EXTRUSION-BASED 3D PRINTING FOR RECYCLABLE GYPSUM

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Abstract. Gypsum is one of the most commonly used construction materials in cladding and non-load-bearing decoration. Recently, 3D printing technology has been involved in creating complex geometry. The particle-based method is the principal approach in 3D gypsum printing. However, the complex device and limited printable range limit the massive production of large-scale building components. This paper proposed a novel extrusion-based gypsum printing method and corresponding robotic fabrication workflow. First, several experiments are conducted to analyze the effect of different admixtures (retarder, activation agent, and accelerator) on the material setting properties. Second, a set-on-demand gypsum-based material is proposed by actively controlling multiple admixtures. Then, a process parameter-based robotic fabrication workflow is proposed, and a set of extrusion-based 3D gypsum printing equipment is built. A curved gypsum panel sample is printed as experimental verification. By comparing to the particle-based method, The test sample shows that the extrusion-based method can effectively improve the production efficiency and reduce the production cost. Therefore, the proposed method gives a relatively efficient and cost-effective way to produce recyclable gypsum material massively.

Keywords. 3D Gypsum Printing; Extrusion-based; Set-on-Demand Material; Material Modification; Robotic Fabrication Workflow; SDG 9.

1. Introduction

Gypsum-based composites have been widely used in interior linings such as walls and ceilings due to their unique advantages: low cost, good habitability, and good fire resistance (Jia et al., 2021). With the rapid development of industry in China, gypsum as a by-product is stacked as waste, not being effectively treated. It is imperative to develop efficient and feasible treating methods to reduce the harm of this solid waste to humans and the environment and create economic benefits by turning the waste into

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a resource (Huang et al., 2021). According to the research, in the past period of time, conventional gypsum products are generally produced by casting (Zhou et al., 2015).

3D printing technology is an emerging rapid prototyping technology and develops rapidly in the manufacturing sector, which is the core element of digital fabrication (Huang et al., 2021). Powder-bed binder jetting (PBBJ) and extrusion-based 3D printing are two commonly used 3D printing methods for gypsum-based material (Huang et al., 2021). In comparison with the machining of slip cast structures, there are many advantages of PBBJ. One of the most important is the form freedom, once many details impossible or very hard to be machined can be produced by 3D printing (Dantas et al., 2016).

However, The PBBJ printing product has low strength due to the low level of hydration caused by poor mixing of powder and water and porous structure within the product caused during powder spreading. Compared with PBBJ, extrusion-based 3D printing, also known as a direct ink writing technique, has advantages over PBBJ (Huang et al., 2021). Since the hydration-hardening process of gypsum materials is difficult to control, there is a need to modify the gypsum treatment and propose material control parameters related to the process.

The main contribution of this paper is to propose a set-on-demand materials by the active control of multiple material modification components and Parameter-based fabrication workflow.

Currently, extrusion-based methods have become the underlying methodology for many 3D printing digital fabrication technologies, such as spatial printing, modified plastic printing, and concrete printing. Compared with other printing technologies, gypsum 3D printing technology is also a derivative of extrusion-based method; however, unlike other printing technologies, gypsum 3D printing requires a two-step modification operation of gypsum hardening in a rather short period of time, and both interventions result in chemical rather than physical changes; therefore, the research based on the material modification aspect is also a major contribution.

2. Method

To realize the objective of this research, we conducted material modification studies, explored the parameter-based workflow, selected proper printing equipment, and successfully obtained a 600mm×75mm×130mm curved gypsum panel using a KUKA six-axis robot (KR90r2900).

During the hydration of calcium sulfate hemihydrate, calcium sulfate dihydrate (gypsum plaster) is formed. Three steps can be distinguished in the hydration reaction of calcium sulfate hemihydrate: the dissolution of hemihydrate yielding a partially saturated gypsum solution, the nucleation and growth of gypsum crystals, and the final formation of solid material through the entanglement of gypsum needle-like crystals (Mucha et al., 2020).

