found that the active sites of microcosm in the presence of a plasticizer (despite the formation of a film on its surface) also produce calcium silicate and its subsequent hydration, as evidenced by the change in the pH of the medium: after 3 hours, the pH increased from 6.8 to 7.4, after 24 hours - to 8.2.

The effectiveness of additives was evaluated by improving the mechanical and physical-chemical properties of the modified materials. A range of 5% by weight of cement was used to determine the optimal content of micro-silica in the concrete mix intended for the production of effective reinforced concrete sleepers for high-speed highways. The optimal content of additives was determined by changing the compressive strength of 15×15×15 cm cube samples after 28 days of normal hardening. The test results presented in table 1 and figure 1 indicate that the optimal content of microsiliicon is 15%, and the increase in strength relative to the control sample is 33.39%.

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Table 1. The composition and test results of concrete

| №  | Materials          | Composition, kg / m³ | Test (10% MK) | №2 (15% MK) | №3 (20% MK) | №4 (25% MK) |
|----|--------------------|----------------------|---------------|-------------|-------------|-------------|
| 1  | CEM I 42,5H        | 420                  | 378           | 357         | 336         | 315         |
| 2  | Water              | 147                  | 147           | 147         | 147         | 147         |
| 3  | Crushed granite   | 950                  | 950           | 950         | 950         | 950         |
| 4  | Sand               | 845                  | 845           | 845         | 845         | 845         |
| 5  | Superplasticizer "Plasticine RK" | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 |
| 6  | Micro-silica MK-85 | -                    | 42            | 63          | 84          | 105         |
| 7  | W/S (C + SF)       | 0.35                 | 0.35          | 0.35        | 0.35        | 0.35        |
| 8  | Compression strength at 28 days, MPa | 47.04 | 62.76 | 45.03 | 30.81 |

Figure 1. The dependence of the tensile strength of the concrete in the compression of fuel additive

Using spectroscopy, shown in figure 2, the infrared (IR) spectra of microsilicon (MC) are shown: in the dry state and treated with activated waters of the "acidic water (KV)" and "alkaline water (SCHV)" types, as well as the IR spectrum of quartz glass, which was taken as a reference sample.
Figure 2. IR spectra of samples: 1-MK; 2-MK, processed type KV; 3-MK, processed type SCHV; 4-quartz glass

The IR spectra show (figure 2) that there was a coincidence of the oscillation region of quartz glass with micro-silica mixed with water treated by electrolysis with pH=2.1-3, enriched with oxonium Н₃О⁺ ions (type KV) and with water treated by electrolysis with pH=10-11, enriched with hydroxyl ОН⁻ ions (type SCHV).

Thus, we can conclude that when treating microcosm with water of the KV and SCHV types, we obtained dimers of orthosilicic acid Si(ОН)₄, which is proof of chemical activation of microcosm. After it was found that the process of dispersing microcosm to the state of orthosilicic acid Si(ОН)₄ and its dimers (the range of oscillations in the region of 1027-1195 cm⁻¹) is affected by: oxonium Н₃О⁺ ions in an acidic environment, and hydroxyl ОН⁻ ions in an alkaline environment.

Based on the experimental data obtained, we can propose a theoretical scheme for the chemical activation of microsilicon with water treated by electrolysis with pH=10-11, enriched with OH⁻hydroxyl ions (type of SCHV). In the future, it was decided to treat the micro-silica with water obtained by electrolysis with pH=10-11.

It is known that a complex additive containing inorganic particles related to the crystal chemical structure, such as SiO₂, is the most optimal for modifying cement stone. However, the use of a dispersed silica-based modifier may be technologically difficult, since it is necessary to ensure pre-dispersion of the particles and their uniform distribution over the volume of the material. This problem can be solved if the additive is obtained in an aqueous medium, which is the mixing water in the presence of a superplasticizer (SP). At the same time, the SP introduced into the complex additive performs a double function: on the one hand, it stabilizes the growth of colloidal aggregates of silica, and further solves the technological problem of uniform distribution of the complex additive in the cement system. In our experiments, a complex additive was obtained by initially mixing micro-silica with water treated by electrolysis with pH=10-11 and holding for 10 minutes, then adding a superplasticizer, the quantitative ratios of the components are shown in table 1. To activate the micro-silica, we used: pre-treated water by electrolysis with pH=10-11, superplasticizer "PLASTICITE RK" and micro-silica of the MK-85 brand.

