Compounding Features of Special Molding Mixes for 3D Printing Technology

E. S. Glagolev, N. V. Chernysheva(✉), V. S. Lesovik, and E. N. Lesnichenko

Belgorod State Technological University named after V.G. Shukhov, Belgorod, Russia
chernysheva56@rambler.ru

Abstract. World experience shows that to ensure the speed of building construction and minimize labor costs, the technology of layer-by-layer synthesis (3D printing or three-dimensional extrusion) will develop rapidly in the next decade. In modern Russian conditions, 3D printing is ideal for mass and individual construction of low-rise houses and cottages. The main idea of construction printing is to create a finished product or structure with a single device. For a stable technological process of construction of low-rise buildings by layer-by-layer synthesis, special fast-hardening molding mixes are offered, including clinker minerals, gypsum binders, mineral and organic additives, as well as fine aggregate. The joint insertion of gypsum binders of α - and β - modification (G-5BII and GVVS-16) into the composition of CGB contributes to the early structure formation of stone on CGB. The insertion of modifying additives into its composition - the hyperplasticizer MARP SU 84, the thickener MARF (Forbocrete 9010) and the hydrophobic rheological additive MAPF №T 10 can significantly reduce the water demand of the binder by 28…56%) and improve plasticity, while the compressive strength increases by 2 times in 2 h, by 1.7 times in 1 day, and by 1.5 times in 7 days. Developed for 3D additive technologies, molding mixtures based on CGB and quartz sand quickly harden and gain strength, providing concrete compressive strength class B3.5 in the early stages of hardening (1 day), and at the age of 7 days – B7.5.

Keywords: Construction 3D printing · Molding mixes · Composite gypsum binder

1 Introduction

In recent years, Russia has paid special attention to such a direction of the construction industry as low-rise construction. This rapidly developing area requires the development and implementation of new construction technologies and building materials. One of the most advanced trends in the development of construction technologies is construction printing. According to a large number of publications [1–9], its advantage is an increase in the pace of construction, the ability to create structures of a wide variety of configurations.

S. V. Klyuev and A. V. Klyuev (Eds.): ICICC 2021, LNCE 147, pp. 250–257, 2021.
https://doi.org/10.1007/978-3-030-68984-1_37

Multi-component molding mixes with various mineral and organic modifying additives are used for low-rise construction using 3D printing. The use of traditional hydraulic binders due to their slow hardening, and air binders-gypsum, due to low water resistance, is not rational. In this regard, in our opinion, building systems of layer-by-layer molding from a special fine-grained molding mixture based on effective fast-hardening binders [10, 11] with a low content of clinker–composite gypsum binders (CGB) – can be promising for these purposes in monolithic low-rise construction.

In terms of physical and mechanical properties and durability, forming mixtures on CGB are similar to concrete mixtures on Portland cement, but they have significant advantages in the ability to control their setting time and hardening speed within a wide range. In addition, the low energy consumption and simplicity of their production are extremely important in the technology of layer-by-layer synthesis (the consumption of conventional fuel for the production of gypsum is 3…5 times less than that of Portland cement). In Belgorod region there are unlimited supplies of raw materials of technogenic origin (dropouts of crushing quartz sand stone – QSS, waste of wet magnetic separation of ferruginous quartzite– WMS waste, etc.) whose use as mineral admixtures and fine aggregate can significantly reduce the cost and materials intensity of monolithic low-rise construction with the help of 3D technology.

Thus, the development of 3D printing with special fast-hardening fine-grained molding mixtures based on CGB will make the technology attractive for small and medium-sized businesses, as well as open up new opportunities for its use.

This area requires additional targeted research.

The solidified molding mix on CGB is a very complex multiphase system. The use of chemical modifiers and active mineral additives, various fillers and aggregates allows regulating directly the water demand and the processes of structure formation of the hardening composite. Workability, plasticity and setting time of the special molding mix are especially important that allows maintaining the dimensional stability of the layers of the structure in the 3D printing process and rapid curing in the early stages of hardening, which contributes to quick lock structure, finding design load capacity and further hardening.