Therefore, the modification treatment of gypsum is mainly carried out in these following three directions：

2.1. MATERIAL

Commercially available α-hemihydrate (α-HH) gypsum that meets the requirement of Chinese standard GB/T 9776–2008 was used in this research. This kind of α-HH was made from natural gypsum with high purity, reducing the influence of inherent impurities. The chemical composition analyzed by XRF is shown in Table 1.

Table 1. Chemical composition of gypsum (Qi et al., 2021).

	CaO	SO_3	Fe_2O_3	MgO	SiO_2	Al_2O_3	K_2O	LOI.
Gypsum wt.%	39.96	51.65	0.076	0.393	0.335	0.116	0.026	10.29

2.1.1. Retarder

After environment scanning electron microscope (ESEM) observation, it was learned that small hemihydrate particles rapidly dissolved and hydrated, forming dihydrate crystals network around large hemihydrate particles, which makes an increasingly dense microstructure and promotes the setting of gypsum slurry (Liu et al., 2019).

In this study, Protein Salt (PS) was used as the main retarding additive. PS is made of protein macromolecule, surfactants, and inorganic ions. Functional groups in surfactants can hinder the dissolution of gypsum, and the gypsum crystal nucleus is wrapped in the protein macromolecule (Zhi et al., 2017).

Commonly, polycarboxylate superplasticizer (PCE), which is the most effective water-reducing agent, is used to achieve high fluidity and low porosity; hydroxypropylmethylcellulose (HPMC), one of the most widely used thickeners, is also used to ensure that the proper viscosity can be achieved to avoid bleeding and segregation (Zhi et al., 2018).

So, PCE and HPMC were used as secondary additives to ensure good rheological properties and to set rates (Zhi et al., 2018).

2.1.2. Activation Agent

To ensure the retarded slurry solidifies rapidly after extrusion, sodium oxalate (Peng et al.,2009) and dihydrate gypsum powder were used as an activation agent in this research.

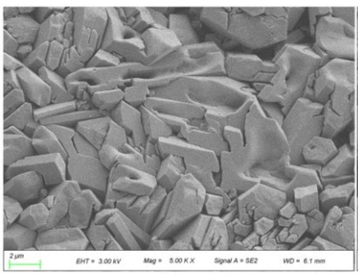
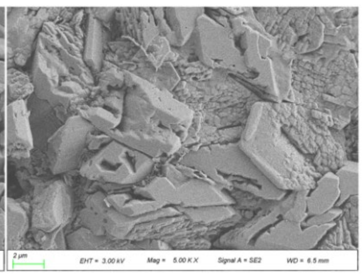

Figure 1. Left: Micro-structure of gypsum crystal without active excitation component (Group A)

Figure 2. Right: Micro-structure of gypsum crystal with active excitation component (Group B)

The micro-structure of gypsum crystal can explain the action mechanism of active excitation components to a certain extent. Through scanning electron microscope (SEM), we can observe that the crystal structure of gypsum crystal with active excitation component (Group B) (Figure 2) is more compact than that of gypsum crystal without active excitation component (Group A) (Figure 1). $Na_2C_2O_4$ promotes the dissolution of gypsum, increases the supersaturation of gypsum dihydrate, decreases its critical nucleation radius, accelerates the nucleation and growth rate of crystals, and the formation of SO_4^{2-} rich liquid phase by $Na_2C_2O_4$ facilitates the formation of gypsum dihydrate crystal matrix and increases the nucleation centre of gypsum dihydrate crystals (Peng et al.,2009).

2.1.3. Water demand of retarded slurry

By process arrangement, when the material was extruded by the printer, the materials were built layer by layer (building stage) and allowed to be cured (curing stage) to develop strength. In the latter two stages, the material would solidify. Compared to the former and latter two stages, the material needs to transform rapidly from fluid to solid (Huang et al., 2021).

