Formation of the properties of nano-modified concretes

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Abstract. Nanomodified concrete is obtained from multicomponent dry building mixes based on Portland cement containing nanoscale filler particles. This paper examines the cement-sand mixture activated in a high-energy mill as a nanomodifier. The result is the gain in strength of concrete in the initial hardening time. The influence of fractional characteristics of sand on the activation process is analyzed. Three sand samples of different deposits of the Kaliningrad region characterized by different size and content of dust and clay particles were studied. The results of tests of samples of fine-grained concrete with activated and non-activated components for the initial compressive strength at the age of 0-90 minutes after the preparation of the mixture are presented. It is noted that the mechanical activation of cement-sand mixture is most effective when there are large fractions in the activated sand.

1. Introduction
Modern construction composite materials are multicomponent and polydisperse systems that include various modifying additives, ultrafine components, etc. One of the key factors of nanotechnology in construction material science should be to achieve the desired or maximum quality of material at minimum cost resource. As a primary nanomaterial in this paper we consider a fine-ground mixture of Portland cement and sand, obtained by joint mechanical activation in a high-speed ball mill. Mechanical activation provides an increase in the speed of concrete setting and more complete use of cement binding properties [1]. According to the results of previous works, it was proved that this type of activation is the most effective [2]. The concrete mixture containing fine ground cement-sand mixture sets faster and shows a significant increase in strength in the initial setting period. This mixture can be used in construction 3D printing with concrete as it meets the requirements for strength to withstand the weight of the above-printed layers [3-6].

2. Materials and methods
Sands from various locations of the Kaliningrad region are used as the components for activation: sea sand (SS) of the medium size (Fineness modulus = 2.1); sand from the quarry near village Sinyavino (SQS) of the fine size (Fineness modulus = 2.0); sand from the quarry Rybachye (SQR) of the very fine size (Fineness modulus = 1.34). The size of sand was determined according to GOST 8735-88 through the fineness modulus. Conducted joint mechanical activation of cement and sand in the RetschEMax high speed ball mill measured initial strength of the samples. According to the results of earlier works on the selection of composition for additive technologies in construction, the optimal composition meeting the requirements of 3D printing with concrete was determined [7]. Mixtures of fine-grained concrete with activated and non-activated components are made of this composition.
2.1. Materials
The following materials were used for the preparation of samples:

- Portland cement Eurocem super 500, CEM I 42.5H, Petersburg Cement;
- Sand: for the composition No. 1: sea sand from the coast of the urban-type settlement Yantarny, Kaliningrad region; for the composition No. 2: sand from the quarry near village Sinyavino, Kaliningrad region; for the composition No. 3: sand from the quarry Rybachye, Kaliningrad region.
- Polypropylene fiber: length of 12 mm, thickness of 35 μm, country of origin: Russia;
- Silica fume (SF): wastes of the metallurgical industry, country of origin: Poland;
- Highly active metakaolin (MK): white, country of origin: Russia, Chelyabinsk region, Synergyo;
- STACHEMENT 1267 hyperplasticizer based on polycarboxylates for the production of ready-mixed concrete: country of origin: Poland.

The consumption of materials per 1 m³ of the concrete mixture is given in table 1.

Table 1. Materials per 1 m³.

| W/C ratio | Cement (kg m³) | Sand (kg m³) | Water (l m³) | Silica fume (SF) (kg m³) | Metakaolin (MK) (kg m³) | Fiber (kg m³) | Hyperplast. (l m³) |
|-----------|----------------|--------------|--------------|--------------------------|-------------------------|--------------|-------------------|
| 0.66      | 545            | 1168         | 360          | 156                      | 78                      | 1.2          | 11.7              |

Characteristics of sand are presented in table 2. All the characteristics were determined according to Russian State standards GOST 8736-2014 "Sand for construction work. Specifications" [8] and GOST 8735-88 "Sand for construction work. Testing methods" [9].

