Development and optimization of 3D printable cementitious composites for printing applications

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**DEVELOPMENT AND OPTIMIZATION OF 3D PRINTABLE
CEMENTITIOUS COMPOSITES FOR
PRINTING APPLICATIONS**

WENG YIWEI
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
2019

**DEVELOPMENT AND OPTIMIZATION OF 3D PRINTABLE
CEMENTITIOUS COMPOSITES FOR
PRINTING APPLICATIONS**

WENG YIWEI

School of Civil and Environmental Engineering

A thesis submitted to the Nanyang Technological University
In partial fulfillment of the requirements for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials, and has not been submitted for a higher degree to any other University or Institution.

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Authorship Attribution Statement

This thesis contains material from 4 manuscripts published/submitted/under preparation where I am the first and/or corresponding author.

(1) Chapter 3

Chapter 3 has been published as Y. Weng, B. Lu, M. Li, M.J. Tan, S. Qian. Empirical models to predict rheological properties of fiber reinforced cementitious composites for 3D printing. *Construction and Building Materials* 189, 676-686. DOI: 10.1016/j.conbuildmat.2018.09.039. The contributions of the co-authors are as follows:

A/Prof Qian is in overall charge of the research topic and provide guidance/supervision throughout the study. A/Prof Shunzhi Qian and A/Prof Ming Jen Tan edited the manuscript drafts. Mr. Bing Lu and I proposed the research area and prepared the manuscript drafts. The manuscript was revised by Dr Mingyang Li. I co-designed the study with Lu Bing and performed all the laboratory work at the School of Civil and Environmental Engineering and the Singapore Centre for 3D Printing. Mr. Bing Lu and I also analyzed the data. All experiments were conducted by Mr. Bing Lu and me in the Protection Engineering lab and Building and Construction lab.

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29/May/2019

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SUMMARY

3D concrete printing (3DCP) builds up objectives in a layer-atop-layer manner and has attracted much attention recently due to many advantages, such as customized production, reduced waste, and diminished lead-time of the rapid prototype. A number of works have been conducted in 3DCP in recent years. However, limitations remain in 3DCP, especially in the field of developing consistent and reliable cementitious materials for 3DCP.

This thesis proposes a holistic approach to develop consistent and reliable 3D printable cementitious materials for large-scale printing applications. Three levels are included in the conceptualized methodology. Rheology control serves as a vital factor at the lowest level to ensure that material fresh properties can satisfy the printing requirement in terms of buildability, pumpability, setting control and shape retention capability. Afterwards, material design are the critical factors at the intermedium level to ensure that hardened properties of printed materials are suitable for structural or non-structural applications. Hardened properties are focused on compressive and flexure performance in this thesis. Process design focuses on the optimization of printing parameters for better material distribution and interlayer properties. Finally, integration of building information modeling (BIM) and architecture with 3DCP is expected to promote automatic construction fabrication for digitalized products at the third level. Due to time constraint of this PhD study, this thesis focused on the first two levels and the third level is discussed in the section on future work.

The first level study focused on the influence of various factors on material rheological properties. Firstly, empirical models are constructed to predict the rheological properties based on material constituents and chemical admixtures. Secondly, theoretical models are developed to link rheological properties with printability in terms of buildability, which was validated by a new testing method proposed in this study. Thirdly, a class of rapid hardening materials, magnesia phosphate cement-based materials, is also developed.

SUMMARY

The second level study characterized the hardened properties of developed printable materials. Three different types of printable materials were investigated, i.e. plain cementitious materials, fiber reinforced cementitious materials, and rapid hardening cementitious materials, respectively. The hardened properties were studied in terms of compressive and flexural strength.

LIST OF PUBLICATIONS

All the publications derived from the work conducted during the Ph.D. period are listed below:

Book chapter:

1. **Yiwei Weng**, Mingyang Li, Ming Jen Tan, Shunzhi Qian. Design 3D printing cementitious materials via Fuller Thompson theory and Marson-Percy model. In Sanjayan, Nazari & Nematollahi (Eds). *3D Concrete Printing Technology*, Elsevier. ISBN: 9780128154816. 219, 2019 (Chapter)

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2. **Yiwei Weng**, Mingyang Li, Zhixin Liu, Wenxin Lao, Bing Lu, Dong Zhang, Ming Jen Tan. Printability and fire performance of a developed 3D printable fibre reinforced cementitious composites under elevated temperatures [J]. *Virtual and Physical Prototyping*, 2018, 14 (3): 284-292.
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4. **Yiwei Weng**, Bing Lu, Ming Jen Tan, Shunzhi Qian. Rheology and Printability of Engineered Cementitious Composites-A Literature Review[J]. Proceedings of the 2nd International Conference on Progress in Additive Manufacturing (Pro-AM 2016), 2016, 427-432

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3. **Yiwei Weng**, Mingyang Li, Ming Jen Tan, Shunzhi Qian. A novel mixture of printable fiber reinforced concrete for large-scale applications. 2019

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LIST OF SYMBOLS

τ (Pa): shear stress

τ_0 (Pa): yield stress

$\dot{\gamma}$ (1/s): shear rate

T (N·m): torque

N (rpm): rotation speed of the rheometer

G (N·m): flow resistance

$\tau_{0,0}$ (Pa): initial yield stress

ρ (g/cm³): density of materials

g (m/ s²): gravitational constant

H_L (mm): the height of the vertical structure

σ_v : vertical stress

R_c : the rate of construction

t_{ct} : construction time

σ_c : critical stress

α_{geom} : geometric factor

H_m (mm): maximum printed height

P (Pa): pumping pressure

R_{hose} (mm): the radius of a hose

L_{hose} (m): the length of a hose

Q (m³/s): the average volumetric flow rate of materials

μ_p : plastic viscosity

t_{rest} : resting time

A_{thix} : thixotropy parameter

$\tau_0(0)$: yield stress at resting time zero

t_v : the moment at which the slurry reaches 1000 Pa·s.

t_c : a characteristic time

$\mu_0(0)$: viscosity at resting time zero

LIST OF SYMBOLS

D_d : the diameter of a printed column

ϕ : packing fraction

ϕ_m : maximum packing fraction

ϕ_0 : the percolation threshold

b : the average particle size

H_s : the surface to surface separation distance at contact points

F : interparticle force

τ_s (Pa): static yield stress

τ_d (Pa): dynamic yield stress

H : printed height

p_i : the percentage of material that pass the i^{th} sieve

d_i (mm): the opening size of the i^{th} sieve

D (mm): the maximum particle size

$u_b(\dot{\gamma})$ (Pa·s): the shear viscosity of the binder

ω (rad/s): the rotational speed of the outer barrel

l (m): length and radius of the probe

R_1 (m): radius of the probe

R_2 (m): radius of the outer barrel.

C_a : a geometric factor of a hollow cylinder

u_r, u_z : material flow velocities in r and z direction for a cylindrical coordinate system

C : undetermined constant

$I_2(r, z)$: second invariant

$\sigma_{ij}^{(d)}$: stress tensor

E (min): time of last penetration greater than 25 mm

H (min): time of first penetration less than 25 mm

C (mm): penetration depth reading at time E

D_p (mm): penetration depth reading at time H

Chapter 1 Introduction

This chapter introduces the background and motivation, and the outline of this dissertation.

1.1 Background: digital fabrication and printable concrete

Concrete is one of the most widely used construction materials in the world. It possesses many excellent properties, such as convenience in application, wide raw material sources and generally highly reliable performance (Li et al., 2016; Qiu, 2016; Safiuddin, Salam, & Jumaat, 2011). In the United States alone, the concrete industry represents a €23.3 billion of sales per year (Buswell et al., 2007; Buswell et al., 2005; Gardiner). Figure 1-1 shows the consumption of cement in the world from 1997 to 2015. As can be seen easily, consumption increases rapidly in the last 20 years. In the year 2015, over 4.1 billion tons of cement were consumed in the world (U.S. Geological Survey, 2015).

Figure 1-1 Comparison of cement consumption in the world from 1997 to 2015 (U.S. Geological Survey, 2015)

One of the unique properties of concrete is phase transition, where concrete goes naturally from a fluid to a solid-state and is capable to flow and fill a mold as well as

sustain a load upon hardening (Li, 2011). This unique property of concrete gives great flexibility in terms of material handling and placement, which is greatly valued in the world of digital fabrication, especially 3D concrete printing.

3D concrete printing (3DCP) has attracted intensive attention in the last decade and a number of groups worldwide are currently engaged in the research due to its advantages (Tay et al., 2017). The primary advantage of 3DCP, including customizable structures and accurate material placements, can be value-added by its additional merits, such as increased construction speed, reduced labor and formwork costs, and improved worker safety (Gardiner et al., 2016; Hager, Golonka, & Putanowicz, 2016; Wangler et al., 2016; Wu, Wang, & Wang, 2016). Besides, by placing materials precisely in efficient structural design, 3D concrete printing is expected to be a more sustainable construction method (Buswell, 2018; Labonnote & Rüther, 2016). Meanwhile, as a result of more efficient construction, especially with respect to formwork elimination, 3D concrete printing can reduce waste generation during construction as well (Gosselin et al., 2016; Salet et al., 2018).

Although a number of works have been conducted in 3DCP as aforementioned, some limitations still remain in the field of large-scale printing. For example, research to date has been focusing on demonstration of concepts (Buchi et al., 2018; Buswell et al., 2007; Cesaretti et al., 2014; Gosselin et al., 2016; Khoshnevis, 2004a) and few works have applied the technology of 3DCP in large-scale applications (Salet et al., 2018). One main reason is that 3DCP process at the current stage is inconsistent and unreliable arising from many aspects, including material properties, which is affected by various factors such as material constituents (Svermova, Sonebi, & Bartos, 2003), chemical admixtures (Asaga & Roy, 1980), etc. Therefore, developing consistent and reliable 3D printable concrete is crucial for large-scale applications.

In the pursuit of consistent and reliable 3D printable cementitious materials, two vital aspects should be taken into consideration, i.e. fresh properties and hardened properties. Fresh properties, especially rheological properties, are fundamentally important to ensure that materials are capable to be conveyed to the nozzle via a

delivery system and placed in a layer-atop-layer manner to build up objectives (Le et al., 2012; Weng et al., 2018b). Rheological properties should be optimized to satisfy several unique requirements, such as pumpability, buildability, extrudability, shape retention capability, open time, etc. (Buchi et al., 2018; Roussel, 2018). The pumpability dictates how easily the material can be conveyed, and the buildability implies how well the materials can be stacked stably (Lim et al., 2012). The extrudability indicates the ability of a material to be extruded through the nozzle with minimal energy consumption (Salet et al., 2018). The shape retention capability characterizes the ability of materials to maintain the cross-section of printed filament (Lim et al., 2018), and it significantly affects the surface finish and structural stability of printed objectives (Li et al., 2017; Ma, Li, & Wang, 2018). The relationship between rheological properties and the aforementioned printing requirements will be discussed in Chapter 2.

The hardened property of 3D printable materials is another issue that needs to be considered. It seems that as a result of a high-pressure extrusion process, the hardened property of printed materials could be better than that of cast materials, and a densifier matrix could be achieved as well (Malaeb et al., 2015). However, results reported by many research works are far below expectations (Lim et al., 2009). One reason may be that fabricating objectives from a conglomeration of extruded filaments predisposes printed objects to anisotropy, which influences the end-use performance of materials (Le et al., 2012). Therefore, a critical driver for current research in 3DCP is to understand those effects, which can be explored through a number of topics (Buswell, 2018), including interlayer performance, shrinkage, durability, tensile reinforcement, bulk density, under-filling, measurement methods for hardened material properties, etc.

In summary, 3D printing can be applied in concrete to increase the automatic degree of civil engineering as well as broaden the application horizon of civil engineering because of its excellent advantages compared with the traditional construction approach. However, 3DCP requires materials to have unique fresh and hardened properties to fulfill the demand for large-scale printing applications. It is a challenge

for both researchers and engineers to optimize material formulations for consistent and reliable 3D printable cementitious materials such that both the requirements of fresh and hardened properties can be satisfied.

1.2 Research objectives

This Ph.D. study focuses on the formulation design of cementitious materials and the process optimization of the 3D concrete printing for newly developed materials such that the material properties can be optimized for 3DCP. The main challenge is to ensure that developed cementitious materials possess appropriate fresh properties as well as desirable hardened properties such that it can be applied in the practical engineering applications. Therefore, the main objectives of this Ph.D. thesis are set as follows accordingly.

(i) Development of rheological models in terms of material constituents or chemical admixtures

Rheological property control is the key aspect for 3D printable cementitious materials to achieve a large-scale printing. Material rheology is mainly influenced by material constituents and chemical admixtures. Therefore, theoretical or statistical models should be established to optimize material constituents or chemical admixtures to efficiently predict rheological property in terms of yield stress, plastic viscosity, and thixotropy.

(ii) Exploration of the relation between rheological properties and printability

Printability is mainly represented by pumpability and buildability. Pumpability implies how easily materials can be conveyed and a continuous pumping process can be achieved by an appropriately designed delivering system and pumpable material. Buildability indicates how well materials can be stacked and it is widely accepted that buildability is determined by material rheology. Quantitative models are to be

established to correlate the buildability and rheology such that the model can act as a guideline for researchers and engineers to design material formulation to satisfy the requirement of printing height. Besides, an appropriate printing test method should be designed to validate the proposed models.

(iii) Development of cementitious materials for large-scale printing application

Two types of novel formulations of 3D printable materials are developed according to the aforementioned rheological control and buildability model. The feasibility of material for large-scale printing is demonstrated by a practical printing test. The first type is a class of plain 3D printable cementitious materials. Another formulation of fiber-reinforced 3D printable cementitious material is developed for enhanced hardened property as well as large-scale printing.

(iv) Investigation of rapid hardening materials for 3D concrete printing

In this part, a type of 3D rapid hardening printable magnesium potassium phosphate cement paste (MKPC) through optimizing rheological and mechanical properties is designed. Fly ash was adopted to partially replace reactive magnesium oxide, consequently further reducing the environmental impact and modifying the rheological property of developed material. Meanwhile, silica fume acting as an efficient ingredient to adjust the fresh properties of pastes for 3D printing was attempted along with different magnesia-to-borax ratios.

Figure 1-2 illustrates the methodology of this thesis, which provides a systematic guideline for material development in 3DCP. The thesis is organized according to the methodology. Firstly, rheological tailoring and control measures were employed to ensure the printability of materials. Secondly, the hardened properties of printed specimens are optimized through material design. Finally, in the future, Building Information Modelling (BIM) and architecture can be potentially integrated with 3DCP to achieve automated construction.

Figure 1-2 Research roadmap for the material development of a 3D printing process

1.3 Thesis outline

This thesis organization is shown in Figure 1-3. Following a brief introduction on these chapters, Chapter 1 provides the research background related to this thesis topic and research significance. The research objectives, methodology, and organization are also mentioned in this chapter.

Figure 1-3 Framework of the thesis

Chapter 2 reviews the state-of-art 3D concrete printing technology with a focus on the extrusion-based process. Rheological properties of cementitious materials are reviewed in terms of yield stress, plastic viscosity, and thixotropy, and methods to control the rheological property are also discussed. Additionally, a literature review on introducing reinforcement and developing rapid hardening binders for 3DCP will be discussed.

Chapter 3 and Chapter 4 present statistical models to link the relationship between rheological properties and material constituents or chemical admixtures. Factorial design method and center composited design method, adopted for experimental design, are discussed. The accuracy of the proposed models is verified. The printing test is conducted to qualitatively demonstrate the influence of material rheological properties on printability.

Chapter 5 proposes a theoretical model to predict the buildability in terms of rheological properties, especially the static yield stress. The accuracy of the proposed

theoretical model is verified by a designed printing test. Additionally, according to the Fuller Thompson theory and the Marson-Percy model, the influence and importance of particle size distribution on the rheological property are discussed. A new material formulation is designed through optimizing particle size distribution. Finally, a large-scale printing test is used to validate the printability of developed materials.

Chapter 6 formulates a new design for 3D printable rapid hardening materials with waste cementitious materials, which increases its sustainability and cost-effectiveness. This work proposes an environmentally friendly 3D printable cementitious material involving the use of magnesium potassium phosphate cement (MKPC) with various ratios of fly ash replacement ranging from 0 to 60 wt% to increase the working time of the binder. Silica fume was used at up to 10 wt% to adjust rheological and mechanical properties.

Chapter 7 presents a new mixture design of 3D printable fiber reinforced cementitious materials for large-scale printing. The properties of developed materials are thoroughly characterized in terms of rheology and working time.

Finally, major contributions that have been achieved in this thesis research are summarized and future works are recommended in Chapter 8.

Chapter 2 Literature review

According to the hierarchy of methodology in the introduction part, a thorough and systematic literature review is provided in this chapter. Firstly, a fundamental understanding of 3DCP and the effect of printing parameters on the printable material are provided. Secondly, a literature review of rheological technology to ensure printability is discussed. Thirdly, various methods to introduce reinforcement and using rapid hardening cementitious materials for 3DCP are discussed. Finally, the problems and knowledge gaps of current research are summarized.

2.1 Extrusion-based 3D concrete printing process

2.1.1 Generals

The gantry-based system and robot-based system are the typical printing systems when it comes to 3D printing. A typical gantry system used for concrete printing is illustrated in Figure 2-1 (Bos et al., 2016). As can be seen from Figure 2-1, materials are firstly mixed and then conveyed to the nozzle head through a mixer-pump in the printing process. After materials reaching nozzle head, the gantry system controls the nozzle movement to place materials precisely according to the designed CAD file. The robotic-based printer has been developed to increase the flexibility of printer in 3DCP (Gardiner et al., 2016; Gosselin et al., 2016; Pham, Lim, & Pham, 2016), as schematically shown in Figure 2-2 (Gosselin et al., 2016). The pioneering work on 3DCP, i.e., Contour Crafting was conducted by Khoshnevis et al. as early as 2004 (Hwang & Khoshnevis, 2006; Khoshnevis, 2004; Khoshnevis et al., 2006), with the aim to print high-rise buildings and houses with a concrete printer (Khoshnevis & Zhang, 2015). Recently, 3DCP approach has been adopted by the industry and academia in a variety of 3D concrete printing projects all over the world.

Figure 2-1 Typical gantry-based system in 3DCP (Bos et al., 2016)

Figure 2-2 Schematic of the robotic 3D printing setup: 0. System command; 1. Robot controller; 2. Printing controller; 3. Robotic arm; 4. Printing head; 5. Accelerating agent; 6. Peristaltic pump for accelerating agent; 7. Peristaltic pump for premix; 8. Premix mixer; 9. 3D printed object (Gosselin et al., 2016)

One such example is the company WinSun in Shanghai, who succeeded in printing full-scale houses within 24 hours by modular printing and assembling various parts of the structure (Davison, 2015). Other examples include the company Total Kustom

from architect Andrey Rudenko, who recently produced a 3D printed hotel in the Philippines (Printer, 2017), and the project WASP, which launched the world's biggest 3D printer with 12 m height (Wasp, 2015). Another Chinese company HuaShang Tengda has 3D printed a 400 m² villa around reinforcement through the use of novel nozzle design, seemingly eliminating one of the major challenges of 3DCP using horizontal extrusion-based technology (Alec, 2016). XTreeE team built several architectural structures in France (XtreeE, 2018). The research team in the Technology University of Eindhoven fabricated a 3D printed bridge with the cable reinforcement and prestressed system (Figure 2-3 a) (Bos et al., 2016).

Figure 2-3 Noteworthy examples of projects using 3DCP in institutes: (a) 3D printed bridge by TUE (Bos et al., 2016); (b) Curvy printing in UK, by Loughborough University (Buswell et al., 2007; Le et al., 2012); (c) 3D printed reinforced element by University of Naples Federico (Asprone et al., 2018); (d) 3D printed structure with 78 × 60 × 90 cm (L × W × H) via using fiber reinforced cementitious composites by Nanyang Technological University (Weng et al., 2018a); (e) Multiple mobile robots concurrently printing process by Nanyang Technological University (Zhang et al., 2018)

Burgeoning research interest has led to the establishment of materials-based approaches in recently launched projects including Loughborough University since

2010 (Figure 2-3 b) (Buswell et al., 2007; Le et al., 2012). The research team in Nanyang Technological University (NTU) developed a type of 3D printable fiber reinforced cementitious composites, which has been adopted for large-scale printing (Figure 2-3 c) (Weng et al., 2018a). Researchers proposed a novel method to fabricate reinforced concrete elements and subsequently assembled them in the University of Naples Federico (Figure 2-3 d) (Asprone et al., 2018). A team of multiple mobile robots concurrently printing process has been developed for large-scale printing in NTU recently (Figure 2-3 e) (Zhang et al., 2018).

Although extensive works have been conducted in 3DCP, many challenges remain. Firstly, the fresh property of printable materials should be optimized so that the designed material can be flowable enough to be pumpable and support its own weight and the weight of materials to be subsequently placed. Secondly, material hardened properties should be sufficient for structural or non-structural applications and ideally be equivalent to that of the cast ones. This is rather challenging as several works reported that the hardened property of 3D printed materials is worse than cast material (Le et al., 2012; Lim et al., 2012a; Malaeb et al., 2015), partly attributed to relatively poor interlayer strength and its anisotropic behavior. Finally, reinforcement should be introduced in printable cementitious materials since concrete is brittle material with low tensile strength and crack resistance, which limits its further engineering applications (Neville, 1995). However, incorporation of reinforcement is difficult, as steel rebar must not impede the movement of the printer head.

Developing appropriate printable materials are the focus of this thesis to address the issues arising from the requirement of the printability, hardened property, reinforcement, etc. Since material rheology plays an important part in the printability of 3D printable materials, which influences the printability significantly (Perrot et al., 2016; Roussel & Cussigh, 2008; Roussel et al., 2012), it is crucial to understand the the relationship between rheology and printability for designing appropriate materials for 3DCP. Short-fibers has been commonly used as the secondary reinforcement in conventional concrete for strengthening hardened properties, and developing 3D printable materials reinforced with short fibers is a potential approach to solving the

issue arising from the requirement of reinforcement and hardened property (Li & Li, 2011; Li, 2003). A literature review is provided in the next sections accordingly.

