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CEMENTITIOUS MATERIAL DEVELOPMENT FOR ADDITIVE FABRICATION

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Abstract. For the 3D STAR project and 3D printing purposes, a special fine-grained cement mixture from locally available raw materials was developed. The reason for the development of the custom mixture was the possibility of arbitrary optimization of the developed mixture at any stage of the project and for any type of application. Mix design, printing head and the entire system from mixing to extrusion was the subject of research and development for this project. It was therefore necessary to address both issues in parallel and to respond in both sectors to the realities arising from the partial results of the different groups involved in the development.

Keywords: 3D printing, cementitious material, optimization, testing, material properties.

1. Introduction

Cement binders require a cement hydration process to cure, which under normal conditions takes place at its fastest stage at a significantly slower rate of days and is not fully completed even within a few years. Cement hydration is the process of first setting and then hardening of the cement-bonded material [1, 2]. The setting process depends on many factors, but generally this phase takes place within hours. The hardening process is loosely related to the setting process. A fundamental issue, 3D printing of cementitious composites is facing, is designing the mixture in such way that after extrusion and repeated layering, it resists its own weight, and the printed element can be printed/built up vertically. The mixture must be of a suitable consistency to be pumpable and subsequently easy to leave the extruder, but at the same time it must set quickly enough after extrusion or have a rigid consistency to allow the layers to be reapplied on top of each other. This is further related to the very issue of the stability of a freshly printed object that is not sufficiently cured [3, 4]. These mixture requirements ultimately lead to the design of a cementitious composite of a rather complicated composition containing several different additives, including setting accelerators. The resulting mechanical strength is certainly also important to the overall design of the final element, but less important in terms of the extrusion process itself [5, 6].

2. Experimental part

2.1. Preliminary tests

At the beginning, fine-grained micro concrete was compound (e.g. see Table 1). According to requirements on maximum size of grain, sand with grains of 1.25 mm was used. A requirement for the compressive strength of the molding to be at least 60 MPa was required, therefore CEM II 52,5 N cement was used in combination with a superplasticizer. Also, polypropylene (PP) fibres with length of 12 mm were added to prevent plastic shrinkage.

Fine sand 0.10 – 0.63 mm	587	$kg\,m^{-3}$
Fine sand 0.63 – 1.25 mm	841	
CEM II 52.5 N	528	
Superplasticizer	23	
Water	200	
12 mm PP fibres	1.0	

Table 1. Mix design of preliminary tests.

This basic mixture was tested to buildability when the viscosity modifying admixture (VMA) is added. The question was, if we are able to provide such material, that can be build by layers. Adding VMA to the mixture cause increase of material stiffness and thixotropy. These charakteristics allow to print individual layer that withstand the pressure of the layers above it without plastic deformation due to compression, spreading, etc. Varienty of VMAs were tested. After few trials for each type of VMA, printable cement based material was produced (e.g. see Figure 1). By using pistol (e.g. see Figure 2) filled by fresh mixture, the layers were manually printed out. For each type of VMA, the optimum dosage for manually printed material was experimentaly determined. In Table 2, type of VMA, water content, quantity of admixture, consistecy of fresh mixed material determining by the method specified by standard EN 1015-3, bulk density of the material, flexular strength and compressive strength, are listed. Bulk density, com-

Type of VMA	**VMA content** [kg m^{-3}]	**Water content** [kg m^{-3}]	**Flow (EN 1015-3)** [mm]	**Bulk density** [kg m^{-3}]	**Flexural strenght** [MPa]	**Compressive strenght** [MPa]
Modified starch	5.2	215	120 × 120	2 200	14.0	88.0
Modified hydroxyethyl methylcellulose	1.0	225	130 × 135	2 170	16.2	83.5
Activated bentonite	40.0	225	135 × 135	2 190	17.8	86.0
Modified starch + Activated bentonite	20.0 / 2.0	235	125 × 130	2 160	15.9	85.0

TABLE 2. Mix design of preliminary tests.

FIGURE 1. Printed layers of cement based material.

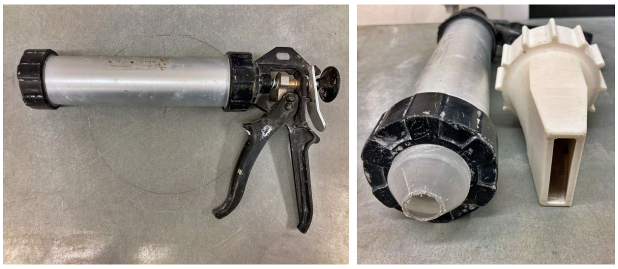

FIGURE 2. Pistol for manually printed cement based material.

pressive and flexural strength are determined on beam specimens with dimensions of 40 × 40 × 160 mm at the age of the material of 28 days.

