High-performance concretes with modifying micro additives of microsilica and diopside

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Abstract. This paper presents the results of the complex modifying additive’s effect consisting of a dispersed inert additive (diopside) and an active mineral additive (microsilica) and plasticizer on the strength properties and salt resistance of fine-grained concrete. It is shown that reducing the particle size of the inert mineral additive decreases its amount required to provide maximum curing of concrete specimens. The optimal ratio of microsilica, diopside, and plasticizer required to achieve maximum performance characteristics (compressive and bending strengths and, salt resistance) is determined.

1. Introduction

The rapidly developing construction industry places ever higher demands on building materials, in particular, concrete. The high mechanical of concrete strength is one of its most important performance properties. It is determined by a variety of factors: the water–cement ratio, the amount of entrained air, the quality of the binder and aggregates, etc. The influence of these factors has been studied well (see, for example, [1–3] and the literature cited therein), they are regulated by various standards and normative documents in the domestic construction industry.

It is also known that the strength of concrete is increased by the microadditives addition of different chemical composition. Microsilica (silica fume) is commonly used for this purpose [4, 5]. The effect of dispersed mineral additives on the heavy-weight concrete strength has been studied [5–8]. It has been found that the addition of both silica and diopside microadditives increases the strength of concrete, but different mass fractions of these additives are required to achieve the same increase. In our opinion, this may be due to the different particle size of the microadditives used. To answer this question, it is necessary to study the strength of concrete using microsilica and diopside additives with different particle sizes. It is also necessary to simultaneously vary the mass fractions of the additives used. In addition, it is necessary to investigate the mutual influence of these additives on the strength of cement conglomerates. This is the objective of the present study. The experimental data obtained will be used to testing the numerical model of the fine-grained concrete developed by the authors.

2. Materials and methods

In this work, TsEM I 42.5 N Portland cement (PC) (GOST 31108-2003, with a specific surface of 354 m²/kg) produced by the Topkinskii Tsement company was used. The concrete aggregate was sand produced by the Kamnerechenskii Kamennyi Kar’er Company and sieved and graded in accordance with GOST 26633-2012 Heavy-Weight and Sand Concretes Specifications. The fineness modulus of the sand was 2.5.
MK-85 microsilica (Kuznetskie Ferrosplavy, Chelyabinsk) and diopside were used as modifying additives. Microsilica was light gray, with a specific surface of 2180 m²/kg and an average particle size of 1.25 μm. According to the specification, the microsilica particle size distribution was as follows: less than 2.0 μm, 90.07%; 2–2.36 μm, 1.17%; 2.36–3.4 μm, 0.86%; 3.4–5.4 μm, 1.47%; 5.4–8.3 μm, 1.51%; 8.3–15.3 μm, 2.86%; 15.3–20.0 μm, 1.0%; 20.0–46.3 μm, 1.06%. The chemical composition was determined by the French company Filter Media at the request of the manufacturer. This microsilica was found to include 93.2 wt.% SiO₂, 0.74 wt.% Al₂O₃, 0.68 wt.% Fe₂O₃, 0.81 wt.% CaO, 0.91 wt.% MgO, 0.79 wt.% Na₂O, 1.38 wt.% K₂O, 1.20 wt.% C, and 0.29 wt.% S.

Diopside used in this work was crushed rock, a waste from the processing of phlogopite ore. Its density was equal to 3300 kg/m³. The composition of the mineral was determined by quantitative chemical analysis using 10 specimens collected in the Slyudyanskoye field. The results of the analysis were as follows: 53.44 wt.% SiO₂, 26.23 wt.% CaO, 17.90 wt.% MgO, 0.20 wt.% Al₂O₃, 0.09 wt.% Fe₂O₃, 0.11 wt.% R₂O, 0.10 wt.% TiO₂, and 1.93 wt.% LOI.

The certified MS-PowerFlow plasticizer, brown in color, was used. Its density was 1030–1090 kg/m³. The maximum content of chlorides and alkalis did not exceed 0.1 and 2%, respectively.

One of these study objectives was to investigate the dependence of sand concrete on the particle size of the diopside additive. The original diopside was ground in two types of mills: MShL-50 ball mill and an AGO continuous disk mill. The particle size of the resulting powders was determined by the BET method, and it was determined that the powders had a specific surface area of 400 m²/kg and 500 m²/kg, respectively. Thus, the powders had an average grain size \( D_d = 0.46 \) and 0.35 μm.