2.1.2 Effect of printing parameters on the printed material

Material properties are affected by many factors in 3DCP, where materials are first batch-mixed or inline-mixed, and then delivered to the nozzle head. Afterward, the printer controls the nozzle travel around and prints the structure according to the designed CAD file. Several parameters can be varied in the printing process, such as time-gap between two layers, pumping speed, nozzle travel speed, nozzle standoff distance, nozzle size and shape, printing path design, etc. Understanding the influence of printing parameters on the printed material can help us gain a better view of 3DCP. The influence of printing parameters on the material property is discussed in this part.

(i) Time-gap

The time-gap is defined as the time that a nozzle needs to reach the same location on the subsequent layer when the nozzle travels to print the structure. The time-gap is dependent on the nozzle travel speed and the distance that the nozzle needs to travel for a single layer. It may result in a weak bonding at the interface between two consecutive layers (Tay et al., 2018), especially in the large-scale printing where a long time-gap exists.

Many works have been conducted to explore the effect of time-gap on interface adhesion. Sanjayan and Xia reported that with the increase of time-gap, the surface moisture of the initial layer decreases, which consequently reduces interface adhesion. Tay et al. reported that the porosity on the interface increases with the increase of time-gap (Tay et al., 2018). Keita et al. presented that water loss is localized in a dry region at the free surface leading to an incomplete cement hydration and high local porosity (Keita, 2019), and the surface water loss is a function of resting time, as

shown in Figure 2-9. As a consequence, with the increase of time-gap, the interface adhesion decreases.

Figure 2-4 Relative water loss in the first layer (i.e. ratio between the amount of evaporated water and initial water content in the sample) as a function of resting time in a wind tunnel, in laboratory room and sealed (Keita, 2019)

(ii) Standoff distance and printing speed

Material delivering speed, nozzle travel speed, and standoff distance are three printing machine-related parameters. Material delivering speed refers to the pump rotational speed. Nozzle travel speed indicates how fast the printer moves around. Standoff distance defines the distance between the nozzle opening and the top surface of printed layer, as shown in Figure 2-5. Panda et al. found that with the decrease of standoff distance, the interface adhesion of geopolymers increases (Panda et al., 2018). However, Wolf et al. reported that there was no clear relation between interlayer adhesion and standoff distance (Wolfs et al., 2019). Due to limited results from literature, further investigation is required to explore the effect of standoff distance on the interface adhesion.

Figure 2-5 Schematic show of standoff distance

Panda et al. also explored the effect of nozzle travel speed on the interlayer adhesion (Panda et al., 2018). The results imply that with the increase of nozzle travel speed, the interface adhesion decreases, and the possible reason is that the higher travel speed generates more microvoids between layers. However, more studies are needed in this area since the current relation between printing speed and material interlayer adhesion is not clear in 3DCP.

In summary, standoff distance and nozzle travel speed are critical parameters, which affect the printed material property. However, the conclusion is not consistent based on current research works and the relationship between standoff distance, nozzle travel speed, and material property is not clear. Additionally, few studies have been conducted to investigate the effect of material delivering speed on the printed material property, and therefore, more works should be carried out in this area.

(iii) Nozzle design and printing path design

The shape of the printed filament is largely determined by the nozzle opening design. The most common used nozzle for printing is round shape nozzle and rectangular shape nozzle. Zareiuam and Khoshnevis optimized the design of nozzle opening to introduce the interlocking between layers, and consequently the interlayer property can be strengthened (Zareiuam & Khonshnevis, 2017), as shown in Figure 2-6 where the length of nozzle teeth was varied.

Printed filament surface finish is relevant to the nozzle shape and material property. Lao et al. proposed a machine-learning method to optimize the nozzle shape for improving the surface finish of printed filaments in terms of material rheological property (Lao et al., 2017), as shown in Figure 2-7. Additionally, Xu et al. developed a variable-size square nozzle to manufacture architectural ornaments (Xu et al., 2019).

Figure 2-6 Effect of interlocking on the mechanical property of printed specimens; (a) Preliminary study on the size of the interlocking; (b) Direction of applied force on the specimens

Figure 2-7 Effect of nozzle shape on the cross section of printed filament (nozzle design on left and corresponding extrudate cross section on right): (A) Rectangular shape nozzle; (B) Trapezoid shape nozzle ; (C) Optimized nozzle shape (Lao et al., 2017)

3D concrete printed structure is constructed by stacking layers of printed filament, whose direction may affect the final product property. Hambach and Volkmer

investigated the influence of printing path on the printed structural property, and various path was adopted to print the same specimen (Hambach & Volkmer, 2017), as shown in Figure 2-8. The result indicates that the mechanical performance of specimens can be enhanced by optimized the designed printing path (Hambach & Volkmer, 2017). Furthermore, Moini et al. found that concrete structure designed based on bioinspired Bouligand structures can generate unique damage mechanisms, which allow inherently brittle hardened cement paste materials to attain flaw-tolerant properties and novel performance characteristics (Moini et al., 2018).

Figure 2-8 3D-print path models in 3D-printing software and photographs of specimens fabricated via (a) print path A and (b) print path B for 3-point bending test (Hambach & Volkmer, 2017)

Nozzle and printing path design are attractive areas to facilitate 3DCP. The nozzle design is focusing on nozzle opening shape design at current stage. Apart from this, developing functional nozzles to introduce various ingredients is vital in future work, such as chemical additive adding nozzle, fiber mixing nozzle, etc. Research works in printing path design are at the preliminary stage, and designing printing path to achieve functional structure for better durability and structural performance is necessary for future research works.

2.2 Rheological control for 3D printable cementitious materials

Rheology describes the deformation and flow behavior of materials (Neville, 1995). Bingham model is commonly used for cement pastes due to its simplicity and wide acceptance in civil engineering (Austin et al. 1999). The relationship between shear stress τ (Pa) and shear rate $\dot{\gamma}$ (1/s) in the Bingham model is described as follows:

$$\tau = \tau_0 + \mu_p \dot{\gamma} \quad (2.1)$$

where τ_0 (Pa) and μ_p (Pa·s) are yield stress and plastic viscosity, respectively. Yield stress τ_0 represents minimum shear stress required to initiate or maintain the flow of a material, while plastic viscosity μ_p describes the change of shear stress with altering shear rate. These two rheological parameters are measured by a rotational rheometer test, in which Bingham model can also be expressed as the following formula for convenience of experiment design and data analysis:

$$T = G + hN \quad (2.2)$$

Eq. (2.2) describes the relationship between the measured torque T (N·m) and the rotational speed N (rpm). The parameter G (N·m) is flow resistance, representing the minimum torque required to initiate or maintain the flow of material. The parameter h (N·m·min) is the torque viscosity. Similar to the μ_p in Eq.(2.1), the parameter h describes the change of applied torque with altering rotational speed.

Bingham model indicates that if both parameters (yield stress τ_0 and plastic viscosity μ_p) are kept at a higher level, the material is difficult to flow at any given speed. As indicated in the study of pumpable concrete, the rise of τ_0 and μ_p yields the increase of pumping pressure (Okamura et al. 2000) in the case of slip flow, which is undesirable to the pumping process and delivering process. In the printing phase, to restrain deformation due to subsequently printed layers requires high yield stress τ_0 (Perrot et al., 2016). Considering the delivering phase and the printing phase as a whole, yield stress should be enhanced whilst plastic viscosity should be kept at a low level to achieve appropriate rheological control of 3D printable cementitious

composites. The influence of rheology on printability (buildability, pumpability and extrudability) is discussed in Section 2.2.1.

The rheology of cementitious materials evolves with time because of the hydration process and flocculation. The hydration process is due to the chemical reaction in the cementitious material system. Flocculation is due to colloidal interactions and Calcium Silicate Hydrate (CSH) nucleation at the contact points between cement grains (Roussel et al., 2012).

To quantify the evolution of rheology, thixotropy is investigated, which describes the reversible and time-dependent reduction of material viscosity, which is due to the build-up of a structure in fresh concrete at rest (Taboada et al., 2018; Rahman et al. 2014; Wallevik, 2009). The influence of thixotropy on yield stress and plastic viscosity evolution is discussed in Section 2.2.2. Finally, methods to control material rheological properties are provided in Section 2.2.3.

2.2.1 Rheology and printability

In 3DCP, printability can be defined as the property of a material to satisfy printing requirements without the formation of weak layer-to-layer interface bonds. This parameter is relevant to the material buildability, pumpability, and extrudability, which are related to material rheological property. In this part, the relationship between material rheological property and printability is discussed.

(i) Rheology and buildability

The relationship between yield stress and buildability is discussed in this part. Buildability is defined as the ability of an extruded cement-based material to retain its geometry (shape and size) under sustained and increasing loads in the fresh or transient state (Nerella et al., 2018). For this reason, printable materials should exhibit

sufficient static yield stress and structuration rate at the time of deposition in the fresh state.

In the case of layered extrusion of concrete to fabricate a wall or column, a cementitious material is extruded, and objectives are built up in a layer-atop-layer manner, as depicted in Figure 2-9. After extrusion, the initial yield stress of any layer (rectangular shape), $\tau_{0,0}$, must support its self-weight (Schowalter & Christensen, 1998), as expressed follows:

$$\tau_{0,0} = \rho g H_L / \sqrt{3} \quad (2.3)$$

where ρ (kg/m³), g (m/s²), and H_L (m) are the density, gravity constant and layer height, respectively.

Then during the printing process, the vertical stress σ_v applied on the bottom layer is expressed as follows (Perrot et al., 2016):

$$\sigma_v = \rho g H_L(t) = \rho g R_c t_c \quad (2.4)$$

where R_c (mm/s) is the rate of construction; t_c (s) is the construction time; $H_L(t)$ (m) is the height of the vertical structure.

The stability of the first layer can be measured by comparing the vertical stress given by Eq. (2.4) with critical failure stress, which is linearly correlated to the yield stress of the first placed material:

$$\sigma_c = \alpha_{\text{geom}} \cdot \tau_{0,0} \quad (2.5)$$

where α_{geom} is the geometric factor, depending on the built structure.

After completing the printing process, the yield stress of the bottom layer should be sufficient to sustain the entire height (H_m), written as follows:

$$\sigma_v = \rho g H_m \leq \sigma_c = \alpha_{\text{geom}} \cdot \tau_{0,0} \quad (2.6)$$

therefore, the maximum height (H_m) can be acquired and expressed as follows (Wangler et al., 2016):

$$H_m \leq \frac{\alpha_{\text{geom}} \cdot \tau_{0,0}}{\rho g} \quad (2.7)$$

Figure 2-9 Schematic of a layered extrusion process with concrete (Wangler et al., 2016)

In summary, the printed height of materials depends on the structural geometry (α_{geom}), material density (ρ), and yield stress ($\tau_{0,0}$). However, structural design is out of the scope of this thesis, and material density varies from 1.5 g/cm^3 to 2.5 g/cm^3 for concrete while the yield stress can vary from several Pa to thousands Pa. Therefore, yield stress should play a dominant role in material buildability during printing process compared with material density. To achieve better buildability, higher yield stress of materials is required.

(ii) Rheology and pumpability

Concrete pumping is achieved by pushing concrete at high pressure into pipes. In this process, pumpability is mainly characterized by the pumping pressure in the material delivering process. The applied pressure provides the necessary thrust to move the concrete forward in the pumping process, i.e., it causes the concrete material to deform in the direction of the applied force and, hence, to transmit the force further. Since coarse aggregates cannot be deformed easily, fresh mortar plays a major role in the deformation behavior of concrete. For most of the concretes it is evident from previous studies that concrete flows as a plug in the pumping hose (Kaplan, Larrard, & Sedran, 2005; Kwon, Jang, Kim, & Shah, 2016). Coarse aggregates move towards the center of pipe forming a core (plug), and for Bingham fluid in the pipe (Schutter

& Feys, 2016), the relationship between rheological parameters and pumping pressure is generally expressed as follows (Chhabra & Richardson, 1959):

$$P = \left[\frac{8\tau_{0,0}}{3R_{\text{hose}}} + \frac{8\mu_p}{\pi R_{\text{hose}}^4} Q \right] L_{\text{hose}} \quad (2.8)$$

where R_{hose} (mm) and L_{hose} (m) are the inner radius and length of a hose, respectively; Q (m³/s) is an average volumetric flow rate of materials. As can be seen from Eq. (2.8), pumping pressure is relevant to yield stress, plastic viscosity and material flow rate, and is proportional to the hose length.

Since the fresh mortar is easily deformed compared with coarse aggregate under high pressure pumping process, lubricating layer is formed at the internal walls of the hose, consequently leading to a considerable reduction in the required pumping pressure. The lubricating mortar layer consists of cement paste and fine aggregates (Mechtcherine et al., 2014).

The Eq. (2.8) for pumping pressure is only valid for slip flow (at low pumping rates) without plug flow. When plug flow with lubrication layer forms and the shear stress (τ_i) at the concrete-pipe wall interface is lower than the yield stress (τ_0) of the concrete, i.e., at lower shear rates, Kaplan et al. proposed a model using Bingham and interface parameters (Kaplan et al., 2005), as expressed:

$$P = \frac{2L_{\text{hose}}}{R_{\text{hose}}} \left[\frac{Q \cdot \mu_i}{\pi \cdot R_{\text{hose}}^2 \cdot k_f} + \tau_0 \right] \quad (2.9)$$

where μ_i is the plastic viscosity of the lubricating layer and k_f is the filling coefficient.

When the interface shear stress (τ_i) at the interface exceeds the yield stress (τ_0) of the concrete in the scenario of plug flow, slip-plus-shear flow occurs. Kaplan et al. proposed another model to predict the pumping pressure using Bingham and interface parameters, as expressed as follows:

$$P = \frac{2L}{R} \left[\frac{\frac{Q}{\pi \cdot R^2 \cdot k_f} - \frac{R}{4 \cdot \mu} \tau_{0i} + \frac{R}{3 \cdot \mu} \tau_0}{1 + \frac{R}{4 \cdot \mu} \mu_i} \cdot \mu_i + \tau_{0i} \right] \quad (2.10)$$

(iii) Rheology and extrudability

Extrudability is the ability of a material to be extruded through the nozzle with minimal energy consumption (Mechtcherine et al., 2019; Salet et al., 2018), which depends on yield stress, plastic viscosity, etc. (Nerella et al., 2019; Nerella et al., 2018). Most of the extrudability measurements reported for printable concretes have been qualitative only (Le et al., 2012). Nerella et al. proposed an extrudability test method for inline, quantitative characterization of the extrudability of printable materials by utilizing the 3D-printer as a test device (Nerella et al., 2019). The energy required for extrusion of concrete at a specified flow rate is measured to quantify its extrudability index and unit extrusion energy (J/cm³). The lower the unit extrusion energy of material under investigation, the higher its extrudability. In this way, optimum compositions are identified by means of a parametric study (Nerella et al., 2019).

2.2.2 Thixotropy: time-dependent effect of yield stress and plastic viscosity

Material rheological property evolves with time due to hydration process and flocculation. Since for most printing process, materials only flow through a short delivering and deposition phases at current stage, the dominant factor for the rheology evolution is the flocculation, which is due to colloidal interactions and CSH nucleation at the contact points between cement grains, as shown in Figure 2-10 (Roussel et al., 2012).

At the end of the mixing stage, cement particles are distributed, as shown in Figure 2-10 (a). The colloidal attractive forces cause cement particles to flocculate in a short

period (few seconds) and a network of interaction particles is formed, which can withstand stress and reveal an initial elastic modulus and an initial yield stress (Figure 2-10 b). This phase is referred to as flocculation, which was shown to result from the competition between attractive colloidal forces between cement particles and viscous dissipation in the interstitial water between the cement grains (Roussel et al., 2012).

At the same time, the nucleation of CSH occurs at the contact points between cement particles within the particle network, even though the material is still in the dormant period. This nucleation transforms locally the soft colloidal interactions between cement particles into higher energy interactions, which can be seen as solid bridges. Consequently, the elastic modulus increases at the macroscopic scale. After several tens of seconds, a percolation path of cement particles interacting purely through CSH bridges forms (Figure 2-10 c).

Further increase of the macroscopic elastic modulus and yield stress is due to the increase of the size or amount of hydrates bridges between percolated cement particles (Figure 2-10 d). This phase is referred to as structuration. It can also be noted that, at a microscopic scale, a non-reversible chemical reaction creates CSH bonds between particles. Nevertheless, these bonds may be weak enough to be broken by shear and/or remixing, while new bonds may appear again at rest as long as the reservoir of chemical species is sufficient. Therefore, from a practical point of view, hydration may have reversible macroscopic consequences as long as the applied mixing power is sufficient to break the hydrates bridges between cement particles. (Roussel et al., 2012).

Figure 2-10 The network evolution of interacting cement particles in the dormant period. (a) Dispersed cement particles at the end of the mixing phase; (b) A couple of seconds after the end of mixing, cement particles are flocculated and colloidal interaction forms between particles. Darker particles belong to a percolation path; at the contact points between particles, nucleation of CSH (black and white dots) starts immediately to turn locally the soft colloidal interaction between cement particles into a rigid interaction; (c) All the particles in the percolation path (black particles) are linked by CSH bridges forming a percolated rigid network in the material; (d) The elastic modulus of the mixture keeps on increasing as the size of the CSH bridges increases. (Roussel et al., 2012)

(i) Time-dependent effect of yield stress

Rheological parameters and models discussed in Sections 2.2.1 neglect the time effect. To take time effect into consideration, thixotropy should be incorporated in former models (Roussel et al., 2012). Roussel (2006) proposed a linear model to quantify the time-dependent effect of yield stress, as shown in follows:

$$\tau_0(t) = \tau_0(0) + A_{\text{thix}} t_{\text{rest}} \quad (2.11)$$

where t_{rest} is resting time; A_{thix} is the thixotropy parameter, which is assumed to be a constant for a given material; $\tau_0(0)$ is yield stress at resting time zero. Generally, a high A_{thix} is required to drive up yield stress overtime to ensure that materials possess enough buildability during the printing process.

Perrot et al. (2015) found that although Roussel's model can fit the evolution of yield stress well before the end of the dormant period, a large variation between the experimental results and model ones occurred after the hydration reaching acceleration stage, as shown in Figure 2-11. Therefore, they proposed an exponential model to correlate the evolution of yield stress with time, as expressed follows:

$$\tau_0(t) = \frac{A_{thix}}{\tau_0(0)} \cdot t_{ct} \cdot (e^{t_{rest}/t_{ct}} - 1) + 1 \quad (2.12)$$

where t_{ct} is a characteristic time, which is adjustable to fit with experimental values.

Figure 2-11 Comparison of yield stresses experimental results (squares) with Roussel's prediction (dashed lines) and the proposed model (solid lines) (Perrot et al., 2016)

Therefore, Eq. (2.7) should be rewritten as follows:

$$H_m \leq \frac{\alpha_{geom}(t) \cdot \tau_{0,0}(t)}{\rho g} \quad (2.13)$$

Substituting the construction rate in Eq. (2.13), the correlation between construction rate and material yield stress can be expressed as follows:

$$R \leq \frac{\tau_0(t) \cdot \alpha_{geom}(t)}{\rho g t_c} \quad (2.14)$$

In the case of printing a column, the geometric factor can be expressed as follows (Perrot et al., 2016):

$$\alpha_{geom}(t) = 2\left(1 + \frac{D_d}{2\sqrt{3}H(t)}\right) = 2\left(1 + \frac{D_d}{2\sqrt{3}R_c t_c}\right) \quad (2.15)$$

where D_d is the diameter of a printed column. Therefore, a safe construction rate can be acquired through substituting Eq. (2.15) into (2.14). The model was validated by Perrot et al. (2016), as shown in Figure 2-12, where different construction rates are applied to the material and the time of failure occurrence is predicted. The experimental results suggested that the measured failure time fits well with the exponential model.

Figure 2-12 Comparison of the evolution of critical stress σ_c and vertical stress σ_v for building rate ranging from 1.1 to 6.2 m/h: the solid circles indicate the experimental failure time and the diagonal crosses indicate the failure time derived from a linear evolution of the yield stress (Perrot et al., 2016)

The safe construction rate defines a maximum vertical velocity R_c , above which the evolution of material yield stress would not fast enough to support the rate of construction. However, the construction rate R_c also cannot be too slow such that the cold joints may form, which has been found in distinct-layer casting process (Roussel & Cussigh, 2008).

(ii) Time effect of plastic viscosity

The time effect on plastic viscosity is expressed as follows (Papo & Caufin, 1991):

$$\mu_p(t) = \mu_p(0) + (1000 - \mu_p(0))(t/t_v)^n \quad (2.16)$$

where t_v is the moment at which the slurry reaches 1000 Pa·s, $\mu_{0,0}$ is plastic viscosity at resting time zero. Eq. (2.8) can be rewritten as follows:

$$P = \left[\frac{8\tau_0(t)}{3R_{\text{hose}}} + \frac{8\mu_p(t)}{\pi R_{\text{hose}}^4} Q \right] L_{\text{hose}} \quad (2.17)$$

(iii) Discontinuity

Discontinuity is a common phenomenon relevant to the material rheology evolving with time. As the resistance of fluid increases with time during printing process, pumpability decreases such that it deteriorates the delivering phase and causes discontinuity of printed filaments (Kaszy et al., 2018; Kazemian et al., 2017; Liu et al., 2018; Panda & Tan, 2018; Zareiyan & Khoshnevis, 2017).

Liu et al.'s work demonstrated the importance of dynamically monitoring material properties and automatically adjusting pump rotational speed. Their results are illustrated in Figure 2-13 (Liu et al., 2018), which implies that the printing process with open-loop control can achieve a superior quality of printed filament and surface finish compared with that without open-loop control.

