Mixture design and processing of novel spray-based cementitious materials for 3D printing

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**Mixture Design and Processing of Novel Spray-based
Cementitious Materials for 3D Printing**

LU BING
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

2019

Mixture Design and Processing of Novel Spray-based Cementitious Materials for 3D Printing

LU BING

School of Civil and Environmental Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

Statement of Originality

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

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Section 2.2 is published as B. Lu, Y. Weng, M. Li, Y. Qian, K.F. Leong, M.J. Tan, S. Qian, A Systematical Review of 3D Printable Cementitious Materials, *Construction and Building Materials*, **207** (2019) 477-490.

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. Assoc Prof Tan Ming Jen provided the initial project direction and research funding support.
- I prepared the draft of manuscript. The manuscript was revised/commented by Dr Li Mingyang, Dr Qian Ye, Assoc Prof Leong Kah Fai, Assoc Prof Tan Ming Jen and A/Prof Qian Shunzhi.
- I did the through literature investigation of 3D printable cementitious materials and had detailed discussions with A/Prof Qian Shunzhi.
- Mr Weng Yiwei, Dr Li Mingyang and Dr Qian Ye assisted in the technical discussions for this literature review work.

Chapter 4 is published as B. Lu, Y. Qian, M. Li, Y. Weng, K.F. Leong, M.J. Tan, S. Qian, Designing Spray-based 3D Printable Cementitious Materials with Fly Ash Cenosphere and Air Entraining Agent, *Construction and Building Materials*, **211** (2019) 1073-1084.

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- A/Prof Qian is in overall charge of the research topic and provide guidance/supervision throughout the study. Assoc Prof Tan Ming Jen provided the initial project direction and research funding support.
- I wrote the drafts of the manuscript. The manuscript was revised/commented by Dr Qian Ye, Dr Li Mingyang, Assoc Prof Leong Kah Fai, Assoc Prof Tan Ming Jen and A/Prof Qian Shunzhi.
- I co-designed the rheological experiments with Dr Qian Ye and had technical discussions with him.
- I performed all the experiments including assessment of fresh properties and spray performance of designed spray-based 3D printable cementitious materials, e.g. rheological measurement, workability evaluation and material distribution analysis in spray-based 3D printing.
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- I prepared the draft of the manuscript. The manuscript was revised/commented by Dr Li Mingyang, A/Prof Qian Shunzhi, Assoc Prof Tan Ming Jen and Assoc Prof Leong Kah Fai.
- I performed all the experiments including material characterization, robotic-arm controlled spray tests and build-up thickness distribution analysis.
- Dr Li Mingyang assisted in empirical model construction and provided useful suggestions for the experiment design and analysis.

- Mr Weng Yiwei and Dr Li Mingyang assisted in the robotic-arm controlled spray tests.
- Mr Lao Wenxin assisted in the image analysis of the cross section of sprayed filament.

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Summary

With new manufacturing technology innovations currently in Industry 4.0, there is a rising trend in the number of research studies and engineering applications of 3D printing. Recently, remarkable progress of 3D concrete printing has been achieved, where the printable cementitious materials are deposited layer-atop-layer to build the desired structures. It further facilitates automation in the construction industry, which saves the labour and improves the overall efficiency compared with the conventional construction methods. In addition, 3D concrete printing generates less waste and contributes to green and sustainable production.

However, commonly adopted extrusion-based 3D concrete printing has certain limitations when printing in in-situ vertical/overhead structures, e.g. decorative profile on the external wall or ceiling structures. The vertical constraints of extrusion-based 3D concrete printing bring about a bottleneck to the overall automation in construction. As the materials cannot be deposited layer-atop-layer in these applications, a new method of 3D printing and corresponding materials are required.

Based on the similarities between the conventional spray concrete technology (also known as *shotcrete*) and 3D concrete printing process, a spray-based 3D printing process of cementitious materials was proposed as a possible approach. Compared to extrusion-based 3D printing, spray-based 3D printing utilizes the compressed air to project the tailor-designed mixture onto the substrate at high speed. The substrate could be at any arbitrary orientations, and the sprayed material can adhere to the substrate to form a desired profile in layer-by-layer manner. In this regard, the need for design of suitable spray-based 3D printable cementitious materials is both urgent and significant. This is the primary motivation for this work as in this research study.

The research study mainly focuses on the design of suitable mixtures and the determination of influence of printing process on material spray-based printing performance. Based on a comprehensive literature review of 3D printable cementitious materials and sprayable cementitious materials, the key properties of the desired

mixtures were established and specified. Meanwhile, the limitations in the previous studies were also identified. To tackle the two major research tasks, specific strategies were adopted in mixture design and printing process investigations. Rheological tests and supplementary experiments were applied to evaluate the overall spray-based printing performance and select the optimal mixture. On the other hand, the printing parameters were investigated for their effects on thickness distribution of sprayed material.

The research of mixture design yields two different cementitious materials for spray-based 3D printing. With the introduction of fly ash cenosphere and air-entraining agent, the first recipe is lightweight cementitious material for spray-based 3D printing. Based on the overall evaluation in delivery and deposition phases, the optimal mixture is achieved. The selection criteria for this mixture are also proposed. With the elimination of cement usage, the second recipe provides a more sustainable recipe of MgO-activated slag for spray-based 3D printing. The experiment results suggest that slag could be effectively activated by MgO, and the rheological properties could be tailored with the addition of fly ash cenosphere.

The research on the printing process has identified the effects of four important printing parameters (i.e., pumping rate, air inject pressure, nozzle travel speed and nozzle standoff distance) on the thickness distribution of sprayed material. An empirical model has been constructed to describe and predict the material distribution. This research helps understand the correlation between the input printing parameters and final spray-print.

Finally, possible future research directions are raised. Feasibility of utilizing foam concrete is also proposed, followed by the suggestion of integration with feedback control to realize a feedback-oriented spray-based 3D printing system. Furthermore, the structural performance of hybrid structure by spray-based 3D printing is briefly discussed.

List of Publications

Journal Papers

1. Bing Lu, Ye Qian, Mingyang Li, Yiwei Weng, Kah Fai Leong, Ming Jen Tan, Shunzhi Qian. Designing Spray-based 3D Printable Cementitious Materials with Fly Ash Cenosphere and Air Entraining Agent, *Construction and Building Materials*, 2019, 211: 1073-1084.
2. Bing Lu, Yiwei Weng, Mingyang Li, Ye Qian, Kah Fai Leong, Ming Jen Tan, Shunzhi Qian. A Systematical Review of 3D Printable Cementitious Materials, *Construction and Building Materials*, 2019, 207: 477-490.
3. Bing Lu, Weiping Zhu, Yiwei Weng, Zhixin Liu, En-Hua Yang, Kah Fai Leong, Ming Jen Tan, Teck Neng Wong, Shunzhi Qian. Study of MgO-activated Slag As a Cementless Material for Sustainable Spray-based 3D Printing, *Journal of Cleaner Production*, under review.
4. Bing Lu, Mingyang Li, Wenxin Lao, Yiwei Weng, Kah Fai Leong, Ming Jen Tan, Shunzhi Qian. Experimental Investigation of Printing Parameters on Material Distribution in Spray-based 3D Printing of Cementitious Material, *Additive Manufacturing*, under preparation.
5. 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, *Virtual and Physical Prototyping*, 2018: 1-9.
6. Yiwei Weng, Bing Lu, Mingyang Li, Zhixin Liu, Ming Jen Tan, Shunzhi Qian. Empirical Models to Optimize Rheological Properties of Fiber Reinforced Cementitious Composites for 3D Printing, *Construction and Building Materials*, 2018, 189: 676-685.

Conference Papers

1. Bing Lu, Mingyang Li, Wenxin Lao, Yiwei Weng, Shunzhi Qian, Ming Jen Tan, Kah Fai Leong. Effect of Spray-based Printing Parameters on Cementitious Material Distribution, *Proceedings of the 29th Annual International Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference*, 2018, Austin, TX, U.S.: University of Texas at Austin, 1989-2002.
2. Bing Lu, Mingyang Li, Shunzhi Qian, Kah Fai Leong, Ming Jen Tan. Develop Cementitious Materials Incorporating Fly Ash Cenosphere for Spray-based 3D Printing, *Proceedings of the 3rd International Conference on Progress in Additive Manufacturing*, 2018, Singapore: Research Publishing Services, 38-43.
3. Yiwei Weng, Bing Lu, Ming Jen Tan, Shunzhi Qian. Rheology and Printability of Engineered Cementitious Composites - A Literature Review, *Proceedings of the 2nd International Conference on Progress in Additive Manufacturing*, 2016, Singapore: Research Publishing Services, 427-432.
4. Bing Lu, Ming Jen Tan, Shunzhi Qian. A Review of 3D Printable Construction Materials and Applications, *Proceedings of the 2nd International Conference on Progress in Additive Manufacturing*, 2016, Singapore: Research Publishing Services, 330-335.

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List of Symbols and Abbreviations

Symbols

γ	Shear strain
t	time
$\dot{\gamma}; d\gamma / dt$	Shear rate
τ	Shear stress
τ_0	Dynamic yield stress
k	Plastic viscosity
T	Equilibrium shearing torque
G	Flow resistance
H_k	Torque (Apparent) viscosity
N	Rotational speed of rheometer
τ_s	Static yield stress
μ	Shear viscosity
Q	Average flow rate
R	Inner radius of hose
L	Length of hose
Δp	Pressure difference in the hose
ϕ	Non-dimensional ratio
τ_w	Shear stress at the wall of the hose

S	Slump value
H_0	Original height of the printed filament
ρ	Fresh density
g_0	Gravitational acceleration
σ_{gr}	Green strength
$H_{\max}$	Theoretical maximum height of the printable material
$n_{\max}$	Number of layers the printable material can build without deformation
h_0	Height of each printed layer
α_{geom}	Geometric factor
R_1	Inner radius of printed hollow cylinder
R_2	Outer radius of printed hollow cylinder
H_c	Height of printed hollow cylinder
C_α	Geometric coefficient of printed hollow cylinder
τ_{sh}	Shear strength
σ_n	Compressive strength
P	Pumping pressure
τ_{0i}	Yield stress at the interface (lubricating layer)
k_i	Plastic viscosity at the interface (lubricating layer)

c_r	Filling coefficient
H	Maximum build-up thickness
$F(\eta)$	Second-order Gaussian Distribution Function
a_i	Fitting coefficient
b_i	Fitting coefficient
$j_p(x, r)$	Mass flow density
$j_{\max}(x)$	Maximum mass flow density
r	Radius from the central of sprayed profile
$r_{\max}$	Radius of the sprayed profile on the receiving plane
$\tilde{A}_i$	Normalized test result
A_i	Original test result
Γ	Material index
Ψ	Compressibility index
ρ'	Three-day air-dry density
v_x	Speed in perpendicular direction to the receiving plane
v_r	Speed in parallel direction to the receiving plane
α	Spray angle
I	Impulse of sprayed material
p_r	Receiving pressure at radius r on the substrate

C_r	Critical ratio
α_p	Pumping pressure
γ_{ts}	Nozzle travel speed
δ	Nozzle standoff distance
W	Width of sprayed filament
R^2	Coefficient of determination
h	Build-up thickness of sprayed filament
s	Non-dimensional filament thickness coordinate

Abbreviations

3DPCM	3D Printable Cementitious Materials
ABS	Acrylonitrile Butadiene Styrene
AEA	Air Entraining Agent
ATR	Attenuated Total Reflection
C ₃ A	Tricalcium Aluminate
CAC	Calcium Aluminate Cement
CAD	Computer Aided Design
C-A-H	Calcium Aluminium Hydrate
C-A-S-H	Calcium Aluminium Silicate Hydrate
C-H	Calcium Hydroxide
C ₃ S	Tricalcium Silicate

CSA	Calcium Sulphoaluminate
C-S-H	Calcium Silicate Hydrate
CVC	Conventional Vibrated Concrete
FAC	Fly Ash Cenosphere
FTIR	Fourier-transform Infrared
GGBS	Ground Granulated Blast-furnace Slag
HMC	Hydrated Magnesium Carbonate
HPMC	Hydroxypropyl Methylcellulose
HRWRA	High-range Water-reducing Admixture
HWC	Highly-Workable Concrete
MgO	Magnesium Oxide
MMD	Multi-level Material Design
M-S-H	Magnesium Silicate Hydrate
PVA	Polyvinyl Alcohol
RMS	Reactive MgO-Slag
SCC	Self-Consolidating Concrete
SCM	Supplementary Cementitious Materials
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
VEA	Viscosity Enhancement Agent

Chapter 1 Introduction

1.1 Research Background

With the transformation of manufacturing technology, the industry has gone through four stages of revolution to the current so-called Industry 4.0 (Lasi et al. 2014, Rüßmann et al. 2015, Zhou et al. 2015). Through the introduction of artificial intelligence and cloud-based control of machinery, the physical and digital worlds are connected seamlessly. The industrial activities are becoming highly automated with improved work efficiency, safer labour environment and less waste production.

In this circumstance, facilitating the automation in construction becomes increasingly important. Over the years, automation in the traditional construction industry is rather low. A lot of labour is required on site for the work such as scaffold and formwork installations, reinforcement installations, concrete casting, formwork demolitions, etc. The working environment carries high risks of potential injuries, and labour productivity in construction industry is very low as compared to other industrial sectors. In comparison, the labour productivity of manufacturing industry is steadily increasing in Industry 4.0 (Bock 2015) (see Fig. 1.1). Furthermore, extensive use of formwork leads to much construction waste, which is contrary to the aim of attaining clean and sustainable production.

Fig. 1.1 Labour productivity in industry generally, and specially in manufacturing industry and construction industry (Bock 2015). Reproduced with permission © Elsevier

3D printing is a fast-evolving manufacturing technology, which was firstly developed in 1980s (Kodama 1981). Through layer-by-layer sequential deposition of material, the target product is manufactured as per designed profile. 3D printing has been widely applied in many industrial fields, such as biomedical treatment (Murphy and Atala 2014, Qin et al. 2014, Seol et al. 2014) and precision manufacturing (Sun et al. 2013, Vaezi et al. 2013). In these applications, adoption of 3D printing reduces manufacturing costs of complicated objects and contributes to customization to personal requirements.

Recently, 3D printing in the construction field has been attracting more and more attention. With tailor-designed concrete materials as printing ink, the designed structures could be manufactured by large-scale 3D printing systems. Fig. 1.2 shows the printing process and final onsite assembly of a 3D printed concrete bridge completed by Eindhoven University of Technology (TU/e) (Salet et al. 2018). Compared to traditional methods, 3D printing eliminates the need of temporary formworks. Thus, it saves construction time and brings about less construction waste. Due to the highly

automatic operation, labour requirement is also reduced. As a result, overall work efficiency and work safety are greatly improved.

Fig. 1.2 Printing and assembly of a 3D printed concrete bridge (Salet et al. 2018): (a) printing of the structure unit; (b) onsite assembly of the bridge. Reproduced under Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0/>, no changes were made to the figures)

The growing application of 3D printing in construction field also further increases the design flexibility of structures. Unique structures could potentially be manufactured by 3D printing, while they could be difficult and time-consuming to construct by traditional construction methods. Fig. 1.3 shows a 3D printed concrete bench with built-in curvatures in Loughborough University (Le et al. 2012a). It is even feasible to construct hyperboloidal structures of high aesthetic values, which requires not only complicated formwork but also highly skilled labour if constructed by traditional construction methods.

Fig. 1.3 Design and printing of a concrete bench with curvature (Le et al. 2012a): (a) designed model; (b) printing process. Reproduced with permission from Springer Nature

The growing application of 3D printing in construction field calls for the research and development of suitable printing ink, i.e. printable cementitious materials. In recent years, there are many corresponding research studies from different groups. Le et al. (Le et al. 2012a) developed a high-performance printing concrete with adjustment of sand/binder ratio and optimization of the dosage of admixtures, e.g. superplasticizer. Weng et al. (Weng et al. 2018c) developed a printable cementitious mixture by statistical optimization of rheological properties. Zhang et al. (Zhang et al. 2018b) developed printable concrete materials with the addition of nanoclay and silica fume. These materials possess good delivery and deposition performance to be applied in 3D printing.

On the other hand, further development of 3D printable cementitious materials calls for cleaner and more sustainable production. With this regard, the utilization of industrial waste/low-carbon impact ingredients were utilized in the research practice. Ma et al. investigated the incorporation of copper tailings in 3D printable cementitious materials (Ma et al. 2018a). Panda et al. (Panda et al. 2017b), Xia et al. (Xia and Sanjayan 2016, Xia et al. 2019) developed green 3D printable materials using geopolymer. Ting et al. investigated the feasibility of incorporating recycled glass in 3D printable cementitious materials (Ting et al. 2019). The utilization of waste materials reduces the environment impact of construction, especially in the countries with limited natural resources like Singapore.

The 3D printing of cementitious materials could be divided into two phases, i.e. delivery and deposition phases (Lu et al. 2019b). In the delivery phase, the printable cementitious material is delivered through the hose to the printing nozzle with the pressure provided by the pump. In the deposition phase, the printable cementitious material is deposited in a layer-by-layer manner to build the desired structure. The movement of the printing nozzle is usually controlled by gantry or robotic arm. The mainstream concrete printing systems utilize the extrusion of cementitious materials, e.g. Contour Crafting developed in University of Southern California (Khoshnevis 2004), Concrete Printing developed in Loughborough University (Lim et al. 2012), and the collaborative robotic arm printing system developed in Nanyang Technological University (Zhang et al. 2018a).

1.2 Motivation

While there are many research studies and engineering applications of extrusion-based concrete printing systems, severe limitations exist. As could be noticed, the printing orientation is limited. In these printing systems, the material is deposited through extrusion and simply laid on the horizontal printing bed to gradually build up. The orientation of the target printing structure may need to be adjusted in the printing process. There are some attempts of printing cementitious materials on inclined substrates (Costanzi et al. 2018) or printing of overhanging structures with temporary supports (Tay et al. 2019). However, as reported in the literature, the inclined angle is

small; the temporary supports need to be removed. Furthermore, extrusion-based 3D printing of cementitious materials is not suitable for the cases of in-situ vertical/overhead applications such as external wall coatings or ceiling structures. The situation calls for the urgent development of new printing method and corresponding printable cementitious materials.

Spray is a conventional construction method for tunnel or retaining wall construction, which relies on the pumping and high-speed projection of sprayable cementitious materials (Neville 2011). The materials could gradually build up to certain thickness on vertical/overhead substrates. Hence, spray is widely applied in in-situ vertical/overhead engineering projects. Compared with the casting of concrete, spray could reduce the usage of formwork. Similar as extrusion-based 3D concrete printing, spray also contains delivery and deposition phases. It is promising to adopt spray process in 3D concrete printing for vertical/overhead surfaces, which could be termed as spray-based 3D printing.

However, suitable cementitious materials need to be developed specifically for spray-based 3D printing due to the severe limitations in current sprayable cementitious materials. With the high-speed projection of sprayable cementitious materials, some portion of sprayed material may bounce off from the substrate, which is referred to as rebound (Neville 2011). The rebound in the current practice of spray is severe, leaving a non-uniform thickness distribution of sprayed material which greatly impact the surface finish of sprayed structures. Hence, to rectify and improve the surface finish caused by non-uniform material distribution, usually post-processing such as manual scraping is required (ACI Committee 506 2005). However, the quality of spray and subsequent scraping is highly dependent on the skills of nozzleman, which is not desirable from quality control viewpoint. On the other hand, coarse aggregate may not be included in the raw ingredients due to the size limitation of nozzle in the case of 3D printing (Panda et al. 2017a). Therefore, corresponding material research should be carried to cater for spray-based 3D printing.

For the successful engineering applications of 3D printing in the construction industry, it is important to know the relationship between the printing parameters and the material distribution of the final printout. The knowledge can be utilized for printing parameter adjustment in a feedback-oriented system to facilitate the automation. Research studies in this area have been conducted in extrusion-based 3D printing (Lao et al. 2017, Li et al. 2018). Similar research should also be conducted in spray-based 3D printing of cementitious materials. Hence, the effects of printing parameters on cementitious material distribution in spray-based 3D printing should be investigated. Based on this result, a model should be constructed to effectively describe and predict the material distribution.

1.3 Research Objectives

To address the issues related to extrusion-based 3D printable cementitious materials and sprayable cementitious materials, the research objectives are listed as follows.

1. Develop suitable cementitious materials for spray-based 3D printing, which can be utilized for in-situ vertical/overhead construction applications.
2. Develop sustainable cementitious materials for spray-based 3D printing, which includes the utilization of industrial waste/low-carbon impact ingredients.
3. Investigate the effects of printing parameters on cementitious material distribution in spray-based 3D printing.
4. Construct a model to describe and predict the cementitious material distribution in spray-based 3D printing.

1.4 Scope of the Study

There are limited research studies about spray-based 3D printable cementitious materials, whether in the mixture design or material performance. Hence, it is critical to systematically design suitable material. Fig. 1.4 shows the multi-level material design of 3D printable cementitious materials (Lu et al. 2019b). It covers three levels of

material development, i.e. mixture design, printing process and composite structure. At each level, all the components contribute to the key aspect. The three levels of material development are connected by the two key aspects, i.e. rheology, pumpability & buildability. The final key aspect is the structural performance of the developed materials.

Fig. 1.4 Multi-level material design of 3D printable cementitious materials (Lu et al. 2019b). Reproduced with permission © Elsevier

Due to limited scope of this study, it mainly focuses on the mixture design and printing process levels. Through the literature review of 3D printable cementitious materials and sprayable cementitious materials, the key properties of materials are specified. A suitable mixture for spray-based 3D printing was developed thereafter. To cater for green and sustainable production, a feasibility study of utilizing MgO for spray-based 3D printing was conducted. On the other hand, the effects of printing parameters on material distribution were investigated. An empirical model was constructed to describe and predict the material distribution of sprayed cementitious materials which was successfully validated. Finally, for future study, three possible directions were proposed, i.e. spray-based 3D printable foam concrete, integration with feedback control and structural performance.

1.5 Organization of Thesis

The thesis consists of seven chapters.

In *Chapter 1*, the overview of the research was introduced. The current status of research development and engineering application of 3D concrete printing were briefly addressed. Meanwhile, the issues of common extrusion-based 3D concrete printing were identified. Hence, developing spray-based 3D printable cementitious materials was proposed as the possible solutions to address these issues. The research scope was specified, and organization of the thesis was described in detail.

In *Chapter 2*, a literature survey was carried out to analyse the previous research work and pinpoint the research gaps. The 3D printable cementitious materials were systematically reviewed. On the other hand, previous studies on sprayable cementitious materials were also investigated. With the literature review work in this chapter, the research gaps were identified thereafter. The chapter provides guidance for further material development and performance tailoring.

In *Chapter 3*, research methodology of the study was described. Necessary experiments for material development was introduced, including rheological tests and supplementary experiments. Suitable testing protocols for rheological measurement were selected. On the other hand, methodology for investigating the influence of printing process was illustrated. Effective control of nozzle movement was introduced, and other printing parameters were mentioned. Empirical models may be applied to link the material distribution with printing parameters.

In *Chapter 4*, development of spray-based 3D printable cementitious materials with fly ash cenosphere (FAC) and air entraining agent (AEA) was illustrated. The introduction of FAC and AEA led to lower density and changed the rheological behaviour of the cementitious materials. Considering the delivery and deposition requirements for spray-based 3D printing, material index was proposed for the selection of optimal mixture. Subsequent spray test was used to confirm the performance of the optimal mixture. Based on experimental research, material selection criteria for spray-based 3D concrete printing was proposed.

