Feasibility study on sustainable magnesium potassium phosphate cement paste for 3D printing

Weng, Yiwei; Ruan, Shaoqin; Li, Mingyang; Mo, Liwu; Unluer, Cise; Tan, Ming Jen; Qian, Shunzhi

2019

Weng, Y., Ruan, S., Li, M., Mo, L., Unluer, C., Tan, M. J., & Qian, S. (2019). Feasibility study on sustainable magnesium potassium phosphate cement paste for 3D printing. *Construction and Building Materials*, 221, 595-603. doi:10.1016/j.conbuildmat.2019.05.053

<https://hdl.handle.net/10356/140134>

<https://doi.org/10.1016/j.conbuildmat.2019.05.053>

© 2019 Elsevier Ltd. All rights reserved. This paper was published in *Construction and Building Materials* and is made available with permission of Elsevier Ltd.

Downloaded on 26 Apr 2023 16:53:30 SGT

Feasibility study on sustainable magnesium potassium phosphate cement paste for 3D printing

Yiwei Weng^{a,b}, Shaoqin Ruan^b, Mingyang Li^a, Liwu Mo^c, Cise Unluer^b, Ming Jen Tan^a,
Shunzhi Qian^{a,b,*}

^aSingapore Centre for 3D Printing, School of Mechanical and Aerospace Engineering,
Nanyang Technological University, Singapore

^bSchool of Civil and Environmental Engineering, Nanyang Technological University,
Singapore

^cState Key Laboratory of Materials Oriented Chemical Engineering, College of Materials
Science and Engineering, Nanjing Technological University, Nanjing, China

*Corresponding author. Tel: +65 6790 4916, Email: SZQIAN@ntu.edu.sg

Abstract:

3D printing of cementitious materials is an innovative and promising approach in the construction sector, attracting much attention over the past few years. Use of waste cementitious materials in the production of 3D printable components increases the sustainability and cost-effectiveness of this process. This work proposes an environmentally friendly 3D printable cementitious material involving the use of magnesium potassium phosphate cement (MKPC) with various ratios of fly ash replacement ranging from 0 to 60 wt% to increase the working time of the binder. Silica fume was used at up to 10 wt% to adjust rheological and mechanical properties. The performance of the developed MKPC binders with different formulations in the context of 3D printing was assessed via a detailed investigation of the workability, extrudability, buildability, compressive strength, porosity and microstructural analysis. Amongst the mixtures studied, the optimum MKPC formulation involving 60 wt% fly ash and 10 wt% silica fume with a borax-to-magnesia ratio of 1:4 was selected for a small-scale printing demonstration in line with its rheological and mechanical

properties. Finally, a 20-layer component with a height of 180 mm was printed in 5 min to demonstrate the feasibility of the adopted mixture in 3D printing.

Keywords: Additive manufacturing; 3D printing, magnesium potassium phosphate cement; supplementary cementitious materials; fresh properties

1 Introduction

3D printing technology has attracted much attention recently [1,2], especially in the field of concrete industry due to its benefits such as customizable design, reduced labor-cost minimized material wastage and formwork-free fabrication [3–6]. Various types of 3D concrete printers and corresponding printing processes were developed in the past decades [7–9]. In addition to the development of 3D printers and printing processes, concurrent development of printable cementitious materials is also essential for 3D printing. To this end, various types of cementitious materials have been developed for 3D printing, including plain mortar [10,11], short fiber reinforced mortar [12,13], and fiber-reinforced-plastic reinforced printable concrete [14].

However, Portland cement-based materials are lack of sustainability due to the high amount of CO₂ emission during manufacturing process, and there is an urgent need to develop alternative sustainable binders for 3D concrete printing, such as earth-based materials [8], waste materials of copper tailings [15] and geopolymers [16–18]. Reactive magnesium oxide cement is also a promising alternative binder for sustainable 3D concrete printing [19,20]. One of the cementitious materials produced with RMC as binder is magnesium potassium phosphate cement (MKPC), which will be discussed in the following part in more details.

Similar to geopolymer, MKPC is also a type of rapid hardening and environmentally friendly materials [19] from the aspect of reducing the Portland cement consumption, and it has been widely adopted in engineering applications [21–23]. The chemical reactions of MKPC systems can be described as shown in Eqn. (1) [24,25]. The main reaction phase (MgKPO₄·6H₂O or struvite-K) is accountable for the strength improvement in MKPC-based systems [26]. The reaction kinetics and overall performance of the MKPC-based cementitious materials are controlled by several major factors, such as magnesia-to-potassium dihydrogen phosphate (KDP) weight ratio, magnesia-to-borax (Na₂B₄O₇·10H₂O) (M/B) weight ratio [27] and water-to-binder (W/B) ratio [25]. Within these binders, borax is used as a retarder to avoid flash set [27]. When MKPC is used for practical applications, fly

ash has been commonly blended due to its beneficial effects in improving fresh mixture workability, reducing heat generation and lowering the production cost [25].

