Fine-grained Concrete with Complex Modifiers for Construction in Extreme Climatic Conditions

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Abstract. It has been established that nanomodification and the use of complex modifiers of concrete mixtures lead to a decrease in the content of loosely bound moisture at an early age and indicate an acceleration of hydration processes in the initial period of hardening. The ascertained fact correlates to data on the dynamics of sample hardening and the results of structural surveys. Optimal formulations of modified fine-grained concrete with high strength properties, which are recommended for the production of building products and structures that operate in extreme climatic conditions, have been developed.

1. Introduction
The construction materials industry is a priority industry that determines the current state of the national economy and its development potential.
In the Development Strategy for the Building Materials Industry [1], priority belongs to the production of new types of composite construction materials that reduce material consumption and increase energy efficiency, reliability, and durability of buildings and structures.

In modern construction, the most popular material for building structures and buildings is concrete. Its share and role in the global construction industry is growing rapidly and accompanies the development of new methods and approaches in the development of composite materials for various purposes.

In the current economic relations, the market for concrete materials needs competitive products of relatively low cost. Such products can be obtained using local natural raw materials.

2. Relevance
Modern research methods and the development of advanced technologies make it possible to affect the structure and properties of cement mortars and concrete directionally and to obtain materials with high technological and physical-technical parameters [2-6]. Currently, the prospect of creating new concrete technologies and the intensification of the existing ones is associated with the development of effective methods for modifying concrete mixtures, which will allow obtaining new, more valuable products [7–9]. Herewith, mineral nano- and finely dispersed fillers, including those from local raw
materials, are the most promising. The parameters of their crystal cells are comparable with the similar parameters of the hydrated phases of cement systems. The present research is aimed to increase the reliability and durability of structures by using modifying additives of natural origin in concrete.

3. Methodology

Portland cement PC 400 D0, which is manufactured by OAO PA Yakutcement and corresponds to GOST 10178-85 “Portland cement and Portland slag cement. Specifications”, was used as a binder. River sand from the floodplain of the river Lena was used as a filler. According to GOST 8736-93 “Sand for construction works. Specifications”, its granulometric composition belongs to Class II, to the category – very fine.

The modifying additives included the following:
- anorthite powder Ca\[Al_2Si_2O_8\] synthesized at the Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk;
- the mechanically activated zeolite of the Kempendyaysky deposit from the most developed reservoir Hongurin III (clinoptilolite content is 75-90%);
- the mechanically activated clay of the Oy-Bessky deposit of RS (Ya), which belongs to the kaolinite-hydromicaceous clay groups and has medium ductility, low sensitivity to drying, low air and general shrinkage;
- complex modifier, including mechanically activated zeolite and anorthite;
- complex modifier, including mechanically activated clay and anorthite.

The modified concrete mixes contained the following: anorthite from 0,005 to 1,0 wt.%, activated zeolite in the complex modifier from 5 to 15 wt.% of the original binder, and activated clay in the complex modifier from 5 to 15 wt.% of the original binder.

The mechanical activation of clay and zeolite was accomplished on the AGO-2 laboratory ball mill, which implements the free-blow method. The activation time of the components was 2 minutes [10]. Mechanical activation of materials increases their specific surface area and reactivity, affecting the formation of concrete structure, its hardening rate, and physical-mechanical properties [11].

To conduct research by vibrocompression, cube-samples with edge length of 70.2 mm (C:P = 1:1.3 at W/C = 0.4) were manufactured. There were 5 samples for each type and duration of the test [12-15]. The obtained concrete samples hardened for 7, 14, and 28 days under the conditions of natural drying at an air temperature of 20 ± 2 °C and air humidity of 50 ± 5%.

The uniform distribution of the modifier nanoparticles in powder form over the volume of dry cement is a complex technological task. The tests of cube concrete specimens have revealed that it is preferable to introduce nanoaditives into the concrete mixture along with mixing water than before mixing. The mixing of the concrete mixture was performed in two stages to obtain an equilibrium cement system. The first stage consisted in mixing the dry mixture for 3 minutes. In the second stage, the mixture was blended with tempering water containing a different concentration of nanomodifier for 5 minutes. This technological technique ensures uniform distribution of the nanomodifier throughout the volume of the concrete mixture and improves the plasticization effect, which increases the viscosity of the liquid phase of the concrete mixture, improves placeability and resistance to disintegration, increases the contact area, and improves the adhesion between the aggregate and cement paste. Thus, the sediment cone (SC) of concrete mixtures with a nanomodifier is increased by 2 units compared with the SC of unmodified mixtures: 10 cm versus 8 cm with the same water-cement ratio (W/C) equal to 0.4.