In *Chapter 5*, considering the environmental impact of spray-based 3D printable cementitious materials, reactive magnesium (MgO) was introduced to activate slag

material and eliminate the usage of cement. FAC of different dosages was added to the mixtures for rheological tailoring to meet the requirement of spray-based 3D printing. Through the assessments of rheological and spray performance, the optimal mixture was selected. A profile was spray-printed with the optimal mixture design to confirm the printing feasibility.

In *Chapter 6*, effect of printing parameters on material distribution were analysed. Through the experimental investigations, effects of pumping rate, air inject pressure, nozzle travel speed and nozzle standoff distance were investigated in detail. Based on the experimental investigation, an empirical model was proposed to describe the thickness distribution of sprayed filaments. The proposed model was further verified by experiment.

In *Chapter 7*, the research findings in this thesis were summarized. Contributions and impact of the research study were pointed out. Based on the investigations in this study, some future directions were proposed to give insights for further development of spray-based 3D printable cementitious materials.

Chapter 2 Literature Review

2.1 Introduction

In this chapter, previous studies pertaining to 3D printing of cementitious materials were reviewed in detail to reveal the state of the art. Through the literature study, rheological performance of cementitious materials was specified, which could be used as reference for material tailoring. A systematical and critical review of 3D printable cementitious materials was carried in this chapter. With the guidance of multi-level material design, the review covers the material design levels from mixture design, printing process to composite structure. On the other hand, previous studies on sprayable cementitious materials were also investigated. Based on the literature review, current limitations were exposed and research gaps were identified.

2.2 A Systematical Review of 3D Printable Cementitious Materials

Content of this section has been published as (Lu, B. et al. 2019). B. Lu, Y. Weng, M. Li, Y. Qian, K.F. Leong, M.J. Tan, S. Qian, A systematical review of 3D printable cementitious materials, Construction and Building Materials, 207 (2019) 477-490. Permission has been granted by Elsevier to use the published paper in the thesis. Revisions have been made in the thesis.

2.2.1 Introduction

3D printing, also known as rapid prototyping and additive manufacturing, is referred to as the process that sequentially deposits materials in a layer-by-layer manner to build expected product as per Computer-Aided Design (CAD) (Gibson et al. 2015, Chua and Leong 2017). In 1981, Kodama invented the first prototype of 3D printing (Kodama 1981). Since then, the development of 3D printing has been very fast with wide applications in a number of industrial sectors, including manufacturing of complex structures and objects (MIT Technology Review 2015, Fantino et al. 2016), medical

treatments (Qin et al. 2014, Seol et al. 2014), food fabrication (Sun et al. 2015) and so on. The adoption of 3D printing reduces the manufacturing costs of complex objects and customized products. With further exploitations and applications, 3D printing can potentially revolutionize the manufacturing industry in the future. Recently, 3D printing has been expanded to the building and construction field. Due to its freeform construction ability and highly automatic operation, 3D printing has distinctive advantages over conventional construction methods, contributing to higher construction efficiency, less intensive labour and less waste production (Weinstein and Nawara 2015, Asprone et al. 2018, Salet et al. 2018).

As the most widely used ink of 3D printing for building and constructions, suitable 3D printable cementitious material (3DPCM) is critical to successful printing. The development of 3DPCM is examined as follows: general 3D printing processes of cementitious material are introduced through various printing systems in *Section 2.2.2*, where the fresh performance requirements of 3DPCM are also specified. To guide the review work and potential future material development in a systematical way, multi-level material design (MMD) approach is proposed for 3DPCM in *Section 2.2.3* considering material related properties/performance at different levels, then the literature study follows the proposed MMD approach to review and analyse the key parameters in developing 3DPCM. This review work covers multiple levels including mixture design, printing-related material properties and structural performance of 3DPCM in *Sections 2.2.4 to 2.2.6* respectively, which are expected to provide insights for future design and exploitation of 3DPCM for intended structural performance.

2.2.2 3D Cementitious Material Printing System

2.2.2.1 Gantry-based 3D cementitious material printing system

Contour Crafting is the first gantry-based large-scale 3D cementitious material printing system. It fabricates objects with smooth surfaces by computer-controlled gantry crane, which is of high efficiency and accuracy (Khoshnevis 2004). In the printing process, the cement-based paste is extruded successively through the nozzle to form the rim of expected structure. A layer is printed when the nozzle moves back to its origin and

forms a closed region. Then the nozzle lifts up to start printing another layer atop the previous layers. With the scraping by top and side trowels, the printed structure has a smooth surface, as can be seen in Fig. 2.1 (a). Materials such as conventional concrete can then be poured into this closed section if needed (see Fig. 2.1 (b)) (Hwang and Khoshnevis 2004). In this case, Contour Crafting creates 3D printed permanent formworks, which will be part of the printed structure.

Fig. 2.1 Contour Crafting (Hwang and Khoshnevis 2004): (a) schematic drawing of printing nozzle; (b) formation of composite structure. Reproduced with permission from IAARC

Concrete Printing developed by Lim et al. (Lim et al. 2012) is also based on the extrusion process of cementitious materials. Compared with Contour Crafting, it has better printing system control and higher printing resolution (Lim et al. 2012). The printing system contains a giant frame mounted with movable beam and nozzle (See

Fig. 2.2 (a)). The nozzle moves along the beam while the beam moves in the other two orthogonal directions to implement free-form 3D printing (Lim et al. 2009, Lim et al. 2011). Compared with Contour Crafting, layered texture can be clearly observed due to the lack of surface scraping in Concrete Printing (See Fig. 2.2 (b)). However, the dimensions of filaments are much smaller than Contour Crafting. Thus, the pixels of the printed concrete surface are very small. The layered texture also exists in the structures printed by similar gantry-based printing system (Bos et al. 2016).

Fig. 2.2 Concrete Printing (Lim et al. 2011, Bos et al. 2016): (a) gantry framework; (b) details of printed structure and scanned surface. Reproduced with permission from IAARC

2.2.2.2 Robot-based 3D cementitious material printing system

In robot-based 3D cementitious material printing system, robot is used to control the movement of printing nozzle as per programmed path (Gosselin et al. 2016, Zhang et

al. 2018a). Fig. 2.3 illustrates the equipment of a robotic arm printing system for large-scale 3D cementitious material printing (Zhang et al. 2018a). The raw ingredients of cementitious material are mixed and then the fresh material is delivered to the nozzle for printing. At the same time, the robotic arm moves with the mounted nozzle to implement the layer-by-layer 3D printing process. Compared with the gantry-based 3D cementitious material printing system, the robot-based 3D cementitious material printing system has less size limitations on the designed structure. On the other hand, the robot-based 3D cementitious material printing system is mounted on a movable platform, which is suitable for onsite printing. Moreover, the collaborative printing by synchronized robots further reduces the size and location limitations of 3D cementitious material printing (Zhang et al. 2018a).

Fig. 2.3 Robotic arm printing system for large-scale 3D cementitious material printing (Zhang et al. 2018a). Reproduced with permission © Elsevier

In addition to the aforementioned major cementitious material printing systems, there are some other similar printing systems, e.g., computer-controlled crane with slewing structures (Kazemian et al. 2017), binder-jetting 3D printing with cement paste penetration (Pierre et al. 2018). From the introduction of different 3D cementitious material printing systems, it can be found that the printing process can be divided into two successive phases. In the first phase, which can be referred to as delivery phase, 3DPCM is prepared and delivered through the hose to the printing nozzle. In the second phase, which can be referred to as deposition phase, the material is extruded from the

moving nozzle and laid atop the supporting platform or printed layers. It should be noted that among the practices reported in the literature, the delivery phase could be slightly different based on the type of material preparation. Some printing systems deal with premix 3DPCM, where the material is only prepared at the beginning of the printing. In contrast, the other printing systems require continuous mixing and preparation of 3DPCM during the printing process. The two categories could also be referred to as off-line mixing and in-line mixing (Wangler 2018) respectively. The different time span from mixing to printing in these two types of material preparation could significantly affect the performance of 3DPCM.

The core equipment in the delivery phase is pump, while the core equipment in the deposition phase is the end effector to control the movement of the nozzle. Based on different operation mechanisms, direct-acting piston pump (Neville 2011), peristaltic squeeze pump (Neville 2011) and screw pump (Weng et al. 2018b) could be applied to deliver the material. With the triggered pressure difference in the hose, the material is forced to move to the printing nozzle and be extruded out. On the other hand, different end effectors contribute to the above different types of printing systems, whether it is associated with gantry, robot, etc.

The printing process requires specific fresh properties for cementitious materials. In the delivery phase, the material should be easy to deliver to the nozzle without causing blockage, which requires good pumpability of the material (Weng et al. 2016). In the deposition phase, the printed material should have little deformation to ensure sufficient support for successive layers. This requirement of little deformation of the printed layer can be labelled as buildability (Tay et al. 2016). Therefore, the material needs to have good buildability in the deposition phase. To summarize, suitable 3DPCM should possess good pumpability for delivery and good buildability for deposition in 3D printing process.

2.2.3 Multi-level Material Design

To systematically capture some of the significant factors in the design of 3DPCMs, the multi-level material design (MMD) is proposed and illustrated in Fig. 2.4. It covers the

design span from raw ingredients to ultimate structural performance. The three pyramids of MMD are corresponding to the three consecutive stages in the design of 3DPCM, i.e. mixture design, printing process and composite structure. These pyramids are linked together by two common apexes. For each pyramid, the factors at the lower three apexes largely influence the properties/performance at upper apex, which in turn significantly impacts the properties/performance at a higher level together with other two factors. The proposed MMD makes the initial attempt to explain the contribution of these significant factors in the material design span. In addition, it gives the insight for future improvement on systematical and standardized designs of 3DPCMs.

Fig. 2.4 Multi-level material design for 3DPCM

At the lowest level (i.e., the lowest pyramid), different raw ingredients of mixture design, including supplementary cementitious materials (SCM), superplasticizer and viscosity enhancement agent (VEA) contribute to the rheological properties of the material. Rheology describes the deformation and flow characteristics of the material (Barnes et al. 1989), which affects the pumpability and buildability of the printing process. In addition to rheology, pumpability and buildability are also influenced by equipment-related parameters, such as tribology, delivery and placement with different pumping facilities. These are reflected in the intermediate level, i.e., the middle pyramid. As an input to the highest level (i.e., the highest pyramid), pumpability and buildability contribute to the structural performance with other inputs from mechanical property and

reinforcement. As 3D cementitious material printing is a very comprehensive topic, organizing the content according to this multi-level material design concept can sharpen the focus of our review work such that the key developments in 3DPCM can be captured.

2.2.4 Influence of Material Composition on the Rheological Properties of 3D Printable Cementitious Materials

In the current 3D cementitious material printing, due to size limitation of the delivery system, coarse aggregate (e.g. particle size larger than 2 mm (Panda et al. 2017a)) typically is not used in the mix design. In this case, 3DPCMs are usually mortars (Kazemian et al. 2017, Wolfs et al. 2018b), instead of concretes. The 3D printing process is a flowing process. The materials are flowing in the pipe during pumping and extruded out of the nozzle. Thus, rheology of the materials is of critical importance.

The most common way to describe the flowability of cementitious materials is to obtain the equilibrium flow curve. It is the relationship between equilibrium shear stress and shear rate. Commonly, the equilibrium shear stress is obtained by applying a constant shear rate. The shear stress would increase to a peak value, and then decay till reaching equilibrium value (Qian and Kawashima 2016a, Qian and Kawashima 2018), as shown in Fig. 2.5. The equilibrium shear stress value and the corresponding shear rate is plotted in Fig. 2.6.

*Fig. 2.5 Stress development under constant shear rate (Qian and Kawashima 2018).
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*Fig. 2.6 The equilibrium flow curve of mortar (Qian and Kawashima 2018).
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It could be seen that for mortars, there is a linear relationship between equilibrium shear stress and shear rate. Thus, the most frequently applied viscosity model is Bingham Plastic model (Austin et al. 1999). Bingham Plastic model depicts a linear relationship between shear stress τ (Pa) and shear rate ($d\gamma/dt$) (1/s), as shown in Eq.(2.1):

$$\tau = \tau_0 + k \frac{d\gamma}{dt} \quad (2.1)$$

where τ_0 (Pa) is referred to as dynamic yield stress, representing the minimum stress needed to maintain flow; k (Pa·s) is referred to as plastic viscosity, representing the stress increment for unit increment of shear rate once dynamic yield stress is exceeded. These two parameters are basic rheological parameters describing the flowability of cementitious materials.

Bingham Plastic model can also be expressed as following Eq.(2.2), which is commonly used in the rheological experiments (Austin et al. 1999):

$$T = G + H_k N \quad (2.2)$$

where T (N·m) is equilibrium shearing torque, N is rotational speed of rheometer (s^{-1} or rpm). G is referred to as flow resistance (N·m), H_k is referred to as torque viscosity (N·m·s). Flow resistance and torque viscosity in Eq.(2.2) correspond to dynamic yield stress and plastic viscosity in Eq.(2.1) respectively and can be converted through Reiner-Riwlin equations (Reiner 1949).

Recent studies (Qian and Kawashima 2016b, Ma et al. 2018b, Yuan et al. 2018) also reveal that there exists another yield stress, which is higher than dynamic yield stress. It is believed to be the yield stress corresponding to the flocculation state before the microstructure is broken down, which is referred to as static yield stress. With the measurement of static yield stress, the structural build-up of cementitious materials can be effectively monitored (Ma et al. 2018b). The information of structural build-up is useful for the buildability assessment (Perrot et al. 2016), which further relates to the structural performance of 3DPCM.

Thus, the rheological parameters of cementitious materials are subjected to the change in mix proportions and time. Early hydrates are formed during the early hydration period, which is usually within 20 mins after the contact between water and cement. In considering the sustainability of the cement industry, supplementary cementitious materials (SCM) are commonly used to replace cement paste. These mineral replacements have different mineral components than cement and hydration rates, thus modifying the early rheological parameters (Tang et al. 2014, Tang et al. 2016). In the

meanwhile, superplasticizers are commonly used as water reducing agent in modern concrete. They usually adsorb on the surface of cement particles / agglomerates and reduce attractive bonding between particles / agglomerates, thus increasing flowability (Qian et al. 2018). It helps to reduce water content and increase the mechanical strength of cementitious materials. For example, pumping of self-consolidating concrete (SCC) requires high flowability. Likewise, in 3D printing, to guaranty the continuous pumping process and prevent clogging, superplasticizers should be added to enhance flowability and pumpability. Furthermore, after pumping and extrusion out of the nozzle, the 3D printable materials are supposed to be strong enough to support its own weight and further layers above; and stiff enough to keep its shape. Cementitious materials become stronger and stiffer over time due to cement hydration. The consumption of water and reaction to form hydrates, such as C-S-H and C-H make the materials stronger and stiffer (Banfill 1994, Perrot et al. 2016). However, for the usual application of 3D printing, the whole printing period occurs within 2 hours and thought to be dormant period (Neville 2011). Some accelerators could increase hydration and shorten the dormant period, which leads to a narrowed printing window and faster gain of dynamic/static yield stress over time. Certain types of viscosity enhancement agents (VEA), such as nanoclay (Qian and Kawashima 2016b, Panda et al. 2019), could enhance the green strength and static yield stress of materials.

It could be seen that for successful 3D printable materials, it has bi-fold rheological properties. On one hand, the materials should be flowable enough to be pumped and extruded; on the other hand, the materials should be strong and stiff enough to maintain its shape and sustain the weight of its own and the layers above. From the perspectives of rheology, it should have low dynamic yield stress and high static yield stress. According to Qian and Kawashima (Qian and Kawashima 2018), the discrepancy between dynamic and static yield stress is related to thixotropy. Thus, the 3D printable materials should have high thixotropy, as has been discussed by previous researchers (Bos et al. 2016, Wolfs et al. 2018b).

2.2.4.1 Supplementary Cementitious Materials

The most widely-applied supplementary cementitious materials (SCM) are fly ash, ground blast furnace slag and silica fume. All of them contains mineral components and can be triggered to have secondary hydration in the cement hydration process, which are commonly referred to as pozzolanic reaction. As mentioned at the beginning of this section, the incorporation of these SCM can contribute to different rheological behaviours.

There are many experimental studies and theoretical analyses to investigate the rheological effects of SCM incorporation. Jiao et al. (Jiao et al. 2017) have summarized the rheological effects from literature to draft the corresponding rheographs. From these rheographs, Jiao et al. found that there are some contradictory reports. The contradiction may be due to the different sources of SCM and hence different particle size distribution and chemical composition. However, some general conclusions could still be drawn, which can be useful to instruct the design of 3DPCM. In the cases of fly ash, the rheological effects vary a lot among different reports, but class F fly ash can significantly decrease plastic viscosity compared with class C fly ash (Jiao et al. 2017). In the most cases, plastic viscosity is reduced with the increasing dosage of ground blast furnace slag, while yield stress varies due to the competition of prominent micro-filling effect and increased water demand from high specific area. Most reports point out that the increase of silica fume contribute to higher dynamic yield stress and higher plastic viscosity, and the effects are highly associated with the water binder ratio and different types of superplasticizer applied (Jiao et al. 2017).

Rheological behaviour in ternary blends system has also been investigated in details (Jiao et al. 2017). The reports show that the yield stress is dominated by the particle size distribution of these raw ingredients, e.g. addition of cementitious material which has an intermediate particle size distribution between cement and silica fume can lead to the decrease of yield stress. For ternary blends system of cement, fly ash and ground blast furnace slag, both yield stress and plastic viscosity were reported increased (Park et al.

2005). In this case, 20% fly ash with 40% slag combination showed the highest increase in plastic viscosity (Khayat et al. 2008).

2.2.4.2 Superplasticizer

Generally, superplasticizer can be classified into such types: purified lignosulfonates, carboxylate synthetic polymers, sulfonated synthetic polymers and synthetic polymers with mixed functionality (Ramachandran et al. 1998, Nkinamubanzi and Aïtcin 2004). As the superplasticizer is used to improve the workability of mortar or concrete materials, its addition decreases yield stress and plastic viscosity, which has been verified by many rheological experiments (Banfill 1994, Yun et al. 2015b). However, there exist critical and saturation dosages for the superplasticizer specifically. Below the critical dosage (too little amount) or above the saturation dosage (too much amount), superplasticizer has minimal effects on the rheological behaviour (Flatt and Schober 2012). The critical and saturation dosages are dependent on the molecular structure of the superplasticizer, e.g. polycarboxylate and polyphosphonate-based superplasticizer have lower dosage than naphthalene and melamine-based superplasticizer (Nkinamubanzi and Aïtcin 2004).

The rheological effects of superplasticizer are also hinged on the water binder ratio of the material. For the material with high water to cement ratio, there are minimal differences in rheological influence between different superplasticizers. However, in the case of low water to cement ratio such as 0.20, the polynaphthalene sulfonate polymer-based superplasticizer is ineffective to change the rheological properties of the material, while different polycarboxylic ether type superplasticizer shows different extents of reducing rheological parameters (Flatt and Schober 2012, Qian and De Schutter 2018a).

Research studies pointed out that the effectiveness of superplasticizer in rheological changes is highly dependent on its type, e.g. polycarboxylate-based superplasticizer shows a stronger reduction of plastic viscosity but weaker reduction of yield stress compared with naphthalene sulphonate-based superplasticizer (Jiao et al. 2017). Different types of superplasticizer have different molecular structures, which can

account for different efficiency of altering rheological properties, e.g. naphthalene sulfonate formaldehyde polycondensate superplasticizer has a linear structure and reduces the attraction of particles by electrostatic repulsion; polycarboxylic ether superplasticizer has a comb-like structure and reduces the attraction of particles by steric hinderance (Flatt and Schober 2012, Gelardi 2017). Research studies also reported that low side chain density of the superplasticizer contributes to the reduction of yield stress, and the rheological changes brought by effective superplasticizer can be very sensitive to the dosage (Flatt and Schober 2012).

The type of superplasticizer also has impacts on the robustness of rheological effects, which is linked to its compatibility with different cement systems. Lack of robustness and compatibility lead to great rheological changes with small dosage variation, time and possible segregation (Nkinamubanzi and Aïtcin 2004), e.g. polysulfonate-based and polycarboxylate-based superplasticizer possess good compatibility with high alkali and sulphate cement, while polysulfonate-based superplasticizer has poor compatibility with low alkali cement.

2.2.4.3 Viscosity Enhancement Agent

Viscosity Enhancement Agent (VEA) is frequently applied to enhance the fluidity and cohesion of fresh concrete materials, leading to improved robustness (Khayat 1998, Bouras et al. 2012). For concrete materials, the addition of VEA can effectively influence the rheological behaviours. The applied shear stress has a certain influence on the rheological behaviour of concrete materials incorporating VEA. It has been reported that while some material exhibited shear thinning behaviour when subjected to high shear stress, it exhibited the opposite trend when subjected to low shear stress (Bouras et al. 2012).

Similar to superplasticizer, the rheological effectiveness of VEA also depends on its type. Research studies have shown that hydroxypropyl methyl cellulose-based VEA reduces yield stress but increases plastic viscosity (Yun et al. 2015b); polysaccharide-based VEA significantly increases yield stress, while microsilica-based VEA induces low plastic viscosity (Leemann and Winnefeld 2007). In addition, nanoclay-based VEA

can significantly increase static yield stress and enhance thixotropic property of the material (Qian and Kawashima 2016b, Zhang et al. 2018b), which further improves the shape stability of the material (Voigt et al. 2010, Zhang et al. 2018b). It has also been found that the combination of nanoclay and PCE superplasticizer could obtain a cementitious mixture with low dynamic yield stress, yet high thixotropy and high static yield stress (Qian and De Schutter 2018b).

2.2.5 Pumpability and Buildability of 3D Printable Cementitious Materials

From the analysis of 3D cementitious material printing process, it is revealed that 3DPCM should possess good pumpability for delivery and good buildability for deposition. Materials with good pumpability can be easily delivered through the hose to the printing nozzle with low risk of blockage. The blockage in the printing process leads to discontinuity of the extruded material and further impaired structural performance of 3DPCM. Thus, the adoption of material with good pumpability improves the robustness of 3D printing by reducing the risk of blockage. Materials with good buildability can build up to large height with negligible deformation, which ensures the consistency of printed dimensions and structural stability. As mentioned in *Section 2.2.4*, successful 3DPCMs should have bi-fold rheological requirements. In addition to the analysis of rheology, tribology and placement/delivery of the material should also be taken into consideration, which exerts import influence on the printing process. This part of review and analysis covers the second pyramid in the multi-level material design illustrated in Fig. 2.4.

2.2.5.1 Analysis of rheology

As rheology describes the flow characteristics of the material, it is necessary to analyse how rheological parameters affect the pumpability and buildability of 3DPCM respectively. Pumpability can be assessed by shear viscosity of the material in the hose (Yamaguchi 2008). Considering Bingham Plastic model, shear viscosity μ (Pa·s) is calculated as follows in Eq.(2.3):

$$\mu = \frac{\tau}{d\gamma / dt} = \frac{\tau_0}{d\gamma / dt} + k \quad (2.3)$$

With constant equipment-related control such as adoption of the same pipeline system and constant flow rate, shear viscosity or the consequent pressure drop can be the indicator for pumpability. The flow of cementitious material inside the hose follows plug flow when the flow rate is small (Chhabra and Richardson 2008), of which flow velocity profile and shear stress distribution are shown in Fig. 2.7.