Fly ash (FA) is a by-product of coal combustion in power plants and has been widely employed as a replacement of magnesia or KDP in MKPC to improve workability, reduce hydration heat, diminish the cost and reduce environmental impacts [23]. Some studies indicated that FA is capable of acting as inert fillers when both the magnesia and KDP are replaced with FA while maintaining magnesia-to-phosphate (M/P) molar ratio unchanged [21,26]. Previous investigations also reported that FA is involved in the chemical reactions within MKPC systems [28] after the major binder, magnesia, is substituted with FA partially, consequently reducing M/P molar ratio in the designed binders and achieving better fresh properties, improved microstructures, and enhanced mechanical properties.

In addition to fly ash, silica fume is a by-product of manufacturing silicon metal and is an efficient ingredient to adjust the rheological properties for 3D concrete printing and improve the mechanical properties of MKPC. Intensive research works use silica fume to optimize the rheological properties of materials to satisfy the requirements of 3D concrete printing [29,30]. Additionally, Zheng et al. [31] indicated that silica fume with the dosages less than 15 % of the mass ratio of MgO + KDP can enhance the hardened mechanical properties of MKPC due to a much denser matrix with less crack and porosity achieved.

To the best of our knowledge, this work is among the first in the literature on developing 3D printable MKPC through optimizing rheological and mechanical properties. FA was introduced in MKPC mortars through partially replacing MgO. Meanwhile, silica fume acting as an efficient ingredient to adjust the fresh properties of pastes for 3D printing was attempted along with different magnesia-to-borax ratios. Fresh performance and early-age mechanical properties of mortars with different formulations were characterized through initial setting time, rheological performance and compressive strength test, respectively.

Scanning electron microscopy (SEM), X-ray diffraction (XRD), and μ -CT scan were employed to investigate the hydration products, microstructure and porosity. A small-scale printing test using the optimized MKPC design was conducted as a proof of concept eventually.

2 Material design and preparation

2.1 Materials

Light-burnt magnesia [32] was supplied by Urban Redevelopment Authority, Singapore. Class F fly ash was supplied by Sembcorp Design & Construction Pte Ltd, Singapore. Borax was supplied by Linyi Chemical Reagent Company Ltd., Shandong, China. Undensified silica fume Grade 940 was supplied by Elkem Pte Ltd. Table 1 shows the chemical compositions of magnesia and fly ash. Particle size distribution of magnesia, fly ash and silica fume are presented in Fig. 1. An accelerated reactivity method [33] was used to characterize reactivity of magnesia. The result was plotted in Fig. 2. Fig. 3 depicts the gradation curve of fine sand supplied by Buildmate Pte Ltd Singapore.

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

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

Fig. 1 Particle size distribution of magnesia, fly ash and silica fume

Fig. 2 Reactivity of MgO

Fig. 3 Gradation curve of sand particles

2.2 Sample preparation: mix design and procedures

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

144

Table 2 Mix compositions of the MKPC mortars

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

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

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

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

145

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

149

150

151 **3 Experimental methods**

152

153 **3.1 Characterization of setting behavior**

154

155 Open time, a critical factor for 3D concrete printing, is defined as the period within which
 156 the materials are consistent with acceptable printing quality in the printing process [34].
 157 Setting time has been proved to be an important parameter closely related to the open time
 158 [35]. It should be sufficient long to prevent the material from blocking the hose. Meanwhile,
 159 too long setting time is harmful to buildability and printing speed as the materials need longer

time to gain strength. Setting time was characterized by an automatic Vicat apparatus in this work.

3.2 Rheological characterization and early-age compressive strength

In 3D concrete printing, extrudability and buildability are two somewhat conflicting properties. Extrudability requires that the materials can be pumped smoothly in the hose without blockage in the printing process. Buildability requires that the materials can be stacked stably in a layer-atop-layer manner. Both extrudability and pumpability are influenced by rheological performance of materials in fresh state, where desirable materials should have high flowability during pumping process (under applied shear rate) and can quickly build up internal structure at rest (without applied shear rate).

In this work, rheological performance in the fresh state was characterized by two methods, i.e. mini-cone test [10] and rheometer test (Anton Paar MCR 102) [36]. After being printed out, the material should be able to maintain its shape, which indicates low slump characteristics i.e. high yield stress [36]. Slump characteristics can be presented by the results from mini-cone test. Then, the protocol of rheometer test as shown in Fig. 4 was used to simulate the material rheological behavior in 3D concrete printing process. At step I, a shear rate of 100 s^{-1} was applied for 200 s to simulate the state of materials during pumping process. At step II, the shear rate was 0.01 s^{-1} and held for 30 s to simulate the condition of materials after printing out stage [36].

