3D printable ‘just-add-water glass and water’ geopolymer—an experimental research based on extrusion-based 3D printing practices

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Abstract. The application of 3D printing technique has been bringing construction to a new stage. Development of suitable materials and suitable printing process of printable mixtures are very important issues. The present study aims to understand the strategies for the application of ‘just-add-water glass and water’ geopolymer in extrusion-based 3D printing. The 3D printing practice showed that the satisfactory printing quality, including extrudability, shape retainability, and buildability, can be achieved by adjusting water-to-binder ratio and gap time between layers for the ‘just-add-water glass and water’ geopolymer in fly ash–slag binary system.

1. Introduction
In recent years, 3D printing technology has shown great potential in construction, which offers new approach to buildings. Subsequently, the 3D printed concrete technology was born showing some obvious advantages including substantial energy saving, emission reduction, and improvement of construction efficiency. One of the most challenging for developing 3D printed concrete is the development of suitable 3D printable materials.

Geopolymers are generally understood as alkali-activated aluminosilicates [1], which is an inorganic two component system consisting of (1) a reactive solid source of SiO2 and Al2O3, and (2) an alkali activation solution [2]. They are regarded as amorphous materials consisting of SiO4 and AlO4 tetrahedral units connected by oxygens and charge-balanced by hydrated alkali cations [3]. The solid raw materials, also called alumina and silica sources, mainly come from industry by-products and low-temperature treated minerals, including fly ash, slag, silica fume, metakaolin, gibbsite, red mud, bottom ash, et al [4-6]. Geopolymer is seen as a plausibly green and sustainable cementitious material with a potential alternative to ordinary cement, and an opportunity to convert a variety of waste streams into useful by-products [4,7].

Some researches on the application of geopolymer in 3D printing construction have been done. Panda et al [8] evaluated the potential of fly ash based geopolymer cement for 3D printing by examining fresh properties and mechanical properties of printed geopolymer, and [9] measured the anisotropic mechanical performance of 3D printed fly ash-based geopolymer reinforced by chopped glass fibre. Al-Qutaiffi et al [10] evaluated effects of fibre, time gaps between layers, and layering patterns on structural buildability and hardened mechanical properties, showing that fibre increased the flexural strength and minimum time gaps produced the highest flexural strength results. Nematollahi et al [11] investigated
the influence of polypropylene (PP) fibres on the fresh and hardened properties of 3D-printed fly ash-based geopolymer mortars. The addition of fibre improved both the fresh and hardened states to meet the necessary properties for 3D printing by improving the shape-retention ability and enhancing compressive and flexural strength with a minor reduction in interlayer bond strength. Panda et al [12] investigated the effects of printing time gap between layers, nozzle speed and nozzle standoff distance on the tensile bond strength of 3D printed fly ash-based geopolymer mortar. Panda et al [13] studied the mix proportion in fly ash-slag-silica fume system to obtain a best printable mix by measuring extrudability, shape retention, buildability and open time. Alghamdi et al [14] prepared 3D printing fly ash-based geopolymer supplemented with fine limestone, slag, or Portland cement. Based on the measured shear yield stress at different times and concurrent printing of a filament, the printability window and yield stress bounds for printability, applicable for the chosen printing parameters, are established. Bong et al [15] optimized geopolymer mixture by considering the influence of type of hydroxide solution (HS), the type of silicate solution (HS), and the mass ratio of SS to HS on the workability, extrudability, shape retention ability and mechanical performance of different geopolymer mixtures. Panda et al [16] developed a printable one-part geopolymer mix to solve the troublesome induced by high viscosity of the alkaline solution.

However, the printable geopolymer in above listed literatures was prepared by adding viscosity modifying agent (VMA). The aim of this paper is to develop the strategies for the 3D printing application of ‘just-add-water glass and water’ geopolymer in fly ash-slag binary system, based on the extrusion-based 3D printing practice.

2. materials and methods
The content of this section is the design of test mix ratio and the test method to be followed in the test.