Fig. 2.7 Flow velocity and shear stress distribution of cement mortar material inside the hose

The flow rate of the material Q (m^3/s) can be expressed in the form of pressure drop $\Delta p/L$ (Pa/m), dimensions of the hose (inner radius R (m) and length L (m)) and rheological parameters (yield stress τ_0 (Pa) and plastic viscosity k ($\text{Pa}\cdot\text{s}$)) (Chhabra and Richardson 2008), namely

$$Q = \frac{\pi R^4}{8k} \left(\frac{\Delta p}{L} \right) \left(1 - \frac{4}{3}\phi + \frac{1}{3}\phi^4 \right) \quad (2.4)$$

$$\phi = \frac{\tau_0}{\tau_w} = \left(\frac{L}{\Delta p} \right) \frac{2\tau_0}{R} \leq 1 \quad (2.5)$$

where τ_w (Pa) is the shear stress at the wall of the hose, which is not smaller than yield stress τ_0 . It is observed that lower dynamic yield stress and lower plastic viscosity contribute to smaller pressure drop with the same flow rate, indicating better

pumpability of the material. Hence, lower rheological parameters are desirable in the delivery phase.

Kaplan derived corresponding equations to describe the flow behaviour of cementitious materials inside the hose for large flow rate, which involves viscous flow apart from plug flow (Kaplan 2000). The influence of the lubricating layer formed by the material was also considered in the calculations. From the calculations, the same conclusion was proposed, i.e. lower plastic viscosity and dynamic yield stress contribute to better pumpability. Therefore, the conclusion is applicable to cementitious material in any flow rate.

When the material is extruded from the nozzle to form filaments, good buildability is required. Buildability is heavily influenced by the deformation behaviour of extruded filaments under gravity. The most direct way to assess buildability is to compare the maximum height or number of layers that can be built with the same printing setup. Negligible deformation is required for 3DPCMs. Buildability can also be quantitatively assessed by the green strength of the material. Green strength refers to the maximum stress that the material can withstand in the fresh state (Lomboy et al. 2012, Weng et al. 2018b). Judged by its definition, high green strength increases the ultimate pressure the printed filaments can resist. In the literature (Hoornahad 2014, Khoshnevis et al. 2015), slump value is frequently used as an indirect assessment of buildability. To minimize the deformation of the printed layer, zero slump value is specified for 3DPCMs. To summarize, little slump value or high green strength suggests better buildability of the material.

Khoshnevis et al. have analysed the deformation of the printed sulphur concrete filament with rectangular cross section (Khoshnevis et al. 2015). The analysis depicts the relationship between slump value and rheological parameters. As the deformation analysis does not involve material information of sulphur concrete, it can be applied to all the extrusion-based 3DPCMs. The slump value S (m) can be expressed by Eq.(2.6):

$$S = H_0 - \frac{2\tau_s}{\rho g_0} \left[1 + \ln \left(\frac{\rho g_0 H_0}{2\tau_s} \right) \right] \quad (2.6)$$

where H_0 (m) is the original height of the printed filaments, ρ (kg/m³) is the fresh density of printed material, and g_0 (m/s²) is gravitational acceleration. τ_s is the static yield stress as the material flocculates and recovers the microstructure after it is extruded.

Eq.(2.6) reveals that high static yield stress and low density contribute to low slump value, indicating better buildability. Specifically, if the ratio of static yield stress to fresh density is large enough, there will be no slump for the concrete material. A similar conclusion can be obtained through the calculation of green strength. In the critical case where there is no slump value exactly (i.e. $S = 0$), green strength σ_{gr} can be expressed as:

$$\sigma_{gr} = \rho g_0 H_0 = 2\tau_s \quad (2.7)$$

And the theoretical maximum height $H_{\max}$ (m) and number of layers the material can build without deformation $n_{\max}$ are:

$$H_{\max} = \frac{2\tau_s}{\rho g_0} \quad (2.8)$$

$$n_{\max} = \frac{2\tau_s}{\rho g_0 h_0} \quad (2.9)$$

respectively, where h_0 is the height of each printed layer. Hence, for better buildability of 3DPCM, high static yield stress and low density are desired.

Perrot et al. have constructed a more general model to link green strength with static yield stress (Perrot et al. 2016). The model considers the geometric influence of printed structure and evolution of static yield stress, and in this case, green strength is expressed as:

$$\sigma_{gr} = \alpha_{geom} \tau_s(t) \quad (2.10)$$

where α_{geom} is the geometric factor and $\tau_s(t)$ is the static yield stress considering time effect. The geometric factor α_{geom} varies for different printed structures, e.g. for a hollowed cylinder which is one of the common structures in 3D cementitious material printing, the geometric factor α_{geom} can be computed as follows (Weng et al. 2018b):

$$\begin{aligned} \alpha_{\text{geom}} = & (R_2^2 - R_1^2)^{-1} \left(\frac{1}{2} + \frac{C_\alpha}{R_2^2} \right)^{-1} \sqrt{\frac{3}{4} + \frac{C_\alpha^2}{R_2^4}} \left\{ \frac{4}{H_c} \left[\frac{(R_2^3 - R_1^3)}{6} + C_\alpha (R_2 - R_1) \right] \right. \\ & + 2C_\alpha \left(\sqrt{\frac{3R_2^4}{4C_\alpha^2} + 1} - \sqrt{\frac{3R_1^4}{4C_\alpha^2} + 1} \right) - 2C_\alpha \left[\operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_2^2} \right) - \operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_1^2} \right) \right] \\ & \left. - 2R_1^2 \left(\frac{3}{4} + \frac{C_\alpha^2}{R_1^4} \right)^{-1/2} \left(\frac{1}{4} - \frac{C_\alpha^2}{R_1^4} \right) - 2R_2^2 \left(\frac{3}{4} + \frac{C_\alpha^2}{R_2^4} \right)^{-1/2} \left(\frac{1}{4} - \frac{C_\alpha^2}{R_2^4} \right) \right\} \end{aligned} \quad (2.11)$$

where R_1 and R_2 are the inner radius and outer radius respectively, and H_c is the height of the hollow cylinder. C_α in Eq.(2.11) can be determined by the following equation:

$$\frac{\frac{1}{2} - \frac{C_\alpha}{R_2^2}}{\sqrt{\frac{3}{4} + \frac{C_\alpha^2}{R_2^4}}} - \frac{\frac{1}{2} - \frac{C_\alpha}{R_1^2}}{\sqrt{\frac{3}{4} + \frac{C_\alpha^2}{R_1^4}}} + \operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_2^2} \right) - \operatorname{arcsinh} \left(\frac{2C_\alpha}{\sqrt{3}R_1^2} \right) = 0 \quad (2.12)$$

Based on the proposed model, it is accessible to estimate the failure height of the printed structure.

Experimental studies of buildability of 3DPCMs have been reported by several researchers, which can offer verifications for the proposed models. Le et al. (Le et al. 2012a) have conducted printing tests for different 3DPCMs, and their results show that higher yield stress contributes to more layers that the material can build (see Fig. 2.8). The printed structure is comprised of several parallel filaments next to one another. It was suggested that with increased number of filaments more number of layers can be built, which is due to the increased overall width and therefore better stability of the structure (Suiker 2018). This will be further discussed in *Section 2.2.5*. The same conclusion has been reported by Weng et al. (Weng et al. 2018b). Voigt et al. have

reported that increasing the content of fiber and clay materials such as metakaolin lead to higher green strength, while increasing the content of fly ash makes the material easier to flow (Voigt et al. 2010). Increasing sand-binder ratio (Le et al. 2012a), the addition of polymer resin or thickening agents (Jeon et al. 2013) can lead to smaller deformation of printed structures, indicating better buildability. These results can be explained by their rheological effects, which indirectly verify the theoretical analysis.

Fig. 2.8 Buildability results of 3DPCMs with different yield stress (Le et al. 2012a): (a) experiment results; (b) printed structures comprised of 1 to 5 filaments respectively (from bottom right to upper left). Reproduced with permission from Springer Nature

The analysis of rheology indicates different rheological requirements for 3DPCMs in the delivery and deposition phase. In the delivery phase, the material should possess low plastic viscosity and low dynamic yield stress for better pumpability; in the deposition phase, the material should possess high static yield stress for better buildability. The paradox could be more significant in the printing with off-line mixing. The prepared 3DPCM undergoes more time before delivery compared with the in-line mixing, while generally the yield stress increases with the hydration of the fresh material (Perrot et al. 2016). To meet seemingly conflicting rheological requirements in different phases, tailoring rheological properties with the consideration in the first pyramid is required.

There could be three strategies in the rheological tailoring. As the deposition phase is after the delivery phase, one of the tailoring strategies is to utilize time-dependent

rheological behaviour. Special raw ingredients or additives such as accelerator can be added to the mix to trigger the great increase of yield stress over time. However, the excessively rapid rising of yield stress may lead to poor pumpability or even clogging of hose. In this case, open time is critical to the printing performance of material (Le et al. 2012a, Martens et al. 2018), which identifies the window available for printing. The insight for the second strategy comes from the influence of delivery on buildability. This strategy is to decrease rheological parameters for better pumpability and recover them after the material is printed. The strategy requires large compressibility of the material. In the pumping process, the material with high compressibility is compacted under pressure, which triggers the rheological change. The detailed mechanism will be introduced in *Section 2.2.5.3*. The third strategy is to make compromises in both phases. The material can be designed to have high static yield stress and low fresh density for good buildability as well as low plastic viscosity for better pumpability. Adjusting the raw ingredients or additives, e.g., increasing silica fume/cement ratio can contribute to the desired rheological properties. More information of the rheological effects of different raw ingredients of concrete materials can be found in *Section 2.2.4*. To reduce the fresh density of the material, lightweight aggregates may be adopted in the mix design.

Several experimental studies on the evolution of rheological parameters related to printing have been reported, while most of them focus on yield stress evolution. Yield stress evolution of 3DPCMs containing different supplementary cementitious materials has been investigated (Banfill 1994, Ahari et al. 2015). Cementitious materials containing metakaolin and Class C fly ash have a significant increase in yield stress with time (Ahari et al. 2015). However, no clear trend on the yield stress can be observed for other supplementary cementitious materials. On the other hand, yield stress evolution of 3DPCMs incorporating different additives has also been investigated (Le et al. 2012a, Perrot et al. 2016). In Le et al.'s work (Le et al. 2012a), shear vane apparatus was adopted to assess the shear strength of the material, which is regarded as yield stress in the analysis. Fig. 2.9 shows the evolution of yield stress (shear strength) of the material with different dosages of superplasticizer and retarder. The figures reveal that increasing dosage of superplasticizer can effectively extend the window of

workable yield stress for printing. In this case, the window ranges from 0.3 to 0.9 kPa. In comparison, increasing dosage of retarder does not have consistent effects.

Fig. 2.9 Yield stress (shear strength) evolution (Le et al. 2012a) under: (a) different dosage of superplasticizer; (b) different dosage of retarder (solid curves for agitated samples; dotted curves for non-agitated samples). Reproduced with permission from Springer Nature

The evolution of rheological parameters has also been investigated with different rapid hardening ingredients. Khalil et al. (Khalil et al. 2017) reported the adoption of calcium sulphoaluminate (CSA) cement for 3D printing. By replacing 7% of ordinary Portland cement with CSA cement, yield stress increases rapidly with time. Kim et al. (Kim et al. 2003) found that increasing the ratio of calcium aluminate cement (CAC) to ordinary Portland cement leads to rapid development of viscosity. Similar rheological results can be found for material incorporating rapid hardening ingredient such as Magnesium Potassium phosphate cement (Fu et al. 2016). In addition, through the application of appropriate accelerating agents, rapid setting and hardening can be achieved in several

minutes (Won et al. 2013), which also leads to the rapid increase of rheological parameters.

2.2.5.2 Analysis of tribology

In addition to rheology, tribology of the material should be taken into consideration when the material flows in the hose. There are two types of friction in the delivery phase: (a) internal friction of the material which contributes to rheology (Chhabra and Richardson 2008), and (b) friction between the material and the wall of the hose. Correspondingly, there exist two types of blockage in concrete material pumping (Binns 2003, Neville 2011). In the first type, a mass of concrete material cannot be pumped to move inside the hose under certain pumping pressure. This is due to the high internal friction brought by high rheological parameters, which has been clarified in *Section 2.2.5.1*. In the second type of blockage, water dissipates from the mix under pressure with solid material left behind to cause clogging of the hose.

The second type of blockage is related to the segregation of material under pressure. In the delivery phase, water transmits the pumping pressure to other ingredients (Neville 2011). If the lowest pumping pressure to initiate flow (pumping pressure threshold) is higher than segregation pressure, the pressure-induced segregation happens (Kempster 1968). The segregation leads to the loss of material homogeneity and water is squeezed out from the material. To prevent the second type of blockage, it is critical to prevent severe segregation in the delivery phase. Assaad et al. have investigated the relationship between segregation index and rheological parameters (Assaad et al. 2004), which is shown in Fig. 2.10. The figure reveals that reducing flow resistance or torque viscosity increases segregation index. In other words, decreasing yield stress or viscosity increases segregation tendency. Hence in the material design, both viscosity and yield stress should have minimum design values, which can be examined through column segregation tests, pressure bleeding test or similar experiments.

Fig. 2.10 Relationship between segregation index and rheological parameters (Assaad et al. 2004). Reproduced with permission © American Concrete Institute

The tribological analysis can be verified through concrete pumping practices. Increasing cement content can increase the resistance to segregation when the concrete material is pumped (Johansson and Tuutti 1976). Incorporating more fine particles also reduces the risk of segregation in the pumping process (Neville 2011). The mechanism of these practices in controlling segregation in the pumping process can be attributed to higher rheological parameters of the material (Banfill 1994).

Based on the above discussions, a schematic diagram shows different combinations of yield stress and plastic viscosity in relation to printing, as can be shown in Fig. 2.11. In total, there are five regions in Fig. 2.11. The descending curve sets apart Regions 1, 2 and Regions 3, 4 as the material with good and poor pumpability respectively. The curve is drawn based on the discussion of Eq.(2.4). In Eq.(2.4), all the equipment-related parameters and flow rate are kept the same. The dashed line sets apart the material with good and poor buildability, which is related to Eq.(2.8). Very low yield stress or plastic viscosity can lead to segregation of the material, which is denoted as Region 5.

The previous discussions on rheological tailoring strategies in *Section 2.2.5.1* can be further extended based on Fig. 2.11 correspondingly. The first and second strategies are to design the material with rheological parameters in Region 2 for good pumpability, then bring its rheological parameters to Region 1 and Region 3 in the printing phase for good buildability. The third strategy is to deliberately tailor the rheological parameters

of the material from Regions 2 or 3 to Region 1. Special additives may be added to the mixture to elongate open time for this strategy.

Fig. 2.11 Schematic diagram showing different combinations of yield stress and plastic viscosity in relation to printing

2.2.5.3 Delivery and placement

In 3D cementitious material printing, delivery greatly affects pumpability and buildability of the material. Regarding Eq.(2.4), increasing the inner radius of the hose, reducing the total pipe length can lower pumping pressure required for the material. Material with higher rheological parameters yet the same pumpability can be developed accordingly. Additional air pressure can be added to push the material forward, which has been applied by Keating et al. in their 3D printing of foam concrete material (Keating et al. 2017), as can be seen in Fig. 2.12. To overcome friction in the delivery phase, 3DPCM is compacted under pumping pressure. The compaction of the material leads to higher fresh density and higher yield stress (Beaupre 1994). Therefore, buildability of the material is affected by such compaction in the delivery phase. This process-induced effect is critical to materials with large compressibility, e.g. air-entrained concrete materials.

Fig. 2.12 3D printing of foam concrete materials (Keating et al. 2017). Reproduced with permission © American Association for the Advancement of Science

The compaction of the material in the delivery hose offers a tailoring strategy for 3DPCMs. This strategy was previously applied in developing sprayable concrete materials, and the corresponding rheological change is referred to as slump-killing effect (Jolin and Beaupre 2003). For material with high yield stress, extra air-entraining agent can be added to decrease the rheological parameters for better pumpability (Banfill 1994, Yun et al. 2015b). When the material is printed, higher yield stress caused by the compaction will contribute to better buildability.

Placement of the material also affects the measured buildability. As suggested in Fig. 2.8, printed layer with a wider width, e.g. more parallel filaments lead to a larger number of layers built. It may be attributed to the stability of the printed structures. Small disturbance can lead to the offset of printed layers in the printing process, and the printed structure with narrow layer width is more susceptible to the offset moment. On the other hand, different structures have different geometric factors as described in Eq.(2.10), which certainly affect the maximum printable height. Elastic buckling may happen before the printed material reaches the critical yield stress of plastic collapse (Suiker 2018), e.g. the wall structure with a large height to width ratio may bend over in the printing. This situation also limits the maximum height of the printed structure. Detailed theoretical analysis, simulations or experiments need to be carried to decide whether plastic collapse or elastic buckling dominates the final failure (Suiker 2018, Wolfs et al. 2018b). For large-scale 3D cementitious material printing such as garden villas (Young 2016), the printing duration is significantly longer than the dormant period of cement

hydration. In this case, the evolution of rheological parameters contributes to higher buildability, especially for the material in the bottom layers.

2.2.6 Structural Performance of 3D Printable Cementitious Materials

The structural performance of conventional concrete materials is largely governed by its mechanical property and the reinforcement in the structure, which is also applicable for 3DPCMs given that process difference between casting and 3D printing is adequately considered. Obviously, the layer-by-layer printing process greatly affects the mechanical property and subsequently structural performance of 3DPCMs. Furthermore, the very different methods of reinforcement addition in 3D printing could significantly impact structural performance as well. In addition, for 3DPCMs, the influence of pumpability and buildability on structural performance should also be considered. This section analyses the influence of these factors on the structural performance, which can potentially provide insights when designing 3DP concrete structures with desirable structure performance.

2.2.6.1 Pumpability and buildability

Good pumpability and buildability improve the structural performance of 3DPCMs. In contrast, the poor pumpability of the material increases the difficulty of pumping and hence brings a higher risk of discontinuity. Lack of steady and continuous material flow leads to defects such as tearing and variations of dimensions in the extruded layers, as shown in Fig. 2.13. In this situation, poor pumpability of material results in deteriorated structural performance. On the other hand, poor buildability of the material makes it difficult to reach the designed dimension of structures in one printing, as the structure may collapse during the printing process (Le et al. 2012a). The continuous printing process may be suspended for the printed material to gain enough yield stress with time. As will be discussed in the later section, the long time gap between each printing impairs the interfacial bond of printed structure. Therefore, it is necessary to increase pumpability and buildability for better structural performance.

Fig. 2.13 Defects due to poor pumpability

2.2.6.2 Mechanical property

Due to the layer-by-layer deposition process, the printed structure has a distinctive orientation in manufacturing. The orientation further leads to the direction-dependent structural performance of 3D printed concrete structures, which is also referred to as anisotropic property (Lu et al. 2016). The layer-by-layer 3D printing process introduces interfaces between adjacent layers, which potentially make its mechanical property less desirable compared with conventional concrete structures due to lack of adequate bond between printed layers. Cracks are more likely to initiate and propagate between adjacent printed layers with poor bonding. These cracks accelerate the penetration of detrimental substances into the structure, thus reducing its long-term load-carrying capacity. In addition, lack of bonding between layers may cause structure failure by shear force in horizontal loading cases, e.g. due to seismic loading.

Several experiments (Le et al. 2012b, Feng et al. 2015) have been carried out to investigate the mechanical properties of 3DP structures. Through these experiments, it is found that 3D printed structures have distinctive anisotropic mechanical behaviour. It is revealed that when the loading induces tension between the printed layers, the strength of the printed structure is greatly reduced. The highest strength is measured when the loading induces tension parallel to the printed layers.

Different from conventional cementitious materials, investigation on the mechanical strength of 3D printed cementitious materials at very early ages (e.g. several minutes to several hours) are highly valued. Wolf et al. have reported the very early age mechanical properties of 3D printed cementitious materials (Wolfs et al. 2018a, Wolfs et al. 2018b).

Evolution of compressive strength, Young's modulus and shear strength have been recorded through unconfined compressive tests and direct shear tests, which can be used to predict the elastic buckling or plastic collapse of the printed structure. The empirical Mohr-Coulomb model has been adopted to describe the evolution of shear strength, which is expressed as follows:

$$\tau_{sh} = (0.058t + 3.05) + \sigma_n \tan(20^\circ) \quad (2.13)$$

where τ_{sh} and σ_n are shear strength and compressive strength respectively.

There are several methods to potentially improve the bonding between adjacent printed layers. Le et al. have confirmed that reducing printing time gap can effectively increase bonding strength (Le et al. 2012b). A similar conclusion has been reported by Panda et al. for 3D printed geopolymers concrete material (Panda et al. 2018). Furthermore, the addition of fibers (Christ et al. 2015), adjustment of surface moisture level between layers (Sanjayan et al. 2018) and bonding compound material such as latex (Zhang and Li 2015) are also beneficial to interlayer bond strength.

Printing setup can affect printing quality and the consequent mechanical property of the printed structure. It is noticed that in the long 3D printing process, the printing quality gradually reduces with respect to time (Le et al. 2012b). The gradual built-ups at the nozzle may affect the extrusion, leading to poorer printing quality (Feng et al. 2015). It should also be taken into consideration that in some early printing system, the printed layers may not be able to come in full contact with each other due to nozzle outlet shape (Le et al. 2012b). Defects may arise in the prints with poor morphology. However, the good prints could be made with circular nozzles or trapezoid nozzles (Lao et al. 2017).

2.2.6.3 Reinforcement

Concrete is a brittle material that is easy to generate cracks under tensile and/or flexural loading. To improve the structure ductility, reinforcement is introduced to form reinforced concrete structures as the conventional practice. In 3D cementitious material printing, introducing reinforcement in the printed structure is also necessary for

engineering applications. The current practices of reinforcement in structures fabricated by 3D cementitious material printing can be classified into two general methods: (a) separate placement of reinforcement and cementitious material printing, and (b) simultaneous placement of reinforcement while printing. Both methods are proved effective for reinforcement entraining.

2.2.6.3.1 Separate placement of reinforcement and cementitious material printing

Early practices of 3D cementitious material printing adopt the first reinforcement entraining method, i.e. separate placement of reinforcement and cementitious material printing. In Concrete Printing technology developed by Lim et al. (Lim et al. 2012), the positions of steel reinforcement are reserved during cementitious material printing process. After the completion of the cementitious material printing, steel reinforcement will be placed inside. Complicated profiles can be obtained with the formation of composite structures (Lim et al. 2012) (see Fig. 2.14).

Fig. 2.14 Reinforcement in 3D printed structure by Concrete Printing (Lim et al. 2011). Reproduced with permission from IAARC

In Contour Crafting technology, the composite structures are produced through the printing of permanent formworks first, followed by the reinforcement placement and filling of other construction materials (Khoshnevis et al. 2006) (see Fig. 2.15). Reinforcing form ties are placed inside the printed permanent formwork. This characteristic offers flexibility in the structure design as the filling materials do not necessarily need to be the same as the printing materials. Functional construction materials, e.g., heat-insulating materials, self-compacting concrete can be conveniently introduced in this structure design without the need for additional formwork and/or

support. The filling of construction material can even be skipped to form hollow structures if design permits.

Fig. 2.15 Reinforcement in Contour Crafting (Khoshnevis et al. 2006): (a) permanent formwork printed with inserted form ties; (b) A composite concrete wall made by Contour Crafting. Reproduced with permission © Inderscience

Another practice of separate reinforcement placement and cementitious material printing is skeleton printing-spray technology (Architect Magazine 2015). ABS plastic or other printable plastic materials are used to print the reinforcement cage, which forms the skeleton of the desired structure. The cementitious material is sprayed afterwards, with the printed skeleton serving as the formwork and inner reinforcement. In this structure design, 3D printing offers the possibility to construct composite structures with different functional materials in vertical laminated layers (Gao et al. 2015). The printed plastic reinforcements are easy to be duplicated and stacked in the skeleton printing-spraying system, which makes it possible to apply different construction materials with horizontal lamination. Lamination greatly increases varieties of structure design, which can be fully utilized to realize various functions.

