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Experimental study on mix proportion and fresh properties of fly ash based geopolymer for 3D concrete printing

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Abstract:

This paper presents the material design and fresh properties of geopolymer mortar developed for 3D concrete printing application. Unlike traditional casting, in 3D printing, extruded materials are deposited layer-by-layer to build complex architectural and structural components without the need of any formwork and human intervention. Extrudability, shape retention, buildability and thixotropic open time (TOT) are identified as critical early-age properties to characterize the 3D printable geopolymer material. Five different mix designs of geopolymer are tested in a systematic experimental approach to obtain a best printable mix and later it is used to print a 60-centimeter-tall freeform structure using a concrete gantry printer to validate the formulation.

Keywords: 3D Concrete Printing; Geopolymer; Rheology and Thixotropic
1. **Introduction**

Concrete is the most commonly used construction material. Customarily, it is produced by using Ordinary Portland Cement (OPC) as the binder but OPC's production is highly energy intensive and releases massive amounts of carbon dioxide (CO₂) into atmosphere [1]. In this regard, low-CO₂ binders are needed or alternatively new binders like geopolymer can be formulated by using industries by-products such as fly ash, slag etc., instead of disposing them in an open environment. Geopolymer cements has been widely accepted as green construction material for its superior mechanical and durability properties compared to OPC [2-5]. The chemistry and reaction mechanism was discovered in 1970 by Davidovits [6], which resulted from the hydroxylation and poly-condensation of thermally activated kaolin (metakaolin) in an alkaline solution. Since then, intensive academic research is going on in understanding the geopolymerisation kinetics for variety of new materials (red mud, volcanic ash, bottom ash) and their applications in industries like construction, petroleum, nuclear plants, marine and offshore etc [7].

Like OPC, geopolymers are also used in the traditional casting process where it is placed into formwork and then vibrated to fabricate building components. However, the development of self-compacting concrete (SCC) has eliminated this vibration process and made the construction process much easier, especially for high rise buildings application where it can be pumped up to several hundred meters and placed uniformly in the formwork [8]. Considering typical costings of a concrete structure, it has been found that the formwork can cost up to 50% of the total cost followed by material (concrete) and reinforcement cost. Formwork assembly is purely a labour
intensive process and sometimes it is very difficult to mould if the target design is complex (freeform) in nature. A recent advance meet in the construction technology, known as, “3D printing of concrete” has the potential to address these above challenges and more than that, it can automate our building processes while minimizing the labour counts and material wastages [9-12].

Concrete printing is an innovative construction process for fabricating concrete components employing the additive manufacturing technique [13]. This method can be used to build complex geometrical shapes without formwork, and thus has a unique advantage over conventional construction methods. The potential benefits of this process include: (a) ability to optimize the material distribution according to the need of application (b) ability to use of multi-material according to strength requirements (c) freeform structure printing capability (d) print on demand and (e) reduce material wastage [14,15].

The main challenge in the development of a printable mix is to have no-slump and self-compaction concrete, which are two contradictory aims and this can be partially fulfilled simultaneously. First of all, the material must be extrudable through an extruder head and able to maintain its shape, once deposited over the printing bed. Secondly, the deposited layers should not collapse under the load of subsequent layers and thirdly, a good bond strength between the layers must be ensured for better hardened properties [16-18]. In principle, materials (thixotropic) with high (static) yield stress and low viscosity, are suitable for concrete printing application. But unlike OPC, geopolymer cement does not possess such behavior [34] and therefore, in this paper, a systematic experimental approach is presented to obtain an optimum mix design along with the most favorable printing criteria suitable for geopolymer 3D printing. The proposed approach considers all the advantages and limitations of grout screw pump and a
4-axis gantry concrete printer, used in this research, in ambient condition of 25-degree C and 45% relative humidity.

2. Materials and Experimental methods

The primary raw material used in this study was class F fly ash (FA) obtained from Hebei Baisite Technology Co., Ltd (PR China). Ground granulated blast-furnace slag (GGBS), supplied by Engro Ltd. (Singapore), was used together with FA in the preparation of geopolymer mixes. Undensified micro silica fume G940 (SF), purchased from Elkem Ltd. (Singapore), with a specific surface area (SSA) of 15000-30000 m²/kg, was also included in the binder (FA+GGBS) to increase the cohesiveness of the geopolymer paste. Table 1 shows the chemical composition of the FA, GGBS and SF, obtained by X-ray fluorescence (XRF).