Figure 2-13 Printed products (a) without open-loop control (b) with open-loop control (Liu et al., 2018)

2.2.3 Methods to control rheological properties for 3D printing

Concrete can be classified as two-phase material, i.e. fluid paste and solid aggregate phase. The fluid paste contains cement, mineral admixtures, water, etc. Additionally, chemical admixtures are widely used in modern concrete to adjust rheological properties due to their cost-effectiveness and high efficiency. The rheological property of concrete relies on the quantity and quality of each constituent used and their interactions. The influence of mineral admixtures/fiber, aggregates, and chemical admixtures on rheological properties are discussed in this section.

(i) Mineral admixtures and fibers

Extensive research has been conducted to investigate the influence of mineral admixtures on rheological properties (Lu et al., 2018; Park et al., 2005; Ruan et al., 2018; Yang et al., 2009; Zhu et al., 2018). Ultrafine fly ash is considered as the best mineral admixture that reduces the yield stress and viscosity among six different mineral admixtures including coarse fly ash, fly ash, fine fly ash, ultra-fine fly ash, metakaolin and silica fume (Ferraris et al. 2001). Incorporating slag with an optimum content of 15% by mass to replace cement can increase the workability of concrete (Boukendakdji et al., 2009).

Compared to the control case, mixing silica fume in concrete decreased the workability due to higher surface areas of silica fume particles (Nochaiya et al. 2010), as shown in Figure 2-14 (Nanthagopalan et al., 2008). Increasing the water-binder ratio resulted in a relative reduction of plastic viscosity and relative yield stress (Yang et al., 2009). Additionally, fiber content or dispersion plays an important role in rheological properties, e.g. Li and Li (2012) demonstrated that strong correlation existed between plastic viscosity, PVA fiber dispersion and Engineered Cementitious Composites tensile behavior, as shown in Figure 2-15 and 2-16.

Figure 2-14 Effect of replacement of silica fume on rheological properties (Nanthagopalan et al., 2008)

Figure 2-15 Rheological properties of the ECC mixes: (a) Mash cone flow time (before adding fibers) versus plastic viscosity, (b) mini-slump flow diameter (before and after adding fibers) of the ECC mixers (Li and Li, 2012)

Figure 2-16 Correlations between: (a) tensile strain capacity and fiber dispersion coefficient; (b) fiber dispersion coefficient and Marsh cone flow time; (c) tensile strain capacity and Marsh cone flow time

(ii) Aggregates

Concrete is considered as a two-phase material, consisting of coarse aggregate (CA) and paste (Hu & Larrard, 1996). It is well known that aggregates take up 60-80% of the total volume of concrete materials. Rheological properties of the cementitious material are highly affected by the gradation of aggregate (Ashraf & Noor, 2011; Hu, 2005; Hwang et al. 2012). Good aggregate gradation contributes to the high density and proper rheological properties of materials. Fuller Thompson theory is a classical theory for gradation design. In 1907, W.B Fuller and S.E. Thompson proposed a theory for gradation design based on experimental results (Fuller & Thompson, 1907). Later, the Federal Highway Administration (FHWA) proposed a modified Fuller Thompson equation (Li, 2011). Fuller Thompson theory has been widely used in producing high-performance concrete (Hwang et al., 2012; Mangulkar & Jamkar, 2013), designing sustainable concrete with minimum content of cement (Fennis & Walraven, 2012) and optimizing rheology (Hu & Wang, 2011).

Rheological performance is significantly affected by the packing fraction of a system as well, which is defined as the volume ratio of solids to the total volume. Theoretically, materials designed by the continuous gradation can achieve maximum packing fraction, which describes a condition where the void volume reaches the minimum for a given system. According to the Marson-Percy model, the highest packing fraction of materials results in the lowest plastic viscosity. To fulfill the material rheological property requirements in 3DCP, Fuller Thompson theory and Marson-Percy model should be applied in materials design stage of 3DCP.

(iii) Chemical admixtures

Chemical admixtures are economic and high-efficiency ingredients to adjust rheology of concrete. Employing chemical admixtures to adjust rheological property and hydration process is necessary for 3DCP. Extensive research has been conducted to study the influence of chemical admixtures (superplasticizer, accelerator, and retarder) on rheological properties (Banfill & Swift, 2004; Luckham & Ukeje, 1999; Roussel & Cussigh, 2008; Ruan et al., 2018; Yang et al., 2009). The addition of superplasticizer reduces yield stress and plastic viscosity due to the electrostatic and/or steric hindrance effects (Banfill, 2011), as illustrated in Figure 2-17 (Ma & Wang, 2018). Cement particles possess either positive or negative electrostatic charges and agglomerate together. The addition of superplasticizer provides equal polarity to cement particles such that cement particles are dispersed with repulsive force.

Figure 2-17 Action of superplasticizer on cement particles. (a) Flocculated cement particles; (b) dispersing cement particles by the repulsive force generated by negatively charged superplasticizer; (c) releasing of entrapped water (Ma & Wang, 2018)

The underlying mechanism of the correlation between yield stress and the dosage of superplasticizer can be explained with YODEL (Yield Stress mODEL) (Flatt & Bowen, 2006), which correlates the distance between particles with the yield stress from the first principle. The basic expression is as follows:

$$\tau_0 = m_1 \frac{\phi^2(\phi - \phi_0)}{\phi_{\max}(\phi_{\max} - \phi_0)} \quad (2.18)$$

$$m_1 = \frac{1.8}{\pi^4} \left(\frac{G_{\max}}{b} \right) F \quad (2.19)$$

$$G_{\max} = \frac{A_0}{12H_s^2} \quad (2.20)$$

Where ϕ and $\phi_{\max}$ are the solid volume fraction and maximum packing fraction respectively; ϕ_0 is the percolation threshold; b is the average particle size; H_s is the surface to surface separation distance at contact points; F is interparticle force. The average distance between particles increases with the dosage of superplasticizer such that the yield stress and the degree of flocculation decreases.

Besides superplasticizer, accelerators and retarders are the other two types of chemical admixtures. Accelerators are a class of admixtures commonly used for concrete to accelerate setting, hardening and the development of early strength of concrete. The most commonly used accelerators are non-chloride and non-corrosive (Ma & Wang, 2018). Retarder can be adsorbed on the surface of cement particles to create an insoluble layer, which delays or slows down the hydration of cement. Sodium gluconate (SG), tartaric acid (TA), citric acid (CA) and sugar are usually adopted retarders, which perform desirable retarding effect (Li, 2011).

Although extensive works have been conducted to investigate the influence of various factors on concrete rheology as well as explore the underlying mechanism, limitations still remain on quantifying the correlation between rheology and various factors.

2.3 Reinforcement for 3D concrete printing

The fabrication of novel reinforced concrete structures using digital technologies necessarily requires suitable strategies for reinforcement implementation. The successful integration of existing reinforcement systems, such as steel rebar, rods, wires, fibers or filaments, will indeed allow for printed concrete structures to be designed using standard structural codes. However, it is a challenge for the reinforcement integration to be compatible with either the specific printing technique without affecting the level of form-freedom and automation in 3DCP (Asprone et al., 2018). This part will discuss several potential methods to introduce reinforcement to 3DCP.

(i) Mesh mold reinforcement

In the mesh mold approach, the reinforcement is constructed first and then used as a carrier for the matrix material that is added in a subsequent production step. This approach was first adopted in a project realized in 2016 (Alec, 2016), the reinforced concrete walls of a two-story house were made by first erecting the conventional reinforcement mesh and subsequently depositing concrete with a Material Deposition Method (MDM)-type machine, with two large forked print nozzles that can simultaneously print on each side of the reinforcement (Alec, 2016).

(ii) Continuous fiber reinforcement

To achieve automatic introduction of the reinforcement in the printed material, Bos et al. and Lim et al. developed a novel system to embed the reinforcement in concrete along the printing direction (Bos et al., 2017; Lim et al., 2018), as shown in Figure 2-18 and Figure 2-19. In this approach, the continuous metal cable can be entrained as a reinforcement medium in the printing process.

Lim et al. also investigated the influence of metal cable diameter on the flexural strength, as shown in Figure 2-20 where C10,C15,C20 indicates matrix reinforced

with 1 mm, 1.5 mm, and 2 mm stainless steel cable. As shown in the figure, the maximum load increases with the increase of metal cable diameter.

Figure 2-18 Nozzle design for reinforcement printed along printing direction: (a) Schematic of the nozzle equipped with the cable extruder system; (b) Top view of the cable extruder prototype (Lim, et al., 2018)

Figure 2-19 Early version of reinforcement entrainment device, equipped with chain reinforcement (Bos et al., 2017)

Figure 2-20 Plot of load vs displacement graph for control (C0) and C10, C15, C20 specimen (Lim, et al., 2018)

(iii) Short fiber reinforcement

Short fibers are widely adopted in the construction sector as the secondary reinforcement, including steel fibers, polymer fibers, natural fibers, etc. Hambach and Volkmer (2017) first introduced short fibers as the reinforcement for printable concrete and reported that a higher degree of aligned fibers along the printing direction can be achieved in 3DCP compared with cast one. Weng et al. developed a type of printable fiber reinforced cementitious material, and the printability was demonstrated by a large-scale printing test (Weng et al., 2019).

However, limitations remain in the previous works. First, the fiber content introduced in the matrix is less than 1 % by volume, which limits mechanical property improvement. Secondly, the ductility of developed material is limited, which is not desirable to extend the applications of cementitious materials. Several works have been conducted on developing ductile printable material (Soltan & Li, 2018; Zhu et

al., 2019), and the researchers found that the pumpability decreases with the adoption of fiber. Developing printable strain-hardening cementitious materials should be studied in the future.

2.4 Rapid hardening cementitious materials

Similar to geopolymer, magnesium potassium phosphate cement (MKPC) is also a type of rapid hardening materials (Ruan & Unluer, 2016; Ruan & Unluer, 2017), which has been widely adopted in engineering applications (Gardner et al., 2015a; Liao et al., 2017; Xu et al., 2017). The chemical reactions of MKPC systems can be described as shown in Eq. (2.21) (Ma et al., 2014; Xu et al., 2018). The main reaction phase ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ or struvite-K) is accountable for the strength improvement in MKPC-based systems (Ding & Li, 2005). The reaction kinetics and overall performance of the MKPC-based cementitious materials are controlled by several major factors, such as magnesia-to-potassium dihydrogen phosphate (KDP) weight ratio, magnesia-to-borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) (M/B) weight ratio (Yang & Wu, 1999) and water-to-binder (W/B) ratio (Ma et al., 2014). Within these binders, borax is used as a retarder to avoid flash set (Yang & Wu, 1999). When MKPC is used for practical applications, fly ash has been commonly blended due to its beneficial effects in improving fresh mixture workability, reducing heat generation and lowering the production cost (Ma et al., 2014).

Fly ash (FA), as shown in Figure 2-21, is a by-product of coal combustion in power plants and has been widely employed as a replacement of magnesia or KDP in MKPC to improve workability, reduce hydration heat, diminish the cost and reduce environmental impacts (Gardner et al., 2015a). Some studies indicated that FA is capable of acting as inert fillers when both the magnesia and KDP are replaced with FA while maintaining magnesia-to-phosphate (M/P) molar ratio unchanged (Ding & Li, 2005; Xu et al., 2017). Previous investigations also reported that FA is involved

in the chemical reactions within MKPC systems (Lv et al., 2018) after the major binder, magnesia, is substituted with FA partially, consequently reducing M/P molar ratio in the designed binders and achieving better fresh properties, improved microstructures, and enhanced mechanical properties.

Figure 2-21 Morphology of fly ash

In addition to fly ash, silica fume is a by-product of manufacturing silicon metal and is an effective ingredient to adjust the rheological properties for 3D concrete printing and improve the mechanical properties of MKPC. Intensive research works use silica fume to optimize the rheological properties of materials to satisfy the requirements of 3D concrete printing (Kazemian et al., 2017; Weng et al., 2018). Additionally, Zheng et al. (2016) indicated that silica fume with the dosages less than 15 % of the mass ratio of MgO+KDP could enhance the hardened mechanical properties of MKPC due to a much denser matrix with less crack and porosity achieved.

2.5 Problems and knowledge gaps

The problems and the knowledge gaps within the research scope of this thesis (Figure 1-3) are summarized here based on the literature review.

(i) Rheological models for prediction

Researchers reveal that rheological properties in terms of yield stress, plastic viscosity, and thixotropy, are critical material characteristics for materials to satisfy the requirement of printability. Material constituents and chemical admixtures serve as vital factors influencing material rheological properties.

Extensive research has been conducted to investigate the influence of material constituents on rheological properties (Lu et al., 2018; Park et al., 2005; Ruan et al., 2018; Yang et al., 2009; Zhu et al., 2018). However, limitations remain. Firstly, previous works mainly reach qualitative conclusions. Few quantitative results are established to explain the impact of material constituents on rheological properties. Besides, research needs to be carried out to explore the influence of material constituents on thixotropy, which is an essential time-dependent parameter for the printing process. To overcome these limitations, an efficient approach should be adopted for the experimental design to reduce experimental runs. Meanwhile, quantitative models should be built to provide guidance for the predictions of rheological properties (Chen et al., 2015). The influence of material constituents on thixotropy also needs further exploration.

Design of Experiment (DoE) is a scientific methodology for experimental design and data analysis based on fundamental mathematical statistics (Jones, 2002b). As a powerful approach to exploring the correlation between factors and responses, DoE has been successfully used in various research fields (Chen et al., 2017; Chen et al., 2015; Chen et al., 2015; Liu et al. 2017). Therefore, it potentially adopts DoE to construct the statistical model for correlating material constituents or chemical admixtures with rheological properties.

(ii) Practical models to relate rheology with buildability

Extensive works have been conducted to correlate the rheology with buildability as discussed in Sections (ii) and 2.2.2. However, models established in those two

sections are insufficient for practical applications due to a lack of validation through practical printing tests. To overcome the challenge, a practical buildability model should be proposed to correlate the rheological property and buildability.

(iii) Material development for large-scale printing with reinforcement

A number of works has characterized the influence of various material constituents or chemical admixtures on the rheological property as well as proposed several potential ingredients, which can adjust the rheology to fulfill the requirement of 3D printing for large-scale application, including silica fume (Weng et al., 2018), nano-clays (Qian et al., 2017), viscosity modifying admixtures (Ma et al., 2018), etc. However, the aforementioned works remain in the stage of feasibility investigation and lack validation through a large-scale printing test. Therefore, printable material with reinforcement should be developed as well as validated through the large-scale printing test.

(iv) Development of rapid hardening cementitious materials for 3D concrete printing

3D printing of cementitious materials is an innovative and promising approach in the construction sector, attracting much attention over the past few years. The performance of the developed MKPC binders with different formulations in the context of 3D printing was assessed via a detailed investigation of the workability, extrudability, buildability, compressive strength, porosity, and microstructural analysis. Amongst the mixtures studied, the optimum MKPC formulation involving 60 wt% fly ash and 10 wt% silica fume with a borax-to-magnesia ratio of 1:4 was selected for a small-scale printing demonstration in line with its rheological and mechanical properties.

Chapter 3 Statistical models to predict rheological properties of cementitious materials for 3D printing

The factorial design is more efficient than the traditional one-factor at a time experiment. The method can simplify the experimental process and reduce experimental runs, while enough information still can be extracted for data analysis. Meanwhile, the method can allow the influence of a factor to be estimated at several levels of other factors.

The focus of this chapter is to construct statistical models to predict how different factors influence rheological properties by adopting the factorial design. The pre-determined factors in this work are sand-to-binder ratio, water-to-binder ratio, fly ash-to-cement ratio, silica fume-to-cement, and the dosage of fiber. The responses are flow resistance, torque viscosity and thixotropy of materials. The analysis of variance (ANOVA) was adopted to conduct statistical analysis and create statistical models for predictions. Experimental results indicate that the statistical models can be used to predict material rheological properties with an appropriate degree of accuracy. Although the constructed statistical models may not be universally applicable due to change in material chemical composition, different particle size distribution, etc., the validation test indicates that factorial design is efficient to find the desirable formulation within a given boundary.

3.1 Background and Experimental Design

3.1.1 Bingham model

Rheology describes the deformation and flow behavior of materials (P. F. G. Banfill, 2006). Bingham model is commonly used for cement pastes due to its simplicity and wide acceptance (Austin et al., 1999; Weng et al., 2018). The relationship between shear stress τ (Pa) and shear rate $\dot{\gamma}$ (1/s) in the Bingham model is described as (2.1),

where rheological parameters of yield stress and plastic viscosity are measured by a rotational rheometer test, in which Bingham model can also be expressed as (2.2) for the convenience of experiment design and data analysis. Material rheological property evolves with time, which is discussed in Section 2.2.2. Finally, the requirement of material rheological property for 3DCP is discussed in Section 2.2.

3.1.2 2^k design and 2^{k-p} fractional design

2^k design (factorial design) is a special design method in DoE (Jones, 2002a). In 2^k design, each factor has two levels, i.e. high level and low level. The total number of experiments is 2^k if there are k factors. The 2^k design can effectively reduce a total number of experiments via optimizing experimental runs so that the method saves time and efforts in the material design stage and more factors can be studied in experiments than those studied in conventional experimental design. Additionally, effect values can be calculated through the Analysis of Variance (ANOVA). A total number of 2^k experiments can be further reduced via the 2^{k-p} fractional design, in which p means the number of independent generators. The design method reduces the total number of experiments to $1/2^p$ of the original 2^k design (Jones, 2002a).

3.2 Material properties, mixture proportions and printing investigation

3.2.1 Materials properties

Cement slurry was produced from Ordinary Portland cement (OPC, ASTM type I, Grade 42.5), silica fume (SF, undensified, Grade 940, Elkem Pte. Ltd.), silica sand (S), fly ash (FA, Class F), polyvinyl alcohol (PVA) fibers (Kuraray Pte. Ltd.) (Zhang et al., 2018; Liu & Tan, 2018), water and superplasticizers (SP, 181N, Grace Pte. Ltd.). Particle size distributions of cement, silica fume, silica sand, and fly ash are depicted in Figure 3-1. The physical properties of powder ingredients were analyzed by Mastersizer 2000 and BET surface area analyzer, and results are shown in Table

3-1. The chemical compositions of OPC and FA are summarized in Table 3-2. Characteristics of PVA fiber are presented in Table 3-3.

Figure 3-1 Particle size distribution of powder ingredients

Table 3-1 Physical properties of powder materials used in this study

	Density (g/cm ³)	Specific surface area (m ² /g)
OPC	3.15	2.66
FA	2.43	0.285
SF	2.20	7.92
Silica Sand	2.66	0.305

Table 3-2 Chemical composition of fly ash and Ordinary Portland Cement (OPC)

Formula	Concentration / %	
	Fly ash	Cement
SiO ₂	58.59	24.27
Al ₂ O ₃	30.44	4.56
Fe ₂ O ₃	4.66	3.95
TiO ₂	2.02	0.55
K ₂ O	1.51	0.61
CaO	1.21	62.2
MgO	0.776	3.34
P ₂ O ₅	0.531	0.15
Na ₂ O	-	0.21
SO ₃	0.0914	-
ZrO ₂	0.04	-
MnO	0.0351	-
Cr ₂ O ₃	0.027	-
CuO	0.0254	-

ZnO	0.0229	-
Table 3-3 Characteristics of PVA fiber		
Tensile Strength/ MPa		1560
Modulus/GPa		41
Diameter/ μm		40
Length/mm		8
Elongation at break/%		6.5
Oil coating		1.2% by fiber weight

3.2.2 Mixture proportions

In this study, the rheological properties of fiber-reinforced cementitious materials for 3D printing are measured via the fractional design. Firstly, a 2^{5-1} experiment is designed as shown in Table 3-4, in which the total number of experiments should be conducted is 16. Herein, A, B, C, D, and E represent sand-to-binder ratio (S/B), water-to-binder ratio (W/B), fly ash-to-cement ratio (FA/OPC), silica fume-to-cement ratio (SF/OPC) and the dosage of fiber, respectively. ABCDE is then selected as the generator. The content of S/B, W/B, FA/OPC, SF/OPC is expressed by the mass while the dosages of fiber are expressed by volume. Binder represents the total mass of OPC, FA, and SF. Finally, new experiment runs (2^{5-1} design) can be designed by four factors (A, B, C, and D) (Amziane et al. 2013).

Coded values and actual values of fractional factorial design are shown in Table 3-5 and 6 respectively, in which BCD and ABE are selected as generators. D and E are expressed by BC and AB in the tables, respectively. Taking formulation No.1 for example: the high level and low level of S/B (factor A) are 0.28 and 0.3, respectively; therefore, the mean value of S/B is 0.29 with 0.02 as the range between high level and low level; when the S/B is at a low level, the factor mean and range of S/B are then substituted into Eq. (3.1) to attain the coded value. Similarly, the formula can be applied when the factor is at a high level.

Table 3-4 2^{K-1} design matrix

No.	Run	A	B	C	D	E/%
1	(-)	0.28	0.30	1	0	1
2	a	0.30	0.30	1	0	0
3	b	0.28	0.32	1	0	0
4	ab	0.30	0.32	1	0	1
5	c	0.28	0.30	2	0	0
6	ac	0.30	0.30	2	0	1
7	bc	0.28	0.32	2	0	1
8	abc	0.30	0.32	2	0	0
9	d	0.28	0.30	1	0.1	0
10	ad	0.30	0.30	1	0.1	1
11	bd	0.28	0.32	1	0.1	1
12	abd	0.30	0.32	1	0.1	0
13	cd	0.28	0.30	2	0.1	1
14	acd	0.30	0.30	2	0.1	0
15	bcd	0.28	0.32	2	0.1	0
16	abcd	0.30	0.32	2	0.1	1

*The SP used in all mixture is equal to 1.8 g/L.