There are also some reports for engineering applications adopting similar reinforcement entraining method. In the printing of wall structures by Winsun company, separate cementitious material printing and placement of conventional steel reinforcement including longitudinal rebars and stirrups have been implemented (Sculpteo 2015). In another engineering application by Huashang Tengda company, steel rebars are settled

before cementitious material printing (engineering.com 2016). Special pipe and outlet have been developed in the project, where fresh cementitious material can be extruded to simultaneously form both sides of the wall and cover the settled steel rebars.

2.2.6.3.2 Simultaneous placement of reinforcement while printing

Instead of continuous reinforcement, short dispersed fibers can be introduced into the mix design of 3DPCMs to improve the structural performance. The fibers can be mixed with other raw ingredients and pumped to the nozzle for printing. Mechanical tests show that the introduction of glass fibers can effectively improve the flexural and compressive strength of the material while reducing flexural deflection (Hambach and Volkmer 2017, Panda et al. 2017c). Alignment of fibers to the printing direction has been observed in the printed samples (Hambach and Volkmer 2017), which can further improve the structural performance.

Soltan and Li have developed a self-reinforced cementitious composite for 3D printing by introducing short dispersed Polyvinyl Alcohol (PVA) fiber of 2% volume fraction (Soltan and Li 2018). Due to the fiber alignment effect in 3D printing, printed coupons showed better mechanical properties compared with conventional cast ones. It is noteworthy that the printed coupons can reach nearly 3% tensile capacity, which is around 300 times that of conventional concrete materials (Li 2003). Hence, the study further proves the effectiveness of this fiber reinforcing method in 3D printing.

A recently developed method is to entrain reinforcement while printing, which is shown in Fig. 2.16. The reinforcement can be cable wire or chain, which is entrained in each printed concrete layer (Bos et al. 2017). Compared with the aforementioned methods, adoption of reinforcement entraining while printing reduces the total manufacturing time of reinforced structures. Pullout experiments show that the inserted cable wire has certain adhesive bonding with the matrix, although the ultimate pullout stress is lower compared with the inserted cables in casted samples (see Fig. 2.17).

Fig. 2.16 Reinforcement entraining while printing (Bos et al. 2017). Reproduced with permission from MDPI

Fig. 2.17 Ultimate pullout stress for casted and 3D printed concrete specimens (Bos et al. 2017). Reproduced with permission from MDPI

Bos et al. conducted four-point bending tests to assess the mechanical performance of cable wire reinforced 3D printed filaments (Bos et al. 2017, Bos et al. 2018). Good post-cracking behaviours were observed in the cable wire reinforced filaments, including additional cracks and increased displacements under loading. Thus, the feasibility of this cable wire reinforcing method has been clarified. However, cable wires were placed in filaments parallel to the printing direction, which cannot penetrate the layer interface to strengthen interlayer bonding. Furthermore, large variation and limited post-cracking

moment capacity due to slip of the wire and scatter of quality in printed filament were recorded. These issues need further exploration for the application of this method in 3D printing.

2.3 Previous Studies on Sprayable Cementitious Materials

2.3.1 Introduction

Sprayable cementitious materials, or referred to as shotcrete, can be pumped through the hose and pneumatically sprayed onto the substrate with the injection of compressed air (Neville 2011). The sprayed material can adhere to the substrate and build up to form the structure. Depending on sequence of water addition, sprayable cementitious materials can be classified into dry-mix and wet-mix (ACI Committee 506 2005). Water is added at the nozzle in dry-mix, while in wet-mix the water is added from the beginning and mixed with other ingredients. Generally, wet-mix provides more robust spray quality with less rebound of the sprayed material (Neville 2011) and has been more intensively studied compared with dry-mix.

Compared with traditional casting, spray of cementitious materials has many advantages. Firstly, it reduces the need for formwork. With good adherence to the substrate and its build-up characteristic, the sprayable cementitious material only requires a suitable substrate for it to be attached. There are many choices of substrates, e.g. surrounding rocks (Luo et al. 2017), old concrete structure (Garlock et al. 2012, Gao et al. 2018), 3D printed Acrylonitrile Butadiene Styrene (ABS) skeleton (Busta 2015). In these cases, composite structures are created without the use of traditional formwork. Secondly, the build-up characteristic of sprayed cementitious material makes it suitable for inclined, vertical or even overhead engineering applications (Kim et al. 2003, Zhang and Li 2015). In this regard, the ‘buildability’ characteristic of sprayable cementitious material provides the foundation for spray-based 3D concrete printing.

This section provides a performance-oriented review of wet-mix sprayable cementitious materials. As the rheological effects of raw ingredients have been reviewed in *Section 2.2*, the section only discusses how the rheological properties relate to the delivery and

deposition process. On the other hand, experimental studies about fresh properties of sprayable cementitious materials are introduced as the supplementary information. Finally, the dimensional accuracy and material distribution issues are discussed. On this basis, limitations of current research of sprayable cementitious materials are presented.

2.3.2 Performance of Sprayable Cementitious Materials

Similar to extrusion-based 3D printing, the spray of cementitious materials can be divided into delivery and deposition phases. In the delivery phase, the fresh mixture is loaded and pumped through the hose to spray nozzle. In the deposition phase, the material exits the nozzle and is sprayed onto the substrate at high projection speed with injected compressed air. For a successful design of high-performance sprayable cementitious material, the material performance in both delivery and deposition phases should be carefully considered.

2.3.2.1 Theoretical analysis of delivery performance

The sprayable cementitious materials should possess good pumpability in the delivery phase. Sprayable cementitious materials share similar requirements as 3D printable cementitious materials in the delivery stage (Lu et al. 2019a). As mentioned in *Section 2.2.5*, low plastic viscosity and low dynamic yield stress contribute to low pumping pressure. On the other hand, extremely low plastic viscosity/dynamic yield stress may induce bleeding under the pumping pressure and finally lead to blockage in the hose. The pumping pressure P of sprayable cementitious materials can be calculated by Eq.(2.4) and (2.5), or simplified equation as follows (Chhabra and Richardson 2008):

$$P = \left(\frac{8\tau_0}{3R} + \frac{8k}{\pi R^4} Q \right) L \quad (2.14)$$

where R and L are the inner radius and length of the hose; Q is the volumetric flow rate; τ_0 and k are dynamic yield stress and plastic viscosity, respectively.

Considering lubricating layer, the flow of the material inside the hose can be modelled as friction flow and hybrid flow (friction + viscous flow) depending on the flow rate

(Browne and Bamforth 1977, Jolin et al. 2009), as shown in Fig. 2.18. When the material is pumped at low flow rate (friction flow), the bulk material around the central of pipe remains undeformed. This portion is referred to as block zone. The velocity of pumped material increases from zero (near wall) to the maximum (near block zone) in the friction zone. On the other hand, when the material is pumped at high flow rate, shear zone appears between the friction zone and block zone.

Fig. 2.18 Flow of the material inside the hose (Jolin et al. 2009): (a) friction flow; (b) hybrid flow (friction + viscous flow). Reproduced with permission from the corresponding author of Ref. (Jolin et al. 2009)

Kaplan derived the binary linear expression of pumping pressure as a function of total resultant flow to describe the two cases (Kaplan 2000), namely:

$$P = \begin{cases} \frac{2L}{R} \left[\tau_{0i} + \frac{Q}{3600\pi R^2 c_r} k_i \right], & Q \leq \frac{3600\pi R^2 c_r}{k_i} \left(\frac{4}{3} \tau_0 - \tau_{0i} \right) \\ \frac{2L}{R} \left[\tau_{0i} + \frac{\frac{Q}{3600\pi R^2 c_r} - \frac{R}{4k} \tau_{0i} + \frac{R}{3k} \tau_0}{1 + \frac{R}{4k} k_i} k_i \right], & Q > \frac{3600\pi R^2 c_r}{k_i} \left(\frac{4}{3} \tau_0 - \tau_{0i} \right) \end{cases} \quad (2.15)$$

where τ_{0i} and k_i represent yield stress and plastic viscosity at the interface (lubricating layer), τ_0 and k are yield stress and plastic viscosity of bulk material respectively. c_r is filling coefficient. L and R are the length and diameter of the hose respectively. P is pumping pressure and Q is the average flow rate. The equation describing the first stage is valid only when $P \geq 2L\tau_{0i}/R$, i.e. applied shear stress is larger than yield stress of the lubricating material. From Eq.(2.15), it is clear that low plastic viscosity and yield stress contribute to low pumping pressure, thus making it easier to pump the concrete materials.

2.3.2.2 Theoretical analysis of deposition performance

The deposition of sprayable cementitious materials is comprised of material adhesion to the substrate and subsequent build-up of the sprayed material. Adherence, which measures the tackiness of sprayed material to the substrate (Kawashima 2013), is considered to relate with surface of substrate and rheological properties of the material (Kaci et al. 2011). Lack of adherence may lead to the peeling off of the sprayed material from the substrate in the spray process, resulting in adhesive failure (Austin et al. 2005). It may be improved by rougher surface of substrate. However, adequate material adhesion to substrate alone cannot guarantee the build-up characteristics. Lack of “buildability” to build up results in cohesive failure, where the sprayed material slides downward on the substrate (Austin et al. 2005). The build-up of the sprayed material is believed to closely related with static yield stress, as described in the following paragraphs.

In the theoretical analysis of deposition performance of sprayable cementitious materials, Beaupre proposed a simplified model (Beaupre 1994). In this model, gravity

of the sprayed material induced the shear inside the material and tendency of material flowing downwards on the vertical substrate. The shear force is balanced by the cohesive force generated by static yield stress. Based on static equilibrium, Eq.(2.16) is derived as below:

$$H = \frac{1}{\rho g_0} \tau_s \quad (2.16)$$

where H is the maximum build-up thickness, ρ is fresh density of the sprayed material, g_0 is gravitational acceleration and τ_s is static yield stress. It should be noted that this simplified model assumes uniform distribution of sprayed filaments. However, as observed in the engineering practice, the material distribution of spray concrete is not uniform (ACI Committee 506 2005). For sprayed structure with non-uniform distribution, the theoretical maximum build-up thickness should be expressed as Eq.(2.17):

$$H = \frac{\alpha_{geom}}{\rho g_0} \tau_s \quad (2.17)$$

where α_{geom} is geometric coefficient which relates to the material distribution of sprayed profile. Based on Eq.(2.16) and Eq.(2.17), it is clear that static yield stress positively contribute to build-up thickness. In addition, decreasing the fresh density of the material is also valued for increasing the build-up thickness.

2.3.2.3 Experimental research studies on delivery and deposition performances

Experimental studies on correlation between rheological parameters and pressure loss in the pumping have been conducted by Feys et al. (Feys et al. 2013, Feys et al. 2016). In the experiments, the pressure and flow rate at different locations of long pumping circuit were continuously monitored, as shown in Fig. 2.19. On the other hand, the rheological properties were measured by ICAR rheometer. Several mixtures were tested in the research studies, including conventional vibrated concrete (CVC) and self-consolidating concrete (SCC).

Lay-out of circuit:

- 1 = pump
 - 2, 9 = reducer
 - 3-7 = horizontal straight section, 100 mm pipes
 - 11-15 = horizontal straight section, 125 mm pipes
 - 8 = 90° elbow, 100 mm
 - 10 = 90° elbow, 125 mm
 - 16-20 = inclined part of the loop
- Sections 3, 7, 11 and 15 are equipped with pressure sensors and strain gauges

Fig. 2.19 Layout of pumping circuit in the experiments (Feys et al. 2016). Reproduced with permission © Elsevier

The experiment results show good consistency with the theoretical analysis in previous *Section 2.3.2.1*. The measured pressure loss has positive linear relationship with plastic viscosity (see Fig. 2.20). In addition, the measured pressure loss has positive linear relationship with dynamic yield stress for CVC. Other types of concrete shows general positive relationship without clear indication of linearity. Similar conclusions have been drawn by Feys et al. in another research study (Feys et al. 2013), where the positive synergetic influence of viscosity and volumetric flow rate on pressure loss can be clearly observed (see Fig. 2.21).

Fig. 2.20 Relationship between pressure loss and rheological parameters: (a) plastic viscosity vs. pressure loss; (b) yield stress vs. pressure loss (Feys et al. 2016).
Reproduced with permission © Elsevier

Fig. 2.21 Relationship between pressure loss, viscosity and volumetric flow rate (Feys et al. 2013). Reproduced with permission from Springer Nature

Yun et al. proposed “shootability” to describe the deposition performance of sprayable cementitious materials (Yun et al. 2015a). Material with good shootability has the following characteristics: a) good adhesion to substrate; b) large build-up thickness; c) small rebound in the spray process. Build-up thickness and rebound rate have been examined and correlated with rheological parameters, as can be seen from Fig. 2.22 and Fig. 2.23. Torque viscosity and flow resistance in the figures can be converted to plastic viscosity and dynamic yield stress, as mentioned in Section 2.2.4.

Fig. 2.22 Relationship between build-up thickness and (a) torque viscosity; (b) flow resistance (Yun et al. 2015a). Reproduced with permission © Elsevier

Fig. 2.23 Relationship between rebound rate and (a) torque viscosity; (b) flow resistance (Yun et al. 2015a). Reproducde with permission © Elsevier

Weak correlations were observed in Fig. 2.22 and Fig. 2.23. It can be found that there was no consistent relationship between build-up thickness and plastic viscosity for all the mixtures. The mixtures without fibers showed positive relationship between build-up thickness and flow resistance (dynamic yield stress) while the mixtures with fibers did not have consistent trend. On the other hand, both plastic viscosity and dynamic yield stress had weak correlations with rebound rate. However, as the authors did not examine static yield stress, there was no observation about the relationship between build-up thickness/rebound rate and static yield stress. From Eq.(2.16) and Eq.(2.17), positive correlation between build-up thickness and static yield stress is expected and hence it is necessary to examine this aspect.

Yun et al. also pointed out the negative relationship between rebound rate and build-up thickness (Yun et al. 2015a). As shown in Fig. 2.24, with the increase of build-up thickness less rebound was observed. It indicates that the measures to increase the build-up thickness of sprayable cementitious materials are also beneficial for the reduction of rebound, which further improves the quality of sprayed profile.

Fig. 2.24 Relationship between rebound rate and build-up thickness (Yun et al. 2015a). Reproduced with permission © Elsevier

Researchers have explored effects of raw ingredients on the delivery and deposition performances of sprayable cementitious materials. Yun et al. reported that the addition of air-entraining agent and silica fume improves delivery performance and increases build-up thickness, while the addition of polymeric ingredient and viscosity enhancement agent has adverse effects (Yun et al. 2015a, Yun et al. 2015b). Accelerating agent and synthetic fibers were found to increase build-up thickness (Beaupre 1994, Yun et al. 2015a, Yun et al. 2015b). The observations in the experiments can be well explained by rheological effects of raw ingredients in *Section 2.2.4* and theoretical analysis of delivery and deposition performances in *Sections 2.3.2.1* and *2.3.2.2*.

Addition of air-entraining agent can be beneficial to both delivery and deposition phases. It can lead to the decrease of rheological parameters (Banfill 1994, Yun et al. 2015b), which is beneficial to reducing pumping pressure and thus contribute to better delivery performance. Addition of air-entraining agent increases the air content in fresh concrete and lead to higher compressibility. Due to the compaction in the delivery phase, the air content is greatly reduced after the material is sprayed (Beaupre 1994, Jolin and Beaupre 2003). The reduction of air content leads to the increase of yield stress and thus contribute to larger build-up thickness.

2.3.3 Dimensional Accuracy and Material Distribution

2.3.3.1 Dimensional accuracy

Due to the high-speed projection and rebound of the sprayed material, natural finish of sprayed structure typically has low dimensional accuracy (ACI Committee 506 2005). The sprayed material has a non-uniform thickness distribution, where labour-intensive post-processing needs to be carried out, e.g. manual scraping and screeding (see Fig. 2.25). In addition, the quality of the sprayed profile is highly dependent on the skills of the nozzleman. Overspray may happen at the corner, which leads to sagging of the sprayed material and creates weakness in the structure. The sprayable cementitious material could have large rebound if sprayed in a wrong orientation (ACI Committee 506 2005) (see Fig. 2.26). Therefore, it is extremely difficult to leave a profile with high dimensional accuracy if proper post-processing is not applied.

Fig. 2.25 Manual scraping and screeding for the sprayed wall (ACI Committee 506 2005). Reproduced with permission © American Concrete Institute

Fig. 2.26 Comparison of rebound for different spray nozzle orientations (ACI Committee 506 2005). Reproduced with permission © American Concrete Institute

2.3.3.2 Material distribution

There is limited study on material distribution of sprayed cementitious materials, as labour-intensive post-processing can lead to desired distribution. To facilitate the application of spray-based 3D printing, it is necessary to understand material distribution of sprayed profile to achieve desired distribution and good quality control. However, many literature studies adopt qualitative terminologies (e.g. surface finish, splash) to describe the material distribution (ACI Committee 506 2005, Neville 2011). Another common practice is to compare maximum build-up thickness of the sprayed profile with different materials (Beaupre 1994, Jolin and Beaupre 2003, Yun et al. 2015a). The drawback of this approach is that the maximum build-up thickness does not reflect the material distribution, e.g. the build-up thickness of each point on spray substrate.

Ginouse and Jolin investigated the mechanism of placement in sprayed concrete (Ginouse and Jolin 2015, Ginouse and Jolin 2016). Their experiment setup is shown in Fig. 2.27. The horizontal spray nozzle was placed at a specified distance from the vertical substrate. A load cell was connected to the suspended substrate for measuring the placement rate of sprayed concrete. After the spray process, small tubes were placed and penetrated the sprayed profile to obtain the local build-up thickness (see Fig. 2.28). Based on this result, the build-up thickness distribution was quantitatively depicted. An empirical model was proposed thereafter.

Fig. 2.27 Experiment setup to investigate the mechanism of placement in sprayed concrete (Ginouse and Jolin 2016). Reproduced with permission © Elsevier

Fig. 2.28 Sampling in determining the build-up thickness distribution (Ginouse and Jolin 2016). Reproduced with permission © Elsevier

Ginouse and Jolin proposed a second-order Gaussian distribution model to describe the build-up thickness distribution of sprayed concrete (Ginouse and Jolin 2016), as shown in Eq.(2.18) and Eq.(2.19):

$$F(\eta) = a_1 \cdot e^{-\frac{(\eta-a_2)}{a_3}} + b_1 \cdot e^{-\frac{(\eta-b_2)}{b_3}} \quad (2.18)$$

$$j_p(x, r) = \begin{cases} j_{\max}(x) \cdot F\left(\frac{r}{r_{\max}(x)}\right) & \text{for } 0 \leq r \leq r_{\max}(x) \\ 0 & \text{for } r > r_{\max}(x) \end{cases} \quad (2.19)$$

where a_1, a_2, a_3, b_1, b_2 and b_3 are coefficient by fitting in Eq.(2.18); $j_p(x, r)$ is the mass flux density and $j_{\max}(x)$ is the maximum mass flux density; r is the radius from the central of sprayed profile. The constructed build-up thickness distribution is shown in Fig. 2.29. It was noticed that the material distribution in sprayed concrete is far from uniform distribution: most of the material were found near the central of spray nozzle, and sprayed range is quite large compared with the diameter of spray nozzle (32 mm).

Fig. 2.29 Build-up thickness distribution in sprayed concrete (Ginouse and Jolin 2016): (a) 3D contour; (b) plots on substrate plane. Reproduced with permission © Elsevier

However, it should be noted that there are some limitations to their work. Firstly, the nozzle is fixed during spray process, and nozzle is placed far away from the substrate (0.5 m/1.0 m). The material distribution could be greatly influenced by the movement of spray nozzle and decrease of distance between nozzle and substrate. It calls for a construction of a new model to describe and predict the material distribution in spray-based 3D printing. Secondly, the proposed model does not involve the inputs of spray parameters such as pumping rate. It limits the proposed model to a description of the process only and cannot be practically utilized for prediction of the material distribution in sprayed concrete. Furthermore, Ginouse and Jolin mentioned that the flatter portion appears near the central of sprayed profile in some cases (Ginouse and Jolin 2016). It may be linked with the rheological properties of the material. Rheological tailoring is

proposed for the material design, and a more uniform material distribution could be realized for spray-based 3D printing.

2.4 Discussions and Research Gaps

2.4.1 Discussions

As revealed in *Sections 2.2* and *2.3*, the spray technology shares many similarities with 3D printing of cementitious materials. Spray of cementitious materials could be divided into delivery and deposition phases. In the delivery phase, the material needs to be pumped to the spray nozzle and entangled with injected compressed air to spray. In the deposition phase, newly sprayed material additively builds on substrate to reach desired build-up thickness. Similarly, 3D printing process also consists of delivery and deposition phases. In the delivery phase, cementitious material is pumped to printing nozzle through the hose. In the deposition phase, the cementitious material is deposited layer-by-layer with the controlled movement of printing nozzle (Khoshnevis 2004, Lim et al. 2012, Jeffrey 2014, Gosselin et al. 2016). These similarities indicate the feasibility of spray-based 3D printing, which could further improve the degree of automation in in-situ vertical and overhead construction.

On the other hand, target applications of conventional spray technology and spray-based 3D printing are different. Conventional spray technology is usually applied in rock strengthening (Luo et al. 2017), repair of concrete structures (Garlock et al. 2012, Gao et al. 2018), tunnel linings (Hu et al. 2018), etc. In these applications, requirement on dimensional accuracy is low and coarse aggregates may be incorporated in the mixture design (ACI Committee 506 2005). In contrast, spray-based 3D printing targets at in-situ automated construction of decorative vertical/overhead structure. Due to size limitation of the delivery system in spray-based 3D printing, coarse aggregate may not be used in the mixture design.

Unlike conventional spray technology, spray-based 3D printing puts a high requirement on dimensional accuracy of sprayed profile. Conventional sprayable cementitious materials have non-uniform distribution after being sprayed on the substrate, and build-

up thickness varies greatly at different locations (ACI Committee 506 2005). As a result, the cross sections of the sprayed structure are irregular. Necessary post-processing such as manual scraping is required for rectification (ACI Committee 506 2005), which greatly increases labour costs and construction time. The low dimensional accuracy issue limits the application of this technique in the construction of vertical decorative structure, where high precision is crucial and becomes the target application of this study.

In spray-based 3D printing, the accuracy issue of spray may be solved by feedback-oriented adaptive control algorithm (Lindemann et al. 2018) and material development. After the material is sprayed, the information of material distribution is detected by sensors to construct the real-time profile. It can then be compared with the designed profile to calculate the location and amount of additional material required. Afterwards, the information is passed back to the controller to adjust printing parameters such as robotic arm movement. In addition to feedback control, developing suitable cementitious material for spray-based 3D printing is also an option, which motivates the research of this study. Compared with the advanced control solution which requires sophisticated sensors and feedback control system, material-based approach may provide an alternative and cost-effective solution. With improved accuracy, it is possible to utilize spray to build decorative structure without post-processing, as can be seen in Fig. 2.30.

Fig. 2.30 NTU logo manufactured by overhead spray-based 3D printing

2.4.2 Research Gaps

With a close review of literature described in *Sections 2.2* and *2.3*, the limitations in the previous research on 3D printable and sprayable cementitious materials were identified. The research gaps are summarized in four points below and they serve as a guide to the research in this study:

1. Lack of suitable mixtures for spray-based 3D concrete printing. Current extrusion-based 3D concrete printing and corresponding materials cannot be directly adopted for the in-situ vertical/overhead engineering applications.
2. Limited research on material optimization for both delivery and deposition performance. The rheological requirements in the delivery and deposition phases could be contradictory to one another, and an evaluation should be carried to select the material with overall best performance.
3. Lack of quantitative methods to describe the cementitious material distribution in spray-based 3D printing. Most of the research studies about sprayable cementitious materials adopt qualitative approaches. The existing empirical models may not be applicable to the spray-based 3D printing of cementitious materials.
4. Limited research on the correlation between printing parameters and material distribution in spray-based 3D printing. It is necessary to quantify their relation so that the prediction of material distribution can be possible in spray-based 3D printing.