![Figure 1. X-ray diffraction patterns of powders.](image)

X-ray powder diffraction analysis of ground diopside powders using a DRON-3 X-ray diffractometer, (CuKα radiation, Bragg-Brentano focusing geometry) showed that the grinding of the mineral changed its structure. X-ray diffraction patterns of powders with an average particle diameter of 4.6 μm (upper line) and 3.5 μm (bottom line) are presented in Figure 1. The main reflections of SiO₂ (crystobalite) are marked by filled squares, and all other reflections belong to the CaO•MgO•2SiO₂ compound. The highest intensities of the CaO•MgO•2SiO₂ compound reflections and their significant decrease after milling indicate preferential crystallization of diopside in the given plane. The powder with the smallest particles (bottom line) has a more defective structure, and its amorphization occurs.
The strength characteristics of sand concrete were determined by beam tests using 40×40×160 mm beam specimens after 28 days of curing under normal conditions. The prepared specimens in molds were stored in a water seal bath for 24 hours, and after removal from the mold, they were stored in a horizontal position, without contacting each other, in a bath with pure water for 27 days. After the specified period, the specimens were removed from water, wiped, and tested no later than in 30 min.

Bending tests were carried out using a MII-100 testing machine at an average loading rate of (2.0–0.5) MPa/s. The compressive strength of the specimens was determined on a P-50 press, which satisfies the requirements of GOST 28840 and provides pure compressive loading. The bending strength was averaged over the tests’ results for three specimens, and the compressive strength was averaged over the results for six specimens.

3. Results of experiments

3.1. Effect of impurities in sand on the concrete strength

The strength properties of concrete depend significantly on the aggregate quality. Therefore, as a first step, of the impurities amount influence Δ was studied. Two series of concrete specimens were prepared using natural and clean (washed and dried) sand. In the preparation of all specimens, Portland cement and sand were mixed in a proportion of one to three. The strength characteristics of fine-grained concrete (bending strength $S_b$ and compressive strength $S_c$) were determined for 40×40×160 mm specimens after 28 days of curing under normal conditions. The tests’ results are presented in Table 1. Analysis of the results shows that for concrete specimens with clean sand, the compressive strength is 11.9% higher and the bending strength is 6.8% higher than those for concrete with natural sand. Therefore, clean sand was used to eliminate the effect of impurities in the aggregate on concrete strength in subsequent experiments.

Table 1. Effect of impurities in the aggregate on the concrete strength.

| $\Delta$, % | $S_b$, MPa | $S_c$, MPa |
|-----------|-------------|-------------|
| 8.0       | 7.4         | 29.5        |
| 0.3       | 7.9         | 33.0        |

3.2. Modification by microsilica

If the objective of this study was to investigate the strength of fine-grained concrete modified by the simultaneous addition of microdispersed silica and diopside, it would be the first required to elucidate the effect of each of these additives separately. In the experiments, the mass fraction of silica ($m_s$) ranged from zero to fourteen percent. The measured strength characteristics are presented in Table 2, so, it can be seen that the dependence of the concrete strength on the mass fraction of microsilica is not monotonic. Maximum strength values are attained at a mass fraction of 12%; in this case, the compressive strength increased by almost 55%, and the bending strength by almost 14%.

Table 2. Effect of the mass fraction of microsilica on the concrete strength.

| $m_s$, % | 0 | 4 | 8 | 12 | 14 |
|----------|---|---|---|----|----|
| $S_b$, MPa | 7.9 | 8.8 | 8.9 | 9.0 | 8.9 |
| $S_c$, MPa | 33.0 | 36.8 | 43.9 | 51.0 | 44.2 |

3.3. Modification by diopside

In the experiments, the mass fraction of diopside ($m_d$) ranged from zero to 9%, and the average particle size ($D_d$) was 0.35 and 0.46 μm. The measured strength characteristics are shown in Table 3. The experimental results show that modifying sand concrete with diopside additives in all cases increases its strength. However, the nature of the mass fraction effect is not universal and is determined by the average size of the modifying particles. As $D_d$ decreases, the mass fraction of the additive, the maximum
strength is reached also decreases. For the additive with the smallest particles, the optimal mass fraction is 5%, and for the additive with the largest particles, it is 7%.

Table 3. Effect of the mass fraction and particle size of diopside on the concrete strength.

| $D_d, \mu$m | 0.35 | 0.46 |
|-----------|------|------|
| $m_{di}$, % | $S_b$, MPa | $S_c$, MPa | $S_b$, MPa | $S_c$, MPa |
| 0 | 7.9 | 33.0 | 7.9 | 33.0 |
| 1 | 7.9 | 37.4 | 8.0 | 36.8 |
| 3 | 8.0 | 43.6 | 8.4 | 41.9 |
| 5 | 8.4 | 46.3 | 8.6 | 45.2 |
| 7 | 8.2 | 42.7 | 8.6 | 48.4 |
| 9 | 7.9 | 39.2 | 8.3 | 42.2 |

3.4. Modification by simultaneous addition of microsilica and diopside.

In the fourth series of experiments, sand concrete was modified by the simultaneous addition of microsilica and diopside. We used two diopside powders, with an average particle diameter of 0.35 and 0.46 µm at a concentration of 5 and 7%, respectively. In the preparation of a concrete mixture, diopside was pre-mixed with Portland cement in a ball mill for 1.5 hours, and microsilica was added to the mixture together with the mixing water. The results of measuring the strength of the obtained sand concretes are given in Table 4.