The study of the modified concrete microstructure was accomplished on JSM-6480 LV JEOL scanning electron microscope (Japan). Thermogravimetric analysis was performed on a NETZSCH – STA 449C Jupiter synchronous thermal analysis instrument. The test portions of the samples in the form of fragments were heated from room temperature up to 1000 °C at a rate of 10 °C/min in argon.
4. Discussion of results
The previously obtained results on the modification of fine-grained concrete with finely dispersed mineral additives (zeolite, clay) [16] showed that there is a fundamental possibility of increasing the strength characteristics of concrete by introducing nanoadditives of aluminosilicate composition related to a cement binder.

According to the analysis of the literature data, the nanomodification of cement systems improves the technological and physical-mechanical properties of mortars and concrete due to the formation of low-basic hydrosilicates, changes in the ratios of capillary and gel micropores, intensification of early hydration, and regulation of temperature and volumetric changes in hardening compositions [17-19].

It has been established that when non-autoclaved hardening of anorthite is introduced into concrete in an amount of 0.005-0.01 wt.% of the cement weight, concrete strength increases up to 1.5 times at design age. Herewith, nanomodification contributes to a quick strength development of concrete samples in the early stages of hardening (Table 1).

| Introduction of Ca[Al\(_2\)Si\(_2\)O\(_8\)], % of the cement weight | W/C | Compression strength, Mpa |
|---|---|---|
| 1 | 0 | 10.9 | 12.3 | 23.0 |
| 2 | 0.005 | 21.9 | 27.1 | 26.1 |
| 3 | 0.0075 | 24.9 | 28.9 | 30.8 |
| 4 | 0.01 | 26.3 | 29.7 | 35.3 |
| 5 | 0.05 | 24.3 | 27.5 | 32.4 |
| 6 | 0.1 | 23.7 | 27.0 | 33.2 |
| 7 | 0.5 | 22.9 | 23.6 | 23.8 |
| 8 | 1 | 20.1 | 23.1 | 27.1 |

Moreover, high resistance of modified concrete to moisture and low temperatures has been established. Thus, the compressive strength decreases only to 10% after 25 cycles of freezing-thawing of water-saturated samples of nanomodified concrete, while the softening coefficient is 0.8.

The high persistence of properties of the nanomodified concrete after freezing-thawing in a moisture-saturated state is probably ensured by nanopowders, which have increased surface energy and, accordingly, greater mobility. The nanopowders involve a larger number of cement particles in hydration processes, uniformly distribute them throughout the hardening system, and contribute to better compaction of cement stone by blocking pores of comparable size [17].

The results of microscopic studies of samples reveal densification of the structure of concrete materials in Figure 1.

The initial sample is looser in structure (Figure 1A). Platelet forms are visible, and portlandite formations are observed in some places, which indicates an incomplete hydration process. When the structure of the sample of fine-grained concrete with the addition of anorthite (Figure 1 B) is denser, a uniform even layer of binder hydration products is observed. It fills intergranular cavities with fibrous neoplasms, forming a network of strong spatial bonds, which lead to an increase in the density and, accordingly, grade strength of the concrete product.
An analysis of the results revealed the possibility of using anorthite as a modifier of concrete mixtures for obtaining fine-grained concrete with enhanced physical-mechanical properties. The data obtained were the basis for the development of complex modifiers with the use of mineral additives from local raw materials of Yakutia.

Mechanically activated zeolite and clay are used as mineral additives. Since finely dispersed fillers increase the water demand of the concrete mixture, their introduction into cement is impractical. In this regard, mechanically activated mineral additives were introduced into the concrete mixture in a dry state instead of part of the cement. The additives served not only as an active additive that improves the quality of the binder but also as a micro filler, which actively influences the structure formation processes of concrete.

An increase in the compressive strength of samples modified with a complex additive has been established (Table 2). Moreover, the maximum effect is achieved with the use of mechanically activated clay. The strength increased up to 56%.

Table 2. Hardening kinetics of modified samples.

| Age, days | Nanopowder, wt.% of cement weight | Strength, Mpa | Mineral additive, wt.% of cement weight |
|-----------|----------------------------------|---------------|----------------------------------------|
|           |                                  | 5             | 10                       | 15                       |
|           | clay                             | zeolite       | clay         | zeolite       | clay         | zeolite       |
| 3         | 0                                | 14,9          | 16,2         | 19,3          | 13,7         | 20,4          | 9,7            |
|           | 0,01                            | 27,0          | 18,1         | 22,1          | 13,9         | 23,7          | 11,7           |
| 7         | 0                                | 16,9          | 19,9         | 22,8          | 15,8         | 23,2          | 11,4           |
|           | 0,01                            | 30,7          | 20,3         | 25,0          | 16,8         | 27,5          | 20,1           |
| 28        | 0                                | 20,7          | 34,1         | 26,8          | 32,3         | 28,3          | 19,9           |
|           | 0,01                            | 36,1          | 33,5         | 29,4          | 24,1         | 31,6          | 25,4           |

Besides, the test results (Table 2) indicate that concretes made with additives of a multicomponent composition are characterized by accelerated kinetics of curing compared to concrete samples without additives. Acceleration of hydration processes and increase in concrete strength are due to the...
intensification of crystallization processes on seeds from nanodispersed particles of anorthite, which chemically relates to materials with cement components [18]. This correlates with structural studies.