Chapter 3 Research Methodology

3.1 Introduction

This chapter describes the key methodology adopted in this research study. As mentioned in Scope of the Study (*Section 1.4*), the study focuses on the mixture design and printing process of spray-based 3D printable cementitious materials. In other words, the fresh stage of the materials was investigated. To complete the research tasks, certain research strategies/methodology were adopted, which are introduced in the following sections.

3.2 Experiment Setup

3.2.1 Rheological Tests

Through the literature review in *Sections 2.2* and *2.3*, rheological requirements for 3D printable cementitious materials and sprayable cementitious materials are specified. Hence, the designed mixtures for spray-based 3D concrete printing should satisfy these requirements in delivery and deposition phases. Hence, rheological experiments and analysis are necessary in the material development. The results of rheological experiments, i.e. plastic viscosity, dynamic and static yield stress can be further utilized for assessments of pumpability in the delivery phase and buildability in the deposition phase. Statistical methods may be applied to select the desired material.

Measurement of rheological properties in this study were conducted using the Anton Paar Modular Compact Rheometer 102 (MCR 102). A four-blade stirrer probe with a diameter of 30 mm and a height of 40 mm was used. The construction cell has a diameter of 70 mm. In the rheological experiments, the stirrer probe rotates as per testing protocol (rotational speed vs. time), while the construction cell was mounted stationarily. Sensors in the stirrer probe records the shearing torque during the test, which can be further processed to get the rheological parameters. Three replicates were carried out to obtain the average values and standard deviations of rheological parameters.

The classical testing protocol for rheological measurement is shown in Fig. 3.1 (Austin et al. 1999, Weng et al. 2018c), which is comprised of a ramp linear increasing curve followed by a ramp linear decreasing curve. It has been adopted by a number of researchers to investigate the rheological properties of 3D printable cementitious materials (Weng et al. 2018b, Weng et al. 2018c, Zhang et al. 2018b).

*Fig. 3.1 Classical testing protocol for rheological measurement(Weng et al. 2018c).
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Fig. 3.2 shows the typical response curves of cementitious materials corresponding to the classical testing protocol. In the first stage where the rotational speed increases, the response curve shows an initial increase, followed by a gradual decrease. This represents the break-down of microstructure, and the shear stress at peak point is corresponding to static torque (which can be converted to static yield stress). In the second stage where the rotational speed decreases, the response curve shows a linear decrease which can be fitted with Bingham model. The gradient of the fitting line is torque viscosity (which can be converted to plastic viscosity), while the intercept on y-axis is corresponding to dynamic yield stress (which can be converted to dynamic yield stress) (Austin et al. 1999).

However, through laboratory experiments, it is found that the repeatability of the ramp linear protocol is poor. The measured rheological properties have large variations. It can be explained in the following two aspects. Firstly, the classical testing protocols does

not contain horizontal stages for the cementitious material to reach shear equilibrium mentioned in *Section 2.2.4*. At each datapoint, the measured shear stress is higher than the actual shear stress of equilibrium. On the other hand, the residue stress caused by the previous shearing in the cementitious material has great influence on rheological tests (Qian 2017). Hence, the calculated rheological parameters with the classical testing protocols are not accurate.

Fig. 3.2 Response of classical testing protocol for rheological measurement (Weng et al. 2018b). Reproduced with permission © Elsevier

To improve the accuracy and repeatability of rheological tests, step-down shearing protocol and quasi-static shearing protocol have been proposed (Qian 2017). Corresponding figures can be referred to in Fig. 3.3 (Lu et al. 2019a). Both testing protocols contain the high-rate pre-shear to break the microstructure and eliminate the residual stress. Constant shear rate at each step allows for the material to achieve equilibrium. Hence, the step-down protocol gives more accurate shear stress-shear rate relationship to extract plastic viscosity and dynamic yield stress (Qian and De Schutter 2018b, Qian et al. 2018). On the other hand, very low rotational speed in quasi-static shearing protocol makes it more accurate to acquire the static yield stress (Mahaut et al. 2008). Therefore, the revised testing protocols for rheological measurement were adopted in this study.

Fig. 3.3 Advanced testing protocols for rheological measurement (Lu et al. 2019a): (a) step-down shearing protocol; (b) quasi-static shearing protocol. Reproduced with permission © Elsevier

The detailed procedure of rheological test is described as follows. After material preparation, the fresh material was poured into the construction cell. Before each test, the material was hand tampered for 1 minute using a small whisk. Then the stirrer probe was quickly put in position and lowered to the designated position. As shown in Fig. 3.3, after pre-shearing at 600 rpm for 240 s and resting for 60 s, either stepping down from 600, 500, 400, 300, 200 to 100 rpm for 60 s each or maintaining constant angular velocity at 0.1 rpm for 600 s was applied. The torque was recorded at 4 data points per second.

Using the revised testing protocols, the equilibrium flow curve was thus obtained as the equilibrium torque vs. angular velocity. The equilibrium torque and angular velocity are commonly transferred to shear stress and shear rate respectively. In this study, the Reiner-Riwlin equations for flow of Bingham materials (Reiner 1949) were adopted to obtain the equilibrium shear stresses and shear rates of cementitious materials. Hence, plastic viscosity and dynamic/static yield stress can be calculated.

3.2.2 Spray-based 3D Printing

As mentioned in *Section 2.2*, spray performance of cementitious materials could be greatly affected by printing parameters, e.g. the distance between the nozzle and substrate. Hence, it is critical to keep constant printing parameters to exclude their influence in the material development. On the other hand, these printing parameters need to be controlled at designated values for process investigation of spray-based 3D printing. Furthermore, with the programmed control of nozzle traveling path is essential for 3D printing. Hence, a lab-scale spray-based 3D printing system was constructed for the research study and demonstration.

Fig. 3.4 illustrates the constituents and lab setup of spray-based 3D printing system, respectively. The lab-scale spray-based 3D printing system consists of pump, hose, spray nozzle, compressed air system, robotic arm and substrate. In the material development, the pumping rate was set as 900 rpm unless otherwise stated (corresponding volumetric flow rate: 3.78 L/min). The spray nozzle was mounted to the end of the robotic arm and connected to the pump through a hose (inner radius: 0.0127 m (0.5 inch), length: 2.5 m). The compressed air system was connected to the spray nozzle by a connecting vessel, and the air inject pressure could be adjusted by the valve. The substrate was installed on a movable framework. Before each spray-based 3D printing, the distance between the nozzle and substrate is adjusted to the desired value. After which, the framework is locked to prevent any movement. The material is delivered from the pump to the spray nozzle and sprayed onto the substrate with injected air. At the same time, the robotic arm moves as per the pre-set printing path. The profile

is hence printed through the layer-by-layer spray deposition. Fig. 3.5 shows an example of profile spray-printing (tai-chi pattern).

Fig. 3.4 Spray-based 3D printing system: (a) constituents; (b) laboratory setup

Fig. 3.5 Profile spray-printing: Tai-chi pattern

The printing quality of spray-based 3D printing can be demonstrated by its material distribution through spray test. Due to gravity load, the sprayed material may peel off from the substrate, or have severe offset to the downside flow of the material. In addition, the sprayed material may be blown away from the centre by inject pressure. Thus, non-uniform material distribution may occur. This non-uniform material distribution can

result in inaccuracy in the build-up direction, especially in multiple-layer spray. Hence, assessment of material distribution should be applied, after which the distribution can be quantitatively described and predicted.

3.2.3 Supplementary Experiments

Supplementary experiments were conducted for initial selection of mixtures in this research study. These experiments were mainly correlated with assessments of fresh density, workability and hydration characteristics of the designed mixtures. The setup of all the supplementary experiments in this research study was introduced in the following subsections.

3.2.3.1 Assessment of fresh density

As the material needs to resist the gravity-induced shear when sprayed on vertical walls or ceilings, it is critical to assess the fresh density. The fresh density will also be utilized to calculate the critical ratio introduced in *Section 3.3.1*. After material preparation, the fresh mixtures were filled into cubic moulds and weighed immediately. The fresh density values were calculated based on the measured weights and the volume of cubic moulds. For each mixture, three samples were assessed to obtain the average value and standard deviation of fresh density.

3.2.3.2 Flow table test

Flow table test is a frequently used method to intuitively assess the workability of extrusion-based 3D printable cementitious materials, which can be characterised by slump and flow diameter of the material (Paul et al. 2018, Zhang et al. 2018b). The flow table test was carried according to ASTM C 1437 (ASTM 2001). The fresh mixture was filled in the mini-slump cone, and the cone was quickly lifted to measure the slump of the mixture. Then the mixture was struck for 25 times to measure the flow diameter. Slump and flow diameter were measured every 15 minutes in an hour to track the time dependency of workability. Each test was repeated three times, based on which the average values and standard deviations of slump and flow diameter were calculated.

3.2.3.3 Vicat test

Setting behaviour of the mixtures were measured by an automated Vicat testing apparatus (H-3052.4F, Humboldt). The penetration depth of needle was monitored every 20 min and the resulting penetration depth versus time diagram was used to determine the setting behaviour of each mixture. In addition, the penetration depth of needle with time reflects the evolution of workability in different mixtures.

3.2.3.4 Fourier-Transform Infrared (FTIR) spectroscopy test

A ThermoFisher Scientific Nicolet iS50 spectrometer with a built-in attenuated total reflection (ATR) model was applied to collect the FTIR spectra of the fresh mixtures and the hardened samples. The FTIR spectra were collected with quick scanning for 64 times to achieve good resolution. To reveal possible chemical activation at very early age, FTIR spectra of the fresh mixtures were examined. Upon completion of mixing, the fresh mixture was stored in a covered container to prevent water evaporation. Random sampling of fresh mixture was made at regular intervals (i.e., every 20 min and up to 120 min from the addition of water) for FTIR test. The fresh sample was placed on the centre of the diamond ATR sampling station, and then pressed by a constant force of 267 N to ensure tight contact with the station. FTIR spectra of 28-d hardened samples were also collected. After mixing, the fresh mixture was cast into cubic molds and air-cured for 28 d in the lab environment (22.5°C, 58 RH%). The cubic specimen was then ground into powder. The powder was then randomly sampled and placed on the centre of the ATR sampling station. Similarly, a constant force of 267 N was applied to ensure tight contact between the sample and the station.

Vicat test and FTIR test were conducted in the development of MgO-slag mixtures for spray-based 3D printing (*Chapter 5*). It is due to the hydration difference between MgO-activated slag mixture and cement-based mixture. The hydration of slag is very slow due to the presence of impervious layers of amorphous silica and alumina that form around slag particles in the early hydration (Escalante-García et al. 2003). Compared with conventional alkali activator such as NaOH and KOH, the alkalinity of MgO is relatively weaker. In this case, it is essential to assess setting and hydration to decide

the optimal ratio of MgO to slag in the MgO-activated slag mixture for successful printing.

3.3 Evaluation Methods

3.3.1 Delivery and Deposition Performances

The information of dynamic yield stress and plastic viscosity could be further utilized to predict the pumping pressure in the delivery phase of spray-based 3D printing. Small pumping pressure indicates that the material is easier to be delivered. In contrast, large predicted pumping pressure indicates the requirement of more powerful pumping equipment and the printed profile may have discontinuities. With the constant flow of material in the hose, there exists pressure drop due to the internal friction and the friction between the material and the wall of hose. The relationship between pumping pressure P (Pa), inner radius of the hose R (m), length of the hose L (m) and volumetric flow rate Q (m³/s) could be described as following Eq.(3.1) (Chhabra and Richardson 2008):

$$P = \left(\frac{8\tau_0}{3R} + \frac{8k}{\pi R^4} Q \right) L \quad (3.1)$$

When pumping the material at constant flow rate Q , either increasing dynamic yield stress τ_0 or increasing plastic viscosity k leads to higher pumping pressure, which is not desirable from the viewpoint of printing operation.

Based on Eq.(3.1), the pumping pressure for different mixtures can be calculated to reflect their respective pumpability. In the material development (*Chapters 4 and 5*), the calculation has been carried out with the following parameters: $R = 0.0127$ m (0.5 inch); $L = 2.5$ m; $Q = 3.78$ L/min (corresponding to pumping rate of 900 rpm). All these parameters have been adopted in the evaluation of spray-based 3D printing performance. With all the coefficient calculated, Eq.(3.1) can be expressed as:

$$P = 0.00525\tau_0 + 0.15417k \quad (3.2)$$

where P , τ_0 and k are in the unit of bar, Pa and Pa·s, respectively.

As mentioned in *Sections 2.2* and *2.3*, static yield stress contributes to the buildability of deposited material. The maximum build-up thickness H (m) of extruded or sprayed material (assuming enough material adherence to the substrate) is found to have linear relationship with critical ratio C_r (the ratio of static yield stress τ_s (Pa) to the product of fresh density ρ (kg/m³) and gravitational acceleration g_0 (m/s²)) (Beaupre 1994, Khoshnevis et al. 2015), i.e.:

$$H \propto C_r = \frac{\tau_s}{\rho g_0} \quad (3.3)$$

Eq.(3.3) illustrates that the material with higher static yield stress and lower fresh density has higher maximum build-up thickness, indicating more layers could be printed and thus better buildability. Hence, in case of extrusion-based 3D printable cementitious materials, it is necessary to improve the critical ratio. In comparison, while it is also necessary to achieve high maximum build-up thickness in spray-based 3D printing, the material distribution after deposition is more important. However, there is limited study on the relation between the distribution of sprayed material and rheological properties (Beaupre 1994, Lu et al. 2018). As the material distribution focuses on the build-up thickness values over the spray range, it is reasonable to examine the critical ratio. It is inferred that material with the large critical ratio may have more uniform build-up thickness distribution and more regular cross section, as the sprayed material with higher buildability could better resist gravity-induced shear and does not influence the adjacent region.

3.3.2 Build-up Thickness Distribution

In this research study, the build-up thickness distribution in spray-based 3D printing has been quantitatively assessed. It includes an optical acquisition of cross sections of the sprayed filaments and the subsequent processing to extract corresponding morphology. Further analysis based on the extracted morphology has been conducted afterwards.

After sprayed filaments get enough strength, they will be scraped from the substrate and cut to expose the cross section. Then the cross section will be dyed to increase the

contrast in image processing to guarantee accurate optical acquisition. The images of cross section were processed and analysed by MATLAB, of which details can be referred to in Lao et al. (Lao et al. 2017). Fig. 3.6 shows one example of original image, image by optical acquisition and constructed thickness distribution of the same cross section. The constructed numerical distribution can be utilized to evaluate build-up thickness distribution. Corresponding discussions are carried out in the following chapters.

Fig. 3.6 Images of a cross section: (a) original image; (b) image by optical acquisition; (c) constructed thickness distribution

3.3.3 Supplementary Evaluations

The supplementary evaluations were correlated with the aforementioned supplementary experiments in *Section 3.2.3*. The evaluations and corresponding analyses are illustrated in the results and discussions of the following chapters.

Chapter 4 Designing Spray-based 3D Printable Cementitious Material with Fly Ash Cenosphere and Air Entraining Agent

Content of this chapter has been published as (Lu, B. et al. 2019). B. Lu, Y. Qian, M. Li, Y. Weng, K.F. Leong, M.J. Tan, S. Qian, Designing spray-based 3D printable cementitious materials with fly ash cenosphere and air entraining agent, Construction and Building Materials, 211 (2019) 1073-1084. Permission has been granted by Elsevier to use the published paper in the thesis. Revisions have been made in the thesis.

4.1 Introduction

This chapter discusses the cement-based material solution for spray-based 3D printing. As sprayed material needs to resist gravity-induced shear to build up, reducing fresh density should be the direct way to improve the distribution of sprayed material. The reduction of material density could be achieved by the addition of air entraining agent (AEA), incorporation of lightweight aggregate or elimination of fine aggregate in the mixture (Neville 2011). Considering the size limitation of aggregates in 3D printing (Panda et al. 2017a), the elimination of fine aggregate to form no-fine concrete is not applicable. In this study, AEA and fly ash cenosphere (FAC) were introduced for density reduction. FAC is a hollow spherical lightweight aggregate, which could be sourced from fire power plants (Hanif et al. 2017a, Hanif et al. 2017b). FAC could effectively decrease the material density and was widely used as lightweight filler in the previous studies (Wang et al. 2014, Hanif et al. 2016, Hanif et al. 2017b).

The developed material also needs to meet the rheological requirements of delivery and deposition phases. Previous studies of 3D printing and spray have illustrated rheological requirement of delivery phase (Beaupre 1994, Weng et al. 2018b). However, there is limited study for deposition phase of spray. While there are some reports on the influence of rheology on maximum build-up thickness, very limited study is carried out to investigate the effect of rheological properties on material distribution. On the other hand, previous studies of rheological effect of AEA have conflicting results, and there

is limited study of rheological effects of FAC. Therefore, rheological assessment is necessary for the mixtures with AEA and FAC incorporation.

This study develops a suitable cementitious mixture for spray-based 3D printing with uniform material distribution. Firstly, the mixtures with different AEA and FAC incorporation were designed. Fresh density and rheological properties were assessed, followed by a selection of optimal mixture with the consideration of delivery and deposition requirements. Afterwards, spray tests were carried out to study the material distribution. Based on the material performance in delivery and deposition phase, a suitable mixture for spray-based 3D printing was proposed. The mechanism of uniform distribution was discussed through the analysis of material deposition process.

4.2 Material Preparation

Fig. 4.1 shows the scanning electron microscope (SEM) image of FAC, where the spherical shape and hollow structure can be clearly observed. The true density of FAC is 0.80 g/cm^3 . In the experiment design, silica sand was partially or fully substituted by FAC. As Table 4.1 shows, the substitution percentages were classified into three levels, i.e. 0, 50% and 100%. The AEA used in the study is EMAL-10N (Sodium lauryl sulphate), which is in powder form and fully soluble to water. Similarly, the dosage of AEA was classified into three levels, i.e. 0, 0.1 g/L and 0.2 g/L. The naming code is adopted in the following format: M-<FAC substitution percentage>-<dosage of AEA>, e.g. M-50%-0.1 refers to the mixture with 50% FAC substitution and 0.1 g/L AEA. Mix proportion of other ingredients was kept the same among all the mixtures. Particle size distribution of FAC, silica sand, cement, fly ash and silica fume can be found in Fig. 4.2. The superplasticizer used in this study was ADVA-181N from Grace Pte. Ltd.

Fig. 4.1 SEM image of fly ash cenosphere (FAC)

Fig. 4.2 Particle size distribution of FAC, silica sand, cement, fly ash and silica fume

Table 4.1 Mass proportion of mixtures

Mix	FA / C	SF / C	W / B	Agg. / B	Sp. / B	FAC / Agg.	AEA (g/L)
M-0-0						0%	0
M-50%-0						50%	0
M-100%-0						100%	0
M-0-0.1						0%	0.1
M-50%-0.1	0.50	0.05	0.40	0.29	0.35%	50%	0.1
M-100%-0.1						100%	0.1
M-0-0.2						0%	0.2
M-50%-0.2						50%	0.2
M-100%-0.2						100%	0.2

* Abbreviation: Agg.: aggregate (including silica sand and fly ash cenosphere); B: binder (including cement, fly ash, silica fume); FA: fly ash; C: cement; SF: silica fume; W: water; Sp.: superplasticizer; FAC: fly ash cenosphere; AEA: air entraining agent.

The material preparation process is illustrated as follows. Firstly, AEA is dissolved in the weighed water. All dry powder ingredients are mixed at low speed for 3 min. Then water (with AEA) is added and mixed at low speed for another 3 min. Superplasticizer is added afterwards, followed by the low-speed mixing for 1.5 min and high-speed mixing for 3 min. After completion of the aforementioned mixing process, the fresh material is ready for subsequent tests.

4.3 Assessment of Fresh Properties of Materials

4.3.1 Fresh Density

Fig. 4.3 shows the fresh density of designed mixtures. It could be found that the fresh density decreases with the increase in FAC substitution and dosage of AEA. The decreasing amounts are smaller when FAC substitution increases from 50% to 100%, or when the dosage of AEA rises from 0.1 g/L to 0.2 g/L. The significantly reduced

fresh density illustrates the effectiveness of introducing FAC and AEA. In this study, with the combined incorporation of FAC and AEA, the fresh density could be reduced up to 38.5%. Based on the fresh density results, air content in the different mixtures was calculated (see Fig. 4.4). Air content was significantly increased with more FAC or AEA dosages in the mixtures. However, abnormal point of M-100%-0.2 was observed, which may be due to efficiency issue of AEA in this mixture.

Fig. 4.3 Fresh density of designed mixtures (the error bars are too small to be displayed)

Fig. 4.4 Air content of designed mixtures (the error bars are too small to be displayed)

4.3.2 Workability

The results of slump can be referred to in Fig. 4.5 and Fig. 4.6, while the results of flow diameter are shown in Fig. 4.7 and Fig. 4.8. It is revealed that the introduction of FAC and AEA leads to low slump values and spread diameter of fresh cementitious materials. This suggests the material could have better ability to retain the deposited shape (Hoornahad 2014) and hence possibly contributes to more uniform distribution of sprayed profile. However, the reduced slump values and spread diameter could also lead to poor pumpability of delivery (Neville 2011). The conflict in delivery and deposition performances requires further optimization and selection of suitable mixtures.

Furthermore, AEA tends to result in gentler decreasing or even stabilizing slump value/spread diameter with time. At the dosage of 0.2 g/L, the slump value/spread diameter almost remains constant within one hour. In contrast, large slump reduction could be observed in the mixtures without AEA. These mixtures show more than 40% and 16% reduction of initial slump and spread diameter after one hour, indicating the workability has high time dependence. The high time dependence of workability in the mixtures without AEA could affect the accuracy of printed profile, e.g. non-consistent dimensions of printed filament. Real-time feedback-oriented adaptive adjustments are required, e.g. variable pumping rates to maintain the constant flow rate of the material for accuracy consideration and discontinuity prevention. However, using feedback-oriented adaptive spray printing system is not economical and even not applicable in some engineering applications. The mixture without AEA has high time dependence of workability and hard to control, therefore no spray work was carried out for these mixtures.

Fig. 4.5 Slump of mixtures with different FAC substitution percentages (Dosage of AEA: 0 g/L; 0.2 g/L)

Fig. 4.6 Slump of mixtures with different dosages of AEA (FAC substitution percentage: 100%)

Fig. 4.7 Spread diameter of mixtures with different FAC substitution percentages (Dosage of AEA: 0 g/L; 0.2 g/L)

Fig. 4.8 Spread diameter of mixtures with different dosages of AEA (FAC substitution percentage: 100%)

4.3.3 Rheological Properties

Fig. 4.9 and Fig. 4.10 describe dynamic yield stress and plastic viscosity with respect to FAC substitution level and dosage of AEA. It is revealed that with the existence of AEA, the mixtures with 100% FAC substitution percentage has the lowest dynamic yield stress and plastic viscosity respectively. However, the effect of AEA on dynamic yield stress or plastic viscosity is inconclusive. For mixtures with 0% or 100% FAC substitution, dynamic yield stress decreases and then increases as the dosage of AEA

increases from 0 to 0.2 g/L. In contrast, mixtures with 50% FAC substitution show the opposite trend. The plastic viscosity values of mixtures with 50% FAC substitution remain nearly constant, while mixtures with 0% or 100% FAC substitution show non-consistent trends with increasing dosage of AEA. Among all the mixtures, M-100%-0.1 has the lowest dynamic yield stress and plastic viscosity.

