Modification of Cement Composite Material for Additive Construction Technologies

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Abstract. This work discusses the development of concrete mix compositions using modifying additives, the study of the rheological and strength properties of compositions for construction 3D printing. Cellulose ether (CE), calcium formate (CF), and redispersible polymer powder (RPP) were studied as modifying additives at different percentages by weight of cement. Compression strength tests have shown the most promising compositions for their further study for rheological parameters. The best strength indicators in the early and late periods of hardening were shown by the composition with the introduction of 2% RPP and the composition with 2% CF. The composition with 2% RPP has an increased density and viscosity and relatively low flowability, and also has a shortened setting time, which makes the use of an RPP additive effective for additive construction methods.

1. Introduction
Nowadays, additive technologies are a fast growing branch of the scientific and technological sector around the world. In the construction industry, despite some inherent conservatism, innovative technologies are also being introduced. Despite the fact that large corporations and institutes are conducting their development in this area and there are even some regulatory documents in the territory of the Russian Federation [1–4], experimental research in the field of building materials science is of great interest. In this regard, various developments of concrete mixture compositions, studies of the rheological and strength properties of solutions are of great importance for further use in creating a more elaborate regulatory framework by the time additive technologies are introduced into everyday construction practice.

The composition of the concrete mix plays a critical role in the effectiveness of the use of additive technologies. Many scientific groups devote their research to finding the most rational use of mix components. The exclusion of such a component as a coarse aggregate provides a number of possibilities for replenishing the strength of concrete in the absence of a solid stone frame in it. The use of various additives that improve the properties of concrete, as well as an additional analysis of the applicability of alternative dispersed reinforcement, allows you to optimize the physical and chemical characteristics of the composite. The study of previously unexplored components in the composition of a concrete mixture is of particular interest. Such a study could open up new possibilities for the applicability of concrete in additive technologies.

In this work, cellulose ether (CE), calcium formate (CF), and redispersible polymer powder (RPP) were studied as modifying additives at different percentages by weight of cement. These additives are
widely used in dry building mixtures, plaster mortars, construction adhesives to impart tackiness to a cement-based mortar [5], to improve adhesion [6], to accelerate the setting of cement stone [7].

2. Materials and methods
Based on the analysis of modern scientific research [8-13], as well as the results of earlier work [14, 15], a basic composition was selected that would be optimal for the requirements of concrete 3D printing. The selection of the composition is based on the thesis of the most uniform structuring of the concrete matrix due to the introduction of ultradispersed additives.

In this work, the following materials were used: 1) Portland cement Eurocem super 500, CEM I 42.5H, Petersburg Cement; 2) Construction sand, fractions 2.5-1.25 and 0.63-0.315 mm; origin location: Kaliningrad region; 3) Silica fume (SF): wastes of the metallurgical industry, country of origin: Poland; 4) Highly active metakaolin (MK): white, country of origin: Russia, Chelyabinsk region, Synergo; 5) Polypropylene fiber: length of 12 mm, thickness of 35 μm, country of origin: Russia; 6) STACHEMENT 1267 hyperplasticizer based on polycarboxylates for the production of ready-mixed concrete: country of origin: Poland; 7) Modifying additives: Cellulose ether (CE), Calcium formate (CF), Redispersible polymer powder (RPP).

The corrected consumption of components, taking into account the percentage of the additive introduced, as well as the different water requirements of the mixture compositions, is presented in Table 1. Nine different formulations were considered. Composition No. 1 is control, i.e. without the introduction of additives.

| Components | 1 control | 2 RPP 2% | 3 CF 2% | 4 RPP 1% | 5 CF 1% | 6 RPP 1%+CF 1% | 7 CE 1% | 8 CE 0.25% | 9 RPP 1%+CF 1%+CE 0.25% |
|------------|-----------|----------|--------|----------|--------|----------------|--------|----------|------------------------|
| Water/cement | 0.8 | 0.73 | 0.73 | 0.73 | 0.73 | 0.73 | 0.8 | 0.8 | 0.8 |
| Cement (kg/m³) | 545.3 | 545.3 | 545.3 | 545.3 | 545.3 | 545.3 | 545.3 | 545.3 | 545.3 |
| Sand (kg/m³) | 1168 | 1168 | 1168 | 1168 | 1168 | 1168 | 1168 | 1168 | 1168 |
| Water (l/m³) | 416.6 | 381.9 | 381.9 | 381.9 | 381.9 | 381.9 | 416.6 | 416.6 | 416.6 |
| Silica F (kg/m³) | 156 | 156 | 156 | 156 | 156 | 156 | 156 | 156 | 156 |
| MK (kg/m³) | 78 | 78 | 78 | 78 | 78 | 78 | 78 | 78 | 78 |
| CF (kg/m³) | - | - | 10.4 | - | 5.2 | 5.2 | - | - | 5.2 |
| CE (kg/m³) | - | - | - | - | - | 5.2 | 1.3 | 1.3 |
| RPP (kg/m³) | - | 10.4 | - | 5.2 | - | 5.2 | - | - | 5.2 |
| Fiber (kg/m³) | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 |
| St. 1267 (kg/m³) | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 |