In this regard, the main task of the study was to study the effect of various modifying additives on the properties of hardened special molding mixtures based on CGB, the need for experimental selection of their dosage to a specific binder and fine aggregate due to the lack of a developed knowledge base on compatibility [12–16].

2 Methods and Materials

Experimental research was carried out at the Department of Construction Materials Science, Products and Structures, in the test center "BelGTAS-sertitis" in BSTU named after V.G. Shukhov.

To obtain special molding mixtures, a modified CGB composition was developed, consisting of:

- 58% of gypsum binders (70% G-5BII and 30% GVVS-16(G-16);
- 20% of Portland cement CEMI 42.5 N (PC);
- binary active mineral additive (20% fine ground to a specific surface area of 500 m^2/kg of WMS waste and 0.5%; metacaolin);
- dispersed chalk (1.5%) with a $CaCO_3$ content of at least 96%.

To regulate the mobility of the molding concrete mix and the speed of strength gain, surface-active additives were used (in dry form):

- polycarboxylatehyperplasticizer (HP) MAPP SU 84. For molding mixtures based on CGB, the recommended dosage of HP is 0.1–0.3%;
- CP Kelko - Kelco-Crete dutane gum is a MARF (Forbocrete 9010) thickener with a high response to shear removal. It has little effect on hydration, which allows selecting more accurately the rcompounding. The recommended dosage for molding mixtures based on CGB is 0.07% of the total mass of water;
- rheological additive MAPF №T 10 based on modified bentonite clays, provides the creation of weakly expressed hydrophobic properties (0.1–0.3% of the mass of CGB);
- citric acid is a retarder of the setting time (0.2% by weight of CGB);
- CMC–carboxymethylcellulose (2% by weight of CGB)

Due to the fact that the components of the molding mix originally mixed in concrete mixer and then the resulting mixture is fed into the hopper and the extruder of molding device, we need to comply with the time interval between the start (not earlier than 15 min) and the end of setting (not later than 40 min) of the molding mixture. This is necessary to reduce the number of stops during 3D-layer printing for cleaning the forming head of the extruder, as well as to form and set the necessary initial strength of the hardening mixture before the next layer is laid.

Quartz sand was used as a fine aggregate in the ratio of CGB: sand-1:2, respectively.

During the experiments, the existing basic research methods were used.

3 Results and Discussions

The composition of the modified CGB was developed using a separate technology, according to which WMS waste was initially ground to a specific surface area of 500 m^2/kg, and then mixed together with Portland cement, gypsum binders of β-and α-modifications, with metacaolin and chalk in a laboratory ball mill, combined with short-term re-crushing (for 5 min).

Indicators of the properties of the developed CGB compositions are presented in Table 1.

The values of the compressive strength of the hardened samples after 2 h were 2.8 …14.4 MPa, after 1 day of hardening – 3.9 …19.8 MPa, and at 7 days of age – 8.2 … 34 MPa.

The use of various modifiers affects the water demand and the setting time of the hardening CGB.

Table 1. Indicators of CGB properties.