Table 3-5 The coded table of the fractional factorial design matrix

No.	A	B	C	D	E
1	-1*	-1	-1	1*	1
2	-1	-1	1	-1	1
3	-1	1	-1	-1	-1
4	-1	1	1	1	-1
5	1	-1	-1	1	-1
6	1	-1	1	-1	-1
7	1	1	-1	-1	1
8	1	1	1	1	1

-1 and 1 represents high and low level respectively

Table 3-6 Absolute values of the fractional factorial design matrix

No.	A	B	C	D	E	SP/(g/L)
1	0.28	0.30	1	0.1	1	1.8
2	0.28	0.30	2	0	1	1.8
3	0.28	0.32	1	0	0	1.8
4	0.28	0.32	2	0.1	0	1.8
5	0.30	0.30	1	0.1	0	1.8
6	0.30	0.30	2	0	0	1.8
7	0.30	0.32	1	0	1	1.8
8	0.30	0.32	2	0.1	1	1.8

$$\text{Coded value} = (\text{Actual value} - \text{Factor mean}) / (\text{Range of factorial value} / 2) \quad (3.1)$$

3.2.3 Mixing, testing procedures and printing investigation

A hysteresis loop method is adopted to measure the rheological properties of mixed materials, which are evaluated via Viskomat XL in terms of static torque, flow resistance, torque viscosity, and thixotropy. In this method, torque is recorded with a linear increasing and then decreasing angular velocity or rotating speed of the viscometer. If the test sample is thixotropic, the two torque curves produced do not coincide, causing rather a hysteresis loop (Zhang et al., 2018). The larger the enclosure area, the higher thixotropy. Assuming Bingham flow behavior exists, Eq.(2.2) can be adopted for fitting the descending curve to obtain the flow resistance and torque viscosity (Yang et al., 2009).

The six-blade vane probe and cage were used for the rheological test to avoid slippage of cement paste. Both the diameter and the height of this vane probe are 69 mm, and the gap between probe and cage, and the bottoms of probe and barrel are both 40 mm. During the rheological test, the speed of rheometer is increased linearly from 0 rpm to 60 rpm in 5 min. Afterward, it is decreased linearly to 0 rpm in another 5 min as shown in Figure 3-2 (Yang et al., 2009). The flow curve was recorded for both the

ascending and descending legs of the shear stress-shear rate curve as shown in Figure 3-3. Descending curve was used for fitting the Bingham model. Since the mixing procedures (Kaufmann, Winnefeld, & Hesselbarth, 2004), temperature and time may affect the testing results (Yang et al., 2009), the mixing procedures are fixed and shown in Figure 3-4.

Figure 3-2 Rheological testing programs

Figure 3-3 Typical rheological test result

Figure 3-4 Mixing procedure

The printing tests were then conducted by a robotic printing system (Zhang et al., 2018) as shown in Figure 3-5. Premixed materials were firstly poured into a black funnel (Figure 3-5 (b)) and were then pumped to a nozzle head, which was fixed on the robotic arm that controlled the nozzle to print an object based on a CAD model (Figure 3-5 (c)). The CAD model is 75 mm in triangle edge length and 9 layers.

Figure 3-5 The robotic printing system: (a) Robotic arm; (b) Pictor pump; (c) Designed CAD model

3.3 Results and discussion

3.3.1 Rheological results

Table 3-7 shows rheological test results that were further analyzed via the ANOVA, which was adopted to investigate whether factors have statistically significant effects on responses. The analysis result enables researchers to identify major trends and to predict rheological properties according to derived models. The detailed analysis results are discussed in the following sections.

Table 3-7 Rheological properties results measured via factorial design

No.	S/B	W/B	FA/OPC	SF/OPC	Fiber/%	Torque	Flow	Thixotropy/
						Viscosity /N·mm·min	resistance /N·mm	(N·mm·min ⁻¹)
1	0.28	0.30	1	0.1	1	10.7	1088	813.0
2	0.28	0.30	2	0	1	9.03	141.4	2126
3	0.28	0.32	1	0	0	5.22	99.11	192.5
4	0.28	0.32	2	0.1	0	4.16	159.1	656.2
5	0.30	0.30	1	0.1	0	6.09	465.5	1484
6	0.30	0.30	2	0	0	14.3	122.1	4653
7	0.30	0.32	1	0	0	4.90	110.1	1008
8	0.30	0.32	2	0.1	1	8.75	438.3	4578

3.3.2 ANOVA analysis and derived models

A software of Design Expert (Chen et al., 2015) was used to carry out the ANOVA analysis based on the data listed in Table 3-7 and analyzed results are presented in Table 3-8, 9 and 10. F-value, F_0 , of each factor, was then calculated. The significance of each factor was obtained with a confidence level by comparison of calculated F_0 and the control value in the F-distribution chart.

Table 3-8 ANOVA analysis result for flow resistance

Source	DO F	F- Value	Confidence level/%
S/B	1	1.08	64
W/B	1	0.81	57
FA/C	1	6.02	82
SF	1	9.74	94
F	1	12.33	97
Error	2	—	—
Total	7	—	—

$$F_{0.3,1,2} = 1.92; F_{0.2,1,2} = 3.55; F_{0.15,1,2} = 5.20; F_{0.1,1,2} = 8.52;$$

(Note: above F_{α, ν_1, ν_2} is acquired from the F-distribution chart. $1-\alpha$, ν_1 and ν_2 represent confidence interval, the degree of freedom (DOF) of investigated factor and error, respectively.)

Table 3-9 ANOVA analysis results for torque viscosity

Source	DOF	F-Value	Confidence level/%
S/B	1	1.11	64
W/B	1	0.84	57
FA/C	1	1.01	60
SF	1	0.36	40
F	1	2.36	80
Error	4	—	—
Total	9	—	—

Table 3-10 ANOVA analysis results for thixotropy

Source	DOF	F-Value	Confidence level/%
S/B	1	3.82	80
W/B	1	7.62	89
FA/C	1	4.25	82
SF	1	1.53	66
F	1	1.22	62
Error	4	—	—
Total	9	—	—

Table 3-8 illustrates that the dosage of fiber and SF/OPC have a significant influence on the flow resistance at a very high confidence level, 97 % and 94 %, respectively, followed by FA/OPC with a confidence interval of 82 %. To state that S/B and W/B have a significant influence on flow resistance, the confidence level is only 64 % and 57 %, respectively. Table 3-9 indicates the dosage of fiber has significant effects on the torque viscosity at a high confidence interval (80 %), followed by S/B, FA/OPC and W/B with confidence intervals of 64 %, 60 %, and 57%, respectively. However, the confidence level of SF/OPC is at 40 %. Table 3-10 shows S/B, W/B, and FA/OPC possess significant influence on thixotropy at a high confidence level (above 80 %), followed by SF/OPC and the dosage of fiber with confidence intervals of 66 % and 62 %, respectively.

Table 3-11 Effect of each factor on flow resistance, torque viscosity and thixotropy

Factors	Intersection	S/B	W/B	FA/OPC	SF/OPC	Fiber
Parameters	a	A	B	C	D	E
Torque viscosity	7.89	1.74	-3.70	3.96	-0.49	2.73
Flow resistance	327.89	2.71	-194.03	-145.99	419.18	287.42
Thixotropy	3072	-2125	-822.2	-185.1	1345	397.5

Changes in responses induced by changes of a given factor are shown in Table 3-11. Positive or negative numbers indicate that the factor possesses a positive or negative

influence on the responses, respectively. The greater a number, the more influence a factor has on a response. Obtained parameters of derived models were based on the effects of each factor as shown in Table 3-11.

Table 3-11 presents the dosage of fiber has positive effects on flow resistance, torque viscosity, and thixotropy, whereas increasing W/B declines flow resistance, torque viscosity, and thixotropy. Larger SF/OPC raises flow resistance and thixotropy but reduces torque viscosity, whereas FA/OPC presents an opposite trend. S/B possesses a positive influence on torque viscosity and flow resistance while the negative influence on thixotropy. From the analysis above, SF/OPC seems to be a type of critical ingredients for 3D printable cementitious materials. It not only has significant effects on flow resistance, thixotropy with a high confidence level but also shows a desirable trend for flow resistance, torque viscosity, and thixotropy, i.e. positive for flow resistance and thixotropy but negative for torque viscosity.

Effect values of each factor on responses also represent the coefficient of each factor in the derived models. Therefore, the numbers in Table 3-11 are also the coefficients of statistical rheology models, as shown in Eqs. (4-8 to 4-10). These models correlate rheological properties with various factors, where A, B, C, D, E correspond to S/B, W/B, FA/OPC, SF/OPC, and dosages of fiber, respectively.

$$\text{Flow resistance} = 327.99 + 2.71 \times A - 194.03 \times B - 145.99 \times C + 419.18 \times D + 284.42 \times E \quad (3.2)$$

$$\text{Torque viscosity} = 7.89 + 1.74 \times A - 3.70 \times B + 3.96 \times C - 0.49 \times D + 2.73 \times E \quad (3.3)$$

$$\text{Thixotropy} = 3072 - 2125 \times A - 822.2 \times B - 185.1 \times C + 1345 \times D + 397.5 \times E \quad (3.4)$$

However, these models are only valid for this particular set of materials, production technique and testing techniques within the narrow boundaries of the parameters under investigation. The accuracy of models was estimated by statistical analysis in this study. The results of prediction models are listed in Appendix A. Figure 3-6 show the normability tests, where all the points scattering around a straight line. The result indicates that residuals followed a normal distribution, and flow resistance, torque viscosity, and thixotropy cannot be improved by adopting other curve fitting methods.

Figure 3-6 Normability test: (a) flow resistance; (b) torque viscosity; (c) thixotropy

To exclude the influence of run order on the statistical rheological models, the correlation between the residuals and run order should be confirmed. Figure 3-7 depicts that the points scatter randomly (no grouping) with the run order, and the result indicates that the run order has no significant effects on the responses. Ideally,

the model error (residuals) will consist of normally distributed random variation from the experimental process and measurement systems.

Figure 3-7 Residuals analysis: (a) flow resistance; (b) torque viscosity; (c) thixotropy

Figure 3-8 presents the correlation between prediction results and actual rheological test results based on Table A. 1 to A.3 in Appendix A.

Figure 3-8 Predicted vs actual result: (a) flow resistance; (b) torque viscosity; (c) thixotropy

Afterward, three additional formulations were selected to verify the accuracy of the derived models. The formulations and rheological test results are shown in Table 3-12 and 3-13, respectively. Table 3-13 implies the model can largely predict experimental results well despite the random selection of formulations. Nevertheless, the accuracy

of these first-order models can still be improved, and more accurate models with higher-order interactions incorporated are required to predict rheological properties. However, this is beyond the scope of this study.

Table 3-12 Formulations selected for verification

No.	S/B	W/B	FA/OPC	SF/OPC	Fiber/%
1	0.3	0.3	1	0.05	0
2	0.28	0.3	2	0	1
3	0.28	0.32	2	0.1	0

Table 3-13 Rheological test results

Parameters	No.	Experiment	Model	Error/%
Viscosity / N·mm·min	1	9.17	9.37	2.18
	2	10.69	13.81	29.2
	3	6.91	6.41	7.24
Flow resistance/ N·mm	1	384.5	383.3	0.312
	2	225.5	241.6	7.14
	3	93.23	117	25.5
Thixotropy/ N·mm·min ⁻¹	1	506.7	609.3	20.3
	2	4146	4587	10.6
	3	6024	5534	8.13

3.3.3 Demonstration of 3D printable FRCC

Finally, miniature structures were printed for demonstration purposes via a robotic printing system (Zhang et al., 2018). The No.1 formulation in Table 3-7 was selected for the purpose as it possesses the highest flow resistance among all formulations, 1088 N·mm, and low torque viscosity, 10.7 N·mm·min. No.3 formulation, possessing lowest flow resistance among all formulations, was also selected as the control. Raw

ingredients were firstly mixed in a Hobart mixer. The paste was then conveyed from a concrete pump to a nozzle which was fixed on a robotic arm. The robotic arm then printed the paste with the intended shape as the CAD model. The robotic arm movement speed and pumping speed were 100 mm/s and 2.5 L/min, respectively. A conveyance hose used in the printing process was 25.4 mm in diameter and 3 m in length. A nozzle with 8 mm in diameter was used for the printing test.

The final printed hexagon part of formulation No. 1 is shown in Figure 3-9. For each triangle in printed part, it is with an edge length of 74.83 mm, and the height of final printed part is 84.33 mm. The final printed of formulation No.3 is plotted in Figure 3-10, which indicates that material yield stress was insufficient to sustain subsequently printed layers such that serious deformation occurred.

Figure 3-9 Final printed part (formulation No. 1): (a) top view; (b) side view

Figure 3-10 Final printed part (formulation No.3): (a) top view; (b) side view

3.4 Conclusions

A factorial design was adopted in this research to minimize the experimental runs while the experimental results still retain essential information for data analysis. The method is particularly useful when one has to deal with a great number of variables in an experiment, e.g. in search of printable materials with desirable rheological properties. The confidence interval, first-order models, and the effect values were attained via the factorial design that possesses several advantages compared with a traditional variable-controlling method, e.g. the method can save time and resources as it minimizes the number of experimental runs. The method can also be used to derive statistical models for further predictions.

The influences of material constituents on flow resistance, torque viscosity, and thixotropy were explored in this work. Results indicate that flow resistance and torque viscosity were improved with the increment of the dosage of fiber. S/B possesses a positive influence on torque viscosity and flow resistance while the negative influence on thixotropy. Flow resistance, viscosity, and thixotropy are dropped with the rise of W/B. Torque viscosity is boosted while flow resistance and thixotropy are declined with raising FA/OPC. However, compared with the influence of FA/OPC on rheological properties, the opposite trend remains with the increment of SF/OPC, which is desirable for 3DP materials. Finally, silica fume is an appropriate ingredient to adjust rheological properties for the 3D cementitious materials printing process.

The dosage of fiber and SF/OPC have a significant influence on flow resistance at a very high confidence level (more than 90 %), followed by FA/OPC with a confidence interval of 82 %. However, the confidence level of S/B and W/B on flow resistance is only at around 60 %. The dosage of fiber dosage has a significant effect on the torque viscosity at a relatively high confidence interval (80 %), followed by S/B, FA/OPC, and W/B with confidence intervals at around 60 %. However, the confidence level of SF/OPC is only at 40 %. S/B, W/B, and FA/OPC show significant influence on thixotropy at a relatively high confidence level (above 80 %), followed by SF/OPC and the dosage of fiber with confidence intervals at around 65 %.

High flow resistance and low viscosity are necessary for the 3D printing process. Rheological models are highly needed for researchers to design their material formulations according to the rheological properties required for the 3D printing process. Although the first-order models derived in this work can be further improved, the models can still act as initial guidance for the control of the rheological properties of printable materials to achieve a successful printing process. At the next stage, second-order models will be developed to improve the degree of prediction accuracy of rheological properties, which is beyond the scope of this study.

Chapter 4 CCD optimizing chemical admixtures for 3D printable cementitious materials

One of the useful methods that adopt DoE is called Central Composite Design (CCD), which quantifies the influences of variables on responses through constructing statistical models. The CCD is more efficient than the traditional one-factor at the one-time experiment. The CCD can simplify the experimental process and reduce experimental runs, while enough information still can be extracted from the experiment for data analysis. Meanwhile, the method can allow the influence of a factor to be estimated at several levels of other factors.

To efficiently construct mathematical models in a more systematic manner, Response Surface Methodology (RSM) accompanied by Central Composite Design (CCD) was adopted to construct mathematical models describing the rheological characteristics in terms of yield stress, plastic viscosity and thixotropy as functions of three variables i.e. the dosages of superplasticizers, retarders, and accelerators.

4.1 Response surface methodology, rheology, and time-dependent effect

4.1.1 Response surface methodology and Central composite design

As one of the most reliable statistical methodologies in DoE, Response Surface Method (RSM) is used to construct statistical models for predicting the correlation between responses and variables. The methodology can also optimize the response surface function and predict further responses (Weng et al., 2018b).

The RSM includes various design structures, such as central composite design (CCD) and Box-Behnken. CCD experimental design structure is used in this work as it explores a larger process space and provides a higher prediction quality over the entire space than Box-Behnken. The structure of CCD design includes corner points, axial points and center points (corresponding to ± 1 , ± 1.68 , and 0 in Figure 4-1).

Corner points are the parameters with boundary value. The axial points can make the model in quadratic terms, which can take curvature effects into considerations. The center points were replicated several times to provide information on process reproducibility.

Figure 4-1 Design structure of CCD

4.1.2 Rheology and time-dependent effect

The rheological properties of cementitious materials are characterized by the static/dynamic yield stress and plastic viscosity. Static yield stress τ_s (Pa) and dynamic yield stress τ_d (Pa) are the minimum shear stress to initiate and maintain the flow of materials, respectively. Plastic viscosity μ_p (Pa·s) describes the resistance of flow when the fluid is flowing. All the rheological parameters can be attained from one rheological test.

Rheological properties influence the buildability and pumpability that are characterized by a build-up model and a pumping pressure model, respectively. The

built-up model correlates printed height of structures with material static yield stress, and the model is expressed as follows (Perrot et al., 2016):

$$H = \frac{\alpha}{\rho g} \tau_s(t) \quad (4.1)$$

where H (m) and α are the printed height (buildability) and the geometric factor of printed structures (Perrot et al., 2016), respectively; ρ (kg/m³) and g (m/s²) are the density of materials and gravitational constant, respectively. Eq. (4.1) implies that printed height is positively proportional to the static yield stress for a given material and structure. Pumpability, normally characterized by pumping pressure, is positively related to dynamic viscosity that measures a fluid's resistance to flow when an external force is applied. The time-dependent effect of material rheological property is discussed in Section 2.2.2

4.2 Materials, mixture design and properties characterization

4.2.1 Materials and mixture design

Formulations in this study consist of Ordinary Portland Cement (OPC, ASTM type I, Grade 42.5, silica fume (SF, undensified, Grade 940, Elkem company), fine sand, fly ash (FA, Class F), water, superplasticizers (MasterPozzolith-R168, BASF Pte. Ltd.), accelerators (MasterRoc SA160, BASF Pte. Ltd.), and retarders (MasterReobuild1000, BASF Pte. Ltd.). Particle size distribution and chemical composition of all the raw ingredients used in this work have been stated in the authors' previous work (Lu et al., 2018). All the mixtures used in this study follows the same formulations, as shown in Table 4-1.

Table 4-1 Mixture proportion

OPC	Sand	W	FA	SF
1	0.5	0.3	1.5	0.05

Note: all the ingredients' contents are expressed as a mass proportion of cement content

The dosages of chemical admixtures were designed by CCD, the coded and actual values of the experiment are presented in Table 4-2 and 5-3. The correlation between coded values and actual values is expressed in Eq.(4.2). The details to calculate the actual values and coded values have been reported in the authors' previous work (Weng et al., 2018).

Table 4-2 Coded values via CCD

Test run	Retarder	Accelerator	superplasticizer
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1
9	-1.68	0	0
10	1.68	0	0
11	0	-1.68	0
12	0	1.68	0
13	0	0	-1.68
14	0	0	1.68
15	0	0	0
16	0	0	0
17	0	0	0
18	0	0	0
19	0	0	0
20	0	0	0

Table 4-3 Actual values of chemical admixtures for 6 L materials

Test run	Retarder/g	Accelerator/g	Superplasticizer/g
1	6.78	6.78	3.39
2	13.6	6.78	3.39
3	6.78	13.6	3.39
4	13.6	13.6	3.39
5	6.78	6.78	6.78
6	13.6	6.78	6.78
7	6.78	13.6	6.78
8	13.6	13.6	6.78
9	4.47	10.2	5.08
10	15.9	10.2	5.08
11	10.2	4.47	5.08
12	10.2	15.9	5.08
13	10.2	10.2	2.24
14	10.2	10.2	7.93
15	10.2	10.2	5.08
16	10.2	10.2	5.08
17	10.2	10.2	5.08
18	10.2	10.2	5.08
19	10.2	10.2	5.08
20	10.2	10.2	5.08

$$\text{Coded value} = (\text{Actual value} - \text{Factor mean}) / (\text{Range of factorial value} / 2) \quad (4.2)$$

4.2.2 Mixing process and properties characterization

A Hobart mixer X200L was used for mixing. Since the rheological properties of cement slurries are influenced by a number of factors. Mixing procedures in this study were fixed to minimize the differences among batches. Firstly, the powders of all solid ingredients were dry mixed for 1 minute in stir speed. Water, superplasticizers,

and retarders were then added, and the mixing process continued for 1 minute in stir speed followed by 1 minute in speed I; the accelerators were then added, and the mixing process continued for 1 minute in speed I. After finishing the mixing, rheological property was measured.

Rheological properties were characterized in terms of static torque, flow resistance, torque viscosity, and thixotropy via a Viskomat XL. The testing protocol can be found in Section 3.2.3. Figure 4-2 presents the typical rheological test result via a Viskomat XL rheometer with vane probe. Assuming a Bingham flow behavior exists, when a shear stress is applied to the cementitious materials, a static yield stress is required to initiate material flow, corresponding to the maximum static torque in Figure 4-2. Based on the linear fitting of the descending curve, its slope and intersection with Y-axis are defined as torque viscosity and flow resistance respectively, which can then be converted into plastic viscosity and dynamic yield stress in Bingham Plastic model. The difference between Figure 4-2 and 3.3 is that the material used for Section 3 has a high flowability and the rheometer can break the microstructure fast. The data acquisition frequency of Viskomat XL is not sufficient to record the material static yield stress.

Figure 4-2 Typical rheological test result

The rheological performance in this part is characterized in terms of static yield stress and dynamic yield stress. The shear stress can be computed by Chhabra and Richardson (Chhabra & Richardson, 1959):

$$\Gamma = \frac{4\pi R_1^2 R_2^2 l \eta}{R_2^2 - R_1^2} \omega - \frac{4\pi R_1^2 R_2^2 l \tau_0}{R_2^2 - R_1^2} \ln \frac{R_1}{R_2} \quad (4.3)$$

where Γ (N·m) is the torque, ω (rad/s) is the rotational speed of outer barrel, l (m) and R_1 (m) are the length and radius of the probe, respectively, and R_2 (m) is the radius of the outer barrel. For the static yields stress, it can be directly obtained by applying static torque in Eq.(4.3). The dynamic yield stress and plastic viscosity can be obtained by converting flow resistance and torque viscosity via Eq.(4.3). The relationship between shear rate and rotational speed is expressed as follows:

$$\dot{\gamma} = 1 + \frac{\tau_s}{k\omega} \left[1 + \ln r - \frac{R_2^2}{2R_1^2} \left(1 + \frac{1}{r^2} \right) \right], r \in \left[1, \frac{R_2}{R_1} \right] \quad (4.4)$$

4.2.3 Printability test

Finally, a printing test was conducted to investigate the printability of designed mixture. As shown in Figure 4-3, a gantry printer with a 1.2 m × 1.2 m × 1.0 m (L × W × H) printing volume was used to control nozzle position for printing. 3D model used in the printing test is shown in Figure 4-4.

