Application of P.O and R-SAC mortar for 3D printing in construction

J C Lin\textsuperscript{1}, X Wu, W Yang, R X Zhao and L G Qiao

National Enterprise Technology Center, China State Construction Ready Mix Concrete CO., LTD, Wuhan, China

\textsuperscript{1}\textit{E-mail:} Sillybear@yeah.net

\textbf{Abstract.} Compared with traditional properties of building materials, 3D printing materials should have controllable setting time, appropriate workability and superior mechanical properties. Adaptability of two types of cementitious system on the 3D printing were investigated in this paper. Results showed that both of them can match of 3D printing process with the working window time required (10-90min) by using the compound adjustable solidification agents, which have the high mechanical properties ($3\text{d} \geq 30\text{MPa}$, $28\text{d} > 63\text{MPa}$), and appropriate suitable parameter range of fluidity (R-SAC: 210-240mm, P.O: 200-220mm).

1. Introduction

3D printing technology, also known as the additive manufacturing technology. Nowadays 3D printing contain much more multidisciplinary advanced technology such as digital modeling technology, material science, computer technology, sensors technology, etc. This technology is called one of the samples of the third industrial revolution.

3D printing materials are designed for the conditions of 3D process and requirements. There are four general forms of the materials: powder, filament, lamellar, liquid. The major varieties include engineering plastics, photosensitive resin, metals and ceramics, and it is widely used in the mold manufacturing, medical treatment, aerospace and other fields. But because of the issue of cost, technology, practicability, etc., the 3D printing materials mentioned above are not appropriate for the construction building. However, the cementitious a large class of building materials has the advantages of high strength, high durability, self-coagulation and low cost, Combined with the technology of "contour process", the One-piece building elements of 3D-printing is achievable with cementitious materials.

1.1. Analysis of performance requirements of 3D printing cementitious materials

3D printing with cementitious materials is an innovative construction process for fabricating concrete components employing an additive, layer-based, manufacturing technique, also called freeform construction \cite{1,2}.The material needs to have good flow performance, but also provides a certain degree of strength to support the subsequent accumulation after the extrusion of the printing head. With the current technique of building manufacturing process, cementitious materials are achieved long the setting time and excellent working performance Therefore, different from the traditional construction of the material properties, 3D printing material performance should be designed to meet the following requirements:

(1) Appropriate work performance
3D printing materials need to have an acceptable degree of extrudability to be extruded through an extrusion printing head containing nozzles to form small materials filaments. The filaments must bond together to form each layer, as the fresh materials is continuously extruded to form consecutive filaments layered on the previous ones to build complete 3D components.

(2) Controllable setting time
The materials should not only have small amount of deformation with high printing speed, but also must provide sufficient support strength in a short period of time, so the material's setting should be relatively rapid. At the same time, the material working window time is not fixed to avoid the material setting too fast or loosely bound of layers. And the material should provide a controlled adjustment of condensation hardening range from 10-90min.

(3) Superior mechanical properties and durability
The layered structure of 3D printing is likely to congenital defects of compactness, the structural strength of 3D printing construction is less than the prefabricated in order to ensure the safety and integrity of the component of 3D print structure, 3D printing materials require higher mechanical strength and good durability.

Therefore, compared with traditional high performance development of concrete materials, the performance design of 3D printing materials is not convergence, and how to choose the 3D printing cementitious materials is very important. With this, the matching of the materials under R-SAC cement and P.O system with 3D printing is explored.