№	HP	TH	RA	W/B_{in}	Spread, m	Setting time, min,-s		R_{comp}, MPa,in terms		
						Beginning	Ending	2 h	1day	7 day
1	–	–	–	0.46	0.110	5-00	7-00	4.4	6.5	8.4
2	–	–	–	0.53	0.120	10-30	11-30	3.3	5.8	9.6
3	–	–	–	0.6	0.200	12-40	15-00	2.8	3.9	8.2
4	0.1	–	–	0.46	0.200	11-00	13-20	3.8	6.0	10.8
5	0.1	–	–	0.38	0.110	7-30	9-00	4.5	6.7	11.3
6	0.3	–	–	0.30	0.260	14-00	16-30	6.2	9.2	17.9
7	0.3	–	–	0.26	0.230	12-30	14-00	6.7	9.8	22.2
8	0.3	–	–	0.23	0.120	10-30	12-00	13.3	19.1	28.4
9	0.3	0.07	–	0.26	0.120	10-00	11-00	14.0	16.4	32.2
10	0.3	0.07	0.1	0.26	0.120	9-30	10-30	14.4	19.8	34.0
11	0.3	0.07	0.1	0.27	0.170	12-00	13-00	8.1	11.3	23.7
12	0.3	0.07	0.2	0.26	0.120	9-20	10-20	10.0	11.8	24.6
13	0.3	0.07	0.3	0.26	0.120	9-10	10-10	8.2	11.2	23.6

Note. Composition of CGB – gypsum binder 58% (G-5-40%, G-16-18%,); PC-20%, fine ground WMS waste-20%, metacaolin-0.5%, chalk-1.5%.
HP – hyperplasticizer MAPPSU84, TH – thickener MAPF (Forbocrete 9010), RA - rheological additive of the MAPF brand № T 10.

The dosage of HP (0.1–0.3% of the weight of CGB), allows for 28…56%, respectively, to reduce the W/B_{in} ratio almost without reducing the strength (compositions 2, 5, 8).

There is some delayed dilution of the molding mixture over time, which is the result of competitive adsorption, due to which the GP MAPP SU 84 begins to work after binding more strongly charged particles of the binder components.

The MARF thickener (Forbocrete 9010) at a low dosage (0.07% by water) allows stabilizing highly mobile systems (compositions 7, 9) and getting a higher early strength. The binding mixture becomes more plastic, while the compressive strength increases by 2 times in 2 h, by 1.67 times in 1 day, and by 1.5 times in 7 days.

Rheological additive of the MAPF brand №T 10 at a rational dosage of 0.1% of the mass of CGB due to the lamellar structure of bentonite clays in their composition acts as a lubricant, as well as an associative thickener (compositions 9, 10).

The X-ray phase analysis results confirm the stability of the formed structures of the solidified binder at the age of 7 days (Fig. 1).

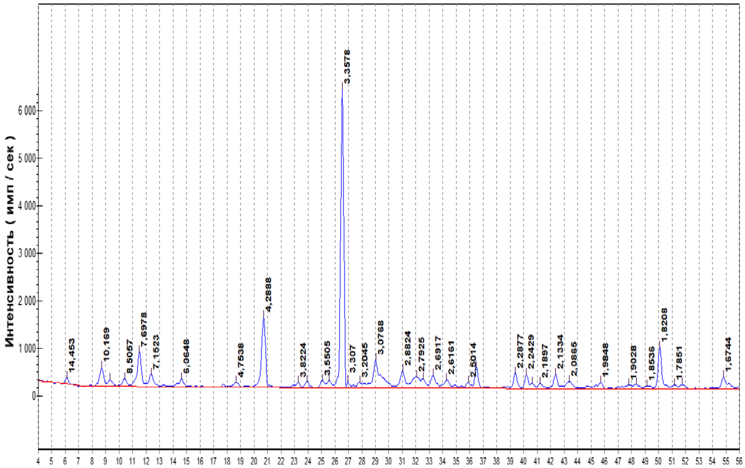

Fig. 1. X-ray phase analysisof solidified CGB (7 days).

In the studied sample, calcium dihydrate(d = 7.69; 4.29; 3.82; 3.076; 2.882…Å) is mainly present as hydration products of CGB; quartz (d = 3.35; 2.54; 2.46; 2.22; 2.28; 2.133; 2.08; 1.54…Å); calcium carbonate (d = 2.086; 1.902 … Å). The radiograph shows traces of portlandite $Ca(OH)_2$ (d = 4.93; 2.61; 1.78…Å). The absence of ettrintite (d = 9.7; 5.6; 4.92…Å) indicates the creation of conditions for the interaction of the amorphous SiO_2 phase in the WMS waste, as well as metacaolin with $Ca(OH)_2$ to form CSN (B), a partially crystallized tobermorite-like calcium hydrosilicate (d = 3.07; 2.88; 2.13; 1.82…Å). And chalk particles act as additional centers of crystallization for various hydroaluminate new formations, which contributes to the rapid strength gain of the composite in the early stages of hardening.