Table 1. Oxide composition of the FA, GGBS and SF

<table>
<thead>
<tr>
<th>Component</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>SO₃</th>
<th>Others</th>
<th>LOI</th>
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<tr>
<td>FA</td>
<td>49.15</td>
<td>39.35</td>
<td>2.94</td>
<td>3.48</td>
<td>0.39</td>
<td>1.17</td>
<td>1.88</td>
<td>1.64</td>
</tr>
<tr>
<td>GGBS</td>
<td>29.65</td>
<td>15.56</td>
<td>39.37</td>
<td>0.35</td>
<td>7.54</td>
<td>4.32</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>SF</td>
<td>98.37</td>
<td>0.19</td>
<td>0.35</td>
<td>0.08</td>
<td>0.15</td>
<td>0.19</td>
<td></td>
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Alkaline solutions, used as activator, were formulated by blending a commercial potassium silicate solution (viscosity = 18 cP) with 24.32 wt.% SiO₂, 18.71 wt.% Na₂O, together with 45 wt.% NaOH solution, to reach the desired modulus (Mₛ = molar SiO₂/Na₂O ratio) of 1.8. Later, fine river sand (maximum 2 mm particle size) was added to the geopolymer paste in different
sand/binder ratios (1.1, 1.3, 1.5, 1.7, and 1.9) and uniformly blended for 1-2 minutes with slight addition of tap water.

Figure 1 shows particle size grading curve of all the dry ingredients used in this research. The sand content was increased from 1.1 to 1.9 by weight of binder in the Mix G1 to G5 whilst the binder formulation was kept constant with 28-days compressive strength of 25 MPa (see Table 2).

![Figure 1. Particle size distribution of the raw materials and mixes](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>Mix proportions (Kg/m³)</th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
<th>G5</th>
</tr>
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<tbody>
<tr>
<td>FA</td>
<td>671.65</td>
<td>635.21</td>
<td>602.53</td>
<td>573.04</td>
<td>546.30</td>
<td></td>
</tr>
<tr>
<td>GGBS</td>
<td>118.52</td>
<td>112.09</td>
<td>106.32</td>
<td>101.12</td>
<td>96.40</td>
<td></td>
</tr>
<tr>
<td>SF</td>
<td>65.84</td>
<td>62.27</td>
<td>59.07</td>
<td>56.18</td>
<td>53.55</td>
<td></td>
</tr>
<tr>
<td>Alkaline reagent</td>
<td>355.58</td>
<td>336.29</td>
<td>318.98</td>
<td>303.37</td>
<td>289.22</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>65.84</td>
<td>62.27</td>
<td>59.07</td>
<td>56.18</td>
<td>53.55</td>
<td></td>
</tr>
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Initially, all the five mixes were tested for extrudability to find right combination of grading and paste content. Then the most suitable mix was further improved with addition of fiber (micro glass fiber: 4 mm length) and highly-purified attapulgite clay (~ particle length = 1.75 mm and ~ particle diameter = 3 nm) for printing a 60 cm tall free form structure.

As suggested in [20], we have used shear strength of the material to characterize the early age properties for 3D concrete printing application.

### 2.1 Extrudability

In concrete printing, extrudability can be defined as the material ability to be pumped out smoothly through an extruder without any disruption/clogging in the pipe flow. As this phenomenon is allied with fresh property of the material, many authors have characterized it with respect to well-known Bingham parameters and other flow properties [21,22]. These studies conclude that materials possessing very high (static) yield stress are difficult to extrude and may result discontinuities during the extrusion process [23-25], which is also subjected to the type of pump used for it.

