Study of mineral additives for cement materials for 3D-printing in construction

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Abstract. The present work provides the results of a study of the effect of thermally activated brown coal fly ash from the coal basin in Podmoskovye, microsilica, Crimean shell rock flour and quartz flour on the rheological and physical and mechanical properties of the model system (of the cement mixture) in order to select the most effective mineral components for cement materials for 3D-printing. Optimization of the structure in order to form a dense and tight structure of high-quality concrete on cement binders can be carried out by introducing fine mineral additives of different material composition. In the presence of polycarboxylate plasticizers, such additives allow to regulate the mobility of cement systems at constant W/C ratio. At the same time, the increase in strength characteristics can be achieved both by introducing reaction active additives (microsilica, fly ash, shell rock flour) and components that perform the structural and topological function (shell rock flour, quartz flour). The effectiveness of regional mineral additives for use in cement systems is presented.

1. Introduction
The technology of 3D-printing is of great interest within various industries. The experience of application of layer-by-layer creation technology is also expanding in construction. The automation of processes allows the developers of equipment for such technology to formulate a wide range of applications: from cheap social housing in countries with a high level of poverty to the construction of the first objects on the surface of other planets and their satellites [1-3].

Despite the appeal of the new technological solution for the construction of building structures and the existing international experience of implementing this process in practice, there are many problems without the solution of which the potential of 3D-printing in construction cannot be fully realized. Fine-grained concrete on cement binders, as the most common and affordable material for construction, is the base for the implementation of 3D-printing technology in construction [4-7], both in Russia and in other countries. However, the peculiarity of layer-by-layer construction of structures is the conditions for molding and hardening of concrete, which in its turn requires the selection of components that, on the one hand, provide the necessary rheological and physical and mechanical properties, and are accessible in the chosen construction region, on the other.

There is a wealth of theoretical and practical experience and expertise in the world concerning the study of fine-grained concrete [8-13], which can be used to formulate requirements for materials for 3D-printing on a cement basis, and to optimize and universalize their formulations in order to improve quality. One of the features of high-quality and high-strength concretes, in contrast to traditional ones, is the presence in the composition of a highly disperse mineral additive that allows changing the
structure of the mixture, regulating mobility, affecting the density and strength of the composite [14-20]. In combination with effective polycarboxylate superplasticizers, mineral additives allow controlling the rheology of the mixture, reducing the W/C ratio, increasing mobility or changing the viscosity, providing the required concrete workability [8, 10, 14, 17].

2. Material and methods
The present work shows a study conducted in order to evaluate the effect of mineral additives on the rheological and mechanical properties of cement mixtures to select components for effective high-strength lightweight concretes on hollow microspheres. The study was carried out on the model system "binding agent - aggregate - water" with a component ratio Cement/(Sand + Additive) = 1: 3, W/C = 0.4.

To ensure the mobility of the mixture, a hyperplasticizer based on polycarbonate Melflux F1681 was used in an amount of 1% of the weight of the binder agent. The introduction of mineral additives was carried out by replacing part of the concrete aggregate. The following mineral additives were used: condensed microsilica MK-85 of Novolipetsk Metallurgical Complex with a mass fraction of microsilica on dry basis of at least 90%; quartz flour, obtained by grinding washed granular quartz sand; thermally activated brown coal fly ash from the coal basin in Podmoskovye and shell rock flour, which is a fine powder from calcareous porous sedimentary rock, consisting mainly of shells of marine animals, from the peninsula of Crimea. A typical material composition of the mineral additives studied is presented in Table 1.

| №  | Mineral additive       | Substance / Content, % wt. |
|----|------------------------|----------------------------|
|    |                        | SiO₂ | CaO+CaCO₃ | Al₂O₃ | FeO+Fe₂O₃ | MgO+MgCO₃ | Other |
| 1  | Microsilica            | 90.0 | 3.5       | –     | –         | 6.5       | –     |
| 2  | Quartz sand            | 94.5 | 0.3       | –     | 2.5       | 0.1       | 2.3   |
| 3  | Fly ash                | 50.0 | 2.5       | 37.0  | 4.5       | 0.5       | 5.5   |
| 4  | Shell rock flour       | 21.2 | 65.0      | 1.5   | 0.5       | 0.4       | 11.4  |

Evaluation of the effect of mineral additives was carried out according to the rheological parameters (mobility of the mixture within the diameter of the cone flow) and physical and mechanical properties (in particular, ultimate working capacity under bending and compressive strength in accordance with EN 196-1 with the help of the servohydraulic press "Advantest 9").

