Modifying additive for concrete based on shungite processing waste

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Abstract. The paper is devoted to the study of waste processing of shungite rocks, which are formed in the process of mining and technological operations. However, the market of national modifying additives based on local raw materials is not developed at the appropriate level in the presence of a rich resource base of the mining industry. In this regard, it is of great interest to obtain additives based on shungite rock processing waste, which allow expanding the range of mineral additives and providing qualitatively new properties for concrete and reinforced concrete products and structures. Such technologies for the production of additives are isolated and not developed at the proper level due to insufficient knowledge of shungite rocks. Analysis of the state of research on concrete and the market for modifying materials showed that the development of production of energy-efficient and environmentally friendly materials due to increasing regulatory requirements for them, as well as to environmental ecology and the obvious need to recycle industrial waste initiated the progressive development of concrete science. One of its latest achievements is modified concrete with special properties, which marked a new stage in the development of concrete. In its production technology, significant progress has been made in improving its chemical additives, special modifiers, as well as active and inactive fillers. In Kazakhstan, the main volume of modifying additives is imported from abroad, which significantly increases their cost, so their choice is limited.

This paper is devoted to the research of waste processing of shungite rocks as a modifying mineral additive of concrete. Its influence on the main indicators of concrete is investigated and the features of the processes that occur in the hardening silicate system “cement - dispersed shungite particles” and contribute to increasing the strength of concrete, as well as reducing the duration of its heat-and-water treatment are studied.

1. Introduction

Currently, technologies related to the development of new methods for obtaining effective nanomodifying additives that allow to regulate the properties of composites based on mineral and organic binders are being intensively developed in the construction materials science [1-4].

The analysis of the issue showed that to improve the strength and other performance properties of concretes, solutions, polymers, the most acceptable are carbon nanoparticles, which include Kazakhstan shungite, which is a unique natural nanotechnological material [5-8].
Kazakhstan shungite is a natural nanostructured composite consisting mainly of a carbonaceous substance close to graphite and microcrystalline silica in mineralogical composition. The reserves of the shungite deposit, located only in the Almaty region, amount to more than 50 million tons. Therefore, the ecological and nanostructural potential of shungite, realized in its application as an effective mineral additive in concretes and solutions, seems promising and long-term [9-13].

Shungites of the Koksu Deposit are shungite rocks with a carbon content of up to 20% and have a wide ecological potential. The composition of shungite includes trace contaminants: Ti; K; Na; Mn; Ba; Zr; Sr; V; Zn; Ni; Y; Sc; P; Cr; Co; Mo; Li; Pb; Cu; Nb; Ga; Sn; Be; W; As; (the content of decreasing from 0.5 % to 0.5 ppm of the listed range of trace contaminants). Koksu shungites have an average chemical composition of macro components that do not contain toxic impurities or their dangerous concentrations [14-15].

Prerequisites for the use of shungite as a mineral additive are the development of the most effective and environmentally friendly technologies for obtaining nanomaterials for the modification of building materials [16-19].

2. Materials and methods

As a mineral additive of concrete, shungite waste was used under the brand “Taurite” of the mining company “Koksu”. Taurite is a fine material with a size of 0-1 mm and up to 20 microns, which is based on the processes of mechanical activation and enrichment at a temperature of 400 to 600°C. Properties of the mineral additive “TK-A”, grain sizes 0-1 mm are shown in table 1.

| Name of indicators | Values |
|--------------------|--------|
| Mass fraction of silicon dioxide (SiO₂), % | 52.76 |
| Content of water-soluble substances, % | 0.73 |
| pH of aqueous suspension | 8.28 |
| Bulk density, kg/m³ | 674.3 |
| Humidity, % | 2.0 |

The properties of the mineral additive “TK-D-A” with grain sizes of 10 microns are shown in table 2.

| Name of indicators | Values |
|--------------------|--------|
| Mass fraction of silicon dioxide (SiO₂), % | 36.76 |
| Content of water-soluble substances, % | 0.7 |
| pH of aqueous suspension | 8.36 |
| Bulk density, kg/m³ | 512 |
| Humidity, % | 0.7 |

Portland cement and all samples of cement stone were studied by a complex of physical and chemical analysis methods: x-ray phase and differential thermal.

Radiographs were obtained using a DRON-3M diffractometer with a copper anti-cathode in the angle range of 4-64 degrees. Samples in the form of fine-ground powder were pressed into a plexiglass cuvette.

Thermo grams were taken on a Q-1500D derivatograph from 10 to 1000°C with a temperature rise rate of 100°C per minute.
3. Results and discussions

Reducing the water demand of cement composite materials with mineral additives is achieved by the complex use of mineral additives with a superplasticizer, which has a significant water-reducing effect.