Literature reveals particle size, gradation, surface area, paste/aggregate volume etc. governs yield stress and viscosity of the material which can be linked to flow properties inside any pipe or complex shaped channel [26,27]. Though, some standard tests such as flow table test and drop test [28] have been previously used by the researchers to quantify the flow behavior, in this research, the data obtained from rheometer was used to study the extrudability of our custom-made geopolymer mortar developed for 3D printing application. Five different mixes (shown in Table 1) were tested using Anton Par MCR 102 rotational rheometer as discussed in [29] and

<table>
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<tr>
<th>River sand</th>
<th>869.20</th>
<th>971.51</th>
<th>1063.29</th>
<th>1146.09</th>
<th>1221.16</th>
</tr>
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...
their respective Bingham parameters were recorded. Later, these mixes were extruded out by a screw pump to co-relate the rheology data for a favorable extrusion criterion. The vane geometry and rheometer set up, used in this paper, is shown in figure 2.

Figure 2. Rheometer used for material fresh property testing (left) and its vane geometry (right)

2.2 Shape retention

Like extrudability, shape retention is also a crucial factor for 3D concrete printing. After extruding, the material must retain its shape as per the extruder dimension and it can be quantified by a dimensionless number called shape retention factor (SRF) which is

\[
SRF = \frac{\text{Cross sectional area of 3D sample before demoulding}}{\text{Cross sectional area of 3D sample after demoulding}}
\]

To obtain high SRF, material must possess low slump characteristics i.e high yield stress so that it will be remain stable under its own weight. Of course, high yield stress can result in high SRF,
however the stress factor should not cross a certain value, so that it cannot be extrudable. In this paper, we used only the extrudable mixes to check SRF after extruding out by the screw pump.

2.3 Thixotropy Open Time (TOT)

Thixotropy open time (TOT), often confused with setting time of the material, can be defined as the time interval beyond which material loses its extrudability property and for extrusion-based concrete printing, it is always earlier than the usual setting (initial) time of the material. In geopolymer chemistry due to the poly-condensation process, material hardens over time and simultaneously causes problem in pumping, leading to discontinuity in the pipe flow. Therefore, it is necessary to tune the TOT of the material according to total printing time and 3D printer capabilities.

In this paper, instead of adding an accelerator/retarder, we replaced 5, 10 and 15% FA with GGBS to vary the TOT, and it was captured by change of the yield stress over time for the selected mix that was extrudable and had good shape retention property. Flow curve test was adopted to measure the yield stress of the material until the mix was workable. For this test, we mixed 24 liters geopolymer mortar, for three different slag percentages (8 liter each) and each time tested 0.5-liter material (as per the capacity of rheometer cup) for ten minutes’ time interval setting. The obtained results were discussed in section 3.3.

2.4 Buildability
In 3D concrete printing, buildability is a challenging issue and to overcome it, the freshly deposited material (after extrusion) must recover its original viscosity and yield stress before the second layer starts falling over it. Since the geopolymer mix behaves like a shear thinning material, the apparent viscosity usually drops during the pumping process, but its recovery is not fast enough to hold another layer on top of it. Therefore, in this research, some attapulgite clay was added to a selected mix (G3) and its recovery behavior was measured from rheology results by mimicking the 3D printing process [30]. The whole test was consisted of three steps. At Step I, a shear rate of 0.1 s\(^{-1}\) was applied for 60 seconds. This step simulated the initial state of a geopolymer before printing. At Step II, the shear rate was increased to 100 s\(^{-1}\) and held for 30 seconds. This step simulated the condition for a geopolymer under a certain shear rate during the printing process. At Step III, the shear rate was reduced to 0.1 s\(^{-1}\) and held for 60 seconds to simulate a condition similar to the final state of the geopolymer after printing.

Additionally, Plate stacking test was also conducted by adding incremental load (0.1N/sec) on the clay modified geopolymer mix to simulate the buildability of our final mix. Some microfibers are also added at this stage to further improve the buildability properties. We used Instron 5969 universal testing machine to apply the pre-calculated load while considering weight of single layer of material and time gap between the layers. The test was continued until the deformation value exceeds 6 mm for the given input settings. Obtained results were later discussed in the result and discussion section.