3. Results and discussion
The rheological properties of the mixture are the most important characteristics that predetermine the formation of the structure and the operational properties of building materials. Therefore, in technology it is important to control the rheology by establishing the patterns of their changes in the choice of mineral components for cement composites.

4. Acknowledgment
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It is known that the amount of energy necessary to move disperse systems depends on the amount of dispersed phase and the thickness of the interlayer of the disperse medium [21]. The amount of the dispersion phase (of quartz sand) in the systems under study varies in proportion to the amount of cement-mineral matrix consisting of a binding agent and a mineral additive. In this case, the mobility
of such a mixture is affected by the interaction of the particles of the mineral additive, the dispersion
and amount of which results in a change in the thickness of the water interlayer both in the cement-
mineral matrix and in the composition.

In the composites studied, the change in the mineral additive content was carried out by reducing
the amount of aggregate, and the mobility of the mixture would depend on the thickness of the
interlayer of the cement-mineral matrix and the size of the aggregate particles. Furthermore, it is
obvious that the introduction of fine components into the mixture is accompanied by an increase in the
specific surface of dry components, which requires more water for their wetting. Therefore, the
dependence of the change in rheological and physical and mechanical properties on the formulary and
structural parameters of the studied systems is established in the work.

To estimate the structural changes and to reveal the regularities of their influence on the physical
and mechanical properties of the systems under study, Table 2 presents the calculated parameters of
the structure and the value of the controlled characteristics of the mixtures.

Table 2. Recipe features, structural parameters and physical and mechanical properties of the
composites studied.

| No | Designation of composition | A/S, % | A/C, % | \(v_{\text{cmm}}\), microns | \(h_{\text{cmm}}\), microns | \(S_{\text{f}}\), m² | \(h_{\text{s}}\), microns | D, mm | \(\rho_{\text{f}}\), kg/m³ | \(R_{\text{cmm}}\), MPa | \(R_{\text{cm}}\), MPa |
|----|-----------------------------|-------|-------|-----------------------------|-----------------------------|-----------------|-----------------|------|------------------|------------------|------------------|
|    |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
|    | Control composition         |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 0  |                             | 1.1   | M-1.5 | 30.3 | 89.8 | 22.3 | 8.97 | 140.8 | 2.21 | 6.31           | 70.3           |
|    |                             | 1.2   | M-3.0 | 31.4 | 93.5 | 24.4 | 8.21 | 159.3 | 2.26 | 8.35           | 81.1           |
|    |                             | 1.3   | M-4.5 | 32.5 | 97.4 | 26.4 | 7.57 | 177.0 | 2.28 | 9.33           | 97.1           |
|    |                             | 1.4   | M-6.0 | 33.5 | 101.3 | 28.5 | 7.02 | 220.8 | 2.29 | 8.62           | 101.5          |
|    |                             | 1.5   | M-7.5 | 34.6 | 105.4 | 30.5 | 6.55 | 178.8 | 2.28 | 7.44           | 99.1           |
|    | 1. Compositions with microsilica |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 2.1 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 2.2 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 2.3 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 2.4 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 2.5 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 3.1 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 3.2 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 3.3 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 3.4 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 3.5 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 4.1 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 4.2 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 4.3 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 4.4 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 4.5 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 4.6 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |
| 4.7 |                             |       |       |                             |                             |                 |                 |      |                  |                  |                  |

Notes: *– diameter of the mixture spread exceeds the diameter of the flow table; A/S – the amount of
mineral additive in proportion to the mass of quartz sand in the control composition; A/C - the
amount of additive in proportion to the mass of cement; \(v_{\text{cmm}}\) – mass fraction of cement-mineral matrix; \(h_{\text{cmm}}\) –
the thickness of the interlayer of the cement-mineral matrix that envelops the aggregate particles,
according to; \( S_i \) is the total surface area of the dry components; \( h_w \) – the calculated thickness of the water film evenly spread over the surface of the dry components; \( D_s \) - the diameter of the spread of the mortar mixture from the truncated cone after 30 shakings; \( \rho \) – the average density of the mixture; \( R_{\text{umc}} \) - ultimate working capacity; \( R_{\text{com}} \) – is the compressive strength.