Fig. 4 Protocol for rheological characterization

In a hardened state, the buildability of cementitious materials is influenced by the development of early-age mechanical properties [37]. Vaitkevicius et al.'s work implied that the early-age compressive strength of the materials achieving 1MPa (20 min) and 4.93 MPa (1 day) is sufficient for most of the requirements in various 3D printing [35]. The influence of MgO, fly ash, silica fume and borax on early-age compressive strength were investigated accordingly in macroscale, which was conducted on cubic specimens with dimensions of 50×50×50 mm at the age of 30 min, 60 min, and 90 min respectively [15]. The average of three samples was reported for each data point.

3.3 XRD, μ -CT and SEM analyses

The hardened properties of MKPC are influenced by several factors in microscale, including hydration products, microstructure, porosity, etc. As indicated in Eq.(1), struvite-K is the main contributor to the mechanical properties of MKPC. To explore the influence of time on the struvite-K, selected specimens at 30 min and 90 min were prepared for XRD analysis.

Silica fume presents the superior filler effect, which influences the porosity and microstructure, consequently affecting the mechanical performance of MKPC as discussed by Ma and Xu [38] that a high ratio of struvite-K-to-space is beneficial to mechanical properties, especially the compressive strength. The μ -CT scan, a non-destructive and environmentally friendly test method compared with MIP, was adopted for quantifying the porosity of selected specimens at 90 min to study the influence of silica fume on the porosity of MKPC. Detailed characterizing procedures can be found in Bossa et al's work [39]. Selected specimens at 90 min were prepared to observe the influence of silica fume on the microstructure via SEM as well.

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

3.4 Printability test

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

Fig. 5 Gantry printer

Fig. 6 CAD model for printability test

4 Results and discussions

4.1 Setting performance

Fig. 7 shows the results of setting time, where black dash line indicates the initial setting time. As can be seen from Fig. 7, the initial setting time of MKPC pastes increases with the growth of the replacement ratio of FA or the decrease of the dosage of SF in the paste. The influence of fly ash on setting time can be both chemical and physical [40]. In the physical sense, with less amount of magnesia in the binders due to higher fly ash replacement ratio, inadequate reaction occurs between magnesia and KDP. Chemically the fly ash can react with KDP while the reaction rate is significantly slower than that of magnesia and KDP [21]. The setting time of the mixture was also influenced by silica fume physically [41]. Silica fume may act as inert fillers, which reduces bleeding and increases the packing fraction of solid materials by occupying space between other particles. These physical effects of the silica fume may contribute to the decrease of setting time.

With the increase of the dosage of borax (Fig. 7), a longer initial setting time was observed since the setting time of MKPC is mainly controlled by the borax-to-magnesia ratio [27]. Comparing pastes with a MgO-to-borax ratio of 1:4 and 1:8, their initial setting time were quite similar, indicating that there is a certain upper limit on the retarding effect of borax.

Fig. 7 The results of setting time

4.2 Rheological characterization and early-age compressive strength

The results of mini-cone test are shown in Fig. 8. As can be seen from Fig. 8, with the increase of the ratio of FA replacement, the spread diameter increases, which reveals that the materials tend to be high-slump characterise. However, spread diameter decreased from 225.7 mm to 101.3 mm by simply introducing 10 % silica fume, which indicates that silica fume has a significant contribution to improving yield stress and shape retention capability [42]. The reason may be that the addition of silica fume can significantly increase the packing fraction, consequently enhancing the interparticle force dramatically [43]. The figure also shows that spread diameter increased from 101.3 mm to 109.6 mm via raising the magnesia-to-borax ratio. Meanwhile, as can be seen from Fig. 7 and 8, with the increase of borax -to-MgO ratio from 1:1 to 4:1, the working time of M40FA60S10-4 increases more than 3 times while the spread diameter almost maintains a constant compared with that of M40FA60S10-1.

Fig. 8 Results of mini-slump test

Rheometer test results are shown in Fig. 9 and Fig. 10. During rheometer test, mixtures of M100FA0S0-1, M60FA40S0-1, M50FA50S0-1, M40FA60S10-1 hardened quite fast and was beyond the test capacity of equipment during the measurement. Therefore only M40F60S10-4 and M40F60S10-8 were analyzed by rheometer. As can be seen from Fig. 4 Fig. 9 and Fig. 10, at step I (Fig. 4), the materials can be quite flowable with low torque under high shear rate (Fig. 9), which is around 20 Pa. This is beneficial to the pumping process. Then, after the materials being printed out (step II, Fig. 4), the high shear rate is removed, and the torque can increase fast (Fig. 10), and it is favorable to the building process as the materials can obtain green strength in a short period. These results reveal that tested materials are desirable for 3D printing in the fresh state as low torque is beneficial for pumping

process (extrudability) under constant high shear rate. Meantime, quick built-up of torque is beneficial for buildability after materials being printed out.