A systematic flow chart of aforementioned methods for laboratory testing 3D printable concrete is shown in figure 3.
3. Result and Discussion

3.1 Extrudability

The extrudability of the mixes were found to be significantly affected by the incremental addition of sand from 1.1 to 1.9 ratio. Geopolymer mix G5 and G4 were not at all extrudable and caused clogging at the outlet due to high static yield stress (see figure 4) of the material, and even the addition of extra water did improve the mix. The materials were segregated by the high shearing force in the pump and hence, 1.9 and 1.7 sand/binder ratio seem to be too high for geopolymer extrusion for the said volume of binder. Mix G3 and G2 were easily extrudable continuously and therefore, G1 mix was not tried for the extrudability test.
Figure 4. Plot of torque versus rotation speed of the geopolymer mixes

Figure 5. Static yield stresses of the geopolymer mixes
Considering yield stress of the mix designs, it is clear from figure 5 that, the materials having high static yield stress (i.e. G5 and G4), are difficult to extrude as they need high pumping pressure to initiate the flow which was not possible using our screw pump setup. In the same line, it should not be misunderstood that high static yield stress material always causes problem in the extrusion since the presence of thixotropic material in cement science contradicts this behavior by having high yield stress at rest and low viscosity when flowing under shear force or any applied pressure [31,32]. Unlikely, here (for G5 and G4) the cause of yield stress increment was due to gradual addition of sand to a fixed amount of binder, which in turn created more interlocking and particle friction and ultimately clogged the hose pipe. It was found that for higher sand/binder ratio, some commercially available rheometers are not able to provide enough torque for viscosity measurement and in some cases, the vane itself rotates in the center creating so called “plug”. Therefore, it should be subject of research before accepting these rheological parameters that may not provide true material properties for high viscous materials.

Based on the experimental finding, 0.6 to 1.0 KPa yield stress was found to be a favorable range for smooth extrusion of geopolymer mortar and G3 was selected as the most suitable mix within this range.

3.2 Shape retention

Shape retention, as defined by, SRF was only measured for extrudable G3, G2 and G1 mix designs. SRFs were found to be proportional to the yield stress that allows the material to retain its shape under own weight. Figure 6 shows co-relation between yield stress and SRF of the three mixes and it is very clear from the trend that higher yield strength mixes possess better shape stability and less deformation in the slump test.
Out of the three mixes (G3, G2 and G1), G3 was found to have highest SRF, but its yield stress may not be enough to carry additional 60 layers according to our 60 cm tall digital model (Section 4) and hence, we have added some clay and micro fibers to this mix and improved the G3 property later in the buildability section.

3.3 Thixotropy Open Time (TOT)

Thixotropic open time (TOT) was measured for different GGBS percentages while replacing FA content in G3 mix. It has been found by other researchers that an increase in GGBS content usually decreases the setting time of the geopolymer cement [33]. In this research, a similar trend was also observed for increasing slag percentage from 5 to 15. Figure 7 shows the increasing yield stress with time, which directly affects workability of the material for our extrusion
process. Comparing the effects of GGBS slag, it is clear that, for higher content of slag, the geopolymer mortar quickly jumps to its setting zone and thus cannot be used for long time during 3D printing. Alternatively, less amount of slag seems to be a better option, if batch mixing is used for printing.

![Figure 7. Variation of thixotropic open time (TOT) with GGBS percentages (Number preceding G3 indicates percentage of slag in G3 mix)](image)

These results are useful in a sense that if the target printing time is around 15-20 minutes, high percentage of slag can be considered for better buildability. The secret of concrete printing lies in having a thixotropic material with an open time of 10-15 minutes where it is possible deposit few layers and then it can start to harden for holding the subsequent layers. Of course, for such process, we require a continuous mixer where material is mixed and pumped out immediately, without any resting like in case of batch mixing. In summary, considering the effect of TOT, material can be always pre-designed to fit total printing time and complexity of the printed part.
3.4 Buildability

In concrete printing, a material is most beneficial, when it can quickly recover its original viscosity after the extrusion process and depending upon the printing time, it can accelerate its stiffening rate (structuration rate), before the subsequent layers are loaded on it. Since the G3 mix passed our previous tests, in this section, we will investigate and improve the buildability of G3 mix for large scale 3D printing application.