As seen on Figure 1, the surface of printed material was not optimal. The surface was rough and contained large voids. To make surface smoother, material with fine particles needs to be add. For that purpose ground limestone, silica fume and ground quarts were added. At the same time, 12 mm PP fibres were replace to fibres with length of 5 mm. Considering the maximum size of grain, 5 mm PP fibres should be sufficient. The dosage of PP fibres was not changed, so due to its geometry the number of fibres had more than doubled. Along with these changes, the amount of cement was reduced by 30 %. The composition of designed mixture is shown in Table 3. Partical size cumulative distribution is shown in Figure 3.

This material with adjusted composition was also tested for its ability to print layers manually with pistol. As seen on the Figure 4, the surface was much smoother than previous pictured on Figure 1, however, if dosage of VMA is high or water content is low, the surface could still show defects. As optimal for printing layer the combination of bentonite and modified starch as VMA was selected.

Fine sand 0.10 – 0.63 mm	412	
Fine sand 0.63 – 1.25 mm	589	
CEM II 52.5 N	370	
Ground quartz 1	188	
Ground quartz 2	188	
Ground limestone	41	kg m^{-3}
Silica fume	94	
5 mm PP fibres	1	
Superplasticizer	28	
Water	Quantity by type of VMA	
VMA	Quantity by type of VMA	

TABLE 3. Mix design of preliminary tests.

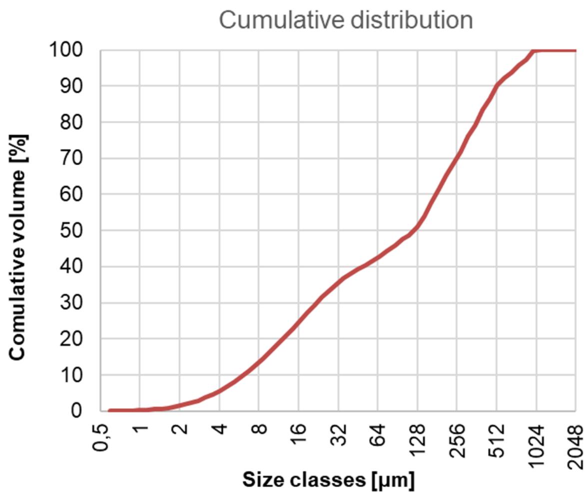

FIGURE 3. Partical size cumulative distribution.

2.2. MECHANICAL PROPERTIES OF THE MATERIAL

As part of the experimental program, several different types of tests were carried out on the material properties of the mixture. Table 4 lists various material parameters at a specific age of the material.

2.3. SETTING ACCELERATOR APPLICATION

To improve the buildability of the printed material and stability of the printed structures the setting accelerator was applicated. Usage of powdery setting accelerators was rejected. These ingredients had to be dosed into the dry mixture and the reaction time is thus started as soon as the water is added. Based on experience, we concluded that pumping the printing mixture with an accelerator can be very risky in terms of unplanned technological breaks, changes in printing speed and other marginal conditions.

Figure 4. Manually printed material with adjusted composition.

Material age [day]	Compressive strenght (EN 196-1) [MPa]	Flexural strenght (EN 196-1) [MPa]	Modulus of elasticity (ISO 1920-10) [GPa]	Layer cohesion (EN 14488-4) [MPa]	Shrinkage (EN 12808-4) [$mm\,m^{-1}$]
1	10.0	3.0	–	–	–
2	24.0	5.7	20.3	–	0.12
5	37.5	7.8	–	–	0.53
7	41.5	8.3	–	–	0.84
14	54.0	10.2	29.4	–	1.04
21	60.0	10.8	–	–	1.16
28	64.5	11.1	32.1	1.8	1.18
56	73.0	11.9	–	–	1.37
90	76.5	12.2	–	–	1.49

Table 4. Mechanical properties of the material.