In further studies in the laboratory, layer-by-layer synthesis of model structures was carried out on an experimental laboratory 3D printer, taking into account its features with a fine-grained molding mixture [12].

For tests on an experimental laboratory device for 3D construction printing, the preparation of a special molding mixture on the CGB was carried out as follows. Initially, citric acid (0.2% by weight of CGB) was inserted into the required amount of water to increase the time interval between the beginning and ending of setting of the molding mixture. Then, with constant stirring (at least 3 min), a pre-prepared dry mixture was added, including CGB with modifying additives and quartz sand (in a ratio of 1:2, by weight, respectively) and 2% of the mass of the binding carboxymethyl cellulose (CMC) to give the molding mixture the required viscosity and plasticity.

During the extrusion process, the mobility of the molding mixture, its setting time, shape stability, uniformity and strength set of the molded layers of the structure were recorded. Experimental verification of the strength characteristics of solidified molding mixtures in the initial hardening period (at the age of 2 h, 1 day and 7 days) was carried out when testing samples-cubes with a size of 7.07 × 7.07 × 7.07 cm.

Composition and results of physical and mechanical tests of a special molding mixture on CGB (composition 10, Table 1) and the solidified composite are shown in Table 2.

Table 2. Composition and properties of the hardened molding compounds on CGB.

Ratio of CGB:TH	Citric acid, %	CMC, %	W/B_{in}	Spread, m	Setting time, min,-s		R_{comp}, MPain terms		
					Beginning	Ending	2 h	1 day	7 day
1:2	0.2	2	0.47	0.120	36-00	40-00	3.2	5.6	9.4

The laboratory experimental device for 3D construction printing consists of a moving platform, a mixer, a hopper, a vertical and horizontal forming head with replaceable nozzles, a vibrator and a control panel (Fig. 2).

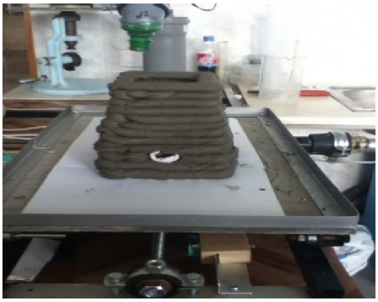

Fig. 2. Experimental laboratory device for 3D construction printing.

The device is managed manually. The speed controller for extrusion of the molding mixture by the extruder is located on the control panel. Together with the mixer, a vibrator is turned on, which does not allow the mixture to set.

4 Conclusion

Based on the conducted research, the following was found. The joint insertion of gypsum binders of α - and β-modification (G-5BII and GVVS-16) into the composition of CGB contributes to the early structure formation of stone on CGB.

Optimization of the CGB structure formation process with the insertion of modifying additives-the hyperplasticizer MAPP SU 84, the thickener MARF (Forbocrete 9010) and the hydrophobic rheological additive MAPF № T 10 can significantly reduce the water demand of the mixture by 28…56%) and improve its plasticity, while the compressive strength increases by 2 times in 2 h, by 1.7 times in 1 day, and by 1.5 times in 7 days.

Developed for 3D additive technologies, molding mixtures based on CGB and quartz sand quickly harden and gain strength, providing a concrete compressive strength class of B3.5 in the early stages of hardening (1 day), and B7.5 at the age of 7 days.

Acknowledgements. The work was carried out as part of the implementation of the Development Program of the reference university on the basis of BSTU named after V.G. Shukhov until 2021. Contract No. A-82/20. Research topic: Aerated concrete based on water-resistant gypsum binders for heat-insulating and heat-insulating structural layers of building envelopes constructed using the construction printing method.