Fig. 9 Torque development under shear rate of 100 s⁻¹

Fig. 10 Torque development with shear rate 0.01 s⁻¹

The compressive strength development of MKPC mortars from 30 min to 90 min are plotted in Fig. 11. As can be seen from the Fig. 11, the compressive strength of all investigated

mixtures is higher than 1 MPa at 30 min, and higher than 4 MPa at 90 min. The results imply that all investigated mixtures are sufficient in civil engineering from the aspect of the development of early-age mechanical performance [35]. When dealing with buildability and open time in general, readers should nevertheless refer to recent reference works [34-36]. Specifically, M100FA0S0-1 samples revealed the highest compressive strength at all curing ages, which could be associated with the higher amount of struvite-K formation due to the larger magnesia content, which enhances the chemical reaction between MgO and KDA. M40FA60S10-1 samples outperformed M40FA60S0-1 samples in terms of compressive strength due to the addition of silica fume, which acts as inert fillers and is capable of filling the pores and cracks within paste, consequently leading to an improved pore structure and packing fraction as well as compressive strength of MKPC [31]. M40FA60S10-4 samples shown almost the worst mechanical properties within all curing ages due to high content of borax. Excessive borax incorporation in MKPC system slows down the hydration process in MKPC-based materials [44], resulting in a lower content of struvite-K and inferior mechanical performance.

Although the reaction of FA and KH_2PO_4 occurred to some extent [45,46], their reaction degree is much lower compared with the reaction between the magnesia and KH_2PO_4 , leaving an abundance of KH_2PO_4 unreacted, consequently increasing the porosity of materials. Additionally, the dissolution of unreacted KH_2PO_4 in water would also decrease the pH of the system, thus destabilizing struvite-K in the system. Furthermore, the strength of mixes would be deteriorated with a high fraction of FA incorporation in water [47].

Therefore, M100FA0S0-1 samples without any addition of FA revealed the highest mechanical strength compared with the rest of the group.

Fig. 11 Early-age compressive strength development of the MKPC pastes with various formulations

4.3 XRD, μ -CT and SEM analyses

The XRD diffractograms of selected hydrated MKPC pastes are displayed in Fig. 12. Some of the main phases usually observed within these systems are magnesia, KDP and struvite-K, whose strongest characteristic peaks were located can be found in Yang et al.'s work [48]. As can be seen from Fig. 12, no KDP characteristic peaks were detected in the presented patterns. The characteristic peaks of MgO and struvite-K were displayed, albeit with low intensities. This could be due to the relatively short curing duration (i.e. 90 min) that these samples were exposed to, thereby limiting the degree of hydration. The amount of the reaction product (intensity in Fig. 12), MKP, that formed within these samples increased with time due to continuous hydration.

Fig. 12 XRD patterns of selected MKPC samples at different curing ages

M40FA60SF0-1 and M40FA60SF10-1 samples were selected in the porosity analysis to investigate the influence of silica fume on porosity. Fig. 13 shows the μ -CT scan images produced on the selected samples. The shadow X-ray image of the sample is presented in Fig. 13 (a), while the typical reconstructed cross-sectional image of the sample is shown in Fig. 13 (b). Fig. 13 (c) shows pores and solid phases, which are represented by black and white areas, respectively.

Fig. 13 Tomographic images showing (a) x-ray shadow image of the typical sample, (b) typical image of X-ray scan data from cross-section x-x and (c) processed data from the selected plane of the sample to show pore regions

A three-dimensional volume of the boxed area (Fig. 14 (a)) was created by stacking together sequential slices of two-dimensional μ -CT images, as shown in Fig. 14 (b). Afterwards, pores were separated from the reconstructed volume. Black areas in Fig. 14 (b) represent pores in the specimen.

Fig. 14 Three-dimensional rendering of μ -CT scan data showing (a) 3D model and (b) pore dispersion

Typical sliced images and pore size distributions of M40FA60SF0-1 and M40FA60SF10-1 samples are plotted in Fig. 15 and Fig. 16, respectively. As can be seen from Fig. 15, fewer pore areas were observed from the sliced image of M40FA60SF10-1 samples than those of M40FA60SF0-1 samples. Pore size distribution and porosity were then calculated through CTAnalyzer, and the result is plotted in Fig. 16. The pore volume of scanned areas in M40FA60SF0-1 and M40FA60SF10-1 samples is 3.54 mm³ and 1.05 mm³, respectively. In line with sliced images, the figures indicate that the addition of silica fume in MKPC system decreases the porosity greatly, and a denser matrix can be achieved, consequently a better mechanical performance. Detailed image processing procedures were discussed by Rattanasak and Kendall [49].