Table 3 shows the composition of concretes with mineral additives of taurite and polymethylene-naphthalene-sulfonate additive of the Kratasol brand.

| № of composition | Cement, kg | Rubble, kg | Sand, kg | Mineral additive “TK-A”, kg | Mineral additive “TK-D-A”, kg | Superplasticizer “Kratasol”, kg | W/C |
|------------------|-----------|-----------|---------|---------------------------|-----------------------------|--------------------------------|-----|
| 1                | 380       | 990       | 875     | 19                        | -                           | -                              | 0.64 |
| 2                | 380       | 990       | 875     | 19                        | -                           | 3.8                            | 0.56 |
| 3                | 380       | 990       | 875     | 11.4                      | -                           | 3.8                            | 0.68 |
| 4                | 380       | 990       | 875     | 11.4                      | 3.8                         | 0.64                           |

The samples were solidified at room temperature for a day and after demolding, one series of concrete samples-cubes solidified for 3, 7, 14, 28 days under normal humidity conditions, and the second series of concrete samples-cubes after forming was placed in a heat-humidity treatment chamber after two hours (70°C).

Analysis of table 3 data shows that the use of mineral additives, depending on their composition and content, affects the W/C ratio of the concrete mix, namely fine-grained additives without plasticizer on average 258 l/m³, with superplasticizer 243 l/m³-247 l/m³.

The effect of plasticization with different amounts of mineral and plasticizing additives is different: concrete mix №1 for 60 minutes with c grade on the mobility of PK5 decreased to PK4; concrete mix №2 did not show a change in mobility for the same time; concrete mix №3 with PK5-PK3; concrete mix №4 with PK5-PK4.

The diluting effect of the superplasticizer “Kratasol” allows reducing the amount of closing water significantly and obtaining high-strength concretes with a given mobility of the concrete mix.

The results of research on concrete compressive strength are shown in table 4.

From the data given in table 4, it can be seen that the greatest strength of concrete was shown by compositions №3 and №4, containing mineral additives TK-D-A and superplasticizer “Kratasol”.

| Numbers of compositions | W/C | Workability OK, cm | Tensile strength at compression, MPa | Normal-humidity hardening, days | Hardening in the conditions of HHT, days |
|-------------------------|-----|--------------------|-----------------------------------|--------------------------------|--------------------------------------|
|                         |     |                    | 3 | 7 | 28 | 12 h | 1 | 28 |
| 1                       | 0.58| 20                 | 13.2 | 19.8 | 32.9 | 10.6 | 22.5 | 33.4 |
| 2                       | 0.64| 21                 | 13.5 | 20.1 | 34.1 | 12.4 | 22.8 | 33.6 |
| 3                       | 0.56| 23                 | 15.2 | 22.4 | 34.5 | 14.7 | 22.6 | 33.9 |
| 4                       | 0.68| 22                 | 14.4 | 21.3 | 33.8 | 12.8 | 22.7 | 34.9 |
| 5                       | 0.64| 23                 | 14.1 | 22.3 | 34.0 | 13.5 | 23.4 | 34.3 |

The increase in strength of compositions №2-5 in comparison with the control composition for the 3rd day is from 2.7-15.3%, for the 7th day from 1-27%, for the 28th day 2.5-30% when solidified in normal humidity conditions.
The increase in the strength of concrete compositions №2-5 during heat and humidity treatment in comparison with the control composition in 12 hours is from 24.5-39.6%, after 1 day from 5.3-29.9 %, after 28 days 2.4-25 %.

The processes occurring in the cement-mineral additive system are studied.

Identification of products of hydration and hardening of silicate systems showed that mineral additives have a significant effect on the phase composition of hardening systems, so the microstructure of the solidified solution at the age of 3 days in natural conditions showed that the particles of the mineral additive have been already exposed to the alkaline components of the cement paste at the initial stage of hydration of the hardening silicate system. As a result of this action, the surface of the particles of the mineral additive is hydrated. The thickness of the hydration layer is 1 ... 5 microns. The hydrated part of the grains forms a “border” around them, without separating from the remaining main part. In some cases, the intermediate cementing phase, on the contrary, penetrates into the grain structure of the mineral component.

Analyzing the obtained data on the study of the microstructure of the solidified solution we can draw the following conclusions:

- initially, there is a mechanical interaction between the mineral additive and the clinker components due to the roughness of the surface of its particles;
- due to their amorphous nature, SiO₂ microparticles serve as centers of crystal formation for hydrates, such as calcium silicate hydrate (CSH), which explains the formation of an additional number of crystallites that initiate the setting process. In addition, SiO₂ silica reacts with portlandite [Ca(OH)₂] via the mechanism described in the reaction:
  \[ \text{SiO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CSH} \]
- in the hardening silicate system, the grains of the micro-filler are mainly hydrated, creating a border around the residual part with a thickness of 1...5 microns;
- components of cement, hydrating and releasing the hydrate phase, actively affect the grain of the micro-filler;
- as a result of active hydration and surface hydration of the grains, an intermediate hydrate layer occurs between them, linking the cement stone and the aggregate (filler);
- this position of the intermediate hydrated layer between the grains of the micro-filler and the cement stone contributes to a significant strengthening and compaction of the solution.