For the purpose of 3D printing, alkali-free setting accelerator used for shotcrete application, was selected as the most optimal. The entire proposed 3D printing system works with a mixture that is mixed, transported, and pumped in a wet state to the printing head where a liquid accelerator is added in the last extrusion stage. Its quantity is adjusted according to the printing speed, the amount of material to be extruded and the complexity in terms of the shape of the printed element. This system allows for virtually any printing environment (length of hoses required to pump the mixture, location of the mixing device versus the printing device, and marginal parameters such as temperature, humidity, or glare). The mixture is transported in a liquid or plastic state through the entire system without the risk of the mixture solidifying in the system during a potential downtime or technological break. Acceleration occurs only at the very end of the printing process and the reaction time, i.e., the start of the hydration and solidification process, is in the order of minutes. Usual range of the accelerator “work” time is about 5–10 minutes. After this time period mixture starts with hydratation of cement components and printed structure became stable.

The various setting accelerators were mechanically mixed into the mixture of uniform composition and the initial setting time was measured.The traditional devices for monitoring the setting time of cementitious materials are various types of penetrometers. The measurement of setting time for ordinary cement is carried out with a so-called Vicat needle. However, this device and the method itself is not suitable for the expected short times (seconds in extreme cases) that are needed when extruding a mixture for 3D printing. Therefore, a sensory evaluation of the material solidification e.g. see Figure 5. Several variants of the use of the setting accelerating additive were selected from this simple test. These variants were subsequently tested directly during printing using the pump and a printhead.

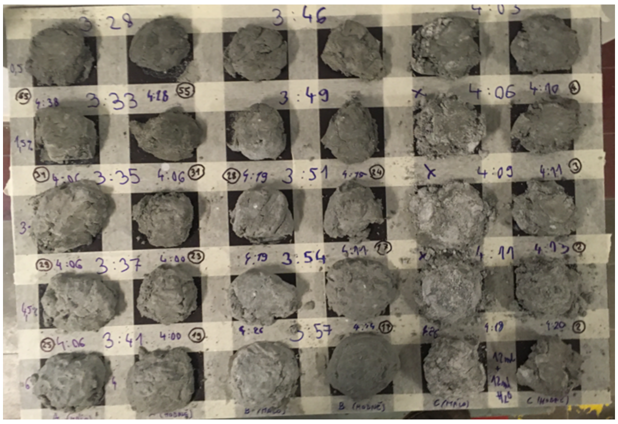

Figure 5. Visual evaluation of the effects of the setting accelerator.

2.4. Mixing equipment

The final designed mixture is capable to be mixed in large mixers.. All dry components (cement, sand,

Figure 6. The mixing device with maximum capacity of 200 l.

Figure 7. Concrete mixture pump with frequency converter.

fine components) are premixed into 20 kg bags to speed up the preparation and mixing process. Large volume mixing plant with a maximum capacity of approximately 200 liters is used for mixing the required volumes for printing test e.g. see Figure 6. This mixer is also suitable for mixing material for continuous printing of large structures. The mixer is equipped with a frequency converter for continuous rotation control. The mixing blades are also variable for a different types of mixtures. This is important for mixing materials with different thixotropic properties.

2.5. Pumping equipment

After initial tests of the base mixture, in which its pumpability was adjusted, the suitable spindle pump for connection to the transport system upstream the printing device e.g. see Figure 7 was selected. The spindle pump is composed of a rotor and a stator where, during movement, temporary chambers are created into which the material is drawn in and then pushed out through the discharge nozzle. The pumping equipment has the hopper volume of 150 litres. The pump control is software-integrated into the printing control system. For the initial prints, the mixture was pumped using a inside DN 25 diameter hose system with a hose length of 12 metres. As the mixture was optimized, the consistency of the mixture was gradually changed and the printing speed increased. These changes resulted in increased friction of the mixture in the hoses and significant heating of the mixture, resulting in uncontrollable solidification of the mixture in the hoses and couplings. For this reason, the entire pumping system was redesigned to DN 35 diameter hoses. These hoses were already 3 m long to make them easier to clean. The length of hose system is 12 metres long. The system is fitted with a pressure gauge to monitor the pressure downstream of the pump outlet and all hoses are fitted with quick couplings for easy assembly and disassembly. When the printing is complete, the entire hose system is disassembled and transported with the pump to the wash bay where all components are washed, lubricated and ready for the next use.