Fig. 15 Typical sliced images of (a) M40FA60SF0-1 and (b) M40FA60SF10-1

Fig. 16 Pore size distribution of different pastes

Fig. 17 shows the SEM results. The microstructure of the M60FA40SF0-1 sample at 90 min is shown in Fig. 17 (a). The observed microstructure involved the presence of crystals with morphologies resembling struvite-K described as bladed prisms [33]. The microstructures of M60FA40SF10-1 samples (90 min) are shown in Fig. 17 (b) and (c). As can be seen from Fig. 15 and 16, compared with M60FA40SF0-1 samples, denser microstructures and less porosity achieved by M60FA40SF10-1 were associated with the presence of a higher amount of SiO₂ within their formulation. The use of silica fume with an amorphous SiO₂ content of 95% in the microstructural development of the prepared formulations led to the formation of a dense network. Abundant SiO₂ that filled the large pores of the prepared samples

contributed to a higher strength achieved by M60FA40SF10-1 samples in comparison to M60FA40SF0-1.

Fig. 17 Microstructural images of (a) M60FA40SF0-1 samples (magnification: x5000), (b) M60FA40SF10-1 samples (magnification: x5000) and (c) M60FA40SF10-1 samples (magnification: x10000)

4.4 Printability test

After finishing the mixing process, a small-scale printing test was conducted in the lab. However, fresh properties of rapid hardening materials evolved very fast. A relatively long setting time was required to prevent damaging the equipment. Besides, a high early-age strength was also needed to ensure the buildability. Thus, the formulation (M40FA60S10-4)

was selected in printability test due to appropriate setting behavior and early-age mechanical properties. The result of printability test is illustrated in Fig. 18. Printing and pumping speed were 2000 mm/min and 650 rpm, respectively. It took 5 min to finish printing the part with 20 layers and 180 mm height. The M40FA60S10-4 paste can be pumped well without blocking hose during the pumping process and can be printed well without significant discontinuity as can be seen in Fig. 18.

Fig. 18 Results of printability test

5 Conclusions

This study explored the feasibility of using MKPC, a rapid-hardening and environmentally friendly building material, in 3D printing applications. The investigation involved the measurement of setting time to indicate the open time for 3D printing, followed by optimization of the fresh properties and early-age mechanical properties of MKPC binders involving 0-60 wt% fly ash and 0-10 wt% silica fume. Finally, a printing test was employed to verify the printability of the designed formulations.

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

Future studies shall focus on optimizing the setting time and/or open time of the developed formulations used in 3D printing. Furthermore, a detailed investigation on the long-term behavior, such as hardened properties, interlayer bonding, etc. of the hardened material involving these novel cementitious binders will enable their application into practice.

Conflict of interest

The authors report that they have NO affiliations with or involvement in any organization or entity with any financial interest in the subject matter or materials discussed in this manuscript.

Acknowledgments