For the slurry treated with retarding components, due to the addition of PCE, the water demand of gypsum under standard consistency will be reduced. At the same time, to ensure sufficient hydration, kaolin is introduced to ensure the integrity and workability of the slurry. Therefore, before the formal printing, the water demand gradient experiment is adopted to determine the water demand in the mixing process (Figure 3).

Figure 3. water demand of retarded slurry research

Experiments have learned that the standard consistency of gypsum slurry after retarder has changed, so in the actual printing, to ensure that the slurry extrusion can be quickly formed, to strictly control the amount of water required for mixing, not only to ensure that the gypsum gets fully hydrated, but also can avoid too much water hindering the formation of early strength.

2.1.4. Accelerator

The setting time of the gypsum slurry was measured by using a Vicat apparatus according to Chinese national standard GB/T 17669.4 (Liu et al., 2018).

It is generally accepted that the mechanism of hydration hardening of gypsum accepts the theory of precipitation-dissolution equilibrium. The action mechanism of the accelerator is to significantly increase the concentration of sulfate ions in the slurry in a short time to form a supersaturated solution of dihydrate gypsum; therefore, the dihydrate gypsum crystal will be precipitated at a reasonably rapid rate. At the same time, the existing gypsum continues to dissolve and is replenished with new calcium and sulfate ions. Under the action of the original active excitation component, the crystallization power of dihydrate gypsum continues to increase. The rate of crystal nucleation and growth increased rapidly and finally achieved the effect of rapid solidification.

Sulfates such as sodium sulfate (NS) and potassium sulfate (KS) were effective accelerators for gypsum(Huang et al., 2021).

2.2. WORKFLOW

2.2.1. Modified gypsum recyclable life cycle

The hardening process of gypsum is the process of a chemical reaction between hemihydrate gypsum and water to form dihydrate gypsum. After a high temperature of 170°C-190°C, dihydrate gypsum can lose crystalline water to form α-hemihydrate gypsum or β-hemihydrate gypsum, and we can make use of this recycling process to realize the recycling of gypsum (Figure 4).

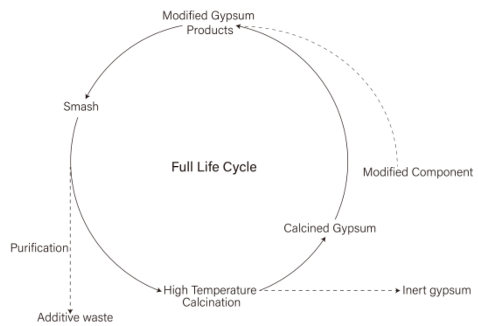

Figure 4. The life cycle of modified gypsum

2.2.2. Parameter-based gypsum 3D printing workflow

The core of the workflow (Figure 5) proposed in this paper lies in the synergy of the material modification study, the conveying-extrusion unit, the robot system, and the control system. The control system（SIEMENS S7-1200PLC） allows real-time adjustment of the operating rate of each motor on the robot, while the intervention of the material directional modification means creates the possibility of long-term stable operation of the large-scale process.