The use of microsilica as a mineral additive in cement systems has been sufficiently studied. The introduction of amorphous silica provides the formation of an additional amount of calcium hydrosilicates by binding the portlandite cement formed during the hydration process. Table 2 shows that the use of microsilica allows not only to increase the concrete compressive strength and ultimate working capacity to 53 and 88%, respectively, but also to form a highly mobile structure of the mortar mixture. This is due to the increase in the thickness of the interlayer of the cement-mineral matrix to 101.3 microns, consisting of cement, mineral additives and water, which envelops particles of quartz sand, reducing the energy costs for their movement. Furthermore, it is worth noting that an increase in the fraction of fine components in the system with a constant amount of water leads to a decrease in the effective thickness of the water layer from 9.88 to 7.02 microns. It can be seen that the amount of microsilica providing an increase in the mass fraction of the cement-mineral matrix to 33.5% corresponds to the best mobility of the mortar mixture and strength characteristics up to 9.33 MPa and up to 101.5 MPa by the concrete compressive strength and ultimate working capacity, respectively (Figure 1).

![Figure 1](image_url)

**Figure 1.** The change of the ultimate working capacity as a result of change in the amount of mineral additive.

The study of compositions with quartz flour shows that – and the similar applies to microsilica – the introduction of such an additive provides similar rheological parameters: the diameter of the spread is 225.8 mm, but with twice the expense (40.6% of the cement mass). At the same time, an equally mobile mortar mix with quartz flour possesses strength lower by 21 MPa, which can be explained by the low activity of the particle surface, in comparison with microsilica. That is, the effect of increasing the mobility of the mixture is more closely related to the particularities of the structure of the mixture, which is characterized for compositions with the highest strength of a cement-mineral matrix thickness of 118.6 \( \mu \)m when the entire surface of dry components is wetted with water by a layer of at least 8.86
μm. The limiting value of these characteristics, when the rheological and physical and mechanical properties of the mixtures under study vary insignificantly, is the share of quartz flour 43.4% of the cement mass. The composition of QS-12 due to the best workability has the best strength characteristics for systems with quartz flour: ultimate working capacity - 7.5 MPa, compressive strength - 80.0 MPa.

Analysis of the results of substitution of quartz sand by fly ash, presented in Table 2, indicate the appearance of a rheological effect when if a coarse fraction is substituted for a finer component, the enhancement of its fluidity is observed. It has been established that the mortar mix, where 7.5% of the aggregate was replaced by fly ash, has a better mobility of 207.8 mm than the control composition. Furthermore, the amount of mineral additive from the mass of cement is 25.3%, which, along with the binder, forms a share of the cement-mineral matrix in the system of 34.3% in weight. The thickness of the water interlayer is similar to the most mobile composition with quartz flour of 8.86 microns. Such an effect of fly ash can be attributed to a change in the structure of the mixture, characterized by a simultaneous increase in the packing density of particles, uniformity of their wetting with water, and a decrease in resistance to free movement.

Table 2 shows that the change in the diameter of the spread of the mortar mixture as a result of change in the amount of fly ash has an extreme dependence: an increase of its amount by more than 25.3% of the cement mass results in a decrease in mobility, which is associated with an increase in the fraction of fine particles in the system with a constant water content. Furthermore, the subsequent increase in the amount of fly ash in the mixture will result in a decrease in the thickness of the water interlayer on the surface of the solid components and in the deterioration of the rheological properties of the mixture. Further increase in the amount of fly ash is accompanied by a decrease in the thickness of the water interlayer below 8.86 microns and affects the mobility of the mixture, reducing it to 177.1 mm with a 10% substitution of quartz sand. This leads to a decrease in strength parameters: ultimate working capacity from 7.2 to 5.2 MPa, compressive strength – from 92.0 to 89.0 MPa (Figure 1 and 2).