2. Raw materials and experimental methods

2.1. Raw materials
(1) Cement:
A) 42.5R sulphoaluminate cement produced by Wang Lou Cement Industry Co., Ltd., which basic performance is shown in table 1.

| Table 1. Physical properties of sulphoaluminate cement. |
|-----------------------------------------------|
| **Standard consistency water consumption (%)** | **Setting time (h:min)** | **Compressive Strength/MPa** | **Flexural Strength/MPa** |
| Initial setting time | Final setting time | 1d | 3d | 28d | 1d | 3d | 28d |
| 27 | 10 | 18 | 30.0 | 41.0 | 45.0 | 5.3 | 5.9 | 6.2 |

B) P· O42.5 cement produced by Hubei Yadong Cement Plant, whose basic performance is shown in table 2.

| Table 2. Basic performance of concrete. |
|-------------------------------------|
| **Standard Consistency/g** | **Density/g·cm** | **Stability** | **Compressive strength/MPa** | **Flexural Strength/MPa** |
| | | | 3d | 28d | 3d | 28d |
| 127 | 3.20 | Qualified | 23.30 | 48.10 | 5.23 | 8.72 |

(2) Coagulant: Calcium formate (industrial pure); Promoting powder; Liquid low-alkali accelerator; AlSO₄ (chemical pure concentration of 20% of the saturated solution), NaF.
(3) Retarder: Boric acid (industrial pure); Sodium gluconate (pure industrial); Sucrose.
(4) Sand: River sand (fineness modulus is 3.0).

2.2. Test methods
Setting time test is performed according to the Standard of test methods for water requirement of normal consistency, setting time and soundness of the P.O (GB/T 1346-2011).

Compressive strength test is performed according to the Standard for Method of testing cements-determination of strength (GB/T 17671-1999).
Mortar fluidity test is performed according to the Standard for Methods of testing uniformity of concrete admixture (GB8077-2012).

3D printing test is performed according to construction process of project developed equipment (figure 1) with the component quality of the mortar, Cement: Microsphere: Slag Powder: Sand: Water=40:9:5:74:15.

**Figure 1.** 3D printer.

3. Experimental results and discussion

3.1. Applicability of sulphoaluminate cement

3.1.1. Controllability of setting time. Sulphoaluminate cement is used for building quick repair materials, and its fast settling speed and higher early strength are more matched for 3D printing construction. The initial setting time of the sulphoaluminate cement used in the trial is about 10min, it is necessary to use retarders to reduce the rate of hydration, the test selected three kinds of common retarder to control the setting time.

![Figure 2. Effect of boric acid on setting time](image)

![Figure 3. Effect of sucrose on setting time](image)

![Figure 4. Effect of sodium gluconate on setting time](image)

The results showed that the effect of different retarders on the setting time of R-SAC is different. Its retarding effect order is boric acid > sodium gluconate > sucrose. The setting time of R-SAC is prolonged with the increasing content of boric acid. When the amount is 0.1%, the initial setting time can be increased by 14% to 24min, but when the amount is 0.3%, the setting time is increased by more than 144%, excessive increase in setting time is not conducive to control, which will increase the use of risk (figure 2). Both sodium gluconate and sucrose are common retarders for P.O, the retardation effect of sodium gluconate is more linear. When the amount of 0.3%, initial setting time is increased by 20 minutes, the retardation effect is more stable(figure 4). With the increase of sucrose amount, the retardation effect of R-SAC is not improved, so it cannot be used as R-SAC retarder(figure 3). It is also found that when the boronic acid amount is 0.15%, the setting time of R-SAC reached the standard of initial setting (> 30 min). Therefore, with 0.15% boric acid, the preparation of R-SAC with stable settling time gradient is carried out by using retarder and quick-setting agent.

As shown in the figure 5, the test group combined with boric acid as a retarder, only the sodium gluconate group has a retardation effect, sucrose group still no retardation effect. In the sodium group, with the increase of the amount of sodium gluconate from 0.1% to 0.4%, the setting time average increase is less than 30%, and the initial setting time is fixed in the range of 75-160 min.
The figure 6 shows that the composite coagulation effect of promoting powder group is the best. When the amount of 0.2%, initial setting time is reduced to 20 minutes, but after that, with the increase in the amount of promoting powder, setting time is essentially flat. The Liquid-low-alkali accelerator has a retarding effect before 5%, when proportion up to 6%, the setting time is shortened to 27min. And calcium formate compound with boric acid has no obvious coagulation effect. In summary, When R-SAC is used as 3D printing material, the R-SAC setting time control formula is shown in the table 3:

| NO. | Setting time/min | Promoting powder/% | Retarder/ Variety | mixing amount/% | initial setting time/min | final setting time/min | Time window/min |
|-----|------------------|---------------------|-------------------|----------------|-------------------------|------------------------|-----------------|
| 1   | 10-20            | 0.2                 | boric acid        | 0.15           | 19                      | 26                     | 7               |
| 2   | 20-30            | /                   | boric acid        | 0.1            | 24                      | 36                     | 12              |
| 3   | 30-40            | /                   | Sodium gluconate  | 0.3            | 32                      | 49                     | 17              |
| 4   | 50-60            | /                   | boric acid        | 0.2            | 60                      | 75                     | 15              |
| 5   | 70-90            | /                   | boric acid + sodium gluconate | 0.15+0.1 | 75                      | 100                    | 25              |

From the table we can see that the R-SAC setting time can be controlled in 10 ~ 90min to match the different construction conditions of 3D printing.

3.1.2. Work performance range. In this experiment, the adjustable solidification agent is chosen as the fifth group in 3.1.1, and the material's setting time is set to 75min. According to the different amount of water reducing agent, fluidity of 150-260mm of the mortar is tested for 3D printing effect, the experimental data is shown in table 4.

| NO. | amount of water reducing agent/% | Fluidity/mm | layer width/cm | The layer number | Printing status   |
|-----|---------------------------------|-------------|----------------|------------------|-------------------|
| 6   | 0.15                            | 150         | 4.1            | /                | /                 |
| 7   | 0.24                            | 175         | 4.1            | 22               | pipe blocking     |
| 8   | 0.33                            | 195         | 4.3            | 22               | pipe blocking     |
| 9   | 0.42                            | 210         | 4.2            | 30               | well              |
| 10  | 0.50                            | 240         | 4.5            | 35               | well              |
| 11  | 0.55                            | 260         | 5.4            | 15               | expanding         |

With the increase of the amount of water reducing agent, the setting time does not change much, the fluidity of cement mortar will gradually increase. But when its amount of more than 0.5%, the mortar is bleeding. When the mortar is super-stiff (fluidity ≤ 150mm), it does not have the extrusion
property, and also can't be connected with the substrate, the print performance is extremely poor; and when the fluidity of mortar is better than 250mm, its extrusion performance is excellent, but the 3D printing maximum number of layers is less than 15, and the component engender deformation. This shows that the fluidity of the mortar has a great influence on the 3D printing performance, and there is suitable parameter range of R-SAC fluidity is 210-240mm.

3.1.3. Mechanical properties. The mechanical properties of mortar with adjustable solidification agents in 3.1.1 are verified, the experimental data is shown in table 5.

| NO. | promoting powder/% | adjustable solidification agents variety | amount /% | initial setting time/min | 3d strength/MPa | 7d strength/MPa | 28d strength/MPa |
|-----|------------------|----------------------------------------|-----------|--------------------------|----------------|----------------|----------------|
| 0   | /                | /                                      | /         | 12                       | 43.2           | 54.4           | 67.9           |
| 1   | 0.2              | boric acid                             | 0.15      | 29                       | 48.7           | 56.7           | 64.5           |
| 2   | /                | boric acid                             | 0.1       | 21                       | 42.6           | 53.2           | 66.6           |
| 3   | /                | Sodium gluconate                       | 0.3       | 29                       | 41.2           | 54.2           | 68.2           |
| 4   | /                | boric acid                             | 0.2       | 67                       | 37.1           | 51.85          | 63.1           |
| 5   | /                | boric acid + sodium gluconate          | 0.15+0.1  | 85                       | 41.0           | 52.9           | 65.2           |

It was found that the addition of retarder had a slight decrease in the strength of 3d, but it did not affect the strength of a late stage. Only when the boric acid amount exceeds 0.2% 3d strength decreased by about 14%.

3.2. Applicability of P.O System

3.2.1. Controllability of setting time. The setting time of P.O material is generally more than 90min. Therefore, three kinds of common accelerators were selected to control the setting time.

