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

Mix design, workability, pumpability, printability, strength, setting accelerator

FOREWORD

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.

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 so 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. 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.

MIXTURE DESIGN

1.1 Matrix design

The mixture was composed of individual selected components typical for fine-grained micro concrete and mortar (fine aggregate, cement, special additives and admixtures) to meet the requirements for mechanical properties, workability and pumpability of the fresh mixture and buildability of the printed material. The basis for the mix design was a thorough analysis of the components in terms of granulometry and the optimal adjustment of their individual proportions. Various cements, aggregates and micro fillers was used in trial mixtures. The mixture has been modified several times due to the gradual development of the printing equipment. Initially, after selecting suitable components, a basic mixture of fine-grained cement paste was designed on which initial mechanical properties and initial manual printability tests were determined. Major changes were made to the mix after the installation of the printing machine itself and the complete pumping equipment on which the mix had to be modified, for example changes due to surface appearance of the layered material e.g. see Fig. 1.

Figure 1. Surfaces of printed material

Suitable plasticizers and superplasticizers were added to the mix to reduce the water-cement ratio and therefore improve the mechanical properties and improve the consistency required for pumping the mix. As a result, basic composition of the mixture is given in the following Table 1:

Component	Content [kg.m-^{3}]
Silica sand 0-1,25 mm	967
Micro fillers	495
Cement CEM II 52,5 N	358
Superplasticizer	25
Water	225

Table 1. Matrix design

1.2 Fibers

In terms plastic shrinkage limitation, the mix was supplemented with dispersed reinforcement in the form of PP fibres. Different fiber lengths and dosages were tested and an optimum length of 5 mm and a content of 0.1 % volume was used.

Initial tests were also carried out with a mixture with added PVA and steel fibers with static function. The aim of the fiber addition is the automated reinforcement of thin-walled elements and dispersed reinforcement (e.g. with steel fibers) is one of the options to reinforce the printed structure. The use of fibers with a static function and the technology of automatically imprinted fibers is now under development. Continuous reinforcing by steel wire was also part of the test but this system for reinforcing was not implemented into wholr printing process yet.

BUILDABILITY AND STABILITY OF PRINTED MATERIAL

Another milestone in the modification of the mixture was to ensure thixotropic behaviour. The mixture is designed as pumpable and at the same time the compactness of the mixture after extrusion needed to be provided. As a result of such behaviour is that mixture does not spread after extrusion and the printed layer can withstand the pressure of the layers printed on top of it as seen on the Figure 2, where layers were manually printed and the buildability was tested. This property is influenced in the mixture by addition of viscosity modifying admixtures (VMA) and also with PP fibers. Organic materials on base of modified starch or cellulose was tested as well as inorganic material such as bentonite. The optimal variant was the combination of these additives with a representation of 2 % by weight of the dry mix. The amount of these additives is strictly controlled because of sensitiveness of the mixture and its behavior (workability).

Figure 2. Manually printed cement layers atop each other – pilot tests of buildability

SETTING ACCELERATOR APPLICATION

To improve the buildability of the printed material and stability of the printed structures the setting accelerator was applicated. An additive that accelerates the setting of the material immediately after extrusion proves to be essential in the case of 3D printing in terms of an immediate increase in basic strength. By basic strength is meant a state in which the individual printed layer can withstand the pressure of the layers above it without plastic deformation due to compression, spreading, etc. At the beginning of the development of the mixture, an analysis of different types of setting accelerators and an initial experimental program was carried out to determine the basic conditions for further development. 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 measurement system to monitor the efficiency of accelerators used for shotcrete in the new Austrian tunnelling method was used in combination with a sensory evaluation of the material solidification e.g. see Fig. 3.