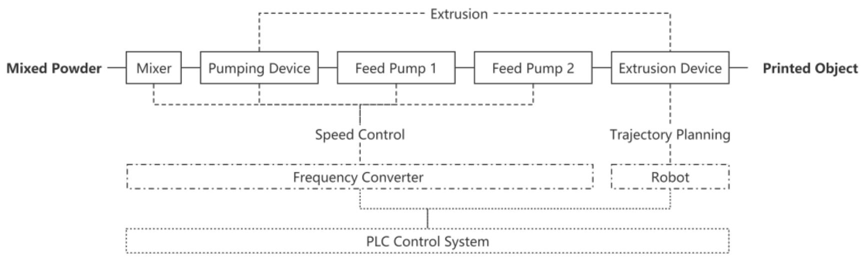

Figure 5. Robot-based gypsum 3Dprinting workflow diagram

3. Experiment

3.1. DIGITAL FABRICATION EQUIPMENT

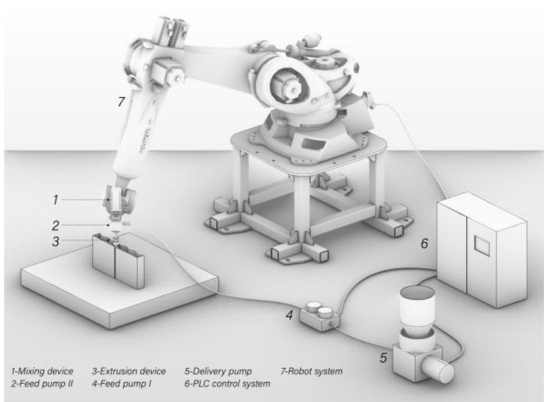

Figure 6. Coupling of model printing speed with process characteristics

The 3D printing device is also designed in a targeted manner based on the characteristic data presented in different stages of the preliminary material modification experiments (Figure 6). Firstly, the slow-setting gypsum slurry can not harden within the effective time while maintaining good fluidity and integrity. Therefore, a dosing screw pump (86 stepper motor) can be used to convey the slow-setting gypsum slurry without worrying that the gypsum will harden in the conveying tube, and the process will not unfold continuously. Secondly, the transported slurry is excited to the active state after passing through the active excitation component dosing pump (dosing pump 1), and the hardening process of the gypsum slurry begins. Therefore, in the actual production, the distance between the charging pump 1 and the fast-setting component (charging pump 2) should not be too long so that the residence time of the active slurry in the delivery pipe is less than the stable holding time of the active slurry to prevent the active gypsum slurry from hardening in the tube. Finally, the charging pump 2 and the stirring device will mix the active slurry with the fast-setting component sufficiently, and the extruded gypsum slurry will achieve initial setting and initial strength formation in a short time.

3.2. PARAMETER-BASED CONTROL EXPERIMENT

The rate control technology of the printing equipment is also an essential factor in determining the outcome of the process route. The robot's movement rate, pumping rate, the pumping rate of the active excitation component, and the pumping rate of the fast-setting component are all used as dependent variables for preset printing requirements, and different printing requirements require different rate control techniques. Moreover, the radius size of the extrusion end is directly related to the width of the print trajectory, so the size and specification of the printed components should be determined before each printing process, and the rates should be determined by the correlation coefficients of the equations, and the process details should be regulated in the signal control system. In the printing experiment, we selected the extrusion end with a radius of 4mm.

The following is a summary of the equations related to rate control based on the test printing process.

V is the pumping volume flowrate.
S_1 is slurry pumping rate.
r is the radius of the extrusion end.
S_2 is the pumping rate of the excitation component.
S_3 is the pumping rate of the quick setting component.
Both α and β are processing coupling parameters.

$V=\pi r^2 \cdot S_1$, $V=\alpha \cdot S_2$, $V=\beta \cdot S_3$

Therefore:

$$S_2 = (\pi r^2/\alpha) \cdot S_1 \quad (1)$$

Similarly:

$$S_3 = (\pi r^2/\beta) \cdot S_1 \quad (2)$$

According to the above equation, we can see that the slurry pumping rate, active excitation component pumping rate, and rapid solidification component pumping rate show a linear relationship under the premise of constant extrusion head radius, but in actual production, this linear correlation coefficient will also fluctuate within a specific error interval due to the difference of ambient temperature and humidity.

The following figure (Figure 7) represents two scenarios of the rate control experiment. The left figure reflects the ratio of S_2 to S_3 is greater than the error range of the specified interval, resulting in the gypsum slurry not being able to achieve rapid curing after extrusion, unable to form structural strength, and the lower trajectory being crushed by the weight of the upper trajectory and structural damage occurring; the right figure reflects the printing effect where the ratio of the two is within the standard error range.