Figures 1 and 2 show the obtained x-ray diffractograms of compositions after 28 days of natural hardening based on cement and mineral additives “TK-A”, “TK-D-A”.

![Figure 1. Diffractogram of cement stone with mineral additive “TK-A”.](image-url)
Articles of mineral filler are susceptible of hydration. The research results showed that the introduction of the mineral additive “Taurite” and naphthalene superplasticizer “Kratosol” increases the strength of normal-humidity hardening concretes and in comparison with the control composition in 3 days is from 2.7-15.3%, 7 days from 1-27%, 28 days 2.5-30%, and concretes of heat-humidity hardening in comparison with the control composition for 12 hours is from 5.5-12.9%, after 1 day from 0.3-19.8%, 28 day 0.6-25 %.

Features of dispersed particles of mineral additives from shungite waste processing in the hardening of silicate systems, namely that the surface of particles of mineral filler are susceptible of hydration that contributes to concrete and mortar with improved physical-mechanical indicators. Amorphous SiO₂ particles in the mineral filler contribute to the formation of foci of crystals of hydroaluminates and calcium hydroxysilicates. The influence of mineral additives on the rate of hydration processes of hardening of silicate systems was studied and established. The main products of hydration of modified mixtures are ettringite, portlandite and gel-like silicate phase. It was found that in the presence of mineral additives, interdependent aluminosilicate and polymer phases are formed, and the additives “TK-A” and “TK-D-A” are inhibitors of structure formation.

4. Summary

The possibility of using a new mineral additive in concrete – “Taurite” of a fine-dispersed size from 0.1 mm and up to 10 microns, which is based on the processes of mechanical activation and enrichment at a temperature of 400 to 600 °C is found. The research results showed that the introduction of the mineral additive “Taurite” and naphthalene superplasticizer “Kratosol” increases the strength of normal-humidity hardening concretes and in comparison with the control composition in 3 days is from 2.7-15.3%, 7 days from 1-27%, 28 days 2.5-30%, and concretes of heat-humidity hardening in comparison with the control composition for 12 hours is from 5.5-12.9%, after 1 day from 0.3-19.8%, 28 day 0.6-25 %. The optimal “soft” mode of heat-and-water treatment of concrete with an isothermal heating temperature of no more than 70 °C is established.

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Figure 2. Diffractogram of cement stone with mineral additive “TK-D-A”.

The lines of tricalcium silicate C₃S (3.035-2.76 Å), bicalcium silicate β-C₂S (2.89 Å) are fixed on the hardening diffractogram with “TK-A” (figure 1), there are quartz lines (4.27-3.346-2.451-2.283-1.988-1.540-1.447 Å) and hydration products: Ca(OH)₂ (4.923-2.624-1.926-1.795-1.687-1.485-1.447 Å), CaCO₃ (3.03-1.861 Å) and ettringite (9.803-5.59-3.874-2.20 Å). On the differential-thermal curve, endoeffects at 100°C and 120°C are associated with dehydration of ettringite and transition to CaO, at 500°C with dehydration of Ca(OH)₂, at 800°C with calcite decomposition.

The lines of tricalcium silicate C₃S (3.037-2.76-2.32-2.188-1.853-1.762-1.48Å), bicalcium silicate β-C₂S (2.89 Å) are fixed on the hardening diffractogram with “TK-D-A” (figure 2), there are quartz lines (4.27-3.34-2.28-1.821-1.539 Å) and hydration products: Ca(OH)₂ (4.917-2.625-1.924-1.793-1.684 Å), CaCO₃ (3.037-2.28-2.093Å) and ettringite (9.73-3.871-2.77-2.18 Å). On the differential-thermal curve, the endoeffects at 120°C and 150°C are associated with the dehydration of ettringite and the transition to CaO, at 520°C with the dehydration of Ca(OH)₂, at 800°C with the decomposition of calcite.

According to the data of x-ray phase analysis, the positive effect of mineral additives “TK-A” and “TK-D-A” on the hydration of clinker minerals was noted, as evidenced by the increase in the intensity of the Ca(OH)₂ line with an inter-plane distance of 4.92 Å and the appearance of a line also related to Ca(OH)₂ of 2.63 Å. On thermograms endoeffects are recorded at 500°C and 520°C associated with the removal of water from the Ca(OH)₂.
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