The number and size of colloidal silica particles obtained during chemical activation of the MC was determined by laser diffraction (particle size analyzer "Analyzette 22". Research results have shown that the additive is x-ray amorphous and consists of spherical colloidal aggregates. Table 2 shows the ratio of the binder components (matrix) to the amount of activator and the test results (figure 3).
Table 2. The developed compositions of matrices with the use of activated silica fume (water treated by electrolysis and is enriched with ions of hydroxyl OH with a pH=10-11)

| №  | Materials                      | Test   | №5 (10% MK) | №6 (15% MK) | №7 (20% MK) | №8 (25% MK) |
|----|--------------------------------|--------|-------------|-------------|-------------|-------------|
| 1  | CEM I 42,5H                   | 357    | 378         | 357         | 336         | 315         |
| 2  | Water with pH=10-11, enriched with ions OH- | -      | 147         | 147         | 147         | 147         |
| 3  | Crushed granite               | 147    | -           | -           | -           | -           |
| 4  | Sand                          | 950    | 950         | 950         | 950         | 950         |
| 5  | Superplasticizer "Plasticine RK" | 845    | 845         | 845         | 845         | 845         |
| 6  | Micro-silica MK-85            | 4.2    | 4.2         | 4.2         | 4.2         | 4.2         |
| 7  | W/S (C + SF)                  | 63     | 42          | 63          | 84          | 105         |
| 8  | Compression strength at 28 days, MPa | 0.35  | 0.35        | 0.35        | 0.35        | 0.35        |
| 9  |                               | 62.76  | 59.11       | 69.98       | 50.39       | 34.78       |

To improve the quality of the matrix obtained from the developed optimal composition of the concrete mix (table 1), samples were manufactured and tested for strength. Experimental formulations were prepared by dosing by weight of the components followed by mixing all the components, but the micro-silica was mixed with water treated by electrolysis and enriched with hydroxyl ions OH- with pH=10-11 before the test, followed by exposure for 10 minutes.

Figure 3. Graph of changes in the strength of concrete at the age of 28 days, depending on the composition
A comparative analysis of the quantitative composition of the control matrix and the experimental one, with the use of preliminary activation of microsilicon with the same qualitative composition, can be concluded:

- preliminary alkaline activation of microcosm allows to increase the strength of the matrix (composition №6) in relation to the composition without using activation of microcosm (control) by 19.09%.

- increasing the strength of the developed matrix composition was carried out due to additional activation of micro-silica with water treated by electrolysis with pH=10-11, enriched with hydroxyl ions OH⁻ in combination with the superplasticizer "Plasticite RK". Using the optimal composition of the developed matrix with a strength of 57.5 MPa, effective concrete with improved performance was obtained.

The technology of substitution of a cement binder with micro-silica is well disclosed in this article [11]. Researchers in their work introduce micro-silica and colloidal nanosilicon into the concrete mix, while reducing the consumption of cement. The authors concluded that 6% of micro-silica and 1.5% of nanosilicon improve strength characteristics, electrical resistance, and reduce capillary absorption. The results of our research really coincide with the research of other scientists [11-14]. Reducing the consumption of cement by replacing it with micro-silica has a positive effect on the physical and mechanical characteristics of concrete.

4. Conclusion

1. The essence physico-chemical activation of inorganic filler and a positive effect of the proposed preconditioning on the processes of structure formation of the hydration system hardening.

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

3. IR spectroscopy confirmed the effect of activation of microcosm in an acidic medium (pH=2.1), enriched with oxonium H₃O⁺ ions and H⁺ cations, and in an alkaline medium (pH=10-11), enriched with hydroxyl groups OH⁻ - anions OH⁻ to obtain dimers of orthosilic acid Si(OH)₄.

4. Chemical activation of micro-silica with water treated by electrolysis and enriched with hydroxyl ions on-with pH=10-11 increased the strength of concrete by 58.8% compared to the control sample of the factory composition (without the use of micro-silica as part of a complex additive).

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