2.6. Extrusion

Through gradually defining the requirements for the printed cement mixture in the course of the research, we decided to pursue the variant where a liquid setting accelerator is injected in the last stage of the printing process. This variant has several advantages for the complex system under development. One of them is the rapid response to changes in the surrounding climatic conditions, which is not possible when printing the mixture with powder accelerator in the bulk mixture. Another advantage is the certainty that the accelerated mixture will not solidify in the conveying hose system when printing is stopped. Another indisputable plus is the possibility of accelerating the setting of the mixture, with initial strength coming within 1 to 10 minutes after application, i.e. extrusion. This rate of setting is suitable for printing column elements that have a relatively short footprint in a single layer, and hence the need for the shortest possible setting time. For such fast-rising prints, a setting speed is necessary in order to build on already printed layers. The printing head with nozzle e.g. see Figure 8 is the final component before the material is extruded. This is also part, where the setting accelerator is applicated. For perfect mixing of mixture with accelerator and control of the printing speed, a system of specially shaped moving blades mechanically coupled to the print mixture dosing drive was developed and several types of shaping of the accelerator inlet itself were tested. The blades must not only mix the mixture perfectly with the setting accelerator, but they should also restrict the flow of material through the printhead as little as possible and not be prone to clogging the print mixture component during printing. After experimental verification of several basic blade shapes, the variant that best met most of the requirements was selected. This variant underwent further development of the mechanical and material design to better withstand the abrasive environment in the

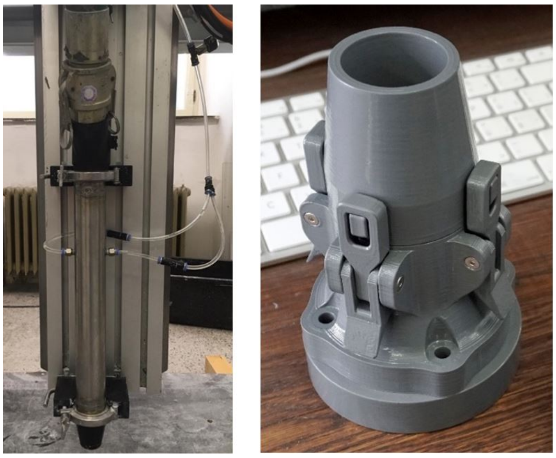

Figure 8. The printhead with setting accelerator injection and nozzle with quick-release system.

print head and shows no significant signs of wear even after several thousand liters of cement mixture flow. All printing nozzles are also developed as parts which are very easy to be printed in small 3D printers so the whole process of parameters changing of the nozzle or simply change of the nozzle can be very smooth and fast.

2.7. Mechanical properties of the material with added setting accelerator

The setting accelerator has a positive effect on the behaviour of the material in the early stage after the printing, but has a negative effect on the final mechanical properties. The degree of influence on the final mechanical properties is dependent on the accelerator dose used. Several test were performed and material characteristics for dosage of 70, 110 and 150 ml min^{-1} was determined at the age of 28 and 90 days.

Figure 9 shows the evaluated values of flexural strength and Figure 10 shows the evaluated values of compressive strength. The test of flexural and compressive strength was performed on specimens with dimensions of 40 × 40 × 160 mm, where material was pressed into the mold from the printhead. Depending of the dose of setting accelerator, the flexural strength is within range of 55 % to 83 % of value of reference material without setting accelerator in the age of material 28 days, the flexural strength is within range of 52 % to 78 % of value of reference material without setting accelerator in the age of material 90 days, the compressive strength is within range of 69 % to 91 % of value of reference material without setting accelerator in the age of material 28 days and the compressive strength is within range of 65 % to 82 % of value of reference material without setting accelerator in the age of material 90 days.

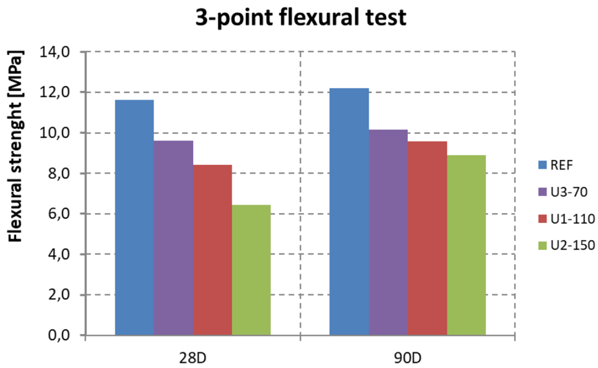

Figure 9. Flefural strength.

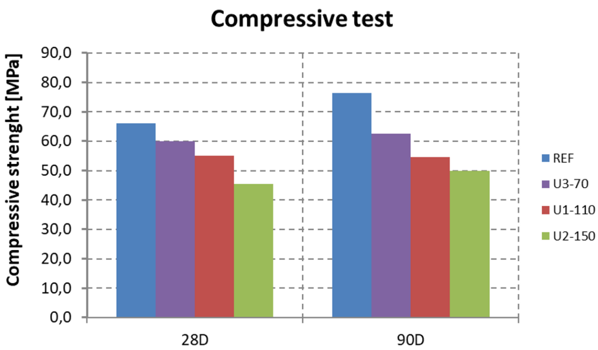

Figure 10. Compressive strenght.