The authors would like to acknowledge National Research Foundation, Prime Minister's Office, Singapore under its Medium- Sized Centre funding scheme, Singapore Centre for 3D Printing and Sembcorp Design & Construction Pte Ltd for their funding and support in this research project. Shaoqin Ruan and Cise Unluer received financial support from the Singapore MOE Academic Research Fund Tier 1 (RG 95/16).

References

- [1] B. Lu, Y. Weng, M. Li, Y. Qian, K.F. Leong, M.J. Tan, S. Qian, A systematical review of 3D printable cementitious materials, *Constr. Build. Mater.* 207 (2019) 477–490. doi:<https://doi.org/10.1016/j.conbuildmat.2019.02.144>.
- [2] F. Bos, R. Wolfs, Z. Ahmed, T. Salet, W. Rob, A. Zeeshan, T. Salet, R. Wolfs, Z. Ahmed, T. Salet, Additive manufacturing of concrete in construction: potentials and challenges of 3D concrete printing, *Virtual Phys. Prototyp.* 2759 (2016) 1–17. doi:10.1080/17452759.2016.1209867.
- [3] Y. Weng, B. Lu, M. Tan, S. Qian, Rheology and Printability of Engineered Cementitious Composites- A Literature Review, in: *Proc. 2nd Int. Conf. Prog. Addit. Manuf. (Pro- AM 2016)*, 2016: pp. 427–432. <https://dr.ntu.edu.sg/handle/10220/41821> (accessed April 1, 2017).
- [4] B. Lu, M.J. Tan, S. Qian, A Review of 3D Printable Construction Materials and Applications, in: *Proc. 2nd Int. Conf. Prog. Addit. Manuf. (Pro-AM 2016)*, Singapore, 2016: pp. 330–335.
- [5] B. Lu, Y. Qian, M. Li, Y. Weng, K.F. Leong, M.J. Tan, S. Qian, Design spray-based 3D printable cementitious materials with FAC and AEA, *Constr. Build. Mater.* (2019). doi:<https://doi.org/10.1016/j.conbuildmat.2019.03.186>.
- [6] B. Lu, M. Li, W. Lao, Y. Weng, S. Qian, M.J. Tan, K.F. Leong, Effect of spray-based printing parameters on cementitious material distribution, in: *Proc. 29th Annu. Int. Solid Free. Fabr. Symp. – An Addit. Manuf. Conf.*, 2018: pp. 1989–2002.
- [7] C. Gosselin, R. Duballet, P. Roux, N. Gaudillière, J. Dirrenberger, P. Morel, Large-scale 3D printing of ultra-high performance concrete - a new processing route for architects and builders, *Mater. Des.* 100 (2016) 102–109. doi:10.1016/j.matdes.2016.03.097.
- [8] A. Perrot, D. Rangeard, E. Courteille, 3D printing of earth-based materials: Processing aspects, *Constr. Build. Mater.* 172 (2018) 670–676. doi:10.1016/j.conbuildmat.2018.04.017.
- [9] X. Zhang, M. Li, J.H.J.H. Lim, Y. Weng, Y.W.D.Y.W.D. Tay, H. Pham, Q.-C.Q.-C. Pham, Large-Scale 3D Printing by a Team of Mobile Robots, *Autom. Constr.* 95 (2018) 98–106. doi:10.1016/j.cageo.2011.03.003.
- [10] Y. Weng, M. Li, M.J. Tan, S. Qian, Design 3D printing cementitious materials via Fuller Thompson theory and Marson-Percy model, *Constr. Build. Mater.* 163 (2018) 600–610. doi:10.1016/j.conbuildmat.2017.12.112.
- [11] Z. Liu, M. Li, Y. Weng, T.N. Wong, M.J. Tan, Mixture Design Approach to optimize the rheological properties of the material used in 3D cementitious material printing, *Constr. Build. Mater.* 198 (2019) 245–255. doi:10.1016/j.conbuildmat.2018.11.252.
- [12] Y. Weng, M. Li, Z. Liu, B. Lu, D. Zhang, M.J. Tan, Printability and fire performance of a developed 3D printable fibre reinforced cementitious composites under elevated temperatures, *Virtual Phys. Prototyp.* 14 (2018) 284–292. doi:<https://doi.org/10.1080/17452759.2018.1555046>.

