Insights into Material Design, Extrusion Rheology, and Properties of 3D-
Printable Alkali-Activated Fly Ash-Based Binders

Hussam Alghamdi1, Sooraj A. O. Nair2, Narayanan Neithalath3,*

Abstract

Material design of alkali activated fly ash-based binders for extrusion-based 3D printing, the rheological responses that are influential in ensuring printability, and the properties of such binders are discussed in this paper. Fly ash is supplemented with fine limestone, slag, or portland cement to provide adequate microstructural packing required for printability. The alkaline activators help reduce the yield stress and enhance the cohesiveness of the mixtures. 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. This approach could be used for mixture qualification for extrusion-based printing. The Benbow-Bridgwater model is implemented on extrusion rheology results of pastes to determine the extrusion yield stress and wall slip shear stress, which are useful process-related parameters. It is shown that these parameters can also be related to shear and extensional rheological properties of alkali-activated pastes, thus ensuring a much-needed link between parameters related to material design and the process of extrusion. Mechanical properties and pore structure similar to those of conventionally cast mixtures are achieved.

Keywords: 3D printing; Alkali activation; Fly ash; Extrusion rheology; Yield stress.
1. Introduction

3D printing (or additive manufacturing) enables fabrication of complex and multi-scale structures through computer-aided design [1,2]. This technology has been successfully applied in aerospace, automotive, and biomedical fields [3–5]. 3D printing of cementitious materials where structures are created by layer-wise construction enables acceleration of the construction process, helps build complex architectural shapes that otherwise are difficult to realize, and facilitates labor and energy reductions [6–10]. 3D printing also enables special components to be fabricated. As an example, low cost syntactic foams (hollow particles filled composite materials) were recently created by 3D printing technique as reported in [11,12]. The commonly used 3D printing technique for concrete is material extrusion and layered printing [8,13–15], even though direct ink writing and powder-based printing have also been attempted [16–19]. These mixes are designed to flow through a barrel-die system and have enough structural stability when stacked in layers to print a stable structure. In extrusion-based printing, the rheological characteristics of the mixtures play a crucial role, and thus several studies have explored the influence of paste rheology in 3D printing of cementitious materials [19–23]. In addition to rheological properties, setting time and mechanical properties of the printed elements are also of interest [24,25], as is the case with any construction material.

A large number of ongoing studies on 3D printing of cementitious materials focus on the use of binders based on ordinary portland cement (OPC), as expected [9,26,27]. Significant advances in the field of mineral and chemical admixtures have aided in the production of OPC-based 3D printed materials whose rheology and early-age response can be tailored. The use of geopolymer binders, which has been widely recognized as a sustainable option to reduce the carbon footprint of concrete, for 3D printing has also been reported [28–32]. It is conceivable that such sustainable binders can be utilized in mass construction, especially in areas where waste/by-product materials like fly ash are abundant. 3D printing of low strength geopolymer binders can also be employed in disaster rehabilitation where temporary structures are needed. This paper examines the aspects that are relevant in the material design of fly ash-based alkali activated binders for 3D printing. Special focus is given to: (i) the use of minor ingredients including fine limestone powder that contributes to improved microstructural packing that provides the network strength in the fresh state to be extruded and layered in a shape-stable manner, and (ii) the influence of alkaline activators on the rotational, extensional, and extrusion rheology of pastes. These studies elucidate the relevant characteristics of the fresh pastes that are influential in printability. Extrusion rheology experiments combined with phenomenological modeling is used to obtain the linkage between
the material design and process-related parameters, thereby enabling better strategies to produce sustainable, alkali-activated 3D printable binder systems.

2. Experimental Program

2.1 Source Materials and Activators

The primary source material utilized in this study was class F fly ash conforming to ASTM C 618. Based on our previous work [20] and several trial mixtures, it was observed that other minor ingredients are required to ensure extrudability and buildability (together termed as printability). Moreover, materials such as slag and ordinary portland cement (OPC), when incorporated into alkali activated fly ash-based systems, improves the setting time and the mechanical properties of the binder. Table 1 lists the binder components utilized in this study, along with their chemical composition. Figure 1 shows the particle size distributions (PSDs) of the source materials used. Sodium hydroxide (NaOH), sodium silicate solution (waterglass), or sodium sulfate (Na$_2$SO$_4$) were used as the activating agents in this study. NaOH was used as the sole activator, or in combination with sodium silicate or sodium sulfate to provide requisite alkalinity to enable aluminosilicate dissolution and precipitation. Waterglass supplied by PQ Corporation has a solids content of 36%, a silica modulus (molar ratio of SiO$_2$-to-Na$_2$O) (M$_s$) of 3.3, and specific gravity of 1.38 g/cm$^3$. The sodium hydroxide and sodium sulfate powders were determined to have specific gravities of 2.13 and 2.66 g/cm$^3$ respectively.

Table 1: Chemical composition of the source materials

<table>
<thead>
<tr>
<th>Components of the binders</th>
<th>Chemical composition (% by mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Fly ash (F)</td>
<td>58.40</td>
</tr>
<tr>
<td>Slag (S)</td>
<td>36.0</td>
</tr>
<tr>
<td>OPC (C)</td>
<td>19.60</td>
</tr>
<tr>
<td>Limestone (L)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaCO$_3$ &gt; 99%</td>
</tr>
<tr>
<td>Alumina powder (A)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1: Particle size distributions (PSD) of the paste constituents.