References

1. Lesovik, V.S., Glagolev, E.S., Volodchenko, A.N., Drebezgova, M.Yu.: Effective composites for 3D additive technologies in construction. Bull. Cent. Territorial Dept. Russ. Acad. Archit. Constr. Sci. Voronezh **15**, 149–156 (2016)
2. Bazhenov, Y.M., Zagorodnjuk, L.H., Lesovik, V.S., Yerofeyeva, I.V., Chernysheva, N.V., Sumskoy, D.A.: Concerning the role of mineral additives in composite binder content. Int. J. Pharm. Technol. **8**(4), 22649–22661 (2016)
3. Permyakov, M.B., Permyakov, A.F., Davydova, A.M.: Additive technologies in construction. Eur. Res. **1**(24), 14–18 (2017)
4. Vatin, N.I., Chumadova, L.I., Goncharov, I.S., Zykova, V.V., Karpenya, A.N., Kim, A.A., Finashenkov, E.A.: 3D printing in construction. Constr. Unique Build. Struct. **1**(52), 27–46 (2017)
5. Tay, Y.W.D., Panda, B., Paul, S.C., Noor Mohamed, N.A., Tan, M.J., Leong, K.F.: 3D printing trends in building and construction industry: a review. Virtualand Phys. Prototyping **12**(3), 261–276 (2017)
6. Luneva, D.A., Kozhevnikova, E.O., Kaloshina, S.V.: Application of 3D printing in construction and prospects for its development. Bull. Perm Natl. Res. Polytech. Univ. Constr. Archit. **8**(1), 90–101 (2017)
7. Drebezgova, M.Yu.: Modern additive technologies in low-rise construction. Bull. BSTU named after V.G. Shukhov **6**, 66–69 (2017)
8. Pustovgar, A.P., Adamtsevich, A.O., Volkov, A.A.: Technology and organization of additive construction. Ind. Civ. Constr. **9**, 12–20 (2018)
9. Inozemtsev, A.S., Korolev, E.V., Zuong, T.K.: Analysis of existing technological solutions for 3D printing in construction. Bull. MSCU **13**(7)(118), 863–876 (2018)
10. Chernysheva, N.V., Lesovik, V.S., Drebezgova, M.Yu., Shatalova, S.V., Alaskhanov A.H.: Composite gypsum binders with silica-containing additives. In: IOP Conference Series: Materials Science and Engineering, vol. 327, p. 032015 (2018)
11. Chernysheva, N.V., Shatalova, S.V., Evsyukova, A.S.: Fischer, Hantz-Bertram: features of selection of rational composition of composite gypsum binder. Constr. Mater. Prod. **1**(2), 45–52 (2018)
12. Klyuev, S.V., Klyuev, A.V., Shorstova, E.S.: Fiber concrete for 3-D additive technologies. Mater. Sci. Forum **974**, 367–372 (2019)
13. Elistratkin, MYu., Minakov, S.V., Shatalova, S.V.: Influence of mineral additives in the composition of a composite binder on the effectiveness of the plasticizer. Constr. Mater. Prod. **2**(2), 10–16 (2019)

14. Klyuev, S.V., Khezhev, T.A., Pukharenko, Y.V., Klyuev, A.V.: To the question of fiber reinforcement of concrete. Mater. Sci. Forum **945**, 25–29 (2018)
15. Klyuev, S.V., Khezhev, T.A., Pukharenko, Y.V., Klyuev, A.V.: Experimental study of fiber-reinforced concrete structures. Mater. Sci. Forum **945**, 115–119 (2018)
16. Markin, V., Nerella, V.N., Schröfl, C., Guseynova, G., Mechtcherine, V.: Material design and performance evaluation of foam concrete for digital fabrication. Materials **12**, 2433 (2019)