Figure 8 shows the recovery behavior of G3 mix and it was seen that, though the G3 mix has initially high viscosity at rest, but after extrusion, the viscosity recovery is only 20%. We have found this typical behavior during printing that can well extrude through a hose pipe however the shearing action of extrusion process made the material shear thickening and the initial yield stress diminished (see figure 9). The practical impact of such behavior is not at all suitable for the printing application because it will not maintain its shape, and pumping pressure will increase with increase in applied shear rate.
A few publications on rheology of geopolymer [34], mentioned that unlike regular cement, geopolymer does not have colloidal interaction (thixotropy effect) which provides initial yield stress because of van der waals force in the fresh stage of material. Instead they observed, hydrodynamic effect present in the material due to the highly viscous nature of potassium silicate reagent. Therefore, to improve this thixotropic property, it desirable to induce some colloidal interaction by addition of nano-clay (attapulgite), compactible with the geopolymer system.

G3’ is our new modified G3 mix that is obtained by addition of 1.2% clay (dosages recommended by the supplier) and its recovery behavior is also shown in figure 8. Comparing with original G3, it has better viscosity recovery property and high yield stress when material was at rest i.e before and after the extrusion scenario. During extrusion, viscosity went down to 30-40 Pa.s, like the G3 mix which is well extrudable without any discontinuity and clogging.
issue though it has high static yield stress. This can be explained by adhering the core concept of thixotropic material that is defined by having high yield stress material at rest but low viscosity under applied pressure or shear force. A higher percentage of this clay was not tried in this research considering high cost of raw material.

It is interesting to take a note that the yield stress value after the addition of clay to G3 mix increased (see figure 9) beyond our defined limit of extrusion (i.e. 1.0 KPa), however it did not cause any problem like clogging, discontinuity etc. This is not surprising as the yield stress of G3’ is caused by thixotropy effect (physical interaction) which can easily break down by the pump pressure during the extrusion process. Therefore, this thixotropy effect cannot be counted in the yield stress limit that was defined by considering increment in volumes of solid particles (sand) in the trail mixes.

To reduce shrinkage and deformation in the plastic state, we added the fiber to G3’ mix at a very low percentage (0.25%) and renamed to G3”. The rheology performance of all three G3 derived mix is shown in figure 10.
As mentioned in the methodology section, we conducted plate stacking test on the modified G3” mix to simulate the printing activity and the obtained results are plotted in below figure 11. It was noted that for the incremental loading of 0.06N/sec on a 50-mm(H) cylindrical block (Figure 11(a)), the initial deformation was increasing rapidly for few seconds and then it slowed down because of strength gain in the material during setting phenomena (figure 11(c)). We simulate this loading test for 30 minutes of printing time and the final deformation was captured as less than 4 mm. A recent study by Wolfs et al. [35] has numerically modelled this buildability property considering early age compression and shear properties of the fresh concrete.

**Figure 10.** Compassion of rheology between G3 and modified G3’, G3” mix
4. 3D Printing of a full-scale freeform model

The results of the above laboratory tests provide us an empirical evidence of the fresh geopolymer properties necessary for 3D concrete printing application. However, production of a full-size component is essential to demonstrate if the proposed criteria and mix design are suitable in practice. To achieve this, a freeform open 3D structure was printed using the optimum mix G3†.
Figure 12. Freeform geopolymer 3D printing (a) CAD model (b) actual printed model (c) model being printed (d) Top view of the model

Figure 12 shows both the CAD and actual model of the component that is printed using a 4-axis gantry concrete printer. The height(H) and width (W) was 60 and 35cm respectively and comprised of 10 mm thickness 60 layers. This design was deliberately architectural to show the possibility of using fly ash based geopolymer for concrete printing application. The total printing time for this component was less than 20 minutes with a printing speed of 80mm/sec and flowrate of 0.5 l/min.

5. Conclusion

In this study, a novel 3D printable geopolymer mortar has been developed, which can be used for printing non-structural building components directly from digital models without the need of any formwork. Critical fresh properties of the printable geopolymer such as extrudability, shape retention, buildability and open time were measured with systematic experimental methods and their workable ranges have been identified. This testing sequence can also be applied to other construction materials, as it mainly focuses on properties of printed layers for an extrusion-based 3D printing technique. Finally, as a word of caution before generalizing the results of the present
study, it is important to note that the suitability of the proposed definition and test methods to characterize printable geopolymer at fresh stage are strongly dependent on the chemical composition of the mixture and equipment used to measure the properties. Any change in either of these may result in different conclusions and accordingly, material limit can be benchmarked for concrete printing application.

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References