Fig. 4.9 Dynamic yield stress of the designed cementitious materials

Fig. 4.10 Plastic viscosity of the designed cementitious materials

Fig. 4.11 shows static yield stress with respect to FAC substitution level and dosage of AEA. It suggests that increasing substitution percentage of silica sand by FAC greatly decreases static yield stress. With FAC substitution percentage increasing from 0%, 50%

to 100%, the increase of AEA generally leads to lower static yield stress. The decreasing trend is most pronounced with 100% FAC substitution.

Fig. 4.11 Static yield stress of the designed cementitious materials

4.3.4 Discussions

4.3.4.1 Evaluation of delivery and deposition performances

To evaluate delivery and deposition performances of the mixtures, the method in *Section 3.3.1* was adopted. The calculated pumping pressure is shown in Fig. 4.12. By comparing the trends when the dosage of AEA increases in Fig. 4.9, Fig. 4.10 and Fig. 4.12, it could be seen that the calculated pumping pressure is largely hinged on the dynamic yield stress of the material. This observation is contradictory to the case of extrusion-based 3D printable cementitious materials, where the pumping pressure is largely hinged on the plastic viscosity of the material (Weng et al. 2018b). The discrepancy could be attributed to the relatively small plastic viscosity of designed sprayable mixtures. Among all the designed mixtures, M-100%-0.1 has the lowest calculated pumping pressure.

Fig. 4.12 Calculated pumping pressure of the designed mixtures

Fig. 4.13 shows the critical ratio for mixtures with AEA. It should be noted that although the mixtures with 0% FAC substitution percentage have high static yield stress, their relatively large density values bring down the ratio. In comparison, as mixtures with 50% and 100% FAC substitution percentages have very similar density, the critical ratio follow the trend of static yield stress.

Fig. 4.13 Critical ratio of the designed mixtures

4.3.4.2 Selection of the optimal mixture

Based on the necessity of low time dependence of workability which has been illustrated in *Section 4.3.2*, mixtures without AEA has been excluded from material selection. From the pumpability evaluation, M-100%-0.1 has the lowest calculated pumping pressure in the delivery phase. However, it also has a relatively small critical ratio, which could compromise the spray performance in the deposition phase. In comparison, M-0-0.1, M-50%-0.1, M-0-0.2 and M-50%-0.2 have large critical ratios, but they have much higher calculated pumping pressure than M-100%-0.1. As the material should achieve good performance in both delivery and deposition phases, a comprehensive material index Γ was proposed.

The material index Γ for each mixture is calculated in two steps. The first step is to normalize the calculated pumping pressure and the critical ratio. The normalization process follows a log-scale normalization procedure described as below (Bunn 1982):

$$\tilde{A}_i = \frac{9}{\log \frac{A_{\max}}{A_{\min}}} \cdot \log \frac{A_i}{A_{\min}} \quad (4.1)$$

where $\tilde{A}_i$ and A_i are the normalized and original test results; $A_{\max}$ and $A_{\min}$ are the maximum and minimum test results. The second step is to assign weights and calculate the material index Γ . The weights are assigned 0.5 for each phase assuming equal importance for material performance in both delivery and deposition phases. As smaller pumping pressure is preferred, the coefficient of the calculated pumping pressure is set to be negative. Thus, the material index Γ_i for each mixture is calculated as follows:

$$\Gamma_i = -0.5\tilde{A}_{i,P} + 0.5\tilde{A}_{i,ratio} \quad (4.2)$$

where $\tilde{A}_{i,P}$ and $\tilde{A}_{i,ratio}$ are the normalized values for calculated pumping pressure and the critical ratio respectively. Corresponding results are shown in Table 4.2, where P and C_r represent for calculated pumping pressure and critical ratio.

Table 4.2 Material index Γ for mixtures with AEA

Mix	P (Pa)	Normalized P	C_r (mm)	Normalized C_r	Γ
M-0-0.1	2.56	6.47	75.78	7.59	0.56
M-50%-0.1	2.43	6.14	76.19	7.64	0.75
M-100%-0.1	0.92	0	49.22	3.78	1.89
M-0-0.2	3.82	9	88.88	9.00	0
M-50%-0.2	2.22	5.57	80.97	8.18	1.30
M-100%-0.2	1.81	4.28	32.09	0.00	-2.14

From Table 4.2, it could be clearly seen that M-100%-0.1 has the largest material index value. Hence, it is regarded as the optimal material for spray-based 3D printing among all the mixtures. The material distribution of M-100%-0.1 was further assessed in the spray test. For comparison, the mixtures with small positive material index (M-0-0.1 and M-50%-0.1) and negative material index (M-100%-0.2) were selected for spray tests. In addition, M-0-0.1 and M-50%-0.1 have larger critical ratios, while M-100%-0.2 has a smaller critical ratio.

4.4 Spray Performance Assessment

The detailed setup of spray-based 3D printing is illustrated in *Section 3.2.2*. In the tests, the air injection pressure was kept at 0.5 bar. The MAI pictor pump was used with the constant pumping rate of 900 rpm (flow rate $Q = 3.78$ L/min). After material preparation, the fresh material was filled in the MAI pictor pump instantly.

Fig. 4.14 illustrates the relative position of the spray nozzle and substrate. The spray nozzle was placed horizontally and perpendicular to the vertical substrate (yz -plane). Two types of spray tests were carried out, i.e. single-layer spray and multiple-layer spray. The initial distance between the nozzle and the substrate was 50 mm. The mounted nozzle travelled along the y -axis for 445 mm at a speed of 100 mm/s to complete a single-layer filament. In the multiple-layer spray, the robotic arm quickly shifted backwards for 10 mm after completion of each layer, then moved in the opposite direction at the same speed to complete another layer. In this study, the number of layers

in the multiple-layer spray was kept at three. After completion of designated layers, the sprayed filaments were covered with plastic sheets for 1 day. The filaments were scraped off from the substrate afterwards and cut to expose the cross-sections. Then the specimens were kept curing in the lab environment (temperature: 22.5 °C, relative humidity: 58%). Due to the acceleration and deceleration of the robotic arm near the endpoints of the filaments, the cross sections were cut at $y = 100$ mm, 150 mm and 200 mm respectively. The morphology and build-up thickness distribution were analysed based on the three cross sections to assess the spray performance of the material.

Fig. 4.14 Relative positions of spray nozzle and substrate: (a) top view of single-layer spray; (b) top view of multiple-layer spray; (c) side view of single-layer and multiple-layer spray

4.4.1 Morphology of Cross Sections

The morphology of cross sections was compared among the sprayed mixtures to offer the qualitative assessment of material distribution. Fig. 4.15 shows the representative cross sections of each mixture (cross sections cut at $y = 150$ mm of each filament). The cross sections were dyed with ink to highlight their morphology.

Fig. 4.15 Morphology of the representative cross sections of each mixture: (a) single-layer spray; (b) multiple-layer spray

It could be found that the mixture M-100%-0.1 has the most regular cross sections, especially in the multiple-layer spray. In comparison, other mixtures have distinctive irregular cross sections and non-uniform material distribution. The cross sections of M-0-0.1 and M-100%-0.2 show that the mixtures have significant offset to the lower side. In multiple-layer spray, the sprayed material of M-0-0.1 shows severe overall offset, while the sprayed material of M-100%-0.2 shows severe offset of the middle layer. The cross sections of M-50%-0.1 show concave curves near the centre in both single-layer spray and multiple-layer spray.

4.4.2 Build-up Thickness Distribution of Sprayed Filaments

The analysis of build-up thickness distribution was based on image processing of exposed cross sections (Lao et al. 2017). It is complementary to the qualitative morphology assessment and offers a quantitative assessment of material distribution. However, the assessment of build-up thickness distribution cannot be applied to M-100%-0.2 due to the offset-induced overhanging (see Fig. 4.15). For other mixtures, the build-up heights were measured at different locations indicated by z values. Zero z value is corresponding to the upper boundary of the sprayed filament, and the positive z -

direction is pointing downwards on actual substrates. The build-up thickness distribution was depicted in Fig. 4.16 and Fig. 4.17.

Fig. 4.16 and Fig. 4.17 show the average material distribution of M-0-0.1, M-50%-0.1 and M-100%-0.1 in single-layer and multiple-layer spray respectively. M-100%-0.1 has slightly lower maximum build-up thickness compared with M-0-0.1 and M-50%-0.1, but the build-up thickness distribution of the material is more uniform, especially for multiple-layer spray. In multiple-layer spray, the build-up thickness distribution of M-100%-0.1 is more approaching isosceles trapezoid. A wide flat zone could be observed near the centre, where the build-up thickness varies very little. In contrast, the distribution of M-0-0.1 and M-50%-0.1 shows significant offset with more materials at the lower side. The build-up thickness has large variations near the centre in the mixture M-0-0.1 and M-50%-0.1. The improvement in material distribution could be further reflected by flat zone percentage and the standard deviation of thickness in the flat zone through least square analysis, as shown in Fig. 4.18. The average flat zone percentage in M-0-0.1 (multiple-layer spray) is 44.01% and the standard deviation of thickness in the flat zone is 1.87 mm. The average flat zone percentage in M-50%-0.1 (multiple-layer spray) is 73.46% and corresponding standard deviation is 2.77 mm. In comparison, the average flat zone percentage in M-100%-0.1 (multiple-layer spray) is 72.00% and the standard deviation of thickness in the flat zone is 1.01 mm. Hence the mixture M-100%-0.1 has the most uniform material distribution.

Fig. 4.16 Average material distribution of mixtures in single-layer spray

Fig. 4.17 Average material distribution of mixtures in multiple-layer spray

Fig. 4.18 Least square analysis of material distribution (multiple-layer spray): (a) M-0-0.1; (b) M-50%-0.1; (c) M-100%-0.1

With the investigation of the morphology of cross sections and build-up thickness distribution, it is revealed that the mixture M-100%-0.1 has the best deposition

performance. The sprayed filaments of the mixture have the most regular cross sections and most uniform build-up thickness distribution. In contrast, the sprayed filaments of other mixtures have severe offset, leading to irregular cross sections and non-uniform build-up thickness distribution.

The results do not fully agree with the assumption that material with larger critical ratio has better spray performance. The mixture M-100%-0.2 has a smaller critical ratio, which shows less uniform material distribution. The mixture M-0-0.1 and M-50%-0.1 have larger critical ratios, but also have less uniform distribution than M-100%-0.1. The discrepancy between the assumption and test results of material distribution is discussed in the following *Section 4.4.3*.

In the material selection, the mixture M-100%-0.1 with the largest material index is predicted to achieve the best balance between the delivery and deposition requirements, but not necessarily the best individual performance in both. However, the mixture shows the best performance in both delivery and deposition phases. The mixture M-100%-0.1 is confirmed the optimal mixture for spray-based 3D printing among all the mixtures in this study.

4.4.3 Discussions

The discrepancy in uniform material distribution should refer to the consideration of spray process. In the spray process, the material is projected at high speed on the substrate. The material may be compacted in the delivery and deposition, which lead to the change of actual volumetric flow rate. On the other hand, the deposition phase needs to be analysed, as the receiving impact pressure of projected material could lead to the change of material distribution.

The influence of compaction could be clearly seen in the analysis of build-up thickness. By comparing Fig. 4.16 and Fig. 4.17, it could be found that the average build-up thickness from multiple-layer spray was smaller than three times that of the single-layer spray. Table 4.3 shows the density of sprayed filaments of M-0-0.1, M-50%-0.1 and M-100%-0.1. It could be found that the 3-day density values of M-0-0.1 and M-50%-0.1

were smaller than their fresh density values, while M-100%-0.1 showed the opposite trend. In general, with the evaporation of water, the density in the lab environment should be smaller than fresh density. However, with the effect of pumping pressure, the material could be compacted and densified (Beaupre 1994). The compressibility of each mixture could be inferred by comparing the relative change of density, which is expressed in the following proposed equation:

$$\Psi = \frac{\rho' - \rho}{\rho} \quad (4.3)$$

where Ψ is defined as compressibility index, ρ' is the average value of 3-day density, and ρ is the average value of fresh density. High compressibility index suggests the material has been largely compacted. The compressibility index values were calculated and shown in Table 4.3. On the other hand, the actual volumetric flow rate could also be calculated by multiplying the cross section area of the sprayed filament and robotic arm moving speed in the single-layer spray. The actual volumetric flow rate was also included in Table 4.3.

Table 4.3 Density and compressibility index

Mixtures	M-0-0.1	M-50%-0.1	M-100%-0.1
3-day density (g/cm ³)	1.71 ± 0.12 (S)	1.23 ± 0.02 (S)	1.25 ± 0.07 (S)
	1.62 ± 0.11 (M)	1.34 ± 0.07 (M)	1.26 ± 0.01 (M)
Fresh density (g/cm ³)	1.76 ± 0.01	1.42 ± 0.02	1.18 ± 0.01
Compressibility index Ψ	-0.05	-0.10	0.06
Actual volumetric flow rate (L/min)	2.62	2.92	2.26

* Annotation: S: single-layer spray; M: multiple-layer spray. The 3-day density is measured in the lab environment (temperature: 22.5 °C, relative humidity: 58%).

The calculation of compressibility index reveals that M-50%-0.1 has the lowest compressibility index, while M-100%-0.1 has the highest compressibility index. Therefore, the actual volumetric flow rate of M-50%-0.1 was much larger than that of

the M-0-0.1 and M-100%-0.1. With further regards to Fig. 4.9, the compressibility of the material seems to have the negative correlation with dynamic yield stress.

Fig. 4.19 shows the speed profile with spray angle α and an infinitesimal annulus at radius r on the substrate. For the speed profile, v_x is the speed in the direction perpendicular to the substrate and v_r is the speed in the direction paralleling to the substrate. The area of the infinitesimal annulus is $2\pi r dr$. During the infinitesimal time dt , the mass through this annulus section dm could be calculated by:

$$dm = \rho \cdot 2\pi r dr \cdot v_x dt \quad (4.4)$$

The impulse of sprayed material dI could be further expressed as:

$$dI = v_x dm = \rho v_x^2 \cdot 2\pi r dr dt \quad (4.5)$$

Hence, the impact pressure by the material p_r could be calculated by:

$$p_r = \frac{dI}{2\pi r dr dt} = \rho v_x^2 < \tau_s \quad (4.6)$$

Fig. 4.19 Speed profile and locus of sprayed material

The impact pressure is balanced by the stress in the sprayed material. The lower volumetric flow rate of the material contributes to lower v_x and resultant lower impact

pressure. Thus, M-100%-0.1 has the lowest v_x and impact pressure. Although M-50%-0.1 has higher static yield stress, the resultant higher impact pressure by the highest volumetric flow rate and density might exceed this value. In this situation, the sprayed material cannot preserve the original distribution and was forced to move. As a result, the distribution of M-50%-0.1 has the concave profile near the centre.

The sprayed filaments of M-0-0.1 does not have the concave profile, which may be attributed to its higher static yield stress and higher compressibility than those of M-50%-0.1. However, the material distribution of M-0-0.1 is also non-uniform. It could be found that more material tends to accumulate in the centre, and the filament also shifts a bit downwards. Some research studies suggested that the material with larger viscosity contributes to smaller spray angle (Chen et al. 1992, Tinprabath et al. 2014). Hence, the material accumulation near the centre may be attributed to the small spray angle of M-0-0.1, while the examination of spray angle is required in further study.

The poor material distribution of M-100%-0.2 is due to the low critical ratio. As can be seen in the multiple-layer spray in Fig. 4.15, the sprayed filament has irregular cross section and non-uniform distribution. Other multiple-layer sprayed filaments of M-100%-0.2 also show the same trend. With a low critical ratio, insufficient static yield stress cannot balance the gravity of large build-up.

With the analysis in this study, the selection criteria for spray-based 3D printable cementitious materials could be constructed. From the discussions in *Section 4.3.4*, low plastic viscosity and dynamic yield stress are preferred for the delivery phase of spray-based 3D printing. On the other hand, the material should have low plastic viscosity, dynamic yield stress, fresh density and high static yield stress for uniform material distribution.

4.5 Conclusions

The adoption of 3D printing contributes to automation, design freedom, sustainability and efficiency in civil engineering. Conventional spray technology shares a number of similarities with 3D printing, indicating the feasibility of spray-based 3D printing.

However, low dimensional accuracy of sprayed profiles with conventional materials greatly affects its quality, the error is typically in centimetre levels and necessary manual post-processing such as scraping must be applied (ACI Committee 506 2005). This hinders the application of spray-based 3D printing and further automation in the building and construction field. The study offers feasible material solution to improve its accuracy by incorporating fly ash cenosphere (FAC) and air entraining agent (AEA) in mixture design. The accuracy improvement of sprayed profile makes the designed mixture feasible for spray-based 3D printing, which could be further utilized for decorative structure without post-processing.

The assessment of fresh density and workability of designed mixtures reveals the effectiveness of introducing FAC and AEA. It is found that FAC and AEA could effectively reduce the fresh density of the mixture. In addition, increasing FAC substitution from 0 to 100% or increasing dosage of AEA from 0 to 0.2 g/L leads to smaller slump and flow diameter. The decrease of slump and spread diameter indicates the improved buildability with the incorporation of FAC and AEA in this study.

The addition of AEA tends to result in gentler decreasing or even stabilizing slump/spread diameter with time. At the dosage of 0.2 g/L, the slump/spread diameter remains nearly constant within one hour from mixing. In comparison, the mixtures without AEA show large decrease of slump/spread diameter, indicating high time dependency of workability. These mixtures were hard to control and thus not applicable for spray-based 3D printing assuming a feedback control system is not readily available.

Rheological tests were carried out to further predict the pumpability and deposition performance of designed mixtures. The results show that the mixture with 100% FAC substitution percentage and 0.1g/L AEA (referred to as M-100%-0.1) has the lowest dynamic yield stress and plastic viscosity, yet not too low static yield stress. Subsequent calculations point out the mixture has the lowest required pumping pressure, while it may compromise the deposition performance. A material index was proposed to evaluate the performance in both of delivery and deposition phases. The mixture with the highest material index is inferred as the optimal mixture for spray-based 3D printing,

which should achieve the best balance between the requirements of delivery and deposition. Through the analysis of cross sections of sprayed filaments and build-up thickness distribution, the optimal mixture M-100%-0.1 was found to have the most uniform material distribution. In multiple-layer spray, the mixture M-100%-0.1 has large flat zone percentage (72.00%) with the lowest standard deviation of thickness in the flat zone (1.01 mm). In comparison, the mixture M-0-0.1 has much smaller flat zone percentage (44.01%) while the mixture M-50%-0.1 has much higher standard deviation of thickness in the flat zone (2.77 mm). It reveals that the optimal mixture could achieve the best performance in delivery and deposition respectively, rather than compromising each other.

The discussion of material deposition process reveals that the material distribution can be affected by many rheological properties. Through the comparison of changes in density, the material with lower dynamic yield stress seems to have higher compressibility. The optimal mixture M-100%-0.1 was mostly compacted in the spray process, leading to the lowest actual volumetric flow rate. The lowest resultant impact pressure of the optimal mixture explains its best deposition performance. The mixture with large plastic viscosity is found to obviously accumulate more material near the centre, which may be attributed to the induced small spray angle. In addition, the mixture with low ratio of static yield stress to the product of fresh density and gravitational acceleration ($\tau_s/(\rho g_0)$) has poor material distribution. The phenomenon could be attributed to the insufficient static yield stress for balancing the gravity of large build up.

With the analysis of delivery and deposition phases, the material design criteria for spray-based 3D printing were proposed. The suitable material should possess low plastic viscosity, dynamic yield stress for better delivery performance and more uniform distribution of sprayed material; in addition, high static yield stress and low density are also required for good deposition performance. The proposed optimal mixture M-100%-0.1 in this study is suitable for spray-based 3D printing, which adopts 0.1 g/L AEA and 100% substitution of silica sand by FAC.

Chapter 5 Study of MgO-activated Slag as A Cementless Material for Sustainable Spray-based 3D Printing

5.1 Introduction

Portland cement which is often used in 3D printing concrete is not an environmentally friendly material. With a calcination temperature of up to 1450°C, it has been reported that cement manufacturing alone accounts for 8% of global anthropogenic CO₂ emissions (Neville 2011, Dung and Unluer 2016, Ruan and Unluer 2016). There is a need to develop a more sustainable 3D printing concrete with less environmental impact to fulfil the aim of clean and sustainable 3D printing construction.

Slag is an industrial waste from the iron production process. It is regarded as a supplementary cementitious material and has been widely used in concrete production. Slag alone reacts slowly with water due to the presence of impervious layers of amorphous silica and alumina that form around slag particles early in the hydration process (Escalante-García et al. 2003). Thus, slag often blends with cement or alkaline activator such as sodium silicate to facilitate slag hydration (Shi et al. 2018, Phul et al. 2019). In slag-blended PC system, the hydration of cement provides the calcium hydroxide and alkaline environment to activate slag hydration (Fu et al. 2002, Mehta and Monteiro 2006, Neville 2011). However, as mentioned, cement production introduces heavy environmental burdens. The alkaline activators are also often produced from energy-intensive processes, which leads to increased greenhouse gas (GHG) emissions and other environmental concerns (Tan et al. 2019).

Reactive magnesium oxide (MgO) can be a potential alternative to activate slag (Jin and Al-Tabbaa 2014, Jin et al. 2015). With 20% replacement of slag by MgO, a 28-d compressive strength of 30 MPa can be obtained (Jin et al. 2015). Furthermore, production of reactive MgO requires a much lower calcination temperatures (700-1000°C) (Shand 2006) and MgO binder gains strength by reacting with CO₂, which leads to the production of stable carbonates, thereby sequestering CO₂ in the process (Unluer and Al-Tabbaa 2013). However, based on the best of our knowledge, there is

no study to investigate the rheological properties of reactive MgO-slag (RMS) system, which is critical for the development of any 3D printable material. A relevant study indicated that the conventional alkali-activated slag materials possess high plastic viscosity and low yield stress (Yang et al. 2018), which could lead to poor performance in the delivery and deposition of 3D printing (Weng et al. 2018a, Lu et al. 2019b). It is therefore necessary to investigate and tailor the rheological properties of RMS for the application of 3D printing.

Different approaches have been proposed to control the rheology of cementitious materials (Banfill 1994, Çınar et al. 2019, Lu et al. 2019b), which is essential for successful 3D printing. Zhang et al. used clay to increase the yield stress of the fresh mixture, which contributes to the deposition performance (Zhang et al. 2018b). However, plastic viscosity was also increased, which is unfavorable for delivery. Weng et al. suggested that the addition of silica fume can significantly increase the yield stress while decreasing the viscosity (Weng et al. 2018c). The resulting mixture showed good delivery and deposition performances in printing a miniature structure. Lu et al. used fly ash cenosphere (FAC) and air entraining admixture (AEA) to reduce the dynamic yield stress and the plastic viscosity and to achieve good pumpability and deposition performance for the spray-based 3D printing (Lu et al. 2019a). Introduction of low-density FAC can effectively bring down the fresh density of the mixture and increase the critical ratio, which contributes to better deposition performance in spray-based 3D printing (Lu et al. 2019a). Furthermore, FAC contributes to the uniform build-up thickness distribution of sprayed material and improves the printing quality. The ball-bearing effect of FAC also leads to good pumpability of the fresh mixture (Niraj et al. 2018, Zhang and Zhang 2018, Lu et al. 2019a).

This study investigates and tailors the rheological properties of RMS materials for spray-based 3D printing. As shown in Fig. 5.1, effects of reactive MgO and FAC addition on setting, plastic viscosity, dynamic and static yield stress of RMS materials were assessed by means of the Vicat needle test, the Fourier-transform infrared (FTIR) spectroscopy, and the rheological test. Thereafter, pumpability and buildability of the designed mixtures were evaluated. An optimal mixture was then selected for spray-

based 3D printing considering delivery and deposition requirements. Finally, the optimal RMS mixture was successfully applied in spray-based 3D printing, which further confirms its feasibility.