Thermogravimetric analysis of concrete samples was accomplished for the complete understanding of the mechanisms of influence of mineral additives on the degree and completeness of concrete hydration [20-23].

An analysis of the data obtained during thermogravimetric studies shows that only endothermic effects appear on the thermograms when heating concrete samples of all formulations from 30 °C to 1000 °C. Three main and two situational DTG effects are distinguished on all thermograms. DTG effect in the range of 88–102 °C is associated with the removal of adsorbed moisture. The extremum at 440-450 °C corresponds to the decomposition of residual portlandite. The effect appears at 578-580 °C due to the polymorphic transformation of quartz (α-quartz → β-quartz). Decomposition of hydrosilicates of calcium, calcite, and, probably, the C–A–S–H phase is observed in the temperature range of 680–750 °C (2 DTG effects). It should be noted that the effects at 680-750 °C are manifested in samples containing activated clay at the design age.

An analysis of the weight loss of concrete samples (Table 3) at an early age shows that the introduction of anorthite reduces the amount of loosely bound moisture by 1.4 times. It is due to the fact that anorthite acts as a plasticizing agent and provides accelerated hydration processes and, consequently, a decrease in the content of weakly bound moisture.

| Age   | Composition of additives | Weight loss in the temperature range, wt.% |
|-------|--------------------------|--------------------------------------------|
|       |                          | 30-300°C | 300-600 °C | 600-1000°C | 30-1000 °C |
| 3 days| Without additives        | 5.28     | 1.96       | 0.99       | 8.19       |
| 3 days| 0.01 wt.% anorthite      | 3.78     | 1.85       | 0.88       | 6.51       |
| 7 days| Without additives        | 3.48     | 2.01       | 1.09       | 6.58       |
| 7 days| 0.01 wt.% anorthite      | 3.51     | 2.06       | 1.03       | 6.60       |
| 28 days| Without additives       | 2.86     | 2.18       | 1.28       | 6.32       |
| 28 days| 0.01 wt.% anorthite      | 4.01     | 2.79       | 1.25       | 8.04       |
| 28 days| 15 wt.% of cement weight m/a zeolite and 0.01 wt.% anorthite | 4.06 | 2.03 | 1.88 | 7.96 |
| 28 days| 15 wt.% of cement weight m/a clay and 0.01 wt.% anorthite | 2.46 | 2.14 | 2.96 | 7.55 |

The weight loss of samples with and without anorthite is the same at the age of 7 days in all considered intervals.

It is seen that the samples containing anorthite and a complex additive of anorthite with zeolite are characterized by a large amount of adsorbed moisture at the design age. The samples with a complex addition of anorthite and mechanically activated clay contain moisture in the same amount as the original sample. This is due to the fact that both anorthite and zeolites are characterized by a developed pore space, which contributes to the retention of moisture in the sample volume. Clay adsorbs a significant part of the moisture on its surface owing to high hydrophilicity and a developed specific surface after mechanical activation. Moisture adsorbed on clay particles gradually enters the cement hydration reaction. Thus, the residual amount of weakly bound moisture ultimately decreases. Moreover, the content of residual portlandite is higher in samples containing only anorthite than that of other samples. The weight loss in the temperature range of 600-1000 °C is 1.3 and 2.4 times higher in samples containing the complex additives zeolite-anorthite and clay-anorthite, respectively. This is due to additional crystalline hydrate forms that appear when using a complex additive with
mechanically activated components characterized by high activity. These forms decompose in the indicated temperature range.

5. Conclusion
Thus, a study of concrete containing mineral additives has revealed that the modification of concrete leads to a decrease in the content of loosely bound moisture at an early age and indicates an acceleration of hydration processes in the initial period of hardening.

6. Scientific novelty
The methods of thermogravimetric analysis has revealed that nanomodification and the use of complex modifiers of concrete mixtures lead to a decrease in the content of weakly bound moisture at an early age and indicate an acceleration of hydration processes in the initial period of hardening.

7. Practical relevance
The optimal formulation of modified fine-grained concrete with the use of mineral nano and complex additives with high strength indicators has been developed. It is recommended for the production of building products and structures of increased resource and reliability for operation in extreme climatic conditions.

8. References
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