2.1. Materials
The chemical compositions of fly ash (FA) and slag used in this study are listed in table 1. The chemical compositions are measured using X-ray Fluorescence Spectrometer (XRF). The activator was commercial water glass with a modulus of 2.4 and solid content of 40%.

| Composition | SiO₂ | CaO | Al₂O₃ | MgO | SO₃ | TiO₂ | Fe₂O₃ | K₂O | MnO | Rb₂O |
|-------------|------|-----|-------|-----|-----|------|-------|-----|-----|------|
| Fly ash     | 22.06| 0.71| 5.95  | 0.25| -   | 0.09 | 6.71  | 5.39| 0.17| 1.20 |
| Slag        | 27.50| 44.60|13.20 | 8.72| 2.05| 1.36 | 0.76  | 0.43| 0.43| -    |

2.2. Preparation of geopolymer paste
Geopolymer pastes were prepared by mixing FA, slag, water glass and water at various FA (slag) content and water-to-binder (W/B) ratio. The binder was the total of FA and slag. The designed mixture proportions are shown in table 2.

| Code | Binder | Alkali content | Water-to-binder ratio |
|------|--------|----------------|-----------------------|
| FA100| 100    | 0              | 4%                    | 0.19-0.25             |
| FA90 | 90     | 10             |                       |                      |
| FA80 | 80     | 20             |                       |                      |
| FA70 | 70     | 30             |                       |                      |

2.3. Setting time.
The setting time was measured using a needle Vicat instrument manufactured, referring to GB / T 1346-2011 "Standard Consumption Water Consumption, Setting Time, and Stability Test Methods".
2.4. Extrusion-based 3D printing
3D printing was conducted using a gantry 3D printer, as shown in figure 1. Once the paste was mixed well, the paste was placed into the feed bin. Then the paste was extruded and deposited according to the model. This printer was controlled by a computer. The line speed of printing was 30 mm/s. The inner diameter of nozzle used in the present study was 30 mm.

![3D printer](image)

Figure 1. 3D printer.

3. Result and discussion

3.1. Minimum water-to-binder ratio for preparing workable paste
The prepared geopolymer mixture should be workable (shown in figure 2 a and b). The minimum W/B ratio for producing workable paste with different FA content from 100% to 70% is presented in figure 2c.

![Mixture images](image)

(a) mixture that did not form workable paste, (b) workable paste, (c) minimum W/B ratio with various FA content.

![Graph](image)

Figure 2. (a) mixture that did not form workable paste, (b) workable paste, (c) minimum W/B ratio with various FA content.

3.2. Setting time
The setting time indicates the workable time. Generally, the extrudability of mixture will reduce earlier than the initial setting time [13, 17], and the mixture begin to become hardened after initial setting time. This means that the mixture should be printed before initial setting time and must be removed from extruder after initial setting time as soon as possible to avoid being hardened in the tube and nozzle.
figure 3 presents the initial and final setting time with decreasing FA content (increasing slag content). The setting time significantly decreased when the slag content increased from 0 to 20%, while, the setting time nearly keep the same when slag content increased from 20% to 30%.

![Setting time graph](image)

**Figure 3. Setting time**

3.3. Extrusion-based 3D printing

3.3.1. Effect of water-to-binder ratio on printability and shape retainability. For the ‘just-add-water glass and water’ geopolymer, the W/B ratio is a key parameter that influence the extrudability and shape retainability. Single layers were printed to check the extrudability and shape retainability. Figure 4 shows the printed layer of 100% FA geopolymer with W/B ratio from 0.19 to 0.22. For the 100 FA geopolymer with W/B ratio of 0.19 and 0.20 (Figure 4a,b), the mixture cannot be printed well with showing unsatisfied printing quality, due to the lack of fluidity of mixture. The printed 100 FA geopolymer with W/B ratio of 0.21 show a satisfactory printing quality with a enough shape retainability (figure 4c). when the W/B ratio increased to 0.22, the printed layer showed a flow of deposited mixture, which means that the printed layer cannot maintain its shape satisfactorily (Figure 4d). Figure 5 and 6 show the printed layer with satisfactory shape retainability for the geopolymer made of various FA and slag contents. Figure 5 shows that 90% FA geopolymer with both W/B ratio of 0.21 and 0.22 could maintain its shape. FA-slag geopolymer has a wider range of W/B ratio to maintain the shape than 100% FA geopolymer.

![Layer images](image)

(a) W/B=0.19  (b) W/B=0.20  (c) W/B=0.21  (d) W/B=0.22

**Figure 4. Extruded and deposited one layer of geopolymer made of 100% fly ash.**
3.3.2. Gap time between layers. The gap time between layers was set to 0 and 20 min. 0 means the followed layers are printed without pause after one layer was printed. 20 min means that the followed layer was printed with a 20 min pause after one layer was printed. The 20 min gap time was set according to the initial setting time measured in Figure 3. Figure 7 shows that the printed multilayers of samples collapsed when the mixtures were printed continuously layer by layer without gap time. When the gap time increased to 20 min, the printed samples with multilayers can be built and maintain their shape with satisfactory buildability.