The granulometric study of sand made it possible to select certain fractions to create the most dense structure of a concrete stone, namely: 70% - sand with a fraction of 2.5-1.25 mm and 30% - sand with a fraction of 0.63-0.315 mm. The coarse fraction of the fine aggregate makes it possible to create a rigid framework in the composite body, and the fine fraction – to fill the pores as much as possible, contributing to the improvement of the structure.

The initial compressive strength of the samples was determined at the ages of 30, 45, 60, 75 and 90 minutes. For this, sample cubes measuring 20x20x20 mm were made from freshly mixed concrete mixture. Determination of the physical and mechanical characteristics of concrete in the early stages of hardening is of particular relevance in the field of additive technologies. The extruded layer of the concrete mix should gain its strength in such a way as to grasp the underlying layer, withstand the weight of the overlying layer without deformation, while the concrete solution should not begin to set inside the extruder.

Universal testing machine INSTRON ElectroPuls E1000 was used to carry out strength tests in the early stages of hardening.
The samples most promising for 3D construction were further tested for compressive and flexural strength at the age of 1, 3, 7 and 28 days on a ToniNORM testing machine with the ToniPRAX modification.

Additionally, the rheological properties of the studied compositions were determined, such as: 1) Determination of the mortar consistency using the Vicat apparatus; 2) Determination of the consistency by cone penetration test; 3) Determination of the workability of the fresh concrete by flow table test; 4) Determination of the setting time using the Vicat apparatus.

3. Results

3.1. Determination of compressive strength

The results of experimental studies are shown in Figure 1.

![Figure 1. Initial compressive strength.](image)

According to the results in Figure 1, it can be noted that the greatest increase in strength is in composition No. 2, which contains an additive of redispersible polymer powder in 2% content. Composition No. 4 with 1% RPP introduction showed high strength results only to 75-90 minutes of hardening. Compositions No. 3 and No. 5 with 2% and 1% calcium formate, respectively, showed a smaller increase in strength relative to control composition No. 1. Composition No. 3 showed a stable increase in strength during the first 75 minutes of hardening. The combined introduction of RPP and CF in composition No. 6 gave a smaller increase in strength compared to compositions with mono-additives. The worst results were shown by compositions No. 7, 8 with the introduction of cellulose ether in the amount of 1% and 0.25%, respectively, yielding in strength even to the control composition. Composition No. 9, including all investigated additives, showed a result similar to compositions No. 7, 8. In this case, we can talk about a tendency to decrease the compressive strength with the introduction of cellulose ether.

The efficiency of the addition of additives $\Delta R$ was determined for samples aged 30 and 90 minutes according to the formula (1) from [16]:

$$\Delta R = \left( \frac{R_{\text{basic}} - R_{\text{control}}}{R_{\text{control}}} \right) \times 100\%$$  \hspace{1cm} (1)

where $R_{\text{basic}}$ and $R_{\text{control}}$ – strength of concretes of basic and control compositions, MPa.

The calculation results are shown in Table 2.
Table 2. Additives efficiency.

| Composition No. | Efficiency (%) |
|-----------------|----------------|
|                 | 30 min | 90 min |
| 2               | 188.60 | 50.04  |
| 3               | 77.38  | 20.84  |
| 4               | 133.41 | 47.51  |
| 5               | 145.63 | 32.01  |
| 6               | 101.75 | 25.55  |
| 7               | -33.71 | -59.80 |
| 8               | -36.64 | -43.06 |
| 9               | -33.36 | -40.63 |

Among the compositions with the introduction of RPP, the most intense increase in strength is observed for composition No. 2 with 2% addition of the additive, this fact is confirmed by the analysis of the efficiency of modifying components. The most stable increase in strength in comparison with other compositions with calcium formate is observed for composition No. 3 (2% FA). Further studies of strength gain at later stages of hardening (1, 3, 7 and 28 days) were carried out for the two indicated compositions in comparison with the control. The results are shown in Table 3.