![Figure 7](image7.png) **Figure 7.** Effect of AlSO₄ on setting time.

![Figure 8](image8.png) **Figure 8.** Effect of NaF on setting time.

![Figure 9](image9.png) **Figure 9.** Effect of Liquid low-alkali accelerator on setting time.

The results shows that the effect of different accelerators on the setting time are similar, and the effect order is NaF> AlSO₄> liquid low-alkali accelerator. It can be seen from figure 7 that with the increase of the amount of AlSO₄, the setting time are shortened rapidly. When the amount of AlSO₄ is 4% ~ 7%, the effect of coagulation is the most significant, and the initial setting time is less than 20min. This is the AFt crystal overlap with each other to form a skeleton [3, 4], but when the amount of AlSO₄ is more than 5%, the setting time tends to be stable. It can be seen from figure 8 that the amount of NaF is more than 1.3%, the initial setting time is less than 20min, and when the amount is more than 1.8%, the setting time is not change greatly. It should be noted that NaF contains alkali metal ions, its dosage should be controlled to avoid the alkali aggregate reaction. As shown in figure 9, the effect of the liquid low-alkali accelerator on setting time is relatively stable increases. When the
amount is over 3%, the initial setting time is shortened to 60min, when the amount is 9%, the initial setting time is less than 10min.

Therefore, When P.O material is used as 3D printing material, the setting time control formula is shown in the table 6:

![Table 6. Setting time control formula of P.O.](image)

From the table we can see that the setting time can be controlled in 10 ~ 90min to match the different construction conditions of 3D printing.

3.2.2. Applicability of work performance. In this experiment, the adjustable solidification agent is chosen as the group 16 in 3.2.1, and the material s ' setting time is set to 80 min. According to the different amount of water reducing agent, fluidity of 150-260 mm of the mortar is tested for 3D printing effect, the experimental data is shown in table 7.

![Table 7. 3D printing performance of P.O mortar.](image)

The results show that with the increase of the water reducer, the fluidity of the mortar gradually increases, and the 3D printing layers stability layers increased first and then decreased. When the mortar is super-stiff (fluidity ≤ 190mm), its extrusion performance is barely, the 3D printing effect is extremely poor as shown in figure 10. And when the fluidity of mortar is better than 245 mm, its extrusion performance is excellent, but it is easy to produce large deformation of the single layer in the printing process shown in figure 11. This shows that the suitable parameter range of fluidity of P.O mortar is 200-220mm.
3.2.3. Mechanical properties. The mechanical properties of mortar with adjustable solidification agents in 3.2.1 are verified, the experimental data is shown in table 8.

Table 8. Mechanical properties of P.O mortar.

| NO | adjustable solidification agents | amount /% | initial setting time /min | The compressive strength/MPa |
|----|---------------------------------|-----------|--------------------------|-----------------------------|
| 12 | AlSO₄                            | 5         | 8                        | 44.5                        |
| 13 | NaF                              | 1.3       | 20                       | 42.5                        |
| 14 | liquid low-alkali accelerator   | 5         | 26                       | 31.5                        |
| 15 | liquid low-alkali accelerator   | 7         | 60                       | 42.4                        |
| 16 | liquid low-alkali accelerator   | 2         | 99                       | 43.2                        |

It is found that the adjustable solidification agents in the suitable amount can be more accurate to control the setting time of the material, and the early mechanical properties of the material can be improved greatly, and the influence on the later performance is less than 10%.

4. Conclusion
In summary, 3D printing materials can choose R-SAC system and P.O system as a cementing material. Both of them can match the working window time required (10-90min) for 3D printing. At the same time, the materials also have excellent mechanical properties, 3d strength ≥ 30MPa, 28d strength > 63MPa. In the actual 3D printing process, the R-SAC mortar has large viscosity and high printing effect than P.O mortar. So the R-SAC suitable parameter range of fluidity is 210-240 mm, the P.O is 200-220mm.

Acknowledgements
This paper is supported by CSCEC Fund Project (cscec-2014-z-33).

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