Figure 4-3 Gantry printer

Figure 4-4 CAD model for printability test

4.3 Results and discussion

4.3.1 ANOVA analysis

The rheological measurement results are presented in Table 4-4. Based on the data listed in Table 4-4, the static/dynamic torque and torque viscosity are converted into static/dynamic yield stress and plastic viscosity.

The ANOVA results are shown in Table 4-5, which shows the significance of the influence of individual and interactive effects of factors on the rheological properties. A, B, C stand for the coded factors of superplasticizers, retarders, and accelerators, respectively. AB, BC, AC represents the interaction effects of superplasticizers and retarders, retarders and accelerators, and superplasticizers and accelerators, respectively.

Table 4-4 Experimental results of CCD

Test run	Static torque (N·mm)	Flow resistance (N·mm)	Torque viscosity (N·mm/rpm)	Static yield stress (Pa)	Dynamic yield stress (Pa)	Plastic viscosity (Pa·s)	Thixotropy (N·mm·min ⁻¹)
1	843.1	194.7	2.58	833.2	192.4	18.84	13243
2	976.3	178.3	2.00	964.8	176.2	14.58	6263
3	1170	233.0	3.53	1156	230.3	25.79	17081
4	937.3	165.4	2.38	926.3	163.5	17.37	8667
5	673.6	164.5	2.90	665.7	162.6	21.19	9898
6	595.6	150.4	2.70	588.6	148.7	19.73	7410
7	1057	213.9	2.08	1045	211.4	15.21	12373
8	639.7	155.3	2.41	632.2	153.5	17.62	9222
9	1082	215.2	3.06	1070	212.7	22.35	15099
10	846.3	155.9	2.17	836.3	154.0	15.88	6893
11	762.8	187.3	1.89	753.9	185.1	13.84	13124
12	996.6	210.9	2.89	984.9	208.4	21.09	17889
13	1099	182.4	2.64	1086	180.2	19.28	11351
14	639.0	149.2	2.46	631.5	147.4	17.97	9233
15	837.9	169.0	2.82	828.1	167.0	20.60	17446
16	834.6	167.2	3.01	824.8	165.3	21.99	17256
17	856.3	166.5	2.64	846.2	164.6	19.29	17126
18	805.6	171.2	2.80	796.1	169.1	20.46	17296
19	825.6	168.5	3.02	815.9	166.5	22.06	18224
20	864.5	169.8	2.90	854.3	167.8	21.19	16585

In ANOVA, P-value and F-value serve as critical parameters for evaluating the significance of the proposed model and individual parameters. The P-value is the probability of achieving the F-value. A small P-value reveals that the effects of the parameters are statistically significant, while the high F-value indicates the variation reported by the model is significantly larger than that inherent in the process (Chen et al., 2015). For instance, the factor AC has an F-value of 16.77 and a P-value of 0.0022 associated with static yield stress, which indicates that there was only a 0.22% chance that the F-value of 16.77 occurs because of noise. As can be seen from ANOVA results, except for some cases in AB, AC, and BC, the *p*-value is generally smaller than 0.05, which implies that the model used for predicting the response is statistically significant.

Table 4-5 The ANOVA results of DoE

	Static yield stress (Pa)		Dynamic yield stress (Pa)		Plastic viscosity (Pa·s)		Thixotropy ($\text{N} \cdot \text{mm} \cdot \text{min}^{-1}$)	
	P	F	P	F	P	F	P	F
	value	value	value	value	value	value	value	value
Model	$< 10^{-4}$	46.15	$< 10^{-4}$	140.6	0.0062	5.64	$< 10^{-4}$	43.18
A	$< 10^{-4}$	61.91	$< 10^{-4}$	577.8	0.0043	13.46	$< 10^{-4}$	106.58
B	$< 10^{-4}$	77.18	$< 10^{-4}$	125.1	0.0482	5.06	0.0003	30.20
C	$< 10^{-4}$	188.8	$< 10^{-4}$	179.8	0.4329	0.6678	0.0148	8.630
AB	$< 10^{-4}$	53.34	$< 10^{-4}$	137.4	0.9525	0.0037	0.4358	0.6589
AC	0.0022	16.77	0.1961	1.920	0.0162	8.34	0.0036	14.26
BC	0.1792	2.090	0.0054	12.48	0.0036	14.29	0.4663	0.5737

Table 4-6 Estimation of model accuracy

Response	Static yield stress (Pa)	Dynamic yield stress (Pa)	Torque viscosity (Pa·s)	Thixotropy ($\text{N} \cdot \text{mm} \cdot \text{min}^{-1}$)
R^2	0.9765	0.9922	0.8354	0.9749
Adjusted R^2	0.9553	0.9851	0.6873	0.9523
Adequate precision	23.26	41.08	11.20	17.90

The accuracy of models was estimated by statistical analysis. The results of prediction models are listed in Appendix B. Figure 4-5 shows the normability tests, where all the points scattering around a straight line. The result indicates that residuals followed a normal distribution, and flow resistance, torque viscosity, and thixotropy cannot be improved by adopting other curve fitting methods.

Figure 4-5 Normal probability plots of residuals for different responses: (a) static yield stress; (b) dynamic yield stress; (c) plastic viscosity; (d) thixotropy

To exclude the run order effects from various statistical rheological models, the relation between the residual and run order should be confirmed (Chen et al., 2015). Figure 4-6 shows that the points scatter randomly (no grouping) with the run order, which indicates that run order has no significant effects on the responses.

Figure 4-6 The relationship between residuals and the run order in which the experiments were performed for different responses: (a) static yield stress; (b) dynamic yield stress; (c) plastic viscosity; (d) thixotropy

Then, the statistical analysis was used to estimate the statistical accuracy. High R^2 value (larger than 0.8) and high adequate precision (larger than 4) imply that the model decided is statically significant. The term adjusted R^2 is used to compensate for the addition of variables to the model. The value of R^2 increases with the addition of intersection variables to the regression models. However, the value of adjusted R^2 can increase or decrease only depending on whether the additional variable adds or detracts to the explanatory power of the model. For this reason, the indicator of adjusted R^2 is generally considered to be more accurate than that of R^2 . The large value of adjusted R^2 indicates that a significant relationship is captured by the model (Chen et al., 2015).

Figure 4-7 Predicted values vs actual values of different responses: (a) static yield stress; (b) dynamic yield stress; (c) plastic viscosity; (d) thixotropy

4.3.2 Prediction models

A positive value in Table 4-7 indicates a positive effect on the response, while a negative value implies a negative effect on the response. The absolute value represents the significance of the factor, which can be used to rank the importance of each factor. Results in Table 4-7 hint that with the increment of dosages of retarders and superplasticizers, all these rheological parameters are decreased while accelerators possess the opposite influence on the rheological properties. The interaction of retarders and accelerators has a negative influence on all the rheological properties. The interaction of retarders and superplasticizers possesses a positive influence on the dynamic yield stress, plastic viscosity, and thixotropy while it has a negative influence on the static yield stress. The interaction of accelerators and

retarders has a positive influence on the yield stress whereas it possesses a negative influence on the plastic viscosity and thixotropy.

Table 4-7 Coefficients of derived models

	Coefficient of models			
	Static yield stress (Pa)	Dynamic yield stress (Pa)	Plastic viscosity (Pa·s)	Thixotropy (N·mm·min ⁻¹)
Interception	829.1	166.82	20.91	17369
A	-71.89	-18.56	-1.65	-2550
B	80.27	8.64	1.01	1357
C	-125.5	-10.35	-0.3685	-725.9
AB	-87.19	-11.83	-0.0360	-262.1
AC	-48.89	1.40	1.70	1219
BC	17.24	3.56	-2.23	-244.5

The derived models for static/dynamic yield stress and plastic viscosity with respect to the three factors can be written as follows:

$$\text{Static yield stress} = 829.1 - 71.89A + 80.27B - 125.5C - 87.19AB - 48.89AC + 17.24BC \quad (4.5)$$

$$\text{Dynamic yield stress} = 166.8 - 18.56A + 8.64B - 10.35C - 11.83AB + 1.40AC + 3.56BC \quad (4.6)$$

$$\text{Plastic viscosity} = 20.91 - 1.65A + 1.01B - 0.37C - 0.036AB + 1.70AC - 2.23BC \quad (4.7)$$

$$\text{Thixotropy} = 17369 - 2550A + 1357B - 725.9C - 262.1AB + 1219AC - 244.5BC \quad (4.8)$$

Figure 4-8 shows the 3D response surface where the coded value of retarders is set as 0. The optimized dosages of accelerators or retarders or superplasticizers can be found from these contour figures to achieve different rheological requirements, e.g. maximum static yield stress or lowest plastic viscosity.

Figure 4-8 3D response surface of different responses: (a) static yield stress; (b) dynamic yield stress; (c) plastic viscosity; (d) thixotropy

4.4 Printability test results

The formulation No.3 and No. 6 in Table 4-4 were selected in printability test. Formulation No. 3 possesses high yield stress (1156 Pa) and high thixotropy (17081 $\text{N}\cdot\text{mm}\cdot\text{min}^{-1}$). No.6 possesses a low yields stress (588.6 Pa) and low thixotropy (7410 $\text{N}\cdot\text{mm}\cdot\text{min}^{-1}$). Printing and pumping speed are 2000 mm/min and 650 rpm, respectively. The result of printability test of formulation No.3 is illustrated in Figure 4-9, which indicates the formulation No.3 can be printed well and that the structure can maintain its shape until completing the test. However, Figure 4-10 plots the printing test results of formulation No.6, which implies that the properties of

formulation No.6 are insufficient for printing. Deformation and misalignment of the structure happen during the printing test and finally, the structure collapses.

Figure 4-9 Results of printability test of formulation No.3

Figure 4-10 Results of printability test of formulation No.6: (a) a slight deformation appear; (b) misalignment happens; (c) collapse occurs

4.5 Conclusions

In this study, Response Surface Methodology (RSM) accompanied by Central Composite Design (CCD) was adopted to investigate the influence of chemical admixtures and associated interactions of decided factors (superplasticizers, retarders, and accelerators) on the rheological properties in terms of static/dynamic yield stress, plastic viscosity and thixotropy. The CCD can minimize the efforts and time consumed in conducting experiments whilst it still can retain essential information from experiments for data analysis. The method is particularly useful when one has to deal with a large number of variables in an experiment. The confidence interval, second-order models and the degree of effect were acquired via CCD. Besides, the method can be used to derive mathematical models to make further predictions.

Three polynomial models are constructed to correlate chemical admixtures with rheological properties. The derived models are shown to be statistically significant based on ANOVA results. The results indicate that with the increment of dosages of superplasticizer or retarders, all the rheological properties are decreased whilst accelerators possess an opposite effect on the rheological properties. The interaction of retarders and accelerators has a negative influence on all rheological properties. The interaction of retarders and superplasticizers possesses a positive influence on the dynamic yield stress, plastic viscosity, and thixotropy while it has a negative influence on the static yield stress. The interaction of accelerators and retarders has a positive influence on the yield stress whereas it possesses a negative influence on the plastic viscosity and thixotropy.

Chapter 5 Design 3D printing cementitious materials via Fuller Thompson theory and Marson-Percy model

To fulfill the material rheological property requirements in 3DCP, Fuller Thompson theory and the Marson-Percy model were applied in materials design of 3DCP. Six different mixtures were prepared with different gradation approaches using five different sands (0.6-1.2 mm, 0.25-0.6 mm, 0.15-0.25 mm, less than 0.15 mm and natural river sand), i.e. mixture A designed by Fuller Thompson theory, mixture B and C designed by uniform-gradations, mixture D and E designed by gap-gradations and mixture F using natural river sand without special gradation design. Rheological tests were carried out to investigate the fresh performance of all mixtures, and printing tests for buildability were conducted among different mixtures via a gantry printer. Density and mechanical performance (compressive and flexural properties) were characterized as well. It should be noted that the time and temperature effect of rheological/material properties is not considered due to the limited scope of this study. Furthermore, all tests including printing are conducted within 30 min after material mixing and under constant lab temperature of 26°C.

5.1 Theory

5.1.1 Built-up theory and the Bingham model

Perrot et al. established the relation between static yield stress and buildability of 3DCP (Perrot et al., 2016). The simplified relation is expressed as follows:

$$H = \frac{\alpha}{\rho g} \tau_s \quad (5.1)$$

where H (m) and α are the printed height (buildability) and the geometric factor (Perrot et al., 2016) of printed structure respectively; ρ (g/cm³) and g (m/s²) are the density of materials and gravitational constant respectively. τ_s (Pa) is the static yield stress, which is corresponding to static torque in Eq. (5.1)

Bingham Plastic model is widely accepted to describe the rheological property of cementitious materials (Banfill, 2006; Banfill et al., 2006; Barnes et al. 1989; Ferraris et al., 2001; Hu & Larrard, 1996; Weng et al., 2016), as expressed by

$$\tau = \tau_d + \mu_p \dot{\gamma} \quad (5.2)$$

where τ_d (Pa) and μ_p (Pa·s) are dynamic yield stress and plastic viscosity, respectively. $\dot{\gamma}$ (1/s) is the shear rate.

From Eq.(5.1), the buildability is proportional to the static yield stress. It should be noted that in this study, the rheological properties are assumed to be constant during the whole printing process as the time consumed for printing test (around 2 min) is much shorter than the rheological test (10 min). The effect of time on rheological performance, printability, and buildability will be investigated in the future. It also worth noting that in this study, we focus on the effect of yield stress and plastic viscosity on the printability and buildability, and the thixotropic behavior and the rate of re-flocculation are out of our scope.

Generally, material pumpability is reflected by pumping pressure during the pumping process, which is related to Bingham Plastic parameters as well. In this work, slip flow without plug and lubrication forming was considered, and the relationship between pumping pressure and the material rheological property is expressed by (2.8).

Eq. (2.8) shows that the increases of dynamic yield stress and plastic viscosity augment the pumping pressure of cementitious material for specific pipe and flow conditions, which reduces the pumpability of cementitious material. In most printing cases of 3DCP, R_{hose} is less than 1 m, which indicates μ_p has a significant effect on the pumping pressure compared with τ_d . Therefore, a low plastic viscosity is required for cementitious materials to decrease the pumping pressure, which will facilitate the safe and economic operation of pumping/printing process.

5.1.2 Fuller Thompson theory and Marson-Percy model

Gradation is an important attribute to produce economical cementitious materials with maximum density and minimum void content. Sand gradation formula proposed via W.B. Fuller and S.E. Thompson is expressed as following (Fuller & Thompson, 1907)

$$p_i = \left(\frac{d_i}{D} \right)^{0.5} \quad (5.3)$$

where p_i is the percent pass the i^{th} sieve, d_i (mm) is the opening size of the i^{th} sieve, and D (mm) is the maximum particle size. Later, in 1962, the Federal Highway Administration (FHWA) published a modified version for Fuller's equation (Neville & Brooks, 1987)

$$p_i = \left(\frac{d_i}{D} \right)^{0.45} \quad (5.4)$$

Three types of gradation are schematically shown in Figure 5-1. Applying Fuller Thompson equation in sand gradation design forms a continuous gradation, in which interaction between particles exists at many points of contact and realizes a maximum densified system. Gap gradation is designed via missing a certain range of sand particle size in the paste, which possesses more voids content, and fewer contact points compared with the continuous grading system. Using single size sand in the mixture can achieve a uniform gradation mixture which has minimum contact points between particles. Since contact points contribute to the friction in the mixture, increasing the contact points between particles can raise the friction and, thus, resulting in increased static yield stress to initiate flow and dynamic yield stress to maintain the flow.

Figure 5-1 Three types of sand gradation

Shear viscosity μ is affected by packing fraction ϕ , maximum packing fraction ϕ_m and shear rate $\dot{\gamma}$. The relationship between packing fraction, shear rate and shear viscosity is commonly expressed by Marson-Percy model (Kalyon & Aktas, 2014)

$$\mu(\phi, \dot{\gamma}) = \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \mu_b(\dot{\gamma}) \quad (5.5)$$

where $\mu_b(\dot{\gamma})(\text{Pa} \cdot \text{s})$ is the shear viscosity of the binder, which is the same among all samples. In our study, ϕ is kept as a constant and ϕ_m is variable for mixtures with different gradations. Theoretically, a mixture designed by Fuller Thompson theory can achieve a maximum density and minimum void system, which means ϕ_m is the maximum among all mixtures, it should possess the lowest shear viscosity μ .

The relation between shear viscosity and plastic viscosity of Eq.(5.2) can also be expressed as follows:

$$\mu = \mu_p + \frac{\tau_d}{\dot{\gamma}} \quad (5.6)$$

When the material particle size gradation is designed by Fuller Thompson theory, as expressed by Eq. (5.4), the mixed material possesses the highest dynamic yield stress

(τ_d) and lowest shear viscosity, μ expressed by Eq. (5.5), compared with mixtures designed by different particle size gradation methods. Consequently, when the shear rate is the same among different mixtures, according to Eq. (5.6), the plastic viscosity (μ_p) of the mixture designed by Fuller Thompson Theory is the smallest, which is desirable for 3DCP as discussed in Section 5.1.1 to facilitate the safe and economic operation of pumping/printing process.

5.2 Materials, and mixture proportions

5.2.1 Materials

Mixtures in this study consist of Ordinary Portland Cement (OPC, ASTM type I, Grade 42.5), silica fume (SF, undensified, Grade 940, Elkem company), silica sand, fly ash (FA, Class F), natural river sand, water and superplasticizer (SP). Figure 5-2 illustrates the particle size distribution of cement, SF and FA, which were analyzed by Mastersizer 2000. Table 5-1 illustrates the chemical composition of OPC and FA, respectively. Silica sand with four different sizes, i.e., 0.6-1.2 mm, 0.25-0.6 mm, 0.15-0.25 mm, and less than 0.15 mm, were used in this study, either as a mono-sized ingredient or a mixture of all four.

Figure 5-2 Particle size distribution of OPC, FA and SF

Table 5-1 Chemical composition of fly ash and Ordinary Portland Cement (OPC)

Formula	Concentration / %	
	Fly ash	Cement
SiO ₂	58.59	24.27
Al ₂ O ₃	30.44	4.56
Fe ₂ O ₃	4.66	3.95
TiO ₂	2.02	0.55
K ₂ O	1.51	0.61
CaO	1.21	62.2
MgO	0.776	3.34
P ₂ O ₅	0.531	0.15
Na ₂ O	-	0.21
SO ₃	0.0914	-
ZrO ₂	0.04	-
MnO	0.0351	-
Cr ₂ O ₃	0.027	-
CuO	0.0254	-
ZnO	0.0229	-

5.2.2 Mixture proportion

Six different mixtures, including five mixtures with silica sands following different gradations and one mixture with natural river sand, were used in this study. The sand gradation curves are shown in Figure 5-3. Sand for mixture A followed the

Fuller Thompson theory to achieve a continuous gradation system. The continuous gradation mixture used in this study is 39.23% of sand size less than 0.15 mm, 10.14% of sand with 0.15-0.25 mm, 23.84% of sand with 0.25-0.6 mm, and 26.80% of sand with 0.6-1.2 mm. Sand for mixture B was a uniform gradation mixture with sand size ranging from 0.6 mm to 1.2 mm. Sand for mixture C was another uniform gradation mixture with sand size ranging 0.15 -0.25 mm.

Figure 5-3 Sand gradation curves for different mixtures

As can be seen in Figure 5-3, mixture D was composed of 39.23% of sand particle size less than 0.15 mm, 10.14% of sand particle size with 0.15-0.25 mm, and 50.63% of sand particle size with 0.6-1.2 mm. Gap gradation 2 (mixture E) removed sand particle size between 0.15-0.25 mm and is composed of 49.37% of sand particle size less than 0.15 mm, 23.84% of sand particle size with 0.25-0.6 mm, and 26.69% of sand particle size with 0.6-1.2 mm.

Mixture F used the natural river sand as the raw materials, while the sand with particle size bigger than 1.2 mm was sieved out. Sieved natural river sand was then analyzed by the sieving machine. The sieved natural river sand consists of 0.86% of sand with particle size less than 0.075 mm, 6.99% of sand ranging from 0.075 to 0.18 mm, 3.68% of sand ranging from 0.18 to 0.212 mm, 11.24% of sand ranging from

0.212 to 0.3 mm, 32.87% of sand ranging from 0.3 to 0.6 mm and 44.36% of sand ranging from 0.6 to 1.2 mm, as shown in Figure 5-3.

All the mixtures mentioned above, except silica sand itself and natural river sand, followed the same mixture proportion, as shown in Table 5-2:

Table 5-2 Mixture proportion

OPC	Sand	W	FA	SF	SP/(g\L)
1	0.5	0.3	1	0.1	1.3

Note: all ingredients content is expressed as a mass weight proportion of cement content

5.3 Mixing and Testing Procedures

5.3.1 Mixing procedures

A Hobart mixer X200L was used for mixing. Since many factors can affect the rheological properties of cement slurries, such as mixing time, mixing speed and temperature (Yang et al., 2009), the mixing procedures in this study were fixed to minimize the differences among batches. Firstly, the powder of all solid ingredients was dry mixed for 3 min in stir speed; then water was added, the mixing process continued for 3 min in stir speed followed by 2 min in speed I; and then the SP was added, the mixing process continued for 1 minute in stir speed followed by 3 min in speed I.