Table 3. Strength at the late stage of hardening.

| Composition No. | Age (days) | Flexural tensile strength | Compressive strength |
|-----------------|------------|--------------------------|----------------------|
|                 |            | Load (kN) | Strength (MPa) | Load (kN) | Strength (MPa) |
| 1               | 28         | 1.95      | 4.7          | 62.72     | 39.2           |
| 2               | 1          | 1.1       | 2.64         | 23.6      | 14.75          |
|                 | 3          | 1.2       | 2.88         | 52.58     | 32.86          |
|                 | 7          | 2         | 4.8          | 67.1      | 41.94          |
|                 | 28         | 1         | 2.4          | 91.4      | 57.13          |
| 3               | 1          | 1.1       | 2.64         | 27.5      | 17.19          |
|                 | 3          | 1.4       | 3.36         | 63.38     | 39.61          |
|                 | 7          | 2.4       | 5.76         | 91.8      | 57.38          |
|                 | 28         | 1.1       | 2.64         | 114.5     | 71.56          |

The results of flexural tensile strength tests did not show an increase in the strength of the modified samples compared to the control. In the case of a study of the compressive strength, the compositions with additives showed an intense increase in strength. By the age of 28 days, the composition with 2% RPP turned out to be 46% more effective, and composition with 2% CF was 83% more effective than the control. Hence, we can conclude that at the early stages of hardening (30, 45, 60, 75, 90 minutes), composition No. 2 with 2% introduction of RPP by weight of cement turned out to be the most effective in carrying out strength tests in compression, and at later periods (1, 3, 7, 28 days) - composition No. 3 with 2% CF content.

3.2. Rheological properties

According to the results of strength tests, composition No. 2 (RPP 2%) was recognized as the most promising, composition No. 3 (FC 2%) can also be noted, which showed a relatively stable increase in strength compared to other concentrations of calcium formate in the composition. At the same time, compositions with the introduction of cellulose ether were recognized as the least effective for achieving high compressive strength and were not subject to further consideration.

The results of studies to identify the rheological characteristics of compositions No. 1 (control), No. 2 and No. 3 are shown in Table 4.
Table 4. Rheological test results.

| Rheological properties                      | Composition No. |
|---------------------------------------------|-----------------|
| Consistency using the Vicat apparatus (mm)  | 31              |
| Consistency by cone penetration test (mm)   | 38              |
| Workability by flow table test (cm)         | -               |
| Setting time:                               |                 |
| beginning                                   | 2h 30min        |
| end                                         | 3h 50min        |
|                                             | 2h 15min        |
|                                             | 3h 25min        |
|                                             | 3h 00min        |
|                                             | 4h 40min        |

A slight increase in the density of the concrete mixture is noted when 2% of the considered additives are added to the composition. This may be due to the fact of the introduction of ultradispersed additives that increase the density of the structure. In this case, a significant decrease in the flowability of the solution is observed. However, based on the results of determining the setting time, composition No. 2 showed a reduction in this period, and composition No. 3 significantly extended them. Understanding the loss of plasticity by grasping without significant development of compressive strength, we can note the great importance of this fact when using the composition in additive technologies. The increase in setting time, which is observed in the composition No. 3, in this case is a negative factor.

According to the study of rheological parameters, composition No. 2 with 2% content of redispersible polymer powder can be distinguished. Such a composition has an increased density and viscosity and relatively low flowability, and also has a reduced setting time. The combination of such indicators makes the use of RPP in 2% by weight of the binder promising for additive construction.

4. Discussions

In this work, the influence of various additives on the strength and rheological characteristics of concrete mixtures was investigated. Based on the results of the work, the following conclusions can be drawn:

1. Introduction to the composition of cellulose ether in the considered concentrations (1%; 0.25%) showed a significant decrease in compressive strength compared to the control composition, which indicates the inexpediency of using this additive in the field of additive technologies;

2. The best results based on the results of strength tests at the early stages of hardening were demonstrated by compositions with mono-additives of 2% redispersible polymer powder (RPP) and 2% calcium formate (CF), which showed the most stable increase in strength compared to other concentrations of these additives;

3. As a result of tests for compressive strength at the age of 28 days, the composition with CF showed an increase in strength in the amount of 83%, and with RPP - 46% compared to the control composition (these compositions were studied as the most promising);

4. Based on the results of studies of rheological characteristics, both compositions showed an increase in the density of the concrete mix, which is a positive factor of applicability in 3D construction;

5. Analysis of the results of the setting time showed a reduction in the setting time for the composition with RPP, while the introduction of 2% CF into the composition led to a significant increase in the hardening period.

Compositions No. 2 and No. 3 were recognized as the most promising based on the results of strength tests at early stages of hardening. Composition No. 3 showed a significant increase in strength at the age of 28 days, however, an increase in hardening time is a negative factor in the technology of layer-by-layer construction. This problem can be solved by introducing a hardening accelerator into the composition, which is the subject of further research. At the same time, the composition No. 2 with
2% RPP meets all the necessary requirements for the characteristics of the concrete mixture for use in additive technologies and requires a more detailed study of other concentrations and possible combinations of this modifying additive.

5. References

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