Compounding features of composite gypsum binders for porous composites in construction printing technologies

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Abstract. At this stage of development of construction technologies and widespread digitalization, one of the most promising and interesting areas of the Russian and international scientific community is construction printing. The main idea of construction printing is to create a finished product or structure with a single installation. The most important task now is to master printing with porous concrete to give structures the required thermal characteristics, without which additive construction cannot fully compete with conventional technologies in the construction of wall structures. One of the promising materials in this case is foam concrete, in which the rapid fixation of the porous structure and the given shape is provided by the use of a composite gypsum binder. The paper considers the possibility of moving away from traditional composition that include active mineral additives by using Portland cement with various mineral additives. The influence of the used foaming agent on the hardening process of the gypsum-Portland cement system with various mineral additives was studied. This solution is designed to simplify the technology, make it more attractive for small and medium-sized businesses, increase the compatibility of the binder with foaming agents, as well as its activity to ensure high mechanical performance of foam concrete.

1. Introduction

One of the most advanced trends in the development of construction technologies is construction printing. According to a large number of publications, its advantage is an increase in the construction rate, the ability to create structures of rational sections of the most diverse configuration [1,2], etc.

Existing industrial models of 3D printers mainly use concrete mix as a building material, which is extruded horizontally on the layer previously laid out by the printer. The structure erected in this way must meet the required regulatory requirements, the most important of which are strength and thermal. If the strength indicators of the structures being built are sufficient for the construction of load-bearing walls of low-rise buildings, the required thermophysical indicators are achievable only with the use of insulation. However, such solutions go against the main ideas of 3D printing – creating a finished product with a single installation [3-6].

In this regard, the development of printing with porous materials that have indicators comparable to those traditionally used is very promising. This will make the technology attractive for small and medium-sized businesses on the one hand, and on the other hand, it will open up new facets of the use of additive technologies.
From this point of view, such materials as expanded clay concrete, foam concrete, non-autoclaved aerated concrete are of interest. According to the analysis of publications in the public domain, this direction is in its infancy. The studies on the possibility of digital printing with expanded clay concrete, foam concrete [7] and non-autoclaved aerated concrete are known [8].

In our opinion, for these purposes, as an alternative to non-autoclaved aerated concrete and other specified materials, it is advisable to use foam concrete, in view of the simplicity of technology, cost-effectiveness, the ability to build load-bearing walls and structural elements with the same properties as on the basis of traditional materials, namely, high thermal insulation, sound absorption and fire resistance.

The foam concrete technology itself has been sufficiently studied [9-11] and others. The main problems for its adaptation to construction printing, in our opinion, are the need for rapid fixation of the structure and the acquisition of the load-bearing capacity of the structure, so that the laid layers are not afraid of external influences. The ability of materials to harden under adverse site conditions, such as rapid dewatering, is also a serious problem that has received little attention.

The use of widely used, traditional hydraulic binders is not rational due to their slow hardening, even when using accelerators. The use of air binders, namely gypsum, is not optimal due to its low water resistance. In this regard, in our opinion, the introduction of fast-hardening composite gypsum binders (CGB) of increased water resistance with active mineral additives of different genesis can be very promising for these purposes [12,13].

However, mineral additives with high activity are expensive, and those that are waste products often have a non-permanent composition and therefore do not have stable properties. In addition, the multi-component composition complicates the production technology and increases the cost of additive construction, which is not profitable for small businesses. Based on this, it is very tempting to obtain CGB without a mineral additive, by mixing only two components, which will increase the content of active components and potentially the strength of foam concrete.

It is known that an active mineral additive in the composition of CGB is necessary for the binding of Ca(OH)$_2$, thus it eliminates the conditions for the formation of ettringite and high-base calcium hydroaluminates [13]. Therefore, in order to exclude these phenomena, it was hypothesized that in highly porous systems, when using Portland cements containing mineral additives, these processes will be minimal.

The second problem in obtaining foam concrete is to which extent the used foaming agent affects the hardening process of the binder.

In this regard, the main task of the study was to study the influence of the type of Portland cement and foaming agent on the strength and stability of CGB.

2. Materials and methods

2.1. Materials

In this work, as the binding base of CGB we used: \(\alpha\)-modification gypsum binder GVVS-16 (G-16) of JSC “Samara gypsum plant”, Portland cement CEM I 42.5 N JSC “Novoroscement” (CEM I) GOST 31108-2016, Portland cement CEM II/A-P 42.5 SS JSC “Novoroscement” (CEM II(SS)) GOST 22266-2013, Portland cement CEM II/B-Sh 42.5 N LLC “South Ural GPC”, GOST 31108-2016 (CEM II(Sh)). As a pore-forming additive, the foaming agent “Penostrom” of LLC “SHIELD” of Shebekino, Belgorod region, corresponding to TU 0250-001-22299560-97 was used.

2.2. Methods

To model the behavior of the system under study, a two-factor three-level experiment was performed for each composition of CGB with different types of Portland cement. The conditions for planning an experiment are shown in table. 1. The amount of the closing water was assumed to be constant W/T=0.45.
Table 1. Conditions for the experiment planning.

| Factor                              | Level of variation | Variation range |
|-------------------------------------|--------------------|-----------------|
| Natural form                        | Encoded form       | -1   | 0    | 1    | 25   | 0.3 |
| Percentage of gypsum in the mix, %  | x₁                 | 25   | 50   | 75   | 25   |     |
| Dosage of foaming agent, %          | x₂                 | 0    | 0.3  | 0.6  | 0.3  |     |

The output parameters were the strength of the hardened composite at the age of 7, 14 and 63 days when stored in air-wet conditions. The choice of these time intervals is determined by the fact that the system indicators at the age of 7 days allow assessing the contribution of gypsum to the formation of composite strength. In addition, the age of 7 days, as practice shows, is the maximum before critical dehydration of the material in unfavorably dry conditions. The increase in the strength of the composite in the interval from 7 to 14 days is mainly due to cement, while the development of destructive phenomena is still minimal. The time interval of up to 63 days provides both the maximum possible hydration of cement in specific conditions, and the development of the main volume of destructive processes. Tests performed at this age are necessary to assess the stability of the resulting system.