Fig. 5.1 Flowchart of the RMS mixture development for spray-based 3D printing

5.2 Materials and Mixture Design

The mixtures were prepared with reactive MgO, ground granulated blast-furnace slag (GGBS) and FAC. The light-burnt MgO was provided by Urban Redevelopment Authority, Singapore. GGBS was provided by Engro Co. Ltd., Singapore. FAC was provided by Hebei Baisite Technology Co. Ltd., China. The chemical compositions of reactive MgO, GGBS and FAC are listed in Table 5.1. Fig. 5.2 shows the scanning electron microscope (SEM) images of reactive MgO, GGBS and FAC. As can be seen, FAC is of spherical shape, while MgO and slag are highly irregular due to the grinding

during manufacturing. Fig. 5.3 and Table 5.2 show the particle size distribution and specific surface area, respectively, of MgO, GGBS and FAC. It could be found that MgO and GGBS have similar particle size distributions and FAC is much coarser than MgO and GGBS. MgO has the largest specific surface area, while FAC has the lowest specific surface area among all three raw ingredients.

Table 5.1 Chemical compositions of MgO, GGBS and FAC

	Compound (wt.%)						
	MgO	SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃	SO ₃	K ₂ O
Reactive MgO	97	1.3	1.3	0.2	0.2	NA	NA
GGBS	2-14	30-40	30-50	0.1-1.8	7-17	NA	NA
FAC	0.8-1.2	56-62	0.2-0.4	2-4	33-38	0.1-0.2	0.5-1.1

Fig. 5.2 SEM images of (a) MgO (2500x magnification); (b) GGBS (2500x magnification); (c) FAC (250x magnification)

Fig. 5.3 Particle size distribution of raw ingredients

Table 5.2 Critical particle diameter and surface area of raw ingredients

	d(0.1)* (μm)	d(0.5) (μm)	d(0.9) (μm)	Specific surface area (cm ² /g)
MgO	2.126	19.175	60.124	11500
GGBS	2.963	18.144	44.158	10500
FAC	13.542	63.762	110.257	3730

***Annotation:** d(0.1) is the particle diameter corresponding to 10% cumulative passing; d(0.5) is the particle diameter corresponding to 50% cumulative passing; d(0.9) is the particle diameter corresponding to 90% cumulative passing.

Table 5.3 shows mass proportions of the mixtures in this study. In mixture M2 and M4, slag was replaced by 20 wt.% and 40 wt.% reactive MgO, respectively. In mixture M4C2 and M4C4, 40 wt.% reactive MgO was used as GGBS replacement and additional FAC was included in the mix. The liquid/solid ratio was kept constant at 0.32 for all the mixtures. The mixture was prepared in a Hobart HL-200 mixer as per the following procedure. Firstly, all the solid ingredients were mixed at low speed for 180 s. Water was then poured into the dry mixture and mixed for another 180 s.

Table 5.3 Mass proportions of the designed mixtures

Mixture	MgO	GGBS	FAC	Water
S	0	1	0	0.32
M2	0.2	0.8	0	0.32
M4	0.4	0.6	0	0.32
M4C2	0.4	0.6	0.2	0.384 (= 0.32*1.2)
M4C4	0.4	0.6	0.4	0.448 (= 0.32*1.4)

5.3 Results and Discussions

5.3.1 Setting and Hydration

Setting relates to the hydration behaviour of the fresh mixtures and is an important parameter governing the working window of 3D printing (Le et al. 2012a, Perrot et al. 2016, Kazemian et al. 2017). While long setting time may lead to buildability issues such as limited printing height, short setting time could lead to narrow working window for offline 3D printing. Fig. 5.4 plots the needle penetration depth of different mixtures. The initial setting time is determined at 25 mm penetration depth (marked in dash line), i.e., the beginning of distinctive decrease of penetration depth. Addition of MgO could effectively accelerate the setting of the fresh GGBS mixture. As can be seen, initial setting time of mixture S without MgO addition is 305 min, while that of mixture M4 is only 67 min (Fig. 5.4 (a)). Furthermore, addition of FAC only slightly retards the initial setting of M4 from 67 min to 100 min (i.e., M4C4 in Fig. 5.4 (b)).

Fig. 5.4 Vicat needle penetration depth of the mixtures with (a) different MgO contents (mixture S, M2 and M4); (b) different FAC contents (mixture M4, M4C2 and M4C4)

FTIR spectroscopy is able to probe the chemical structure of the binder. By monitoring the relevant change of characteristic peaks of chemical radicals, the hydration products could be effectively analysed (Liu et al. 2016, Zhu et al. 2018). Fig. 5.5 shows the FTIR spectra of fresh S, M4 and M4C4 mixtures. Although the peaks in the three mixtures are different due to different chemical compositions of the raw ingredients, there is negligible change of peaks in each mixture with time. It suggests that the chemical

reaction in the first 120 min is negligible for mixture S, M4 and M4C4. Since M4 and M4C4 showed initial setting within 120 min, it is inferred that their early initial setting is plausibly due to physical aspects rather than chemical activation. Reactive MgO contains more fine particles, and more free water is required to wet the solid particle surfaces. Better water retention of mixture M4 and M4C4 could limit the migration of free water towards the surface, which further increases the friction of needle penetration. Therefore, the mixtures with MgO and FAC possess shorter setting time compared with mixture S.

Fig. 5.5 FTIR spectra of fresh (a) mixture S; (b) mixture M4; (c) mixture M4C4 in the first 120 min

Fig. 5.6 (a) shows the FTIR spectra of GGBS and mixture S at 20 min and 28 d. It could be found that there are no characteristic peaks of water (around 3350 cm^{-1} ~ 3390 cm^{-1} and 1640 cm^{-1}) (Yu et al. 1999, Lecomte et al. 2006) at 28 d, indicating the water is lost from the mixture because of negligible hydration and poor bleeding resistance of slag paste. The peaks at 1473 cm^{-1} , 830 cm^{-1} and 875 cm^{-1} are corresponding to CO_3^{2-}

HCO_3^{2-} (Miller and Wilkins 1952, Lodeiro et al. 2009), while the peaks at 646 cm^{-1} and 680 cm^{-1} are attributed to SO_4^{2-} (Miller and Wilkins 1952). Comparing the two spectra of slag and mixture S at 28 d, it was found that no new peak was generated. This suggests the chemical reaction in mixture S is very little, or even negligible, and the slag could not be self-activated. This finding is in line with the previous study (Neville 2011), where the hydration of slag is described as a very slow process due to the necessity of breaking down the glass structure by hydroxyl ions.

Fig. 5.6 FTIR spectra of (a) GGBS and mixture S; (b) mixture M4; (c) mixture M4C4 at 20 min and 28 d

Fig. 5.6 (b) shows the FTIR spectra of mixture M4 at 20 min and 28 d. Compared to the 20-min curve, a new peak at 960 cm^{-1} in the 28-d spectrum is attributed to the formation of C-S-H (Yu et al. 1999, Zhu et al. 2018), indicating the slag was activated by MgO. The expanded peak centered at 1430 cm^{-1} and a shoulder at 855 cm^{-1} are due to the formation of hydrated magnesium carbonates (HMCs) (Abdel-Gawwad and El-Aleem 2015). Furthermore, the intensity reduction of peak at 3694 cm^{-1} indicates the consumption of $\text{Mg}(\text{OH})_2$. Characteristic peaks of water (around $3350\text{--}3390\text{ cm}^{-1}$ and

1640 cm^{-1}) (Yu et al. 1999, Lecomte et al. 2006) could still be found at 28 d in mixture M4 with reduced peak heights, because mixture M4 has better bleeding resistance than mixture S.

Fig. 5.6 (c) shows the FTIR spectra of mixture M4C4 at 20 min and 28 d. The C-S-H and HMC peaks were still observed in the 28-d spectrum with reduced intensities as compared to mixture M4. The incorporation of FAC probably only diluted the MgO but did not inhibit MgO activation of slag. Similarly, the characteristic peaks of water (around 3350-3390 cm^{-1} and 1640 cm^{-1}) (Yu et al. 1999, Lecomte et al. 2006) could also be found at 28 d in mixture M4C4, indicating good bleeding resistance.

From the discussion above, it is expected the reaction of RMS system occurs in two steps. In the first step, hydrolysis of MgO increases the alkalinity of the paste. The hydroxyl group attacks the slag and the chemical bonds such as Ca-O, Mg-O, Si-O-Si and Al-O-Si are broken down. In the second step, Mg^{2+} reacts with Si-O and Al-O to form M-S-H and hydrotalcite-like hydrate, respectively, and Ca^{2+} reacts with Si-O and Al-O to form C-S-H and C-A-S-H, respectively (Jin et al. 2015). Carbonation of brucite could lead to the generation of HMC.

5.3.2 Rheological Properties

5.3.2.1 Plastic viscosity and yield stress

Fig. 5.7 shows the plastic viscosity, the dynamic yield stress, and the static yield stress of the fresh mixtures. With the increase of MgO content, the plastic viscosity firstly increases and then decreases. In comparison, the dynamic yield stress consistently increases with MgO content. On the other hand, comparing mixture M4, M4C2 and M4C4, plastic viscosity is reduced while the trend of dynamic yield stress is not consistent. As for the static yield stress, it increases when MgO and/or FAC are added but without a clear trend.

Fig. 5.7 Rheological parameters of the designed mixtures

As the chemical reactions in the first 120 min are negligible based on FTIR results, change of rheological properties could be attributed to the physical characteristics of raw ingredients. Introduction of MgO greatly increases the particle frictions and consumes more free water due to its irregular shape and high specific surface area. Thus, its dynamic yield stress increases when compared with mixture S. Due to the spherical shape of FAC, addition of FAC leads to decrease of dynamic yield stress and plastic viscosity. Furthermore, introduction of MgO and FAC may increase the thixotropy of the mixtures, which could explain general increasing trend of the static yield stress (Quanji 2010).

5.3.2.2 Pumpability and buildability

Pumpability could be quantitatively evaluated by pumping pressure in the hose. Adopting the evaluation method in *Section 3.3.1*, the pumping pressure P can be calculated by plastic viscosity k and dynamic yield stress τ_0 . Fig. 5.8 shows the pumping pressures for all the designed mixtures. The pumping pressure increases as MgO content increases, however, addition of FAC could effectively reduce the pumping pressure presumably due to ball-bearing effect. Among all the mixtures, M4C4 has the lowest pumping pressure, although the difference is negligible compared with that of M4C2.

Fig. 5.8 Calculated pumping pressure for the designed mixtures

Buildability of the mixtures can be associated with static yield stress τ_s and critical ratio C_r . *Chapter 4* points out that larger critical ratio leads to more uniform distribution of build-up thickness of sprayed material, which improves the quality of spray-based 3D printing. Measured fresh density and calculated critical ratio are shown in Fig. 5.9. Addition of MgO slightly reduces the fresh density, and thus the critical ratio of S, M2 and M4 shows a similar trend to static yield stress. On the other hand, addition of FAC leads to greatly reduced fresh density. Coupled with larger static yield stress, M4C2 and M4C4 have significantly larger critical ratios than the mixtures without FAC. Based on pumpability and buildability consideration, M4C2 and M4C4 were selected for further test of spray-based 3D printing.

Fig. 5.9 Fresh density and critical ratio of the designed mixtures

5.4 Spray-based 3D Printing

5.4.1 Spray-printing of Filament

Spray performance of the mixture M4C2 was evaluated by spray-printing of filament. As a comparison, mixture S was also evaluated in the same test. The layer number of the filament is 3. The nozzle travel speed is set at 200 mm/s and the air inject pressure is set as 0.5 bar. The distance from the nozzle to the substrate is set at 50 mm initially and increases 10 mm after completion of each layer to compensate for thickness of the sprayed layer.

The spray-printed filaments of mixture S and M4C2 are shown in Fig. 5.10. It could be found that mixture S has larger splash width than M4C2. The average splash widths of mixture S and M4C2 are 36.20 mm and 26.57 mm, respectively. Mixture S shows inconsistent build-up thickness along the splash width range, and the surface of the filament is severely influenced by spray pressure (see the ripple pattern marked in Fig. 5.10). In comparison, mixture M4C2 has more consistent build-up thickness and shows a less noticeable ripple pattern. The significant difference is attributed to the rheological properties of mixture S and mixture M4C2, as stated in *Section 5.3.2*. Mixture M4C2 has significantly higher static yield stress with lower fresh density and resulting critical ratio, which leads to better buildability and more uniform thickness distribution in sprayed filament. The higher static yield stress of mixture M4C2 also helps resist spray

pressure and maintain the morphology of sprayed filament (Lu et al. 2019a). Hence mixture M4C2 possesses higher printing quality, and it was applied in profile spray-based 3D printing afterwards.

Fig. 5.10 Spray-printed filaments of (a) mixture S; (b) mixture M4C2 (ripple pattern marked with arrow)

5.4.2 Profile Spray-based 3D Printing

Fig. 5.11 shows the top and isometric views of the designed profile for vertical spray-based printing. It consists of three interconnected equilateral triangles. The layer numbers of the outer triangle, middle triangle and inner triangle are 5, 3 and 1 respectively. The edge length of the outer triangle is 500 mm. Other printing parameters are the same as those in the spray-printing of filament.

Fig. 5.11 Designed profile for vertical spray-based 3D printing: (a) front view; (b) isometric view

The vertical spray-printed profile is shown in Fig. 5.12. It could reflect the characteristics of the designed profile, although the printing resolution is low due to the

splash. Overall width of spray splash increases with the number of layers sprayed, especially when comparing the splash width of the outer triangle (5 layers) and inner triangle (1 layer). However, the build-up thickness remains largely uniform in the spray of single and multiple layers. The profile manufactured by spray-based 3D printing confirms the feasibility of tailoring MgO-activated slag material for spray-based 3D printing.

Fig. 5.12 Spray-printed profile with Mixture M4C2

5.5 Conclusions

This study investigates a reactive MgO-activated slag (RMS) as a cementless material for spray-based 3D printing. Effects of MgO and fly ash cenosphere (FAC) addition on setting, hydration and rheological properties of RMS mixtures were investigated. Results showed that inclusion of MgO greatly accelerates the setting of the fresh mixture. The initial setting is reduced from 305 min to 67 min when 40 wt.% of GGBS is replaced with MgO in the current study. Introduction of FAC generally reduces dynamic yield stress and plastic viscosity and increases static yield stress of the fresh mixture. The resulting mixtures with FAC addition possess lower pumping pressures yet higher critical ratios, suggesting good delivery and deposition performance for 3D printing. Furthermore, RMS with FAC addition shows better spray-printing quality and the build-up thickness remained almost uniform in the single or multiple layers.

The RMS mixture developed in the current study has the potential to be used as a sustainable material for vertical/overhead spray-based 3D printing. Compared with the current spray-based 3D printable mixtures in literature (Lindemann et al. 2018, Lu et al. 2019a), the developed RMS mixture in this study has zero usage of cement, which greatly reduces the CO₂ emission and environmental impact. In addition, the precursor of MgO, *i.e.*, Mg(OH)₂ can be obtained from desalination of seawater (Seeger et al. 2011). Considering this aspect, the developed RMS mixture possesses more sustainability benefits in island countries such as Singapore where desalination of seawater is one of the main sources of clean water.

The synthesis of cementless mixture in this study can guide the future development of MgO-based green geopolymer materials. In these materials, MgO serves as the alkali activator in the geopolymerization reactions, while the waste ingredients provide sources of silicon and aluminium. As suggested in the study, the synthesis can be carried out under room temperature without the adoption of conventional alkali solutions, *e.g.* NaOH. Similar rheological tailoring and optimization can hence be exerted to meet the requirement of concrete printing.

The FTIR spectra inspections during the fresh stage of mixtures can be adopted in the analysis of early hydration in printable concrete materials. The FTIR spectra provides information of possible reactions with the comparison of peak locations and intensities. As shown in this study, the possible chemical reactions of fresh mixtures can be continuously monitored without interference. This outcompetes conventional X-ray diffraction inspection, where the samples need to be dried and grinded.

Furthermore, environmental life cycle assessment can be carried out to investigate the detailed environmental impact of the proposed material as compared to existing spray-based 3D printable cementitious materials. The scope of life cycle assessment can be extended to include maintenance and end-of-life phases of the structure manufactured by spray-based 3D printing.

Chapter 6 Effect of Printing Parameters on Material Distribution in Spray-based 3D Printing

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6.1 Introduction

Most 3D printing in the building and construction is extrusion-based, and the shape of extrudate can be effectively controlled by the design of nozzle outlet (Lao et al. 2017), nozzle standoff height (Bos et al. 2016), printing speed (Panda et al. 2018), etc. However, there is little study of 3D cementitious material printing on the vertical surface, e.g. printing of vertical decorative pattern. Different from printing on the horizontal surface, vertically deposited material needs to resist the shear induced by gravity. In the building and construction area, conventional solution is spraying concrete materials. However, due to the lack of systematic control of spray and large rebound of high-speed sprayed material at far distance, the sprayed material on the substrate is not uniformly distributed and needs subsequent manual scraping work (ACI Committee 506 2005). In contrast, spray-based cementitious material printing process requires higher accuracy on the material distribution without human intervention. However, there is very limited study on spray-based 3D printable cementitious materials (Lu et al. 2018), and no research has been carried focusing on material distribution in spray-based cementitious material printing. The situation motivates the research study in this chapter.

The material distribution in spray-based cementitious material printing is systematically studied in this chapter. Similar to extrusion-based 3D cementitious material printing, material distribution may vary with different printing parameters. The effects of four printing parameters on sprayed material distribution have been investigated, i.e.

pumping rate, air inject pressure, nozzle travel speed, and nozzle standoff distance. An experimental model of material distribution is hereby proposed, which can be utilized for further study of spray-based cementitious material printing.

6.2 Material Design

The sprayable cementitious material used in the experiments was composed of Type-I ordinary Portland cement (OPC), Class-F fly ash, silica fume, sand and tap water. The grading curve of river sand is shown in Fig. 6.1. Superplasticizer of 1 g and Air entraining agent (AEA) of 0.1 g was added to each litre mix. The mix proportion of the sprayable cementitious material is shown in Table 6.1.

Fig. 6.1 Sand gradation

Table 6.1 Mass proportion of the sprayable cementitious material

Cement	Sand / Cement Ratio	Fly ash / Cement Ratio	Silica fume / Cement Ratio	Water / Cement Ratio	Super- plasticizer	AEA
1	0.45	0.5	0.05	0.62	1 g/L	0.1 g/L

The sprayable cementitious material was prepared in Hobart HL-200 mixer as per following procedure. Weighed raw ingredients except water, AEA and superplasticizer were mixed for 180s at slow speed. The water with dissolved AEA was added

afterwards and mixed with other ingredients for another 180s at slow speed. Then superplasticizer was added to the mixture, firstly mixed for 90s at slow speed and followed by another 90s mixing at high speed. Then the material was taken for subsequent investigations.

Some key fresh properties were assessed to check the pumping performance of the designed sprayable cementitious material. The flowability loss of the fresh material was traced by a flow table test, which provides flow diameter of the material after the slump cone is lifted and stroke for 25 strikes (ASTM 2001). As shown in the Fig. 6.2, there is no sudden decrease of flowability within one hour. The viscosity of fresh cementitious material can be described by Bingham Plastic model, and the yield stress and plastic viscosity were measured using rotational rheometer, of which values are 115.18 Pa and 20.27 Pa·s respectively. Pumpability test with printing delivery system showed that the material with such rheological parameters can be pumped consecutively.

Fig. 6.2 Average flow diameter with time

6.3 Experiment Design

Setup of spray-based 3D printing can be referred to in *Section 3.2.2*. The nozzle's orientation and position can be controlled by the movement of robotic arm as per designed programme. The spray nozzle is adjusted to point perpendicularly to the

vertical substrate in the spray-based cementitious material printing process. The nozzle travel path is illustrated in Fig. 6.3. In the experiments, the nozzle travels parallel to the substrate plane at five different speeds to spray straight filaments, i.e. 50 mm/s, 100 mm/s, 150 mm/s, 200 mm/s and 250 mm/s. The distances between spray nozzle and the substrate were set as three different values in different runs of experiments, i.e. 50 mm, 70 mm and 100 mm.

Fig. 6.3 Nozzle travel path with different travel speeds

In addition to the nozzle position and travel speed controlled by robotic arm, pumping rates and air inject pressure were also set to have different levels in the experiments. The pumping rates were set as 600 rpm and 1200 rpm in experiments. Air inject pressure was set as 0.5 bar and 1.0 bar in experiments. The complete experiment design table is shown in Table 6.2.

Table 6.2 Experiment design table

Group	Pumping rate (rpm)	Air inject pressure (bar)	Nozzle standoff distance (mm)	Nozzle travel speed (mm/s)
A	600	0.5	50	50 ~ 250
B	600	0.5	70	50 ~ 250
C	600	0.5	100	50 ~ 250
D	1200	0.5	50	50 ~ 250
E	1200	0.5	70	50 ~ 250
F	1200	0.5	100	50 ~ 250
G	1200	1.0	50	50 ~ 250
H	1200	1.0	70	50 ~ 250
I	1200	1.0	100	50 ~ 250

After completion of spray-based cementitious material printing process, the sprayed filaments were covered with plastic sheet for 24 hours in the lab. This guarantees the sprayed filaments have enough strength to be scraped from the substrate without deformation. Three samples were cut from the centre of each sprayed filament to expose the cross section (see Fig. 6.4). The length of each sample is 30 mm. The images of cross section were processed and analysed by MATLAB. Detailed procedure of image analysis can be found in Lao et al. (Lao et al. 2017).

Fig. 6.4 Exposed cross sections of three samples cut from sprayed filament

6.4 Results and Discussions

Thickness distribution with respect to filament width is used to describe the distribution of sprayed materials. A uniform material distribution should have nearly constant thickness, i.e. the cross section approaches rectangular shape. The integration of

thickness distribution is the cross section area, which suggests how much material is sprayed. The thickness distribution of experiment groups A to I are shown in Fig. 6.5. It has to be pointed out that, due to very thin thickness of sprayed filaments, no data was collected for experiment group C. The integrated cross section area values are shown in Fig. 6.6.

Fig. 6.5 Thickness distribution (Group A to Group I)

Fig. 6.6 Cross section area at different travel speeds in each group

There are some general characteristics in the material distribution. It can be found that increased pump speed can greatly increase the width and thickness of sprayed filament. However, there is no significant difference in width and thickness when air inject pressure increases. The increase of nozzle travel speed decreases the thickness of sprayed filament, especially when the nozzle travel speed increases from 50 mm/s to 100 mm/s. Nevertheless, the thickness difference is not significant when the speed is higher than 100 mm/s in Group A and B; for other groups when the speed is higher than 150 mm/s the thickness difference becomes negligible. Larger standoff distance can enlarge the thickness difference and also increase the width of sprayed filament. In addition, larger standoff distance leads to smaller thickness.

Fig. 6.6 shows cross section area greatly increases with higher pumping rate, especially when the nozzle travel speed is smaller than 200 mm/s. Similar to the trend of thickness distribution, there is little difference on cross section area when the nozzle travels at high speed. The phenomenon can be attributed to the discontinuity in the pumping process, which is traced from decreased density of sprayed filaments as shown in Table 6.3. On the other hand, based on both cross section area and density data, air inject pressure does not seem to significantly impact material distribution.