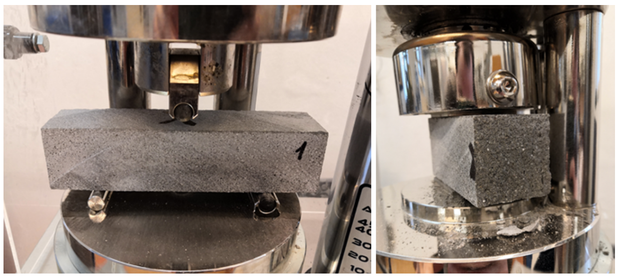

Figure 11. Flexural tensile strength test (left) and compressive strength test (right) on 40 × 40 × 160 mm beams.

2.8. Mechanical properties of the printed material

The possible difference between the laboratory produced specimens (by depositing the material in the moulds) and testing the parameters of the composite after cutting/drilling from the printed object was continuously verified e.g. see Figure 11 and 12. An effort was made to achieve as much consistency and homogeneity of the printed mixture as possible before entry and after extrusion. Modifications to both the printing technology and the mixture resulted in expected differences in the order of 5–10 %. The deterioration in material parameters is expected due to the different deposition (layering and non-compaction) of the mixture. Extrusion increase the air content of the mixture and thus reduce the bulk density. The volumetric mass of the mixture developed is in the

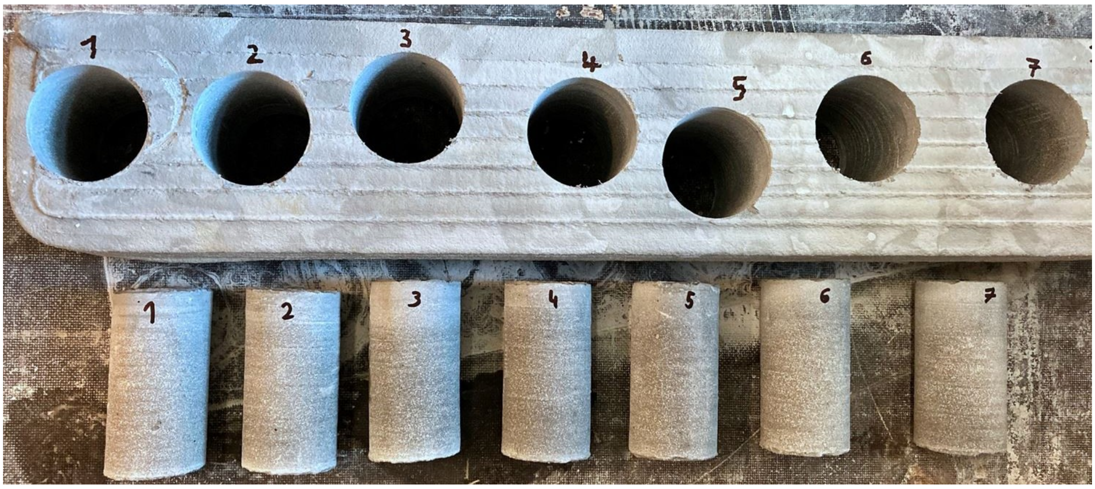

Figure 12. Drilled cores with diameter of 80 mm.

Figure 13. Printed wall and truss beam.

range of 2 080–2 120 kg m^{-3}. Finally a tests on drilled cores (Figure 12) showed practically indentical results as test on samples from formwork.

3. Conclusions

The cement-based material suitable for 3D printing technology was designed. The material was designed for pumping and subsequent printing. The buildability of the material was ensured by the increased thixotropy of the material by adding viscosity modifying admixture and by the alkali-free setting accelerator mixed in the printing head. The compressive strength of the material is around 65 MPa and the bending strength is around 11 MPa at the age of 28 days. Various structures could be printed with this material e.g. see Figure 13. As a final product a set of different construction part was assembled. Main parts of the final structure are: double layered thin walls which are partly filled with liquid insulation Thermowhite, horizontal system consist of truss beam reinforced by added steel reinforcement and there are also several small parts as a isobeam, which connect horizontal and vertical parts. The main outcome from these project is that all developed and printed structures and construction parts are easy transportable and assemble.

Several measurement procedures are ongoing. Also the “final” construction which represents whole research process and program is now installed outside and exposed to all natural influences. The main subject of ongoing monitoring is the development of cracks, durability and the ability to resist external influences.

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