Figure 2. Change in compressive strength as a result of change in the amount of mineral additive.
The improvement in the mobility of the mixture obviously affects the strength characteristics of the mixtures studied. It is established that the nature of the change in physical and mechanical properties correlates with the change in workability: compositions with the best mobility F-7.5 and F-8.5 have the highest values of the ultimate working capacity and compressive strength of 6.44 ... 7.25 and 88.2 ... 92.0 MPa, respectively. At the same time, the ultimate working capacity increases to 45.9%, and compressive strength – to 47.9% (Figure 2). The abovementioned dependences are explained by the influence of two factors: firstly, by the denser packing of particles, which is provided by high mobility (workability), and secondly, by the interaction of fly ash containing up to 55% SiO2, with portlandite formed in the process of cement hydration from the formation of additional the amount of calcium hydrosilicates.

The use of shell rock flour as a mineral additive also has a significant effect on the rheological properties of the mixture. The increase in the proportion of cement-mineral matrix in the mixture to 43.4 ... 49.1% of the mass of cement leads to the formation of an ultra-mobile self-compacting system. This indicates that the additive used is effective for controlling the mobility of cement systems in the presence of a superplasticizer. Furthermore, the thickness of the cement-mineral matrix for such compositions corresponds to a value from 145.6 microns, which corresponds to a similar value for compositions with quartz flour, which have the best combination of rheological and strength properties. The combination of calcium and silicon compounds in shell rock flour that participate in hydration processes provides a comprehensive influence both at the expense of improving the workability of the mixture, and by compaction and strengthening of its structure, which affects the value of the strength parameters. Maximum strength values are the composition of mixtures, where the share of quartz sand is reduced by 20 ... 28%. The content of shell rock flour in such materials in the range of 67.6 ... 94.6% makes it possible to ensure the value of the ultimate working capacity to 8.89 MPa, compressive strength – to 90.1 MPa, which is more by 78.8 and 46.5% respectively in comparison with the control composition.

A comparative analysis of the effect of the studied mineral additives on the mobility of the mixture indicates that in systems with a polycarboxylate plasticizer, each of them promotes an increase in the diameter of the spread, despite an increase in the proportion of dispersed components. The maximal values of the strength characteristics are compositions with a spread diameter of at least 200 mm, which is achieved for each composition with different amounts of mineral additive. It has been established that for the studied cement system, the consumption of mineral additives such as microsilica, quartz flour, fly ash and shell rock flour, which provides the optimal combination of controlled parameters, can be described by the value of the interlayer of a cement-mineral matrix of at least 100 microns or the wetting interlayer of water less than 7.0 microns. Furthermore, it is necessary to form a structure balanced by the distance between the particles of the aggregate and the uniformity of wetting of its solid components, in which such parameters, when introducing fine additives, have a mutually antithetic effect.

Based on the physical and chemical characteristics of each of the additives studied, the effect they exert is significantly different. Thus, the maximum consumption of fly ash is reached at 28.7% of the mass of cement (35.3% of fine fractions), shell rock flour - 94.6% of cement mass (49.1% share of CMM), microcracking - 25.3% % (34.6% share of CMM) and quartz flour - 67.6% of cement mass (43.4% share of CMM).

Thus, it has been shown that the studied mineral additives can be used in plasticized cement systems as rheologically active components that allow them to control their mobility, reduce water consumption or increase strength characteristics, which is especially important for materials for 3D-printing, where the maximum particle size of the main components is limited by the geometric characteristics of the extrusion head parts of the printers.

The possibility of using various regional mineral additives for improving and universalizing materials for 3D-printing is shown. Furthermore, it is necessary to develop compositions that expand the functional designation of structures constructed with such technology: practical design, as well as heat and sound insulating properties, and their aesthetics. High-strength lightweight concrete on
hollow microspheres can be one of such materials [22, 23], its recipe optimization will combine the above-mentioned properties of materials and move away from the practice of using 3D-printing for the construction of a fixed non-removable formwork to realize the potential for constructing functional structures directly at the site.

5. Conclusion
Optimization of the structure for formation of a dense and tight structure of high-quality concrete on cement binders can be carried out by introducing fine mineral additives of different material composition. In the presence of polycarboxylate plasticizers, such additives allow to regulate the mobility of cement systems at constant W/C ratio. At the same time, the increase in strength characteristics can be achieved both by introducing reaction active additives (microsilica, fly ash, shell rock) and components that perform the structural and topological function (shell rock flour, quartz flour). The effectiveness of regional mineral additives for use in cement systems is presented.

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