Figure 7. Rate control experiment

3.3. EXPERIMENT PROCESS

Scale is an unavoidable topic for any laboratory process to develop into a mature industrial process. To develop the existing desktop-scale printing process into a building-scale printing process, it is necessary to ensure a continuous and stable large-scale production workflow.

The workflow of 3D modified gypsum printing is explored by coupling material properties with process characteristics after separate studies of material modification components and 3D printing equipment, which should firstly introduce different material modification components into the gypsum hydration and hardening process in stages according to the different characteristics of different stages of the expected process. The illustration (Figure 8) process is mainly realized through the printing device, while the modified components adjust the setting time, molding strength, and micro-structure of the gypsum slurry.

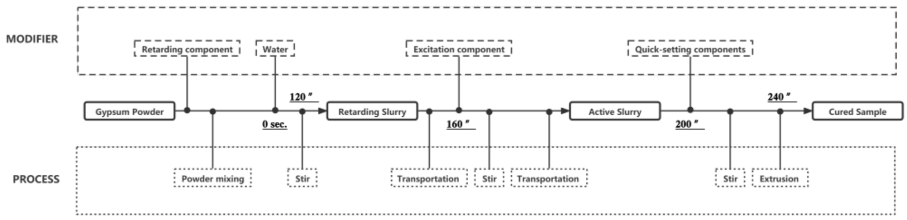

Figure 8. Coupling of process characteristics and material properties

4. Result

In the end, a 600mm×75mm×130mm curved gypsum panel is successfully printed in 30 minutes as experiment verification. By contrast, the PBBJ technique takes far more time to achieve a object of the same size than this technique.

Different printing targets are suitable for different precision printing processes. PBBJ technology has advantages in achieving desktop-level decorations but is not suitable for the manufacture of architectural components, and extrusion-based gupsum printing has made exploration in this direction.

Figure 9. Print process and micro-structure of gypsum treated with modified components

The SEM result shows that, after the gypsum slurry treated with modified components is cured, the intervention of two induced hydration hardening behaviors can be seen. The active excitation component makes the remaining tiny crystals continue to grow on the existing crystal core, quickly form the crystal cluster structure, and realize the rapid hardening of the gypsum slurry (Figure 9).

5. Conclusion and Prospect

The modification status retention time at each stage is the most critical element of the envisioned printing process. After the experiment of curing time of materials, we got the stable holding time of each stage, and the holding time of the retarded state could be maintained over and under 40 minutes, which created conditions for the stable delivery in the process flow; Prompt intervention of rapid curing component within 5 min after the action of active excitation components can allow the gypsum to achieve incipient solidification 2-4 minutes after extrusion from the tool head, achieving the intended conception goals (Table 2).

Table 2. Effect of modified components

Component	Phase	Stabilization Time
PS *PCE* *HPMC*	*Retarding State*	*40±5 min*
Dihydrate Gypsum *Sodium Oxalate*	*Active Excited State*	*7±2 min*
KS *NS*	*Rapid solidification State*	*3±1 min*

This paper takes materials research as the starting point. It proposes three material modification components (slow-setting component, fast-excitation component, and fast- setting component) for the reaction characteristics of natural gypsum materials in the two stages of hydration and hardening, which are used to modulate the original properties of gypsum and adapt them to the robotic construction process. Among them, the introduction of the active excitation component and the rapid hardening component can make the gypsum paste develop strength rapidly after extrusion at the tool end, which can prevent the structural damage caused by the upper print path crushing the lower print path and keep the printed components with good molding stability.

In addition, this paper also designs a set of extrusion-based gypsum 3D printing equipment with the phase characteristics presented by the modified gypsum slurry. It proposes a gypsum 3D printing workflow that couples the process steps with the material properties after continuous experiments. For the recyclable characteristics of gypsum dihydrate, this paper composes a practical flow of the recyclable life cycle of modified gypsum based on industrial production.

Moreover, this research has many subsequent development directions. Issues like how to induce the hydration process of gypsum by temperature control, and how to print lightweight gypsum sheets, etc, are worth further investigation in the future.

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