5.3.2 Rheological characterization

Rheological properties of mixed materials were evaluated via Viskomat XL and mini-slump test. Since rheological properties are affected by various factors, such as mixer types, mixing procedures (Han & Ferron, 2015), mixing intensity (Han & Ferron,

2016), temperature (Yang et al., 2009) and the timing of the SP addition (Perrot et al., 2016). All the aforementioned factors were fixed in this study. Six liters mortars were prepared in the Hobart mixer X200L with a 20 L capacity. The test protocol for Viskomat XL to measure material rheological property can be referred to Section 3.2.3, and the method to calculate the static/dynamic yield stress and plastic viscosity can be found in Section 4.2.2.

Mini-slump test is a classic method to measure materials' workability, which is based on the spread diameter of slurry placed into a cone-shape mold (ASTM C1611 / C1611M, 2017). The mini-slump cone typically has a height of 70 mm, an internal diameter of 50 mm, and 100 mm at the top and bottom, respectively. The cone is placed on a flat, level, and non-absorbent hard surface. During the test, it is filled with fresh material and then raised after a certain amount of time to allow the material to spread. After spreading ceases, two diameters of material mass are measured in the orthogonal direction, and the workability of cementitious material can be characterized by the average of the two diameters.

5.3.3 Printing investigation

Finally, printing tests were conducted to investigate the buildability of different mixtures. As shown in Figure 4-3, a gantry printer with a 1.2 m × 1.2 m × 1.0 m (L×W×H) printing volume was used to control the nozzle position for printing. As shown in Figure 3-5 (b), the materials were pumped by an MAI Pictor pump from the black funnel to the nozzle head through a hose 3 m in length and 2.54 cm in diameter. Figure 5-4 illustrates the 3D model used in the printing test. The circular column with 10 cm inner diameter is composed of 50 layers. Each layer is 20 mm in width and 10 mm in height.

Figure 5-4 3D model for printing test

5.3.4 Density, compressive strength, and flexural performance

All six mixtures were cast into 50 mm × 50 mm × 50 mm cubic molds, consolidated via vibration table and trowel finished. All specimens were then demolded after 24 h. All samples were covered by a plastic sheet and then stored into a plastic container for curing. The density was tested at 7 days, 14 days and 28 days, according to ASTM C642.

After the density test, the compressive strength test was carried on the cubic specimens. The compressive strength was measured by uniaxial loading in triplicates at 7, 14 and 28 days in accordance with the specifications of ASTM C109/C109M-13 (ASTM, 2010). The equipment used for this purpose was a Toni Technik Baustoffprüfsysteme machine with a loading rate of 100 KN/min.

The gantry concrete printer was used to fabricate flexural specimens. The nozzle used for printing was 30 mm × 15 mm (L × W). The printing speed and pumping speed were 4,000 mm/min and 1.8 L/min respectively. The standoff distance was 15 mm for each layer. Printed path and side view of printed filaments are shown in Figure 5-5. Then, the printed specimen was cut into separate filaments with 350 mm in length and 300 mm in height (two layers). Afterward, a four-point bending test with a span length of 240 mm was conducted at 7 days, 14 days and 28 days.

Figure 5-5 Flexural specimen preparation: (a) top view of the printed filament; (b) side view of the printed filament

5.4 Results and Discussion

5.4.1 Rheological analysis

Figure 5-6 illustrates the shear stress and shear rate relation from rheological results based on the Bingham Plastic model. The raw data of static torque, flow resistance, and torque viscosity were shown in Table 5-3, which were then converted to static/dynamic yield stress and plastic viscosity via Eq.(4.3) and shown in the same table.

Figure 5-6 Shear stress and shear rate relation based on the Bingham model

Table 5-3 rheological performance of different mixtures

	Static torque/ N·mm	Flow resistance/ N·mm	Torque viscosity/ (N·mm/rpm)	Static yield stress/Pa	Dynamic yield stress/ Pa	Plastic viscosity/ Pa·s
Mixture A	3390	498.5	2.280	3350	492.7	16.65
Mixture B	2440	264.5	2.601	2411	261.3	19.00
Mixture C	2132	255.8	2.984	2107	252.8	21.81
Mixture D	3358	287.3	2.941	3318	290.6	18.03
Mixture E	2725	277.4	4.560	2693	274.1	33.31
Mixture F	1897	210.9	2.320	1874	208.4	16.95

As can be seen from Figure 5-6 and Table 5-3, mixture A has the highest static yield stress and the smallest plastic viscosity, which is very desirable to ensure low pumping pressure and high buildability based on the previous discussion; mixture E possesses the highest viscosity among all the mixtures, which suggests that the pumpability of mixture E could be the worst.

Figure 5-7 reveals the results of the mini-slump test. As can be seen from Figure 5-7, for all mixtures, the diameter tends to decline along the time. At each time point, mixture A has the lowest slump. After 20 min, the spread diameter of mixture A is approximately 100 mm.

Rheological and mini-slump test results indicate that the most proper materials for 3DCP are mixture A with continuous gradation. With the highest yield stresses and the lowest plastic viscosity, mixture A is expected to reveal better pumpability and buildability among all mixtures investigated in this study.

Figure 5-7 Mini-slump test result

5.4.2 Printing Test

A gantry printer system was used to conduct the printing test of mixtures A to F. Moving speed of nozzle and pumping speed of were 9,000 mm/min and 1.8 L/min, respectively. During the printing test, the printed part can maintain its shape initially. When the printed structure meets the failure criteria at the fresh state, which was described by Perrot et al. (Kalyon & Aktas, 2014), suddenly noticeable deformation occurs. This was followed by misalignment of the printing path and final collapse of the printed structure. The layer numbers with noticeable deformation and final collapse were recorded during the printing test.

Printing test results are summarized in Table 5-4, where the layer number associated with noticeable deformation and final collapse are presented. Taking mixture A as an example, it maintained its shape until the 42nd layer (Figure 5-8 (a)), followed by large deformation (Figure 5-8 (b)), and finally fell down at the 43rd layer (Figure 5-8 (c)). For other mixtures, similar phenomena are observed during the printing test, except that they all showed large deformation and collapsed at a much early stage (smaller layer number). As stated by Perrot et al. (Perrot et al., 2016), the maximum build-up height can be computed by solving equation Eq.(5.1). For a hollow cylinder, the geometric factor can be computed by:

$$\begin{aligned} \alpha = & (R_2^2 - R_1^2)^{-1} \left(\frac{1}{2} + \frac{C_\alpha}{R_2^2} \right)^{-1} \sqrt{\frac{3}{4} + \frac{C_\alpha^2}{R_2^4}} \cdot \left\{ \frac{4}{H} \left[\frac{(R_2^3 - R_1^3)}{6} + C_\alpha (R_2 - R_1) \right] \right. \\ & + 2C_\alpha \left(\sqrt{\frac{3R_2^4}{4C_\alpha^2} + 1} - \sqrt{\frac{3R_1^4}{4C_\alpha^2} + 1} \right) - 2C_\alpha \left[\operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_2^2} \right) - \operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_1^2} \right) \right] \\ & \left. - 2R_1^2 \left(\frac{3}{4} + \frac{C_\alpha^2}{R_1^4} \right)^{-1/2} \left(\frac{1}{4} - \frac{C_\alpha^2}{R_1^4} \right) - 2R_2^2 \left(\frac{3}{4} + \frac{C_\alpha^2}{R_2^4} \right)^{-1/2} \left(\frac{1}{4} - \frac{C_\alpha^2}{R_2^4} \right) \right\} \end{aligned} \quad (5.7)$$

where C_α can be solved from equation

$$\frac{\frac{1}{2} - \frac{C_\alpha}{R_2^2}}{\sqrt{\frac{3}{4} + \frac{C_\alpha^2}{R_2^4}}} - \frac{\frac{1}{2} - \frac{C_\alpha}{R_1^2}}{\sqrt{\frac{3}{4} + \frac{C_\alpha^2}{R_1^4}}} + \operatorname{arcsinh}\left(\frac{2C_\alpha}{\sqrt{3}R_2^2}\right) - \operatorname{arcsinh}\left(\frac{2C_\alpha}{\sqrt{3}R_1^2}\right) = 0 \quad (5.8)$$

The detailed derivation process following geometric factor for cylinder derived by Roussel and Lanos (Roussel & Lanos, 2003) is enclosed in Appendix C. The comparison between prediction and experimental maximum built-up heights is shown in Figure 5-9. As can be seen from Figure 5-9, the model can well predict the deformation/collapse layer number. It is worth noting that the derivation of the predicted and actual result of deformation layer of mixture D is quite significant, which is possibly caused by other unexpected factors.

Table 5-4 Summary of the layer number during which noticeable deformation and final collapse occurred

	layer number with noticeable deformation	layer number with the final collapse
Mixture A	42 nd	43 rd
Mixture B	30 th	31 st
Mixture C	27 th	32 nd
Mixture D	31 st	41 st
Mixture E	32 nd	34 th
Mixture F	24 th	25 th

Figure 5-8 The printing test result of mixture A: (a) maintained the shape until 42nd layer; (b) sudden deformation at the 42nd layer and (c) fell down at 43rd layer

Figure 5-9 Comparison between prediction and experimental maximum built-up heights

Afterward, a large printing test was conducted using mixture A. A circular nozzle with 20 mm in diameter was used in this printing. Moving speed of the nozzle and pumping speed of the pump were 9,000 mm/min and 1.8 L/min, respectively. 3D printing model is shown in Figure 5-10. As can be seen from the top view of the 3D model (Figure 5-10 a), it is composed of 4 semicircles and 4 quarter circles with 10 cm in diameter and 2 cm in thickness. Then the total layer numbers are 80 for printing and the layer height is 10 mm (Figure 5-10 b). The final printed part is shown in Figure 5-11.

Figure 5-10 3D model for large-scale printing: (a) top-view; (b) side-view

Figure 5-11 Gantry printed part: (a) Final printed part; (b) Height and layer thickness and (c) Top view of the printed part

5.4.3 Density, compressive strength, and flexural strength

The density of the cementitious material is related to its packing. Better packing from continuous gradation yields high density. The result of the density of all mixtures is shown in Figure 5-12. As expected, mixture A possesses the highest density among all mixtures at 7 days, 14 days and 28 days. Furthermore, although the density of all mixtures increases with time, a comparison of all the density results at different curing ages indicates that there are not statistically different (i.e., the 95% confidence level $p = 0.0581 \geq 0.05$)

Figure 5-13 and 5-14 present the result of the compressive strength and flexural strength of all mixtures. The mechanical strength of all mixtures increases with time as expected. Mixture A possesses appropriate compressive and flexural strength at 28 days, which are 49.7 MPa and 3.73 MPa, respectively.

Figure 5-12 Density of all mixtures

Figure 5-13 Compressive strength of all mixtures

Figure 5-14 Flexural strength of different mixtures

5.5 Summary and Conclusions

3DCP requires the material to have low plastic viscosity and high yield stresses to meet the requirements for both pumpability and buildability. Fuller Thompson theory and the Marson-Percy model were adopted as a guideline to design construction materials with proper rheological properties for 3DCP. Six different mixtures (i.e., mixtures A-F) were prepared with various gradations using five different sands (0.6-

1.2 mm, 0.25-0.6 mm, 0.15-0.25 mm, less than 0.15 mm and natural river sand). The gradation of mixture A followed the Fuller Thompson theory to achieve a continuous gradation system. Mixtures B and C were two different uniform-gradation mixtures with sand particles of 0.6-1.2 mm and 0.15-0.25 mm respectively. Mixtures D and E followed the gap-gradation method, where ranges of 0.25-0.6 mm and 0.15-0.25 mm were removed, respectively. Mixture F used river sand with particle size bigger than 1.2 mm sieved out.

Rheological tests illustrate that mixture A has the highest yield stresses and the lowest plastic viscosity. During the printing test for buildability, it can reach as high as 40 cm (40 layers) without notable deformation. On the contrary, all other mixtures appeared noticeable deformation at around the 30th layer. Finally, a large-scale printing with mixture A was conducted and the final printed part can be as high as 80 cm without visible deformation. Furthermore, when mixture E with the highest plastic viscosity was used for printing test, pumping pressure significantly increased compared with others. Mechanical properties, including density, compressive and flexural strength of all mixtures have also been measured.

In summary, Fuller Thompson method and the Marson-Percy model can be used as the design guideline to tailor the materials to acquire appropriate rheological properties and mechanical performance for 3DCP. More specifically, with this design guideline, a desirable combination of plastic viscosity and yield stress can be achieved where low plastic viscosity is essential for good pumpability and high yield stresses for buildability. While the direct adoption of sand gradation and mix proportion in practice is not very practical due to the availability of materials and other constraints, simple design guideline by adopting classic theory like Fuller Thompson method and Marson-Percy model still offers meaning insights in the further development of 3D printable material for building and construction industry.

In this research, only the sand particle gradation was investigated. In the future, it is essential to extend the gradation analysis to include other filler-like materials such as silica fume and fly ash in the fresh state. These materials contribute very little to the

hydration process and therefore, mainly play the role of filler like sand at least in the fresh state. Furthermore, a more quantitative link between particle size distribution/particle interactions and rheological properties needs to be established in the context of 3D printing.

Chapter 6 Feasibility study of magnesia phosphate cement of 3D printing application

To the best of our knowledge, this work is among the first in the literature on developing 3D printable MKPC through optimizing rheological and mechanical properties. FA was introduced in MKPC mortars through partially replacing MgO. Meanwhile, silica fume acting as an efficient ingredient to adjust the fresh properties of pastes for 3D printing was attempted along with different magnesia-to-borax ratios. Fresh performance and early-age mechanical properties of mortars with different formulations were characterized through initial setting time, rheological performance and compressive strength test, respectively. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and μ -CT scan were employed to investigate the hydration products, microstructure, and porosity. A small-scale printing test using the optimized MKPC design was conducted as a proof of concept eventually.

6.1 Material design and preparation

6.1.1 Materials

Light-burnt magnesia (Yue et al. 2014) was supplied by Urban Redevelopment Authority, Singapore. Class F fly ash was supplied by Sembcorp Design & Construction Pte Ltd, Singapore. Borax was supplied by Linyi Chemical Reagent Company Ltd., Shandong, China. Undensified silica fume Grade 940 was supplied by Elkem Pte Ltd. Table 6-1 shows the chemical compositions of magnesia and fly ash. The particle size distribution of magnesia fly ash and silica fume are presented in Figure 6-1. An accelerated reactivity method (Chau & Li, 2008; Xu et al. s 2014) was used to characterize reactivity of magnesia. In this test, 5.0 g of the magnesia powder was mixed and stirred in 100 mL of acetic solution with a concentration of 1.0 mol/L. The pH change of the suspension with reaction time was recorded by a pH meter (Xplorer GLX, PASCO), with a recording time step of 1 s. The reactivity index

of the magnesia powders was determined as the time in min to completely neutralize the acetic acid at pH= 7. The result was plotted in Figure 6-2. Figure 6-3 depicts the gradation curve of fine sand supplied by Buildmate Pte Ltd Singapore.

Table 6-1 Chemical compositions of light-burnt magnesia and fly ash powders

	Compound (wt%)										
	MgO	SiO ₂	CaO	Fe ₂ O ₃	P ₂ O ₅	MnO	Al ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	SO ₃
Magnesia	97	1.3	1.3	0.2	-	-	0.2	-	-	-	-
Fly ash	0.776	58.59	1.21	4.66	0.531	0.0351	30.44	N.A	1.51	2.02	0.09

Figure 6-1 Particle size distribution of magnesia, fly ash and silica fume

Figure 6-2 Reactivity of MgO

Figure 6-3 Gradation curve of sand particles

6.1.2 Sample preparation: mix design and procedures

Table 6-2 shows the mix compositions of MKPC mortars with different formulations. Binders include light-burnt magnesia, fly ash, and KDP. The sand-to-binder (S/B) ratio and W/B ratio of all mixes were kept constant values with 0.45 and 0.3 respectively, and the mass ratio of KDP over the sum weight of magnesia and fly ash was 0.43. Fly ash was incorporated in the MKPC mortars as a replacement of magnesia only with adopting four different replacement ratios (0 wt%, 40 wt%, 50 wt%, and 60 wt%). As illustrated in Table 6-2, different magnesia-to-borax ratios and silica fume-to-binder ratios were investigated to tailor material printability.

Table 6-2 Mix compositions of the MKPC mortars

Series	Binder			Borax ^b	W/B	S/B	SF/% ^c
	Magnesia	FA	KDP ^a				
M100FA0S0-1	1	0	0.43	1	0.3	0.45	0
M60FA40S0-1	0.6	0.4	0.43	1	0.3	0.45	0
M50FA50S0-1	0.5	0.5	0.43	1	0.3	0.45	0
M40FA60S0-1	0.4	0.6	0.43	1	0.3	0.45	0
M40FA60S5-1	0.4	0.6	0.43	1	0.3	0.45	5
M40FA60S10-1	0.4	0.6	0.43	1	0.3	0.45	10
M40FA60S10-4	0.4	0.6	0.43	4	0.3	0.45	10
M40FA60S10-8	0.4	0.6	0.43	8	0.3	0.45	10

a, the KDP dosage is expressed as the weight ratio of the sum of magnesia and fly ash

b, the borax dosage is expressed as the weight ratio of the sum of magnesia and FA

c, the SF dosage is express as the weight ratio of binder

MKPC mortars were prepared in a Hobart Mixer. Firstly, powder materials were dry-mixed for one min with speed I. Tap water was then added into the mixture. The wet-mixing process was continued for one min with speed I, followed by another one min with speed II.

6.2 Experimental methods

6.3.1 Characterization of setting behavior

Open time, a critical factor for 3D concrete printing, is defined as the period within which the materials are consistent with acceptable printing quality in the printing process (Lim et al., 2012). Setting time has been proved to be an important parameter closely related to the open time (Vaitkevičius et al. 2018). It should be sufficiently long to prevent the material from blocking the hose. Meanwhile, too long setting time is harmful to buildability, and printing speed as the materials need longer time to gain strength. Setting time was characterized by an automatic Vicat apparatus in this work.

6.3.2 Rheological characterization and early-age compressive strength

In 3D concrete printing, pumpability and buildability are two somewhat conflicting properties. Extrudability requires that the materials can be pumped smoothly in the hose without blockage in the printing process. Buildability requires that the materials can be stacked stably in a layer-atop-layer manner. Both pumpability and buildability are influenced by rheological performance of materials in fresh state.

In this work, rheological performance in the fresh state was characterized by two methods, i.e mini-cone test and rheometer test (Anton Paar MCR 102). After being printed out, the material should be able to maintain its shape, which indicates low slump characteristics i.e. high yield stress (Panda & Tan, 2018). Slump characteristics can be presented by the results from mini-cone test. Then, the protocol of rheometer test as shown in Figure 6-4 was used to simulate the material rheological behavior in 3D concrete printing process. At step I, a shear rate of 100 s^{-1} was applied for 200 s to simulate the state of materials during pumping process. At step II, the shear rate was 0.1 s^{-1} and held for 30 s to simulate the condition of materials after printing out stage (Panda & Tan, 2018). Since a small shear strain applied to material can break the colloidal force interaction between particle, with continuous breaking the colloidal force interaction, the evolution of interaction force between particles can be measured, which contributes to material rheological property and is relevant to material buildability.

Figure 6-4 Protocol for rheological characterization

In a hardened state, the buildability of cementitious materials is influenced by the development of early-age mechanical properties (Wolfs, Bos, & Salet, 2018). Vaitkevicius et al.'s work implied that the early-age compressive strength of the materials achieving 1MPa (20 min) and 4.93 MPa (1 day) is sufficient for most of the requirements in various 3D printing (Vaitkevicius et al., 2018). The influence of MgO, fly ash, silica fume and borax on early-age compressive strength were investigated accordingly in macroscale, which was conducted on cubic specimens with dimensions of 50×50×50 mm at the age of 30 min, 60 min, and 90 min respectively (Ma et al., 2018). The average of three samples was reported for each data point.

6.3.3 XRD, μ -CT and SEM analyses

The hardened properties of MKPC are influenced by several factors in microscale, including hydration products, microstructure, porosity, etc. As indicated in Eq. (2.21), struvite-K is the main contributor to the mechanical properties of MKPC. To explore the influence of time on the struvite-K, selected specimens at 30 min and 90 min were prepared for XRD analysis.

Silica fume presents the superior filler effect, which influences the porosity and microstructure, consequently affecting the mechanical performance of MKPC as

discussed by Ma and Xu (Ma & Xu, 2017) that a high ratio of struvite-K-to-space is beneficial to mechanical properties, especially the compressive strength. The μ -CT scan, a non-destructive and environmentally friendly test method compared with MIP, was adopted for quantifying the porosity of selected specimens at 90 min to study the influence of silica fume on the porosity of MKPC. Detailed characterizing procedures can be found in Bossa et al.'s work (Bossa et al., 2015). Selected specimens at 90 min were prepared to observe the influence of silica fume on the microstructure via SEM as well.

Specimens extracted from the cubes crushed during the compressive strength test were immersed in acetone for 3 days to stop hydration, followed by vacuum drying for another 24 hours to prepare for microstructural analysis. Afterward, vacuum dried samples were ground down to pass through a 75 μ m sieve before SEM and XRD analysis. Prior to SEM, the powders were coated with platinum under 30 mA currents with a coating time of 30 seconds. The sample was then investigated via a field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F). XRD was recorded on a Philips PW 1800 spectrometer using Cu-K α radiation (40 kV, 30 mA) with a scanning rate of 2° (2 θ /step) from 5 to 80° (2 θ).

6.3 Printability test

Finally, a printing test was conducted to investigate the printability of the designed mixture. As shown in Figure 4-3, a gantry printer with a 1.2 m $\times$ 1.2 m $\times$ 1.0 m (L $\times$ W $\times$ H) printing volume was used to control nozzle position for printing. 3D model used in the printing test is shown in Figure 6-5. The CAD model for the demonstration of printability has an edge length of 85 mm for the top and bottom surface, and a height of 190 mm. The detailed CAD file can be found in the supplementary data.