Table 2. Sand characteristics.

| Location of origin | Symbol | Size group | Fineness modulus | Content of dust and clay particles (%) | True density (kg m³) | Bulk density, kg m³ | Voidness, % |
|--------------------|--------|------------|-----------------|---------------------------------------|----------------------|---------------------|------------|
| Coast              | SS     | Medium     | 2.1             | -                                     | 2612                 | 1474                | 43.6       |
| Quarry Sinyavino   | SQS    | Fine       | 2               | 2.2                                   | 2642.5               | 1330                | 49.7       |
| Quarry Rybachye    | SQR    | Very fine  | 1.34            | 3.6                                   | 2551                 | 1501                | 41.2       |

The images of the sand are shown in figures 1-3. The images were obtained using an optical electron microscope.

Figure 1. Sea sand (SS).
Figure 2. Sinyavino quarry sand (SQS).
Figure 3. Rybachye quarry sand (SQR).
2.2. Methods

Joint mechanical activation of cement and sand was carried out in the Retsch EMax high-speed ball mill at a speed of 1000 rpm for 5 minutes, since this activation mode is the most effective [1]. Corundum balls with diameters of 6 and 10 mm in a ratio of 1:1 by weight were used as grinding media. The ratio of grindable mixture/grinding media is 1:2.

Six compositions of the initial building mixtures were considered: No. 1 SS – on the basis of non-activated mixture using SS sand; No. 2 CSSA – on the basis of activated mixture using SS sand; No. 3 SQS – on the basis of non-activated mixture using SQS sand; No. 4 CSQSA – on the basis of activated mixture using SQS sand; No. 5 SQR – on the basis of non-activated mixture using SQR sand; No. 6 CSQRA – on the basis of activated mixture using SQR sand.

Next, cubic samples of size 20 × 20 × 20 mm were made with activated and non-activated components in accordance with the consumption of materials presented in Table 1. The samples were tested for compressive strength at the initial setting time (from 0 to 90 minutes every 15 minutes) on an Instron Electropuls E1000 testing machine.

3. Results

The results of the strength tests of the samples at the initial setting time are shown in the graph in figure 4. In the graph, solid lines indicate the increase in strength of samples with non-activated components, the strength of samples with activated components is indicated by a dash line.

![Figure 4. Compressive strength test results.](image-url)

The dependence of the initial strength of samples with non-activated components (compositions No. 1, 3, 5) on the size of the sand is noted. Samples of composition No. 1 with medium-sized sea sand show the lowest strength in the first 90 minutes of hardening, samples of composition No. 5 with very fine sand from the Rybachye quarry have the greatest strength. Samples of composition No. 3 with fine sand show medium strength.
Compositions with joint activation of cement and sand (No. 2, 4, 6) show an increase in strength compared with the corresponding samples without activation (No. 1, 3, 5). There is a significant increase in strength in compositions No. 2 and No. 4. Strength at the age of 90 minutes for composition No. 2 increases by 2.81 times or by 181% relative to composition No. 1. The strength of composition No. 4 at the age of 90 minutes increases by 2.98 times or by 198.4% relative to composition No. 3. At the same time, there is no significant difference in strength between samples No. 5 and 6: at the age of 90 minutes, the strength of composition No. 6 increases by 1.43 times or by 43.3%. Therefore, the mechanical activation of the sands belonging to the group of very fine sand is ineffective. The test results show that the joint activation of cement and sand gives a significant increase in strength at the early setting time only when large fractions are present in the activated sand.

4. Conclusion
The nanomodified additives obtained by the joint activation of cement and sand in high-energy ball mills are considered. The use of such nanomodified additives leads to an increase in the strength of concrete in the initial periods of hardening. Analysis of the effect of the initial characteristics of sand on the activation process showed that the mechanical activation of the cement-sand mixture is most effective when the activated sand contains large fractions.

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