Table 6.3 Density of sprayed filaments

Travel speed (mm/s)	A	B	C	D	E	F	G	H	I
50	1.64	1.65	/	1.67	1.79	1.62	1.64	1.67	1.54
100	1.40	1.47	/	1.57	1.64	1.54	1.57	1.59	1.59
150	1.39	1.23	/	1.52	1.58	1.39	1.61	1.52	1.59
200	1.23	1.05	/	1.39	1.46	1.14	1.48	1.60	1.45
250	1.34	0.98	/	1.26	1.20	0.99	1.36	1.40	1.49

Volume/mass flow rate in this chapter is defined as the volume/mass of material the vertical substrate received per second. Table 6.4 and Table 6.5 show volume flow rate and mass flow rate of each group respectively. As nozzle travel speed increases, volume flow rate increases while the mass flow rate remains similar when travel speed is smaller than 200 mm/s. The different trends of volume flow rate and mass flow rate can be attributed to the discontinuity of sprayed filaments, which results in lower density. With the same travel speed (lower than 200 mm/s), it can be found that both volume flow rate and mass flow rate increase proportionally as pumping rate increases. Additionally, when the nozzle travels at 250 mm/s, no conclusive conclusion can be drawn. Further investigation needs to be taken to study the mechanism of this transition.

Table 6.4 Volume flow rate of experiments (mL/s)

Travel speed (mm/s)	A	B	C	D	E	F	G	H	I
50	33.89	30.16	/	67.06	63.63	69.38	64.99	70.84	75.21
100	35.56	33.01	/	71.69	64.55	66.80	68.94	69.48	68.44
150	48.03	36.38	/	73.06	68.12	79.74	68.49	71.70	66.06
200	62.70	42.54	/	74.23	66.88	110.58	76.57	71.26	80.25
250	78.01	50.36	/	84.93	72.49	106.64	100.05	85.27	89.20

Table 6.5 Mass flow rate of experiments (g/s)

Travel speed (mm/s)	A	B	C	D	E	F	G	H	I
50	55.61	49.67	/	112.22	114.06	112.06	106.39	118.00	116.06
100	49.67	48.56	/	112.44	105.78	102.56	108.11	110.22	109.00
150	66.83	44.67	/	111.17	107.50	111.00	110.17	108.83	104.83
200	77.11	44.67	/	103.33	97.56	125.67	113.56	114.00	116.67
250	104.72	49.44	/	107.22	87.22	105.83	135.83	119.72	132.50

6.5 Construction of Empirical Model

There were three steps to construct the empirical material distribution model. The first step was to check the significances of printing parameters on the width of sprayed filament by statistics model. The second step was considering the physical deposition process and find the relationship between printing parameters and the maximum filament width. The third step was to correlate material distribution with width and thickness data. In this step, the material distribution was described by three linear functions. Least square method was then utilized to construct the parameters of fitting functions.

From experiment results, it is suspected that air inject pressure does not have significant effect on material distribution. Hence, statistical checking was carried to validate this assumption. Table 6.6 shows p-values of printing parameters for checking their correlation with width and maximum thickness of sprayed filaments. The confidence interval is 95%. The p-values of air inject pressure exceed 0.05 significantly in each case, which certifies that air inject pressure does not have significant effect on material distribution. In contrast, all the other p-values are greatly smaller than 0.05, suggesting the other three printing parameters have significant effects on material distribution. Therefore, air inject pressure will not be included in the empirical model.

Table 6.6 *p*-values of printing parameters

Printing parameters	<i>p</i> -value for width	<i>p</i> -value for maximum thickness
Pumping rate	1.23×10^{-6}	0.02
Air inject pressure	0.58	0.72
Nozzle travel speed	3.09×10^{-6}	1.25×10^{-10}
Standoff distance	1.02×10^{-4}	0.02

Considering the physics of the spray and deposition processes: when the material is sprayed out from nozzle, the spray angle can be considered as constant. Therefore, the width of filament should be linearly related to the standoff distance. On the other hand, the width of filament should be proportional to the square root of filament cross section area, which is proportional to the ratio between pumping flow rate and nozzle travel speed. Denote pumping rate as α_p (rpm), nozzle travel speed as γ_{ts} (mm/s) and standoff distance as δ (mm), the function to describe the width of sprayed filament W (mm) should be expressed as follows:

$$W = C_1 \delta \sqrt{\frac{\alpha_p}{\gamma_{ts}}} + C_2 \quad (6.1)$$

where C_1 and C_2 are constants depend on the pump, nozzle and material properties. By fitting experimental maximum filament widths into the proposed model, it can be now described by

$$W = 0.145 \delta \sqrt{\frac{\alpha_p}{\gamma_{ts}}} + 33.9 \quad (6.2)$$

The comparison between experimental results and this fitted model is shown in Fig. 6.7. The coefficient of determination R^2 is 0.752, which suggests that this model has some rationality but still needs some improvement.

Fig. 6.7 Comparison between experimental width and fitted model

The next step of constructing empirical model is to correlate material distribution with width and thickness data. By observation, the non-dimensional thickness distribution of printed filament can be roughly described by a trapezoid model:

$$s(x, a, b, c) = \begin{cases} ax & 0 \leq x \leq b/a \\ b & b/a < x \leq 1 - b/c \\ c(1 - x) & 1 - b/c < x \leq 1 \end{cases} \quad (6.3)$$

where $x = w/W$ is the non-dimensional filament width coordinate, $s = hW/(\alpha_p/\gamma_{ts})$ is the non-dimensional filament thickness coordinate (h is the thickness of the sprayed filaments), a , b , and c are parameters which can be found by curve fitting. One fitting example is shown in Fig. 6.8. All fitted parameters of experiment groups A to I are plotted in Fig. 6.9. It is very difficult to draw any meaningful conclusion from this distribution at current stage. While further investigation will be conducted in the future, the average value of each parameters ($a = 14.5$, $b = 1.81$, $c = 9.56$) were used for the prediction of material distribution in current study.

Fig. 6.8 The comparison between experimental thickness and fitted trapezoid model of Group E with 150 mm/s nozzle travel speed

Fig. 6.9 Fitted parameters for filament thickness distribution

6.6 Verification of Empirical Model

Validation experiments were designed to verify the proposed empirical model. The pumping rate, air inject pressure, nozzle standoff distance of validation experiments were 900 rpm, 0.75 bar, and 70 mm, respectively. The nozzle travel path and speed were the same as all other experiment groups as shown in Fig. 6.3. The same image analysis

process was adopted, and corresponding material distribution has been compared with the prediction based on empirical model. As can be seen in Fig. 6.10, the proposed empirical model can well predict the material distribution of spray-based cementitious material printing when the travel speed is 50, 100, and 250 mm/s. However, the predicted maximum filament widths are not accurate for cases when travel speed is 150 and 200 mm/s.

Fig. 6.10 Comparison between experimental results and predicted material thickness distribution

6.7 Conclusions

In this study, the material distribution in spray-based cementitious material printing was investigated. By adopting robotic arm control, effects of four printing parameters (i.e. pumping rate, air inject pressure, nozzle travel speed and standoff distance) on material distribution were studied. The experimental results showed that the increase of pumping

rate or standoff distance increases the maximum filament width. On the contrary, the increase of nozzle travel speed decreases the maximum filament width, while the change of air inject pressure has negligible effect on material distribution. When the ratio between pumping speed and nozzle travel speed decreases to certain value, the sprayed filament density will decrease, thus the cross section area will only decrease slightly due to lowered density. This phenomenon however needs further in-depth study.

Based on the experimental material distribution results, an empirical model was proposed to describe the material distribution in spray-based cementitious material printing. Different from the conventional concrete spray process, the influence of moving nozzle and extra pressure brought by air flow with projected material have been taken into consideration. This empirical model suggests that the maximum filament width is linearly related to the product of standoff distance and the square root of the ratio of pumping rate to nozzle travel speed. A trapezoid function was applied in the model to describe the material distribution. The verification experiments show that this empirical model can predict the maximum filament width and material distribution reasonably well. In the future, this empirical model will be improved and potentially used in design of spray-based cementitious material printings.

Chapter 7 Concluding Remarks and Future Work

7.1 Research Overview

With the ongoing development of 3D printing in the building and construction field, there are more and more engineering applications in the recent years. The continuous development of 3D printing greatly facilitates the automation in construction and contributes to the transformation of the industry towards Industrial 4.0. Although 3D printing in building and construction field is still in its early stage, its potential in creating less waste, using less labour and working at higher efficiency makes it one of the most promising technologies in the 21st century for the construction industry.

As the ‘ink’ of 3D concrete printing, suitable printable cementitious materials are significant. Development of spray-based 3D printable cementitious materials is one of the major research focuses in this thesis. On this basis, in-situ vertical and overhead engineering applications, e.g. decorative concrete structures on vertical wall and ceilings can be easily customized and manufactured with 3D printing. The research study covers two different mixture designs for spray-based 3D printing, i.e. cement-based mixture with fly ash cenosphere (FAC) and air entraining agent (AEA) and MgO-activated slag mixture. Considering both delivery and deposition aspects, rheological tests and supplementary experiments were applied to evaluate the overall spray-based printing performance and select the optimal mixtures.

Process investigation of spray-based 3D printing is another major research focus in this thesis. Effects of four common printing parameters on material distribution in spray-based 3D printing have been investigated. In addition, an empirical model was constructed to depict and predict the material distribution on vertical substrate via spray-based 3D printing. The research helps understand the correlation between the input printing parameters and final spray-print.

7.2 Contributions of Research

The contributions of research are summarized in the following sections, which are corresponding to the two main research focuses of spray-based 3D printing: material development and process investigation.

7.2.1 Material Development for Spray-based 3D Printing

7.2.1.1 Cement-based mixtures

Considering that sprayed material needs to resist gravity-induced shear to build up, tailoring lightweight cementitious material could be effective in developing spray-based 3D printable cement-based mixtures. In this thesis, the design of spray-based 3D printable cementitious materials was firstly carried out with the introduction of fly ash cenosphere (FAC) and air entraining agent (AEA). Through assessment of fresh properties such as fresh density, workability and rheological properties, effects of FAC and AEA in the mixtures were thoroughly studied. On this basis, material index was proposed to select the optimal mixture. Detailed assessment of spray performance and analysis of build-up thickness distribution were conducted, which confirm the selected optimal mixture is suitable for spray-based 3D printing.

Major contributions in this part of study are summarized as below:

1) *For the first time, an optimal lightweight cement-based mixture was successfully developed for spray-based 3D printing.* Mixture with 100% FAC substitution percentage and 0.1 g/L AEA was found to possess the lowest dynamic yield stress and plastic viscosity, yet adequate static yield stress. Therefore, the mixture also possessed the smallest pumping pressure yet adequate critical ratio (ratio of static yield stress to the product of fresh density and gravitational acceleration), indicating good delivery and deposition performances. The developed mixture was proven to have uniform build-up thickness distribution, which effectively improves the dimensional accuracy of spray-based 3D printing.

2) *Effects of FAC and AEA on fresh density and workability of sprayable mixtures were studied in detail, where the beneficial influence on spray-based 3D printing was clarified.* Fresh density was effectively reduced with the introduction of FAC and AEA, which helped reduce the self-weight of sprayed filament. Smaller slump and spread diameter were reported with the introduction of FAC and AEA, indicating better buildability of the mixtures. In addition, stabilizing slump/spread diameter with time was observed in the mixtures containing AEA, which is beneficial to the spray printing system without adaptive feedback control for constant flow rate.

3) *A comprehensive evaluation method was proposed for spray-based 3D printable materials with rheological consideration from delivery and deposition aspects.* The study proposes material index for comprehensive evaluation of delivery and deposition performances, which including normalization and calculation process of calculated pumping pressure and critical ratio. The mixture with largest material index is considered as the optimal mixture for spray-based 3D printing. Subsequent spray tests confirm the effectiveness of the proposed approach.

4) *A quantitative analysis of build-up thickness distribution of sprayed material was firstly proposed.* In previous studies, the build-up thickness distribution of sprayed cementitious materials can only be qualitatively described, which is subjective and cannot be used for quality control of spray-based 3D printable materials. In this study, the build-up thickness distribution was firstly captured with image processing, followed by the least-square trapezoid fitting. The build-up thickness distribution can be effectively assessed by the flat zone percentage and the standard deviation of thickness in the flat zone. As an application of the analysis, the developed optimal mixture in this study possesses the largest flat zone percentage with the smallest standard deviation of thickness in the flat zone, which confirms its good spray-printing performance.

5) *Mixture selection criteria for spray-based 3D printable cementitious materials were initially constructed.* The study points out that low dynamic yield stress, low fresh density and high static yield stress are beneficial to the uniform thickness distribution.

On the other hand, the material should also have low plastic viscosity to ensure good pumpability in the delivery phase.

7.2.1.2 Sustainable mixtures with MgO-activated slag

As a sustainable cementless material, MgO-activated slag material was tailored for spray-based 3D printing. Effects of MgO and FAC addition on setting, hydration and rheological properties of fresh mixtures were investigated to obtain the optimal mixture. The optimal mixture was successfully applied in the vertical spray-based 3D printing of filament and profile, which confirmed its feasibility in engineering applications.

Major contributions in this part of study are summarized as below:

1) *A cementless mixture has been designed with reactive MgO-activated slag for sustainable spray-based 3D printing.* MgO reduced setting time and served as alkali activator in the geopolymerization reactions, while GGBS and FAC provide sources of silicon and aluminium. FAC served as an effective rheological tailoring ingredient in this study, which generally reduced dynamic yield stress and plastic viscosity while increased static yield stress of the fresh mixture. Hence, the mixture possesses low pumping pressure yet higher critical ratios, suggesting good delivery and deposition performance for spray-based 3D printing. The developed FAC tailored MgO-activated slag mixture showed good printing quality and uniform build-up thickness, which was successfully applied in the vertical spray-based 3D printing.

2) *Fourier-transform Infrared (FTIR) spectroscopy was applied in the investigation of hydration of printable MgO-activated slag material.* FTIR suggests negligible chemical reactions occurred in the early stage (within 2 hours from addition of water) for the MgO-activated slag mixtures. On the other hand, FTIR spectra of MgO-slag mixtures at 28 d showed the characteristic peaks of C-S-H and HMC, which confirms geopolymerization. The characteristic peaks of water can be found in the MgO-activated slag mixtures at 28 d, indicating the good bleeding resistance. This technique can also be applied in the development of other 3D printable cementitious materials.

7.2.2 Process Investigation of Spray-based 3D Printing

As pointed out in the literature review, the printing process can affect the final deposit of 3D printing. Hence, it is important to understand, depict and predict the thickness distribution of printed material to further improve the printing quality. The effects of printing parameters on thickness distribution were investigated in this thesis. Thickness distribution of sprayed material was depicted with trapezoid shape, and an empirical model was proposed to correlate the thickness distribution with the printing parameters.

Major contributions in this part of study are summarized as below:

- 1) *A systematical experimental investigation was conducted to reveal the effects of printing parameters on build-up thickness distribution in spray-based 3D printing.* Four common printing parameters, i.e. pumping rate, air inject pressure, nozzle travel speed and standoff distance were examined in this study. Results show that air inject pressure has negligible effects on material distribution. Maximum width of sprayed filaments can be positively correlated with pumping rate and standoff distance while negatively related with nozzle travel speed. In addition, with high nozzle travel speed, the density of the material decreases while cross section area only decreases slightly, indicating discontinuity of the sprayed material. Further in-depth study needs to be carried out to investigate the discontinuity issue.
- 2) *An empirical model has been proposed to describe and predict material distribution in spray-based 3D printing.* Based on deposition process and effects of printing parameters, the proposed empirical model suggests that the maximum filament width is linearly related to the product of standoff distance and the square root of the ratio of pumping rate to nozzle travel speed. Trapezoid functions were adopted to describe material distribution with least square analysis. The proposed empirical model was well verified with subsequent verification experiments.

7.3 Impacts of Research

The impacts of the research study in this thesis are reflected in the following three aspects:

1) Material development. With the designed mixtures in this thesis, spray-based 3D printing on vertical/horizontal substrates can be successfully realized. The printed profiles with developed mixtures have good printing quality with uniform thickness distribution. Specifically, the developed MgO-activated slag material contributes to less CO₂ emission and alkali pollution. In addition, as the precursor of MgO, Mg(OH)₂ can be obtained from desalination of seawater and thus possesses more sustainability benefits in island countries such as Singapore, where the desalination of seawater is one of the main sources of clean water.

2) Process investigation. In this thesis, process investigation of spray-based cementitious material has been conducted. It contributed to the understandings of relations between printing parameters and material distribution in spray-based 3D printing. The proposed empirical model provides a tool to describe and predict build-up thickness distribution with input printing parameters, which can be further utilized in feedback control system to improve productivity of spray-based 3D printing.

3) Economic values. With successful completion of all the research objectives proposed in *Section 1.3*, research work in this study can actively promote the automation in construction, especially for in-situ vertical/overhead construction applications. Currently, automation in construction saves 20% ~ 25% of the cost compared with a typical traditional construction project (Laubier et al. 2018), and it potentially shortens overall construction time via 24/7 operation. Spray-based 3D printing can be integrated with feedback control and combined with extrusion-based 3D printing to achieve further automation in the construction industry.

7.4 Future Work

7.4.1 Spray-based 3D Printable Foam Concrete

Foam concrete is a lightweight concrete material (density ranges between $400 \text{ kg/m}^3 \sim 1850 \text{ kg/m}^3$), which adopts forming agent to generate random air-voids (Amran et al. 2015). The volumetric percentage of air voids can reach up to 35% (Panesar 2013), which provides foam concrete with some superior performance, e.g. acoustic and thermal insulation (Narayanan and Ramamurthy 2000, Chandra and Berntsson 2002), low dead weight (Amran et al. 2015), fire resistance (Sach and Seifert 1999). Due to these advantages, foam concrete has been widely used in the building and construction field.

It is feasible to develop foam concrete for spray-based 3D printing. It consists of fresh property tailoring and hardened property improvement. Although conventional foam concrete material is very flowable and considered as self-compacting concrete (Jones and McCarthy 2005), the rheological properties can be effectively controlled by the raw ingredients. The water content in the mixture affects the rheological performance, and some additives such as polymer or clay can increase the thixotropy (Roussel 2012, Zhang et al. 2018b) of the mixture. Furthermore, the low density of foam concrete contributes to good buildability. On the other hand, polymer-based fibers can be added to the mixture to prevent the occurrence of shrinkage cracks. With successful design of spray-based 3D printable foam concrete, it is possible to be extended to functional applications such as acoustic barrier and coatings of large span structures.

7.4.2 Integration with Feedback Control

The application of 3D concrete printing can facilitate the automation in the building and construction field. With the deeper understanding of how printing parameters affect the material distribution, it is feasible to integrate the spray-based 3D concrete printing with feedback control. Such integration can potentially raise the automation levels, which further saves the labour cost and increases the work efficiency.

Due to the splash and rebound of spray-based 3D concrete printing, an integrated system with feedback control can be designed and applied in the engineering applications. Fig. 7.1 and Fig. 7.2 show a possible system diagram and flowchart of feedback-oriented spray-based 3D concrete printing system. In this system, the loops of feedback control are implemented to realize spray-based 3D concrete printing and minimize the difference between the original design and actual print. 3D scanning can be adopted to obtain sprayed profile, which can then be compared with the original design after each loop of scan and spray. Thickness difference can be calculated and utilized for regulation of pumping rate, air inject pressure and robotic arm movement in each loop.

Fig. 7.1 System diagram of feedback-oriented spray-based 3D concrete printing system

Fig. 7.2 Flowchart of feedback-oriented spray-based 3D concrete printing system

Lindemann et al. have developed a similar closed-loop spray system with a laser triangulation sensor (Lindemann et al. 2018). Through the lab-scale experiment, the defect in the printed structure can be amended with automatic regulation system (see Fig. 7.3). It should be noted that the defect amendment may take several loops, e.g. nine loops in the lab-scale experiment. On the other hand, the amendment is only related to the collection of data and regulation of printing parameters.

Fig. 7.3 Defect amendment by a closed-loop spray system with a laser triangulation sensor (Lindemann et al. 2018). Reproduced with permission from Springer Nature

For future improvement of efficiency, the empirical material distribution model proposed in *Chapter 6* can be applied in the system. From the proposed model, printing

parameters can be picked at reasonable values. After each spray, original design and actual print are compared to generate the difference of material distribution, which can be minimized by adopting reasonable printing parameters. Hence, the introduction of material distribution model helps reduce the loop to complete defect amendment. Through feedback control, the target profile can be manufactured by spray-based 3D concrete printing with better quality.

7.4.3 Structural Performance

As mentioned in *Section 2.2*, complete multi-level material design for 3D printable cementitious materials should cover the three levels, i.e. mixture design, printing process and composite structure (Lu et al. 2019b). In this research study, different mixture designs of spray-based 3D printable cementitious materials were developed. In addition, the effects of printing parameters on material distribution were also investigated. Hence, the next level of designing spray-based 3D printable cementitious materials is to investigate the structural performance.

The composite structures can be manufactured by hybrid 3D printing. One option is combining spray-based 3D concrete printing with extrusion-based one. Through this combination, main structure component such as external wall can be manufactured by extrusion-based 3D concrete printing, which serves as the substrate for spray-based 3D concrete printing. The decorative profiles on the wall or ceilings can be manufactured by spray-based 3D concrete printing afterwards. Another option is combining plastic printing and spray-based 3D concrete printing, where printed plastic can serve as the internal reinforcement/skeleton in the composite structure. Simulation of the printed composite structure and topological studies may be conducted to optimize the plastic skeleton for better mechanical performance (Bruggi 2009, Martens et al. 2018). Fig. 7.4 shows an example of a simply supported beam after optimization.

Fig. 7.4 Optimization of a simply supported beam (Bruggi 2009). Reproduced with permission © Elsevier

As shown in Fig. 7.4, the downward force is applied at the middle span of the simply supported beam. Through the finite element analysis/calculations, the stress distribution inside the beam can be obtained. The trajectories of principal stress can be drawn and represented by strut-and-tie model, which is the reference of topological designs shown in the left side of Fig. 7.4. The designed topological structure can be printed with plastic by fused deposition modeling (FDM) printer, which serves as the skeleton/reinforcement. Afterwards, the spray-based 3D concrete can be applied to construct the composite beam. The discussion of topological design is described in literature study (Bruggi 2009), where a flowchart of the procedure can be referred to in Fig. 7.5.

Fig. 7.5 Flowchart of topological design procedure (Bruggi 2009). Reproduced with permission © Elsevier

7.4.4 Adhesion between Sprayed Material and Substrate

As mentioned in *Section 2.3*, sufficient material adhesion to the substrate in the experiments was guaranteed in this study. However, lack of material adhesion to substrate can lead to the fall of sprayed materials with large thickness, which may affect material distribution. On the other hand, while there is no relevant study on loading mechanism of overhead spray-based printing, it is suspected that the competition between gravity, cohesion between each layer and adhesion to substrate plays an important role in the deposition. Therefore, it is important to investigate the adhesion between sprayed material and substrate.

Tack test can be carried out to study the adhesion between sprayed material and substrate. The setup of tack test can be referred to in Fig. 7.6 (Kawashima et al. 2014).

In their test, the fresh mixture was filled between two parallel plates. With controlled lifting of upper plate, normal force on the upper plate and distance between the two parallel plates were recorded. Cohesive rupture inside the mixture, adhesive fracture at mixture-plate interface or viscous flow of the mixture are the three failure modes in the tack test (Mohamed Abdelhaye et al. 2008). Insufficient adhesion between the mixture and plates lead to adhesive fracture, where the peak force can be compared for assessment.

Fig. 7.6 Setup of tack test (Kawashima et al. 2014). Reproduced with permission © Elsevier

Substrates made of different materials may also affect the adhesion. In this thesis, timber plates were used as substrates. For more generic applications, other materials such as steel and hardened concrete can be applied in the future study. Tack test can be adopted to assess the adhesion, where thin plates made of substrate materials can be glued to the two parallel testing plates. Alternatively, overhead spray-based 3D printing can be carried out for different substrates with the same mixture. Through comparison of maximum sprayed layers and failure modes, the adhesion between mixture and different substrates can also be assessed.

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