Diopside has a marked effect on concrete strength, modifying sand concrete by the simultaneous addition of microsilica. Comparison of Tables 1–4 shows that when simultaneously using microsilica and diopside, the compressive strength is higher than when using each of them separately. Maximum strengthening of concrete is achieved by introducing a complex additive containing 7 wt.% diopside with 4.6 µm particles and 12% microsilica. In this case, the compressive strength of sand concrete is increased by a factor of 2.5.

Maximum bending strength is achieved when concrete is modified by microsilica (see Table 2). A similar (about one percent smaller) value was obtained with the use of a complex additive containing 5 wt.% diopside with 3.5 µm particles and 4% microsilica. Specimens with the maximum compressive strength have a bending strength about seven percent lower than the maximum value.

Table 4. Effect of simultaneous addition of microsilica and diopside on the concrete strength.

| $D_d, \mu$m | $m_{di}$, % | $m_{ms}$, % | $S_b$, MPa | $S_c$, MPa | $D_d, \mu$m | $m_{di}$, % | $m_{ms}$, % | $S_b$, MPa | $S_c$, MPa |
|-----------|------|------|------|------|-----------|------|------|------|------|
| 0 | 0 | 0 | 7.9 | 33.0 | 0 | 0 | 0 | 7.9 | 33.0 |
| 0 | 8.1 | 48.1 | 0 | 8.6 | 48.4 |
| 4 | 8.9 | 53.4 | 4 | 8.5 | 59.9 |
| 0.35 | 5 | 8 | 8.1 | 55.1 | 0.46 | 7 | 8 | 8.3 | 63.7 |
| 12 | 7.9 | 75.8 | 12 | 8.3 | 82.7 |
| 14 | 7.7 | 69.1 | 14 | 8.3 | 77.9 |

4. Discussion and conclusions

The results of the experiments show that the use of microadditives significantly increases the strength of fine-grained concrete. This fact is well-known. However, the degree of strengthening is different for different micro-additives and depends on the particle size, mass fraction, and chemical activity of the additive. The positive effect of microsilica in cement compositions is explained by the pozzolanic reaction, which involves chemical binding of free calcium hydroxide, Ca(OH)$_2$ with the formation of calcium hydrosilicate crystals constituting cement gel [6, 8]: SiO$_2$ + Ca(OH)$_2$ + H$_2$O = = mCaO·nSiO$_2$·qH$_2$O. Calcium hydroxide crystals have lower strength [4] than calcium silicate hydrates (C-S-H), which is responsible for the lower mechanical properties of control specimens made without microsilica. This is confirmed by the direct study’s results of the specimens structure using a
Phenom G2 Pure scanning electron microscope. The structure of unmodified concrete is shown in Figure 2 (a); concrete has high porosity. Addition of microsilica and mixing water to the composition significantly changes the microstructure of the material and leads to the acicular crystals formation of calcium hydrosilicates (Figure 2 (b)).

![Figure 2](image)

**Figure 2.** Microstructure of specimens at 2500-fold magnification (control specimen (a), and a specimen with MK-85 microsilica (b)).

The addition of diopside has a micro-reinforcing effect on the structure and leads to stress redistribution under an external load [5, 7]. The Mohs hardness of diopside is 7, implying that the elastic modulus of the additive is higher than that of the cement matrix. Therefore, stress concentration will occur on particles of the additive, which will increase the mechanical strength of the specimens. The addition of diopside influences on the cement matrix structure formation: the average pore diameter decreases, and the frost resistance increases.

In specimens simultaneously modified with microsilica and diopside, both of the above strengthening mechanisms take place. As a result, the compressive strength increases severalfold. Further addition of plasticizer allows reducing the amount of mixing water, which also leads to an increase in the sand concrete strength characteristics.

We used MC-PowerFlow 3100 superplasticizer to compensate for the thickening effect due to the addition of fine diopside to the mixture. In our experiments, the superplasticizer was introduced into compositions modified with a complex additive, having the best strength parameters. Its amount varied from 0.2 to 1.1% of the binder weight. The water requirement of the mixture was evaluated when the slump flow diameter on a shaking table reached 114–115 mm, as for the control composition.

It was found that the introduction of the plasticizer reduced the water requirement of the mixture by 22%. At the same time, the compressive strength was increased, on average, by a factor of 1.5. Maximum strengthening was achieved in two compositions: a composition with a complex additive of 5% diopside with a grain size of 0.35 µm, 12% microsilica, and 0.8% plasticizer and a composition with a complex additive of 7% diopside with a grain size of 0.46 µm, 12% microsilica, and 0.5% of the plasticizer. In these compositions, the compressive strength was increased by a factor of 3.7.

Finally, the salt resistance of concrete was studied. It was shown that, modifying a sand concrete composition with a complex additive of diopside and microsilica in combination with a plasticizer provided increased the strength by more than a factor of two even after efflorescence.
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