Figure 6-5 CAD model for printability test

6.4 Results and discussions

6.4.1 Setting performance

Figure 6-6 shows the results of setting time, where black dash line indicates the initial setting time. As can be seen from Figure 6-6, the initial setting time of MKPC pastes increases with the growth of the replacement ratio of FA or the decrease of the dosage of SF in the past. The influence of fly ash on setting time can be both chemical and physical (Ravina, 1986). In the physical sense, with less amount of magnesia in the binders due to higher fly ash replacement ratio, inadequate reaction occurs between magnesia and KDP. Chemically the fly ash can react with KDP while the reaction rate is significantly slower than that of magnesia and KDP (Xu et al., 2017). The setting time of the mixture was also influenced by silica fume physically (Zhang et al. 2012). Silica fume may act as inert fillers, which reduces bleeding and increases the packing fraction of solid materials by occupying space between other particles. These physical effects of the silica fume may contribute to the decrease of setting time.

With the increase of the dosage of borax (Figure 6-6), a longer initial setting time was observed since the setting time of MKPC is mainly controlled by the borax-to-magnesia ratio (Yang & Wu, 1999). Comparing pastes with a MgO-to-borax ratio of

1:4 and 1:8, their initial setting time was quite similar, indicating that there is a certain upper limit on the retarding effect of borax.

Figure 6-6 The results of setting time

6.4.2 Rheological characterization and early-age compressive strength

The results ss time of M40FA60S10-4 increases more than 3 times while the spread diameter almost maintains a constant compared with that of M40FA60S10-1.

Figure 6-7 Results of mini-slump test

Rheometer test results are shown in Figure 6-8 and 6-9. During rheometer test, mixtures of M100FA0S0-1, M60FA40S0-1, M50FA50S0-1, M40FA60S10-1 hardened too fast and was beyond the test capacity of the equipment. Therefore only M40F60S10-4 and M40F60S10-8 were analyzed by rheometer. At step I (Figure 6-4), the torque of materials decreased to a very low level, which is around 20 Pa. Then, after the materials being printed out, the torque resumed to very high level in a short period at step II (Figure 6-4), which indicates that the evolution of colloidal force between particles of tested material is fast. However, when the torque is more than 200 Pa, the equipment cannot measure it due to its limited capacity. These results reveal that tested materials are desirable for 3D printing in the fresh state as low torque is beneficial for pumping process (extrudability) under constant shear while quick built-up of torque is favourable for buildability after materials being printed out.

Figure 6-8 Torque development under shear rate of 100 s^{-1}

Figure 6-9 Torque development with shear rate 0.1 s^{-1}

The compressive strength development of MKPC mortars from 30 min to 90 min are plotted in Figure 6-10. As can be seen from the Figure 6-10, the compressive strength of all investigated mixtures is higher than 1 MPa at 20 min and higher than 4 MPa at 90 min. The results imply that all investigated mixtures are sufficient in civil engineering from the aspect of the development of early-age mechanical performance (Vaitkevičius et al., 2018). Specifically, M100FA0S0-1 samples revealed the highest compressive strength at all curing ages, which could be associated with the higher amount of struvite-K formation due to the larger magnesia content, which enhances the chemical reaction between MgO and KDA. M40FA60S10-1 samples outperformed M40FA60S0-1 samples in terms of compressive strength due to the addition of silica fume, which acts as inert fillers and is capable of filling the pores and cracks within paste, consequently leading to an improved pore structure and packing fraction as well as compressive strength of MKPC (Zheng et al., 2016). M40FA60S10-4 samples shown almost the worst mechanical properties within all curing ages due to high content of borax. Excessive borax incorporation in MKPC system slows down the hydration process in MKPC-based materials (Lahalle et al., 2016), resulting in a lower content of struvite-K and inferior mechanical performance.

Although the reaction of FA and KH_2PO_4 occurred to some extent (Gardner et al., 2015b; Mahyar, 2015), their reaction degree is much lower compared with the

reaction between the magnesia and KH_2PO_4 , leaving an abundance of KH_2PO_4 unreacted, consequently increasing the porosity of materials. Additionally, the dissolution of unreacted KH_2PO_4 in water would also decrease the pH of the system, thus destabilizing struvite-K in the system. Furthermore, the strength of mixes would be deteriorated with a high fraction of FA incorporation in water (Xu et al. 2018). Therefore, M100FA0S0-1 samples without any addition of FA revealed the highest mechanical strength compared with the rest of the group.

Figure 6-10 Early-age compressive strength development of the MKPC pastes with various formulations

6.4.3 XRD, μ -CT and SEM analyses

The XRD diffractograms of selected hydrated MKPC pastes are displayed in Figure 6-11. Some of the main phases usually observed within these systems are magnesia, KDP, and struvite-K, whose strongest characteristic peaks were located can be found in Yang et al.'s work (Yang et al. 2017). As can be seen from Figure 6-11, no KDP characteristic peaks were detected in the presented patterns. The characteristic peaks of MgO and struvite-K were displayed, albeit with low intensities. This could be due to the relatively short curing duration (i.e., 90 min) that these samples were exposed

to, thereby limiting the degree of hydration. The amount of the reaction product (intensity in Figure 6-11), MKP, that formed within these samples increased with time due to continuous hydration.

Figure 6-11 XRD patterns of selected MKPC samples at different curing ages

M40FA60SF0-1 and M40FA60SF10-1 samples were selected in the porosity analysis to investigate the influence of silica fume on porosity. Figure 6-12 shows the μ -CT scan images produced on the selected samples. The shadow X-ray image of the sample is presented in Figure 6-12 (a), while the typical reconstructed cross-sectional image of the sample is shown in Figure 6-12 (b). Figure 6-12 (c) shows pores and solid phases, which are represented by black and white areas, respectively.

Figure 6-12 Tomographic images showing (a) x-ray shadow image of the typical sample, (b) typical image of X-ray scan data from cross-section x-x and (c) processed data from the selected plane of the sample to show pore regions

A three-dimensional volume of the boxed area (Figure 6-13 (a)) was created by stacking together sequential slices of two-dimensional μ -CT images, as shown in Figure 6-13 (b). Afterward, pores were separated from the reconstructed volume. Black areas in Figure 6-13 (b) represent pores in the specimen.

Figure 6-13 Three-dimensional rendering of μ -CT scan data showing: (a) 3D model and (b) Pore dispersion

Typical sliced images and pore size distributions of M40FA60SF0-1 and M40FA60SF10-1 samples are plotted in Figure 6-14 and Figure 6-15, respectively. As can be seen from Figure 6-14, fewer pore areas were observed from the sliced image of M40FA60SF10-1 samples than those of M40FA60SF0-1 samples. Pore size distribution and porosity were then calculated through CTAnalyzer, and the result is plotted in Figure 6-15. The pore volume of scanned areas in M40FA60SF0-1 and

M40FA60SF10-1 samples is 3.54 mm^3 and 1.05 mm^3 , respectively. In line with sliced images, the figures indicate that the addition of silica fume in the MKPC system decreases the porosity significantly, and a denser matrix can be achieved consequently better mechanical performance. Detailed image processing procedures were discussed by Rattanasak and Kendall (Rattanasak & Kendall, 2005) and Dalen and Koster (Dalen & Koster, 2012).

Figure 6-14 Typical sliced images of: (a) M40FA60SF0-1 and (b) M40FA60SF10-1

Figure 6-15 Pore size distribution of different pastes

Figure 6-16 shows the SEM results. The microstructure of the M60FA40SF0-1 sample at 90 min is shown in Figure 6-16 (a). The observed microstructure involved the presence of crystals with morphologies resembling struvite-K described as bladed

prisms (Xu et al., 2014). The microstructures of M60FA40SF10-1 samples (90 min) are shown in Figure 6-16 (b) and (c). As can be seen from Figure 6-14 and Figure 6-15, compared with M60FA40SF0-1 samples, denser microstructures and less porosity achieved by M60FA40SF10-1 were associated with the presence of a higher amount of SiO_2 within their formulation. The use of silica fume with an amorphous SiO_2 content of 95% in the microstructural development of the prepared formulations led to the formation of a dense network. Abundant SiO_2 that filled the large pores of the prepared samples contributed to a higher strength achieved by M60FA40SF10-1 samples in comparison to M60FA40SF0-1.

Figure 6-16 Microstructural images of: (a) M60FA40SF0-1 samples (magnification: x5000), (b) M60FA40SF10-1 samples (magnification: x5000) and (c) M60FA40SF10-1 samples (magnification: x10000)

6.4.4 Printability test

After finishing the mixing process, a small-scale printing test was conducted in the lab for demonstration. However, the fresh properties of rapid hardening materials evolved very fast. Relatively long setting time was required to prevent damaging the equipment. Besides, a high early-age strength was also needed to ensure the buildability. Thus, the formulation (M40FA60S10-4) was selected in printability test due to appropriate setting behavior and early-age mechanical properties. The result of printability test is illustrated in Figure 6-17. Printing and pumping speed were 2000 mm/min and 650 rpm, respectively. It took 5 min to finish printing the part with 20 layers and 180 mm height. The M40FA60S10-4 paste can be pumped well without blocking hose during the pumping process and can be printed well without significant discontinuity as can be seen in Figure 6-17.

Figure 6-17 Results of printability test

6.5 Conclusions

This study explored the feasibility of using MKPC, a rapid-hardening and environmentally friendly building material, in 3D printing applications. The investigation involved the measurement of setting time to indicate the open time for

3D printing, followed by optimization of the fresh properties and early-age mechanical properties of MKPC binders involving 0-60 wt% fly ash and 0-10 wt% silica fume. Finally, a printing test was employed to verify the printability of the designed formulations.

The obtained results indicated that the working time of the developed MKPC formulations could be extended from 2.98 to 19.4 min by replacing 60 wt% of magnesia with fly ash. The yield stress was increased significantly via the introduction of 10 wt% silica fume. A slight drop in the yield stress with an increase in the magnesia-to-borax ratio from 1:1 to 1:4 was observed, along with an increase in the slump value from 101.3 to 109.6 mm. However, the yield stress decreased drastically with increasing FA replacement level. Rheometer test results indicate that rheological properties of M40FA60S10-4 and M40FA60S10-8 are desirable for 3D printing due to low-level yield stress under high shear rate and fast recovery of yield stress with nearly zero shear rate. Furthermore, the hydration rate reduced, thereby increasing the working time from 19.4 to 22.9 min. Early-age compressive strength measurements performed at different curing ages suggested sufficient strengths (2MPa at 20 min and 5.36 MPa at 90 min) for 3D printing within the M40FA60S10-4 sample. The successful completion of the printing process verified that the developed MKPC formulations involving the use of 60 wt% fly ash and 10 wt% silica fume could be used in 3D printing applications.

Future studies shall focus on optimizing the setting time and/or open time of the developed formulations used in 3D printing. A detailed investigation of the long-term properties of the hardened binders involving these novel cementitious materials will enable their application into practice via the development of 3D printed sections.

Chapter 7 Printability of a developed 3D printable fiber reinforced cementitious composites

While some research has reported the development of 3D printable plain concrete (Bos et al., 2016; Le et al., 2012; Lim et al., 2012), it is still a type of brittle materials with low tensile strength and crack resistance. Cracks, as shown in Figure 7-1, are always a concern about adopting such material into engineering applications. As short fibers are ideal ingredients to enhance the mechanical properties of cementitious materials and restrain cracks caused by dry shrinkage in concrete casting (Tang et al., 2015), a number of researchers have worked on developing appropriate types of 3DPFRCCs with different types of fibers or dosages (Hambach & Volkmer, 2017; Soltan & Li, 2018).

However, several limitations remained in formerly developed materials obstruct further implementation of these materials in engineering applications. For example, large-scale printing test is lacking in previous studies to test the printability of the developed materials with realistic dimensions. A number of challenges exist when upscale from lab-scale printing to real building scale printing, e.g. the requirements on pumpability and buildability become more restricted as the scales of equipment and printing become much larger, the setting time of materials should be tailored such that the materials possess proper hydration rate for 3D printing, the mixing capacity/procedure should be able to meet the material consumption rate of printing, etc.

Figure 7-1 Cracks formed on the surface of the printed structure

In the study, a novel mixture of 3DPFRCCs is developed, and both a 900 mm high small-scale structure and a 2800 mm high large-scale structure were printed to demonstrate the printability of the developed materials. Rheological properties were characterized by static/dynamic yield stress and plastic viscosity. The workable time of materials for 3D printing was characterized by setting time.

7.1 Experimental design

7.1.1 Materials and mixing

In this study, the mixture consists of Ordinary Portland Cement type I 42.5 (C), natural river sand (S), class F fly ash with a fineness of 386 m²/kg (FA), silica fume (SF, undensified, Grade 940, Elkem company), and polyvinyl alcohol (PVA) fiber with 40 μm in diameter, 8 mm in length and 0.8% oil coating by the mass weight ratio of the fiber. Superplasticizer was introduced with a dosage of 3 g/L to adjust the rheological properties. Among all the ingredients, fly ash and silica fume are industrial by-products, which were used for 3D concrete printing to decrease the cost and increase the sustainability of the process. Physical and chemical properties of OPC, fly ash, and silica fume are shown in Figure 7-2 and Table 7-1. The gradation curve of natural river sand is shown in Figure 7-3. The influence of each ingredient

on rheological properties was studied in the author's previous work (Weng et al., 2018). The mixture proportion is listed in Table 7-2.

Figure 7-2 Particle size distribution of cement, fly ash and silica fume

Table 7-1 Chemical composition of fly ash and Ordinary Portland Cement (C)

Formula	Concentration / %	
	Fly ash	Cement
SiO ₂	58.59	24.27
Al ₂ O ₃	30.44	4.56
Fe ₂ O ₃	4.66	3.95
TiO ₂	2.02	0.55
K ₂ O	1.51	0.61
CaO	1.21	62.2
MgO	0.776	3.34
P ₂ O ₅	0.531	0.15
Na ₂ O	-	0.21
SO ₃	0.0914	-
ZrO ₂	0.04	-
MnO	0.0351	-
Cr ₂ O ₃	0.027	-
CuO	0.0254	-
ZnO	0.0229	-

Figure 7-3 Gradation curve of sand particles

Table 7-2 Mixture proportions

S/B ^a	W/B	FA/C	SF/%	Fiber/%
0.5	0.28	1.0	0.05	1

^a B indicates the binder that is the sum weight of C, FA, and SF

An 80L Screed Mortar Mixer (Soroto) was used to mix raw ingredients. As rheological properties are affected by many factors, such as temperature, mixing time, etc., the mixing process is fixed to ensure the consistency of the rheological properties of materials. Firstly, the powder of all solid ingredients was dry mixed for 1 min with stir speed. Water was then added while the mixing process continued for 1 minute with stir speed. After that, the superplasticizer was introduced, the mixing process continued for 1 minute at speed I followed by 1 minute at speed II. Finally, the fiber is introduced, and the mixing process continued for 2 min at speed II.

7.1.2 Rheological characterization

Bingham model is a classic rheological model of cementitious materials. According to the Bingham model, fresh cementitious materials can flow after it overcomes its

static yield stress. During the flow, the dynamic yield stress is the minimum stress applied to maintain its flow. The plasticity viscosity measures how easily the materials can flow once the yield stress is overcome.

In this study, the rheological performance was characterized by a Viskomat XL with a six-blade vane probe and a cage, the detailed dimension of the probe, cage, and testing program can be found in authors' previous work (Went et al., 2018). A typical test result is plotted in Figure 4-2. Then, the static torque, flow resistance, and torque viscosity can be converted into static/dynamic yield stress and plastic viscosity via the Eq.(4.3).

Setting time is another essential parameter, which determines the workable time of 3DPFRCC in the printing process. In this work, the setting time of the cement pastes was determined according to ASTM C 191-13 using an automatic Vicat apparatus. The 1.13 mm diameter needle is fixed on a movable rod. A fresh paste specimen with normal consistency is prepared and placed in a 40 mm high container with a diameter of 40 mm. The test consists of the measurement of the penetration depth of the needle, which penetrates the specimen every 4 min. The initial setting time in this study is calculated as follows:

$$\text{Initial setting time} = \left(\frac{H - E}{C - D_p} \right) \times (C - 25) + E \quad (7.1)$$

where E (min) is the time of last penetration greater than 25 mm; H (min) is the time of first penetration less than 25 mm; C (mm) and D_p (mm) are the penetration depth reading at time E and H , respectively.

7.1.3 Printing test

The printing test was conducted by a gantry printer with a printing volume of 1.2 m × 1.2 m × 1.0 m (L × W × H), as shown in Figure 4-3. To demonstrate the advantage of customization in 3D printing, a special structure was designed and shown in Figure 7-4, which illustrates the top-view and overall-view of the 3D model for printing. The

detailed dimension is shown in Figure 7-4 (a). The height of the printed structure is 90 cm due to the dimensional limit of the printer. Then, a robotic printer with a large printing capacity was used for a large-scale printing test, as shown in Figure 7-5.

Figure 7-4 3D printing model: (a) top-view of the designed part (unit: mm); (b) overall-view of the designed part

Figure 7-5 The robotic-based printing system

7.2 Results and discussions

The results of the rheological test indicate that the static yield stress is 3298 Pa and dynamic yield stress is 314.7 Pa, and plastic viscosity is 32.5 Pa·s. The result of setting time is shown in Figure 7-6. According to Figure 7-6 and Eq. (7.1), the initial setting time is 59.2 mins. The static and dynamic yield stress are 3289 Pa and 314.7 Pa, respectively, and the plastic viscosity is 32.5 Pa·s. According to Weng et al.'s work, materials are able to support the weight of printed structure with 300 mm height at fresh state when its static yield stress is above 3000 Pa.

Figure 7-6 Setting time test result

The small-scale printing test result is shown in Figure 7-7. In the printing process, the standoff distance was 10 mm for each layer. A concrete plate with dimensions of 400 mm $\times$ 35 mm $\times$ 15 mm (L $\times$ W $\times$ H) was preprinted to support the overhang structure.

In the small-scale printing process, assuming all print layers are at fresh state, the printed height is limited to 300 mm, which is a lower boundary for height prediction as time effect is ignored. After materials at lower level reach initial setting, the development of static yield stress to sustain the weight of subsequent layers evolves extremely fast compared with that of materials at fresh state. Hence the printer can build up a higher structure than 300 mm without collapse.

In case of small-scale printing (Figure 7-7 a), the total height is 900 mm and for each 300 mm height, the printing process takes 50 min. When the printing height is more than 300 mm, materials at the very lower layers have reached an initial setting state where static yield stress develops fast, which is desirable for large-scale printing. The whole printing process lasted 150 min for 900 mm printing height. The printing result indicates that developed 3DPFRCCs possesses appropriate rheological properties for a meter-level printing and has the potential for future engineering application. Then, according to the successful experience of large-scale structure printing, a large-scale structure was printed via a robotic printer, and the final printed product is shown in Figure 7-7 (b), which takes 9.5 hours to complete.

Figure 7-7 Printability test: (a) Small-scale printing with the dimension of $780 \text{ mm} \times 600 \text{ mm} \times 900 \text{ mm}$ ($L \times W \times H$); (b) Large-scale printing test result, $2200 \text{ mm} \times 2200 \text{ mm} \times 2800 \text{ mm}$ ($L \times W \times H$)

7.3 Conclusions

3D printable cementitious composites require special rheological properties to satisfy the demand of printability (buildability and pumpability). In this work, a novel mixture of 3D printable fiber reinforced cementitious composites (3DPFRCCs) is developed and is capable of large-scale printing, which is verified by printing test. Rheological properties and setting time were characterized. Results indicate that the developed material possesses appropriate rheological properties for large-scale printing. Rheological properties are designed based on previous practical printing tests. The static and dynamic yield stress are 3289 Pa and 314.7 Pa, respectively. The plasticity viscosity is 32.5 Pa·s. The initial setting time is 59.2 mins.

Finally, a $780 \times 600 \times 900$ mm (L $\times$ W $\times$ H) small-scale structure and a 2200 mm $\times$ 2200 mm $\times$ 2800 mm (L $\times$ W $\times$ H) large-scale structure were printed successfully within 150 min and 9.5 hours respectively, which demonstrate that this novel 3DPFRCCs possess acceptable printability.

Chapter 8 Conclusions and Recommendations

This thesis proposes an approach to develop consistent and reliable 3D printable cementitious materials for large-scale printing applications. Three levels are included in the conceptualized methodology. Rheology control serves as a vital factor at the lowest level to ensure that material fresh properties can satisfy the printing requirement in terms of buildability, pumpability, setting control and shape retention capability. Afterward, material design is the critical factor at the intermedium level to ensure that hardened properties of printed materials reach the demand for structural or non-structural applications. Hardened properties are focused on compressive and flexure performance in this thesis. Finally, while not achieved in this thesis work, integrating building information modeling (BIM) and architecture with 3DCP is expected to promote automatic construction fabrication for digitalized products at the third level. Due to time constraint of the Ph.D. study, this thesis focused on the first two levels and the third level is discussed in the section of future work.

The first level focuses on investigating the influence of various factors on material rheological properties. Firstly, statistical rheological models are constructed to correlate rheological properties, material constituents, and chemical admixtures. Secondly, theoretical models are developed to link rheological properties with buildability, and a novel testing method is proposed for validation.

The second level focuses on exploring the hardened properties of developed printable materials. Three different types of printable materials were investigated, i.e. plain cementitious materials, fiber-reinforced cementitious materials, and rapid hardening cementitious materials, respectively. The hardened properties were studied in terms of compressive and flexural strength.

8.1 Findings and achievements

Significant findings and accomplishments made in this thesis are summarized in the following sections.