- [13] Y. Weng, M. Li, M.J. Tan, S. Qian, 3D Printable high performance fiber reinforced cementitious composites for large-scale printing, in: *Proc. 3rd Int. Conf. Prog. Addit. Manuf. (Pro-AM 2018)*, 2018: pp. 19–24. doi:<https://doi.org/10.25341/D4B591>.
- [14] J.H. Lim, Y. Weng, M. Li, Effect of fiber reinforced polymer on mechanical performance of 3D printed cementitious material, in: *Proc. 3rd Int. Conf. Prog. Addit. Manuf. (Pro-AM 2018)*, 2018: pp. 44–49. doi:<https://doi.org/10.25341/D43G6T>.
- [15] G. Ma, Z. Li, L. Wang, Printable properties of cementitious material containing copper tailings for extrusion based 3D printing, *Constr. Build. Mater.* 162 (2018) 613–627. doi:[10.1016/j.conbuildmat.2017.12.051](https://doi.org/10.1016/j.conbuildmat.2017.12.051).
- [16] B. Panda, S.C. Paul, L.J. Hui, Y.W.D. Tay, M.J. Tan, Additive manufacturing of geopolymer for sustainable built environment, *J. Clean. Prod.* 167 (2017) 281–288. doi:[10.1016/j.jclepro.2017.08.165](https://doi.org/10.1016/j.jclepro.2017.08.165).
- [17] M. Xia, B. Nematollahi, J. Sanjayan, Printability, accuracy and strength of geopolymer made using powder-based 3D printing for construction applications, *Autom. Constr.* 101 (2019) 179–189. doi:<https://doi.org/10.1016/j.autcon.2019.01.013>.
- [18] M. Xia, J. Sanjayan, Method of formulating geopolymer for 3D printing for construction applications, *Mater. Des.* 110 (2016) 382–390. doi:[10.1016/j.matdes.2016.07.136](https://doi.org/10.1016/j.matdes.2016.07.136).
- [19] S. Ruan, C. Unluer, Comparative life cycle assessment of reactive MgO and Portland cement production, *J. Clean. Prod.* 137 (2016) 258–273. doi:[10.1016/j.jclepro.2016.07.071](https://doi.org/10.1016/j.jclepro.2016.07.071).
- [20] S. Ruan, J. Qiu, Y. Weng, Y. Yang, E.-H. Yang, J. Chu, C. Unluer, The use of bacterial carbonate precipitation in healing cracks within reactive magnesia cement-based blends, *Cem. Concr. Res.* 115 (2018) 176–188. doi:[10.1016/j.cemconres.2018.10.018](https://doi.org/10.1016/j.cemconres.2018.10.018).
- [21] B. Xu, H. Ma, H. Shao, Z. Li, B. Lothenbach, Influence of fly ash on compressive strength and micro-characteristics of magnesium potassium phosphate cement mortars, *Cem. Concr. Res.* 99 (2017) 86–94. doi:[10.1016/j.cemconres.2017.05.008](https://doi.org/10.1016/j.cemconres.2017.05.008).
- [22] W. Liao, H. Ma, H. Sun, Y. Huang, Y. Wang, Potential large-volume beneficial use of low-grade fly ash in magnesia phosphate cement based materials, *Fuel*. 209 (2017) 490–497. doi:[10.1016/j.fuel.2017.08.028](https://doi.org/10.1016/j.fuel.2017.08.028).
- [23] L.J. Gardner, S.A. Bernal, S.A. Walling, C.L. Corkhill, J.L. Provis, N.C. Hyatt, Characterisation of magnesium potassium phosphate cements blended with fly ash and ground granulated blast furnace slag, *Cem. Concr. Res.* 74 (2015) 78–87. doi:[10.1016/j.cemconres.2015.01.015](https://doi.org/10.1016/j.cemconres.2015.01.015).
- [24] B. Xu, B. Lothenbach, A. Leemann, F. Winnefeld, Research Reaction mechanism of magnesium potassium phosphate cement with high magnesium-to-phosphate ratio, *Cem. Concr. Res.* 108 (2018) 140–151. doi:<https://doi.org/10.1016/j.cemconres.2018.03.013>.
- [25] H. Ma, B. Xu, J. Liu, H. Pei, Z. Li, Effects of water content, magnesia-to-phosphate molar ratio and age on pore structure, strength and permeability of magnesium potassium phosphate cement paste, *J. Mater.* 64 (2014) 497–502. doi:[10.1016/j.matdes.2014.07.073](https://doi.org/10.1016/j.matdes.2014.07.073).
- [26] Z. Ding, Z.J. Li, High-early-strength magnesium phosphate cement with fly ash, *ACI Mater. J.* 102 (2005) 375–381.
- [27] Q. Yang, X. Wu, Factors influencing properties of phosphate cement-based binder for rapid repair of concrete, *Cem. Concr. Res.* 29 (1999) 389–396. doi:[10.1016/S0008-8846\(98\)00230-0](https://doi.org/10.1016/S0008-8846(98)00230-0).
- [28] L. Lv, P. Huang, L. Mo, M. Deng, J. Qian, A. Wang, Properties of magnesium potassium phosphate cement pastes subjected to water curing: A comparison study on the influences of fly ash and metakaolin, *Constr. Build. Mater.* 203 (2019) 589–600. doi:<https://doi.org/10.1016/j.conbuildmat.2019.01.134>.
- [29] A. Kazemian, X. Yuan, E. Cochran, B. Khoshnevis, Cementitious materials for construction-scale 3D printing: Laboratory testing of fresh printing mixture, *Constr. Build. Mater.* 145 (2017) 639–647. doi:[10.1016/j.conbuildmat.2017.04.015](https://doi.org/10.1016/j.conbuildmat.2017.04.015).
- [30] Y. Weng, B. Lu, M. Li, Z. Liu, M.J. Tan, S. Qian, Empirical models to predict rheological properties of fiber reinforced cementitious composites for 3D printing, *Constr. Build. Mater.* 189 (2018) 676–685. doi:[10.1016/j.conbuildmat.2018.09.039](https://doi.org/10.1016/j.conbuildmat.2018.09.039).
- [31] D. Zheng, T. Ji, C. Wang, C. Sun, X. Lin, K. Muhammed, A. Hossain, Effect of the combination of fly ash and silica fume on water resistance of Magnesium – Potassium Phosphate Cement, *Constr. Build. Mater.* 106 (2016) 415–421. doi:[10.1016/j.conbuildmat.2015.12.085](https://doi.org/10.1016/j.conbuildmat.2015.12.085).