4. Conclusion
This paper investigated the application of ‘just-add-water glass and water’ FA-slag geopolymer in the extruded-based 3D printing using a gantry 3D printer. The 3D printing practice showed that the satisfactory extrudability and shape retainability can be achieved by adjusting water-to-binder ratio, and the buildability can be effectively improved by adjusting gap time.
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References
[1] Rożek, P.; M. Król; W. Mozgawa. (2019) Geopolymer-zeolite composites: A review. Journal of Cleaner Production, 230: 557-579.
[2] Buchwald, A.; H. D. Zellmann; C. Kaps. (2011) Condensation of aluminosilicate gels—model system for geopolymer binders. J. Non-Cryst. Solids, 357: 1376-1382.
[3] De Rossi, A.; L. Simão; M. J. Ribeiro; R. M. Novais; J. A. Labrincha; D. Hotza; R. F. P. M. Moreira. (2019) In-situ synthesis of zeolites by polymerization of biomass fly ash and metakaolin. Mater. Lett., 236: 644-648.
[4] McElhan, B. C.; R. P. Williams; J. Lay; A. van Riessen; G. D. Corder. (2011) Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement. Journal of Cleaner Production, 19: 1080-1090.
[5] Hu, W.; Q. Nie; B. Huang; X. Shu; Q. He. (2018) Mechanical and microstructural characterization of geopolymers derived from red mud and fly ashes. Journal of Cleaner Production, 186: 799-806.
[6] Antunes Boca Santa, R. A.; A. M. Bernardino; H. G. Riella; N. C. Kuhnhen. (2013) Geopolymer synthesized from bottom coal ash and calcined paper sludge. Journal of Cleaner Production, 57: 302-307.
[7] Komnitsas, K. A. (2011) Potential of geopolymer technology towards green buildings and sustainable cities. Procedia Engineering, 21: 1023-1032.
[8] Panda, B.; S. C. Paul; L. J. Hui; Y. W. D. Tay; M. J. Tan. (2017) Additive manufacturing of geopolymer for sustainable built environment. Journal of Cleaner Production, 167: 281-288.
[9] Panda, B.; S. C. Paul; M. J. Tan. (2017) Anisotropic mechanical performance of 3d printed fiber reinforced sustainable construction material. Mater. Lett., 209: 146-149.
[10] Al-Qutaifi, S.; A. Nazari; A. Bagheri. (2018) Mechanical properties of layered geopolymer structures applicable in concrete 3d-printing. Constr. Build. Mater., 176: 690-699.
[11] Nematollahi, B.; P. Vijay; J. Sanjayan; A. Nazari; M. Xia; V. N. Nerella; V. Mechtcherine. (2018) Effect of polypropylene fibre addition on properties of geopolymers made by 3d printing for digital construction. Materials, 11.
[12] Panda, B.; S. C. Paul; N. A. N. Mohamed; Y. W. D. Tay; M. J. Tan. (2018) Measurement of tensile bond strength of 3d printed geopolymer mortar. Measurement, 113: 108-116.
[13] Panda, B.; M. J. Tan. (2018) Experimental study on mix proportion and fresh properties of fly ash based geopolymer for 3d concrete printing. Ceram. Int., 44: 10258-10265.
[14] Alghamdi, H.; S. A. O. Nair; N. Neithalath. (2019) Insights into material design, extrusion rheology, and properties of 3d-printable alkali-activated fly ash-based binders. Materials & Design, 167.
[15] Bong, S. H.; B. Nematollahi; A. Nazari; M. Xia; J. Sanjayan. (2019) Method of optimisation for ambient temperature cured sustainable geopolymers for 3d printing construction applications. Materials, 12.
[16] Panda, B.; G. V. P. B. Singh; C. Unluer; M. J. Tan. (2019) Synthesis and characterization of one-part geopolymers for extrusion based 3d concrete printing. Journal of Cleaner Production, 220: 610-619.
[17] Ding, Z.; X. Wang; J. Sanjayan; P. X. W. Zou; Z.-K. Ding. (2018) A feasibility study on hpmc-improved sulfoaluminate cement for 3d printing. Materials, 11.