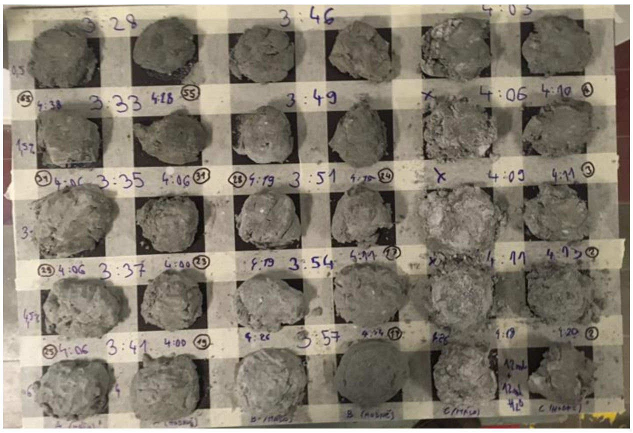

Figure 3. Visual evaluation of the effects of the setting accelerator

In the early stages of development, different types of solidification accelerators were tested not only in the liquid state but also as powdery components. Usage of powdery setting accelerators was soon 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.

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 print 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.

PROPERTIES OF THE PRINTING MIXTURE

The parameters of the resulting mixture were tested before pumping the mixture and after pumping the mixture with the setting accelerator. The important inputs for mixture optimization were the temperature of the mixture after mixing, before and after pumping, the consistency of the mixture and its change over time. These parameters are important in terms of system design for on-site printing or variable environmental boundary conditions. Fresh mix tests were carried out on a shaking table used for conventional mortar workability tests according to the EN 1015 series of standards. This was used to determine the spreading of the mixture after the application of a selected number of blows. The tests were carried out at different times in order to determine the workability time of the mix, in order to determine the workability time in the pumping system and the amount of mix in the pump hopper. Temperature and relative humidity of the print environment is very important also. Printing in higher temperatures leads to faster hydratation process and also it can be very negative in terms of concrete hardening in the hoses or faster setting accelerator reaction.

1.3 Mechanical properties of the material without added setting accelerator

As part of the experimental program, several different types of tests were carried out on the material properties of the printing mixture. Table 2 lists various material parameters at a specific age of the material.

Material age	Compressive strenght (EN 196-1)	Flexural strenght (EN 196-1)	Modulus of elasticity (ISO 1920-10)	Layer cohesion (EN 14488-4)	Shrinkage (EN 12808 - 4)
[day]	[MPa]	[MPa]	[GPa]	[MPa]	[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 2. Mechanical properties of material without added setting accelerator

1.4 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. In the case of compressive strength, the values reach 60 to 95 % compared to the reference material without setting accelerator. In the case of flexural strength, the values reach 60 to 85 % compared to the reference material without setting accelerator. After the optimization process which leads to mixture modification range of the values obtained from the test was between 80 - 85 %.

1.5 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. 4 and 5. 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 range of 2080-2120 kg.m^{-3}. Finally a tests on drilled cores (Figure.5) showed practically indentical results as test on samples from formwork.

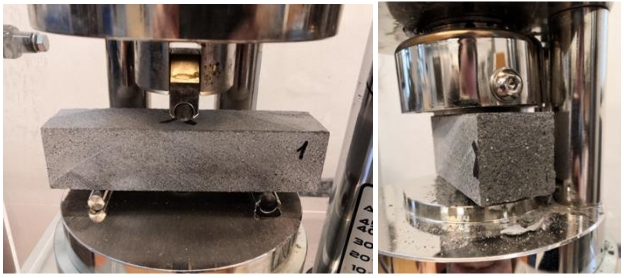

Figure 4. Flexural tensile strength test (left) and compressive strength test (right) on 40×40×160 mm beams

Figure 5. Drilled cores with diameter of 80 mm

PRODUCTION, TRANSPORT AND EXTRUSION

1.6 Mixing equipment

The final designed mixture is capable to be mixed in large mixers. All dry components (cement, sand, 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 Fig. 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 mixures. This is important for mixing materials with different thixotropic properties.

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

1.7 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 Fig. 6 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 (Figure.6). 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 optimised, 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 screw 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.

Figure 6. *Concrete mixture pump with frequency converter*

1.8 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 Fig. 7 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 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 (Figure.7).

Figure 7. *The printhead with setting accelerator injection and nozzle with quick-release system*

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 and by the alkali-free setting accelerator mixed in the print head. The compressive strength of the material is around 65 MPa and the bending strength is around 11 MPa at an age of 28 days. Various structures could be printed with this material e.g. see Fig. 8. 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 this 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 (Figure.8).

Figure 8. *Printed wall and truss beam*

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