3. Results

On the basis of regression equations, the dependences of the dynamics of the strength set of a stone based on CGB with various types of Portland cement were obtained (Fig. 1). The amount of foaming agent (factor x₂=−1) is zero. Factor x₁ (the percentage of gypsum in the mix) varied throughout the considered range. The Figure 2 shows the dependence of the strength of the stone based on CGB with a foaming agent in the amount of 0.3% of the weight of the binder (factor x₂=0). The study was conducted on dense, rather than porous systems in order to avoid the influence of fluctuations in the value of the achieved porosity on the strength indicators.

It is known that when gypsum interacts with the main components of Portland cement clinker, along with hydration products that are favorable for structure formation, compounds are formed in the form of hydrosulfoaluminates and calcium hydrosulfoferrites, which, depending on the conditions of their occurrence, either contribute to strengthening the structure of the hardening binder, or weaken or even destroy it [12]. Therefore, one of the main factors is the content of C₃A and C₄AF. In the cements used in the work, their number decreases in the series CEM I - CEM II (Sh) - CEM II (SS).

It is also known that in the “Portland cement – gypsum – active silica contained in mineral supplements – water” instead of ettringite hydrosilicates and calcium hydroaluminate with reduced basicity, hydrogenate, hydroxyltoluene, hydrochloridechemical can be formed. These new formations are characterized by a lower content of hydrated water in their molecules compared to its content in the ettringite molecule [12].
Comparing the obtained compositions in the ratio “gypsum : clinker : mineral additive” based on CEM II (Sh) (50:20:30) and CEM II (SS) (50:30:20) with the compositions of CGB, where heavy concrete (HC) and quartzite sandstone (QS) were used as mineral additives in the ratio “gypsum : Portland cement : mineral additive” (60:20:20), we have comparable strength indicators of the hardened stone at the age of 28 days (Fig. 3 (a)) and softening coefficients (Fig. 3 (b)).

The second factor affecting the hardening processes of the system under study is the action of the applied foaming agent. According to [14], anionic foaming agent molecules, having a negatively charged group – \( \text{SO}_3^- \), are adsorbed on calcium hydroaluminate particles having a positive surface charge. Therefore, as the C₃A content in the cement increases, the content of non-adsorbed foaming agent in the liquid phase decreases, which worsens the properties of the mixture.

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**Figure 1.** Dynamics of gypsum cement stone hardening on various types of Portland cement: a) CEM I; b) CEM II (Sh), c) CEM II (SS).

**Figure 2.** Dynamics of gypsum cement stone hardening on various types of Portland cement at the concentration of foaming agent – 0.3%: a) CEM I; b) CEM II (Sh), c) CEM II (SS).
4. Discussion
At the age of 63 days for all cements, there is a tendency to increase the strength at the maximum dosage of the foaming agent. Perhaps this is due to the fact that a large amount of foaming agent, slowing down the hydration of cement, stretches the development of destructive processes over time, and reduces their negative impact on strength. This factor manifests itself the more strongly, the worse the cement relates to joint hardening with gypsum in the series CEM II (Sh) - CEM II (SS) - CEM I. At lower dosages, the prevailing factor is the inhibition of cement hardening, at higher dosages - the suppression of destructive processes. Accordingly, it is acceptable and appropriate to use increased dosages of foaming agent in porous systems on CGB, as this simplifies the manufacturing process and suppresses negative phenomena. The inevitable loss of strength in this case for CEM II (Sh) and CEM II (SS) will be 10...15%, for CEM I up to a maximum of 40...50%.

5. Summary
Based on the conducted research, it was concluded that the use of CEM II (Sh) composition “gypsum – clinker – mineral additive” (50:20:30) is suitable from the used cements for foam concrete on CGB. This allows not implementing a separate mineral additive, which simplifies the production technology. At the same time, there is a minimum of destructive phenomena and a neutral attitude to any dosage of the foaming agent is observed. The main disadvantages of CEM II (Sh), such as slow gripping, low initial speed of hardening are fully compensated by a gypsum binder.

6. References
[1] Luneva D. A., Kozhevnikova E. O., Kaloshina S. V. 2017 Application of 3d printing in construction and prospects for its development Bulletin of the Perm national research Polytechnic University Construction and architecture 8(1) 90-101
[2] Yi Wei Daniel Tay, Biranchi Panda, Suvash Chandra Paul, NisarAhamed Noor Mohamed, Ming Jen Tan&Kah Fai Leong. 2017 3D printing trends in building and construction industry: a review Virtual and Physical Prototyping 12(3) 261-276
[3] Elistratkin M.Y., Lesovik V.S., Alfimova N.I., Shurakov I.M. 2019 On the question of mix composition selection for construction 3d printing. Materials Science Forum 945, 218-223
[4] Klyuev S.V., Klyuev A.V., Shorstova E.S. 2019 The micro silicon additive effects on the fine-grassed concrete properties for 3-d additive technologies Materials Science Forum 974 131 – 135
[5] Lesovik V. S., Absemetov M. V., Elistratkin M. Yu., Pospelova M. A., Shatalova S. V. 2019 On the issue of studying the features of structure formation of composite carriers for non-autoclaved aerated concrete Construction Materials and Products 2(3) 41-47
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