8.1.1 Rheological models of material constituents

In this study, a factorial design was adopted to evaluate the influences of five variables (water-to-binder ratio, sand-to-binder ratio, fly ash-to-cement ratio, silica fume-to-cement ratio, and dosage of fiber) on material rheological properties (flow resistance, torque viscosity, and thixotropy). Empirical models were established to predict rheological properties and were verified by experiment. Results imply that the increment of fiber dosage boosts all rheological parameters, while water-to-binder ratio shows an opposite trend. Torque viscosity increases while flow resistance and thixotropy decrease with the rise of fly ash-to-cement ratio. Conversely, the influence of silica fume-to-cement ratio shows an opposite trend on rheological properties as compared to that of fly ash-to-cement ratio. Flow resistance and torque viscosity are improved whilst thixotropy is declined if sand-to-binder ratio increases. Different formulations were adopted in a printing test for demonstration purposes via a robotic arm printing system finally.

8.1.2 Rheological models of chemical admixtures

The printability of cementitious materials is significantly influenced by rheological properties, such as yield stress, plastic viscosity, and thixotropy. The rheological properties are drastically affected by modern concrete chemical admixtures i.e. superplasticizers, retarders, and accelerators. In this work, Response Surface Methodology (RSM) accompanied by Central Composite Design (CCD) was adopted to establish statistical models relating rheological characteristics with the dosages of

superplasticizers, retarders, and accelerators. The analysis of variance (ANOVA) was conducted to assess the significance and adequacy of attained regression models.

Results imply that statistical models obtained have a high degree of accuracy for predictions. Additionally, with the increment of dosages of retarders or superplasticizers, all the rheological parameters are decreased whilst accelerators possess an opposite influence on rheological properties. These rheological properties are negatively proportional to the interaction (second-order effect) of retarders and accelerators. The interaction of retarders and superplasticizers possesses a positive influence on dynamic yield stress, plastic viscosity, and thixotropy whilst a negative influence on static yield stress. The interaction of accelerators and retarders has a positive influence on the yield stress whereas a negative influence was found on the plastic viscosity and thixotropy.

8.1.3 Buildability models

Fuller Thompson theory and Marson-Percy model are classic approaches for sand gradation and packing fraction optimization, respectively. This study attempts to apply Fuller Thompson theory and the Marson-Percy model in designing cementitious materials for 3DCP. Various gradation methods adopted in this study were Fuller Thompson gradation (mixture A), uniform-gradations (mixtures B and C), gap-gradations (mixtures D and E). Besides these mixtures with particular gradation approaches, one mixture using natural river sand (mixture F) was prepared as well. Rheological properties were characterized by static/dynamic yield stress and plastic viscosity in the Bingham Plastic model. Buildability was examined by printing a column with 10 cm inner diameter via a gantry printer.

Rheological test results indicate that the mixture A designed by continuous gradation possesses the highest static/dynamic yield stress and lowest plastic viscosity. During the printing test for buildability, mixture A can easily reach up to 40 layers without notable deformation, while all other mixtures deformed noticeably and fell down

before the 35th layer. Finally, a scaled-up printing test was carried out with mixture A and a structure with a height of 80 cm was printed successfully without notable deformation. Density, compressive strength and flexural strength of printed filaments were also characterized. Mechanical performance test results illustrate mixture A has the highest density and appropriate compressive strength, and a relatively high flexural strength at different curing ages. These results indicate that Fuller Thompson theory and Marson-Percy model can serve as a reasonable guide for material rheology design for 3DCP.

8.1.4 Printable material with fiber reinforcement for applications

3D printable cementitious composites require special rheological performance to satisfy the requirement of printability (buildability and pumpability). In this work, a novel 3DPFRCC was developed. The rheological performance (yield stress, plastic viscosity), setting time, mechanical performance and printability were characterized. The results show that the static yield and dynamic yield stress of this 3DPFRCC are 3289 Pa and 314.7 Pa, respectively; the plastic viscosity is 32.5 Pa·s; the initial setting time is 59.2 min; the flexural strength and compressive strength are 8.5 MPa and 71.2 MPa respectively at 28 days. Finally, a 78 cm × 60 cm × 90 cm (L × W × H) structure was printed in the small-scale printing test, and a 2.2 × 2.2 × 2.8 m was printed in the large-scale printing test, which demonstrates that this new material possesses excellent printability and is capable for large-scale printing.

8.1.5 Feasibility study on the MKPC for 3D printing application

3D printing of cementitious materials is an innovative and promising approach in the construction sector, attracting much attention over the past few years. The use of waste cementitious materials in the production of 3D printable components increases the sustainability and cost-effectiveness of this process. This work proposes an environmentally friendly 3D printable cementitious material involving the use of

magnesium potassium phosphate cement (MKPC) with various ratios of fly ash replacement ranging from 0 to 60 wt% to increase the working time of the binder. Silica fume was used at up to 10 wt% to adjust rheological and mechanical properties. The developed 3D printable MKPC formulations were assessed on their workability, extrudability, buildability, compressive strength, porosity, and microstructure. Amongst the mixtures studied, the optimum MKPC formulation involving 60 wt% fly ash and 10 wt% silica fume with a borax-to-magnesia ratio of 1:4 was selected for a small-scale printing demonstration in line with its rheological and mechanical properties. Finally, a 20-layer structure with a height of 180 mm was printed in 5 min to demonstrate the feasibility of the adopted mixture in 3D printing.

8.2 Future works

8.2.1 Building information modeling

BIM is a revolutionary technology and process for civil engineering to facilitate the integration and management of information throughout the building lifecycle (Lu, Wu, Chang & Li, 2017), thereby providing an opportunity for making the best use of the available design data for sustainable design and performance analysis (Volk, Stengel & Schultmann, 2014).

When the concept and technology related to BIM applications were first discussed since 1999 (Eadie, Browne, Odeyinka, McKeown & McNiff, 2013), intensive efforts have been made in exploring the possibility of BIM in facilitating the development of green buildings (Azhar, 2011; Wu & Issa, 2014). Various functions of BIM have been studied, such as energy performance simulation, lighting analysis, and construction and demolition waste analysis (Bryde, Broquetas & Volm, 2013; Rajendran, Seow & Goh, 2012). Different management aspects associated with BIM adoption have been highlighted, such as its economic benefits and organizational challenges (Ji & Leite, 2018; Porter et al., 2018). A number of BIM applications have been proposed and developed to seamlessly integrate sustainability analysis into a

traditional design, construction, and operation process (Ma, 2012; Wu & Clayton, 2013).

Although BIM possesses a number of advantages and attracts extensive attention from both industry and academia, it still remains largely in the designing and conceptual stage. The uprising of 3DCP provides a great opportunity to integrate the design stage and fabrication stage together to achieve the digitalized fabrication process. The research work should focus on converting BIM files into printing files such that the printer can directly use the file in BIM and build up the object according to the BIM file, as illustrated in Figure 8-1.

Figure 8-1 From BIM to building through 3D concrete printing

8.2.2 Architecture

One of the main advantages of 3D printing is the customized design. The concept of incorporating architecture with 3D printing has been adopted in other 3D printing fields, including metal 3D printing and polymeric 3D printing (Wong & Hernandez, 2012; Yuan, 2017). Their results indicated that the performance and potential value of printed structures could be significantly improved (Mazzoli, 2013). For example, Prasittisopin et al. designed a novel bio-inspired concrete wall panel (as shown in Figure 8-2) and applied the designed structure for the practical application (Prasittisopin et al., 2019). The results indicate that compared with conventional design structure, a house fabricated with the novel design can improve the material

saving by 11%, and the energy consumption can be reduced by 31%. Additionally, the thermal performance can also be improved by 31% (Prasittisopin et al., 2019).

Figure 8-2 Bio-inspired designed concrete wall panel fabricated by 3DCP
(Prasittisopin et al., 2019)

Apart from adopting bio-inspired design for 3DCP, topology optimization is another potential approach to improving the performance of 3D concrete printed structure. Topology optimization process starts from an unknown design (Vantghem et al., 2018), and is independent from an existing and typically non-optimal design. Instead, it generates a new design which is optimized using a mathematical formulation, and the entire design domain is first discretized by a finite element mesh, after which the contribution of every element in the mesh is determined for every new design iteration. The material lay-out is changed by adjusting the density of each element. The final topological result depends on the design objective and its constraints.

Appendix A. Analysis results of prediction models for material constituents

Table A. 1 Statistical analysis results of a prediction model of flow resistance

Run order	Actual value	Predicted value	Residual	Internally studentized residuals
1	141	225	-83.9	-0.536
2	466	382	83.9	0.536
3	110	194	-83.9	-0.536
4	122	37.8	83.9	0.536
5	99.1	-57.6	157	1.87
6	1088	931	157	1.87
7	122	279	-157	-1.87
8	438	595	-157	-1.87

Table A. 2 Statistical analysis results of a prediction model of torque viscosity

Run order	Actual value	Predicted value	Residual	Internally studentized residuals
1	9.03	8.77	0.256	0.143
2	6.09	6.34	-0.256	-0.143
3	4.90	4.64	0.256	0.143
4	6.82	7.07	-0.256	-0.143
5	5.22	7.00	-1.78	-6.94
6	10.7	12.0	-1.78	-6.94
7	14.3	12.5	1.78	6.94
8	8.75	6.96	1.78	6.94

Table A. 3 Statistical analysis results of a prediction model of thixotropy

Run order	Actual value	Predicted value	Residual	Internally studentized residuals
1	813	1257	-444	-0.209
2	2126	1682	444	0.209
3	193	637	-444	-0.209
4	656	212	444	0.209
5	1485	3614	-2129	-4.79
6	4654	6783	-2129	-4.79
7	10077	7948	2129	4.79
8	4578	2449	2129	4.79

Appendix B. Analysis results of prediction models for chemical additives

Table B. 1 Statistical analysis results of prediction model of static yield stress

Run order	Actual value	Predicted value	Residual	Internally studentized residuals
1	833.2	868.2	-35.03	-1.807
2	964.8	996.7	-31.96	-1.649
3	1156	1168	-12.29	-0.6344
4	926.3	948.3	-22.02	-1.136
5	665.7	680.6	-14.94	-0.7712
6	588.6	613.2	-24.67	-1.273
7	1045	1050.0	-5.003	-0.2583
8	632.2	634.1	-1.938	-0.1000
9	1070	1048	22.18	1.049
10	836.3	806.1	30.10	1.424
11	753.9	708.3	45.57	2.156
12	984.9	978.1	6.713	0.3176
13	1086	1043.5	42.42	2.007
14	631.5	621.6	9.865	0.4668
15	828.1	829.0	-0.9618	-0.03124
16	824.8	829.0	-4.261	-0.1384
17	846.2	829.0	17.13	0.5565
18	796.1	829.0	-32.96	-1.070
19	815.9	829.0	-13.16	-0.4274
20	854.3	829.0	25.23	0.8196

Table B. 2 Statistical analysis results of prediction model of dynamic yield stress

Run order	Actual value	Predicted value	Residual	Internally studentized residuals
1	192.4	194.1	-1.767	-1.084
2	176.2	177.8	-1.690	-1.037
3	230.3	227.9	2.303	1.413
4	163.5	164.4	-0.9187	-0.5637
5	162.6	163.5	-0.9653	-0.5923
6	148.7	152.8	-4.187	-2.569
7	211.4	211.5	-0.1939	-0.1190
8	153.5	153.6	-0.1166	-0.07155
9	212.7	213.2	-0.5380	-0.3027
10	154.0	150.7	3.202	1.802
11	185.1	180.8	4.211	2.370
12	208.4	209.9	-1.547	-0.8707
13	180.2	179.8	0.3238	0.1822
14	147.4	145.0	2.340	1.317
15	167.0	166.7	0.2071	0.08000
16	165.3	166.7	-1.492	-0.5765
17	164.6	166.7	-2.192	-0.8469
18	169.1	166.7	2.307	0.8910
19	166.5	166.7	-0.2928	-0.1131
20	167.8	166.7	1.007	0.3889

Table B. 3 Statistical analysis results of prediction model of plastic viscosity

Run order	Actual value	Predicted value	Residual	Internally studentized residuals
1	18.84	19.02	-0.1837	-0.1918
2	14.58	12.37	2.202	2.299
3	25.79	25.58	0.2089	0.2181
4	17.37	18.78	-1.419	-1.482
5	21.19	19.33	1.853	1.935
6	19.73	19.50	0.2246	0.2345
7	15.21	16.97	-1.768	-1.847
8	17.62	17.00	0.6173	0.6446
9	22.35	22.20	0.1439	0.1377
10	15.88	16.63	-0.7571	-0.7249
11	13.84	16.06	-2.226	-2.132
12	21.09	19.47	1.613	1.545
13	19.28	19.55	-0.2714	-0.2598
14	17.97	18.31	-0.3417	-0.3272
15	20.60	20.91	-0.3141	-0.2064
16	21.99	20.91	1.075	0.7070
17	19.29	20.91	-1.624	-1.067
18	20.46	20.91	-0.4541	-0.2984
19	22.06	20.91	1.145	0.7530
20	21.19	20.91	0.2758	0.1812

Table B. 4 Statistical analysis results of prediction model of thixotropy

Run order	Actual value	Predicted value	Residual	Internally studentized residuals
1	13243	13725	-482.4	-0.9194
2	6263	6709	-446.7	-0.8512
3	17081	17454	-373.0	1.592
4	8667	9389	-722.7	1.745
5	9898	10323	-425.7	-1.478
6	7410	8185	-775.4	-1.377
7	12373	13074	-701.7	-0.7110
8	9222	9887	-665.9	1.702
9	15099	14473	625.4	-1.269
10	6893	5894	998.7	-0.2910
11	13124	12410	713.0	-0.1350
12	17889	16977	911.1	1.026
13	11351	10700	650.3	-0.08700
14	9233	8259	973.8	1.136
15	17446	17368	77.3	1.093
16	17256	17368	-112.6	-0.8110
17	17126	17368	-242.6	0.09300
18	17296	17368	-72.6	1.246
19	18224	17368	855.3	1.025
20	16585	17368	-783.6	-0.9397

Appendix C. Derives of geometrical factor

Considering a hollow cylinder has inner radius R_1 (m), outer radius R_2 (m) and height H (m), which is compressed by two plates with uniform velocity v (m/s), the coordinate can be built as shown in Fig. C. 1.

Fig. C. 1 Schematic of a hollow cylinder compressed by constant velocity.

The continuity equation under cylindrical coordinates without angular velocity can be written as

$$\frac{1}{r} \frac{\partial}{\partial r} (ru_r) + \frac{\partial u_z}{\partial z} = 0 \quad (\text{C.1})$$

where the velocities profiles on radial and axial directions satisfying governing equation and boundary conditions are

$$u_r(r, z) = \frac{v}{2H} r + \frac{C}{r} \quad (\text{C.2})$$

$$u_z(r, z) = -\frac{v}{H} z \quad (\text{C.3})$$

where C is an undetermined constant. Thus, the strain rate tensor of this flow is

$$D_{ij} = \begin{bmatrix} \frac{v}{2H} - \frac{C}{r^2} & 0 & 0 \\ 0 & \frac{v}{2H} + \frac{C}{r^2} & 0 \\ 0 & 0 & -\frac{v}{H} \end{bmatrix} \quad (C.4)$$

the second invariant is

$$I_2(r, z) = \frac{3v^2}{4H^2} + \frac{C^2}{r^4} \quad (C.5)$$

and the stress tensor is

$$\begin{aligned} \sigma_{ij}^{(d)} &= \frac{K_i}{\sqrt{I_2}} D_{ij} \\ &= K_i \left(\frac{3v^2}{4H^2} + \frac{C^2}{r^4} \right)^{-\frac{1}{2}} \begin{bmatrix} \frac{v}{2H} - \frac{C}{r^2} & 0 & 0 \\ 0 & \frac{v}{2H} + \frac{C}{r^2} & 0 \\ 0 & 0 & -\frac{v}{H} \end{bmatrix} \end{aligned} \quad (C.6)$$

In the absence of body forces and inertial stresses, the pressure governing equation is

$$\frac{\partial p}{\partial r} = \frac{1}{r} \frac{\partial [r \sigma_r^{(d)}]}{\partial r} - \frac{\sigma_\theta^{(d)}}{r} + \frac{\partial \sigma_{rz}}{\partial z} \quad (C.7)$$

Integrating Eq. (C.7) on $[R_1, R_2]$

$$\begin{aligned} \int_{R_1}^{R_2} \frac{\partial p}{\partial r} dr &= \left(\frac{v}{2H} - \frac{C}{r^2} \right) \left[\left(\frac{3v^2}{4H^2} + \frac{C^2}{r^4} \right)^{-\frac{1}{2}} K_i \right]_{R_1}^{R_2} \\ &\quad + K_i \operatorname{arcsinh} \left(\sqrt{\frac{4H^2}{3v^2}} \frac{C}{r^2} \right) \Bigg|_{R_1}^{R_2} \\ &= 0 \end{aligned} \quad (C.8)$$

Let $C_\alpha = HC/v$, Eq. (C.8) can be rearranged as

$$\begin{aligned}
 & \left(\frac{1}{2} - \frac{C_\alpha}{R_2^2} \right) \left(\frac{3}{4} + \frac{C_\alpha^2}{R_2^4} \right)^{-1/2} - \left(\frac{1}{2} - \frac{C_\alpha}{R_1^2} \right) \left(\frac{3}{4} + \frac{C_\alpha^2}{R_1^4} \right)^{-1/2} \\
 & + \operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_2^2} \right) - \operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_1^2} \right) = 0
 \end{aligned} \tag{C.9}$$

Apparently, 0 is the trivial solution of Eq. (C.9), another solution can be solved numerically from Eq. (C.9). On the plate surface, the dissipation rate is caused by the force between plates and fluids which can be computed by

$$\begin{aligned}
 & 2 \int_{S_p} \sigma_{rz} \left(r, \frac{H}{2} \right) u_r \left(r, \frac{H}{2} \right) dS \\
 & = \frac{4\pi\nu K_i}{H} \left[\frac{(R_2^3 - R_1^3)}{6} + C_\alpha (R_2 - R_1) \right]
 \end{aligned} \tag{C.10}$$

and the dissipation rate inside of the fluid can be calculated by

$$\begin{aligned}
 & \int_V \sigma_{ij}^{(d)} D_{ij} dV - \int_{S_R} \sigma_{ij}^{(d)} D_{ij} dS \\
 & = 2\pi\nu K_i C_\alpha \left(\sqrt{\frac{3R_2^4}{4C_\alpha^2} + 1} - \sqrt{\frac{3R_1^4}{4C_\alpha^2} + 1} \right) \\
 & - 2\pi\nu K_i C_\alpha \left[\operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_2^2} \right) - \operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_1^2} \right) \right] \\
 & - 2\pi\nu K_i R_1^2 \left(\frac{3}{4} + \frac{C_\alpha^2}{R_1^4} \right)^{-1/2} \left(\frac{1}{4} - \frac{C_\alpha^2}{R_1^4} \right) \\
 & - 2\pi\nu K_i R_2^2 \left(\frac{3}{4} + \frac{C_\alpha^2}{R_2^4} \right)^{-1/2} \left(\frac{1}{4} - \frac{C_\alpha^2}{R_2^4} \right)
 \end{aligned} \tag{C.11}$$

Therefore, the work applied on fluid is

$$\begin{aligned}
 F_V = & \frac{4\pi\nu K_i}{H} \left[\frac{(R_2^3 - R_1^3)}{6} + C_\alpha (R_2 - R_1) \right] \\
 & + 2\pi\nu K_i C_\alpha \left(\sqrt{\frac{3R_2^4}{4C_\alpha^2} + 1} - \sqrt{\frac{3R_1^4}{4C_\alpha^2} + 1} \right) \\
 & - 2\pi\nu K_i C_\alpha \left[\operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_2^2} \right) - \operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_1^2} \right) \right] \quad (C.12) \\
 & - 2\pi\nu K_i R_1^2 \left(\frac{3}{4} + \frac{C_\alpha^2}{R_1^4} \right)^{-1/2} \left(\frac{1}{4} - \frac{C_\alpha^2}{R_1^4} \right) \\
 & - 2\pi\nu K_i R_2^2 \left(\frac{3}{4} + \frac{C_\alpha^2}{R_2^4} \right)^{-1/2} \left(\frac{1}{4} - \frac{C_\alpha^2}{R_2^4} \right)
 \end{aligned}$$

For a gravity driven hollow cylinder

$$F = \rho g H \pi (R_2^2 - R_1^2) \quad (C.13)$$

when the fluid starts to flow, it must have

$$\tau_s \alpha = \rho g H \quad (C.14)$$

where

$$\min \left[\sigma_\theta^{(d)} \right] = \sigma_\theta^{(d)} \Big|_{r=R_2} = \tau_s \quad (C.15)$$

Substituting Eqs. (C.13) to (C.15) into Eq. (C.12) and rearranging

$$\begin{aligned}
 \alpha = & \left(R_2^2 - R_1^2\right)^{-1} \left(\frac{1}{2} + \frac{C_\alpha}{R_2^2}\right)^{-1} \sqrt{\frac{3}{4} + \frac{C_\alpha^2}{R_2^4}} \\
 & \cdot \left\{ \frac{4}{H} \left[\frac{(R_2^3 - R_1^3)}{6} + C_\alpha (R_2 - R_1) \right] \right. \\
 & + 2C_\alpha \left(\sqrt{\frac{3R_2^4}{4C_\alpha^2} + 1} - \sqrt{\frac{3R_1^4}{4C_\alpha^2} + 1} \right) \\
 & - 2C_\alpha \left[\operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_2^2} \right) - \operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_1^2} \right) \right] \\
 & - 2R_1^2 \left(\frac{3}{4} + \frac{C_\alpha^2}{R_1^4} \right)^{-1/2} \left(\frac{1}{4} - \frac{C_\alpha^2}{R_1^4} \right) \\
 & \left. - 2R_2^2 \left(\frac{3}{4} + \frac{C_\alpha^2}{R_2^4} \right)^{-1/2} \left(\frac{1}{4} - \frac{C_\alpha^2}{R_2^4} \right) \right\} \tag{C.16}
 \end{aligned}$$

where C_α can be solved from Eq. (C.9).

$$\arcsin\left(\sqrt{\frac{x^2 + y^2}{l_f / 2}}\right) < \arccos\left(\frac{z}{l_f / 2}\right). Q.E.D.$$

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