- [32] L. Yue, S. Jia, C. Bing, Experimental study of magnesia and M/P ratio influencing properties of magnesium phosphate cement, *Constr. Build. Mater.* 65 (2014) 177–183. doi:<https://doi.org/10.1016/j.conbuildmat.2014.04.136>.
- [33] B. Xu, H. Ma, Z. Li, Influence of magnesia-to-phosphate molar ratio on microstructures, mechanical properties and thermal conductivity of magnesium potassium phosphate cement paste with large water-to-solid ratio, *Cem. Concr. Res.* 68 (2014) 1–9. doi:[10.1016/j.cemconres.2014.10.019](https://doi.org/10.1016/j.cemconres.2014.10.019).
- [34] S. Lim, R.A. Buswell, T.T. Le, S.A. Austin, A.G.F. Gibb, T. Thorpe, Developments in construction-scale additive manufacturing processes, *Autom. Constr.* 21 (2012) 262–268. doi:[10.1016/j.autcon.2011.06.010](https://doi.org/10.1016/j.autcon.2011.06.010).
- [35] V. Vaitkevičius, E. Šerelis, V. Kerševičius, Effect of ultra-sonic activation on early hydration process in 3D concrete printing technology, *Constr. Build. Mater.* 169 (2018) 354–363. doi:[10.1016/j.conbuildmat.2018.03.007](https://doi.org/10.1016/j.conbuildmat.2018.03.007).
- [36] B. Panda, M.J. Tan, Experimental study on mix proportion and fresh properties of fly ash based geopolymer for 3D concrete printing, *Ceram. Int.* 44 (2018) 10258–10265. doi:[10.1016/j.ceramint.2018.03.031](https://doi.org/10.1016/j.ceramint.2018.03.031).
- [37] R.J.M. Wolfs, F.P. Bos, T.A.M. Salet, Early age mechanical behaviour of 3D printed concrete: Numerical modelling and experimental testing, *Cem. Concr. Res.* 106 (2018) 103–116. doi:[https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0001991](https://doi.org/10.1061/(ASCE)MT.1943-5533.0001991).
- [38] H. Ma, B. Xu, Potential to design magnesium potassium phosphate cement paste based on an optimal magnesia-to-phosphate ratio, *Mater. Des.* 118 (2017) 81–88. doi:[10.1016/j.matdes.2017.01.012](https://doi.org/10.1016/j.matdes.2017.01.012).
- [39] N. Bossa, P. Chaurand, J. Vicente, D. Borschneck, C. Levard, O. Aguerre-Chariol, J. Rose, Micro- and nano-X-ray computed-tomography: A step forward in the characterization of the pore network of a leached cement paste, *Cem. Concr. Res.* 67 (2015) 138–147. doi:[10.1016/j.cemconres.2014.08.007](https://doi.org/10.1016/j.cemconres.2014.08.007).
- [40] D. Ravina, Properties of fresh concrete containing large amount of fly ash, *Cem. Concr. Res.* 16 (1986) 227–238. doi:[10.1016/0008-8846\(86\)90139-0](https://doi.org/10.1016/0008-8846(86)90139-0).
- [41] M.H. Zhang, J. Islam, S. Peethamparan, Use of nano-silica to increase early strength and reduce setting time of concretes with high volumes of slag, *Cem. Concr. Compos.* 34 (2012) 650–662. doi:[10.1016/j.cemconcomp.2012.02.005](https://doi.org/10.1016/j.cemconcomp.2012.02.005).
- [42] P.K. Mehta, O.E. Gjorv, Properties of portland cement concrete containing fly ash and condensed silica fume, *Cem. Concr. Res.* 12 (1982) 587–595.
- [43] R.J. Flatt, P. Bowen, Yodel: A yield stress model for suspensions, *J. Am. Ceram. Soc.* 89 (2006) 1244–1256. doi:[10.1111/j.1551-2916.2005.00888.x](https://doi.org/10.1111/j.1551-2916.2005.00888.x).
- [44] H. Lahalle, C.C.D. Coumes, A. Mesbah, D. Lambertin, C. Cannes, S. Delpech, S. Gauffinet, Investigation of magnesium phosphate cement hydration in diluted suspension and its retardation by boric acid, *Cem. Concr. Res.* 87 (2016) 77–86. doi:[10.1016/j.cemconres.2016.04.010](https://doi.org/10.1016/j.cemconres.2016.04.010).
- [45] L.J. Gardner, S.A. Bernal, S.A. Walling, C.L. Corkhill, J.L. Provis, N.C. Hyatt, Characterisation of magnesium potassium phosphate cements blended with fly ash and ground granulated blast furnace slag, *Cem. Concr. Res.* 74 (2015) 78–87. doi:[10.1016/j.cemconres.2015.01.015](https://doi.org/10.1016/j.cemconres.2015.01.015).
- [46] M. Mahyar, Phosphate-activated high-calcium fly ash acid-base cements, *Cem. Concr. Compos.* 63 (2015) 96–103. doi:[10.1016/j.cemconcomp.2015.09.002](https://doi.org/10.1016/j.cemconcomp.2015.09.002).
- [47] B. Xu, B. Lothenbach, H. Ma, Properties of fly ash blended magnesium potassium phosphate mortars: Effect of the ratio between fly ash and magnesia, *Cem. Concr. Compos.* 90 (2018) 169–177. doi:[10.1016/j.cemconcomp.2018.04.002](https://doi.org/10.1016/j.cemconcomp.2018.04.002).
- [48] J. Yang, T. L., X. X., Effect of Fine Aggregates on Properties of Magnesium Potassium Phosphate Cement Mortar, *J. Mater. Civ. Eng.* 29 (2017) 6017012. doi:[https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0001991](https://doi.org/10.1061/(ASCE)MT.1943-5533.0001991).
- [49] U. Rattanasak, K. Kendall, Pore structure of cement/pozzolan composites by X-ray microtomography, *Cem. Concr. Res.* 35 (2005) 637–640. doi:[10.1016/j.cemconres.2004.04.022](https://doi.org/10.1016/j.cemconres.2004.04.022).