2.2 Printer and Print Geometries

A desktop printer based on Cartesian configuration [33] was customized with a 100 cm³ barrel to print the alkali activated paste mixtures. The diameter of the barrel ($D_b$) used for paste printing was 35 mm. Two different die exit diameters were adopted in this study (4 mm and 6 mm) with lengths of 35 mm and 20 mm respectively to maintain the die length-to-diameter ratios ($L_d/D_d$) of 9 and 3.33. The die entry diameter was 10 mm. The inner surface of barrel was lubricated to reduce the wall friction and ensure smooth and easy motion of the piston. Several shapes were printed to investigate and visually inspect the printability of mixtures. Slic3r software [34] was used to adjust the printing parameters including printing speed, layer width and height, and infill volume and pattern. The printing parameters used in this study are: layer height of 3mm, layer width of 6 mm, and printing speed of 20 mm/s.

2.3 Material Design for Printability: Multi-Component Binders and Activators

The printability criteria employed in this study were: (i) the ease of extrusion through a tapered nozzle (extrudability), and (ii) the stability of the layered printed shape (buildability). These criteria, together termed as printability, were visually ascertained in the preliminary phase of the study to select a matrix of alkali-activated fly ash-based mixtures for 3D printing. The extrudability and buildability of the selected mixtures are quantified later. Note that these are also dependent on printing parameters including nozzle shape and printing speed. The material design procedure started with class F fly ash as the sole binder, activated by a 5% NaOH solution. Mixtures were prepared using a mass-based liquid-to-binder ratio (l/b)
starting from 0.20, at 0.01 increments. Mixtures developed using the lower end of this l/b range were very stiff and difficult to extrude. A l/b of 0.25 was found to result in a cohesive, extrudable paste; however, this mixture was not buildable, as shown in Figure 2(a). This response is similar to that observed for plain OPC and OPC-fly ash pastes reported in [20], which were also not buildable. The buildability of the cement pastes, for a given set of printing parameters, is a strong function of the initial yield stress of the paste, which depends on the number and quality of interparticle contacts. This in turn, is a function of the particle sizes, arrangement of the particles (including effects of flocculation), and the type of interparticle forces [35]. However, flocculation and its effects are not discussed in this paper. The use of fly ash ($d_{50}$ of ~18 µm) alone as the binder is likely to result in an insufficient number of interparticle contacts to provide sufficient yield stress to the paste. Thus, fine limestone ($d_{50}$ of 1.5 µm) was used as a filler material [36], replacing 15% of fly ash by mass, to enhance the number of interparticle contacts in a given volume and give better fresh state rigidity to the system to resist the overburden pressure without instability. The printability was substantially improved through this minor compositional change, as shown in Figure 2(b). The l/b was increased to 0.27 to ensure extrudability, attributable to the presence of fine limestone particles.

![Figure 2](image)

Figure 2: Hollow cube geometry printed using fly ash-based binders activated using 5% NaOH: (a) 100% class F fly ash paste (l/b=0.25), showing shape instability, and (b) improvement in printability and buildability when 15% fine limestone is incorporated into the paste (l/b=0.27).

Next, the activator concentration was increased from 5% to 10% NaOH. With a 10% NaOH content in the activator solution, an extrudable mixture containing fly ash alone was obtained with a l/b of 0.20 (as compared to a l/b of 0.25 for 5% NaOH activation). The increase in activator viscosity with increase in NaOH concentration enhances the cohesiveness of the mixture [37]. The combined effects of: (i) reduced interparticle spacing at a lower l/b, (ii) increased activator viscosity, and (iii) greater negative surface charges on fly ash particles at higher NaOH concentrations that result in increased interparticle repulsion [37] enable the production of an extrudable mixture as shown in Figure 3(a) and (b), at a l/b of 0.20. However, the mixture was too cohesive, to the extent of being very “sticky”, that resulted in layer
deformation at corners during the printing process (as the print head drags already laid material), as can be noticed in these figures. To compensate for this effect, the l/b was increased to 0.24, along with the replacement of 15% of fly ash with fine limestone powder. Figure 3(c) shows that, while the mixture consistency and water retention was improved (note the shine in Figure 3(a) and (b), which is due to water draining from the paste, while Figure 3(c) shows improved water retention due to limestone addition), the print quality was still inconsistent. Minor compositional changes could account for these effects, but in order to create a more diverse composition, the limestone content was increased to 30%, and the l/b to 0.27, to result in a satisfactorily extrudable and buildable mixture as shown in Figure 3(d). Note that the l/b is same for the selected mixtures with 15% and 30% limestone powder (Figure 2(b) and 3(d)). It has been suggested that higher hydroxide contents in particulate suspensions might have an effect similar to that of superplasticizers [37].

Figure 3: Hollow cube geometry printed using fly ash-based binders activated using 10% NaOH: (a and b) 100% Class F fly ash paste (l/b=0.20) showing layer deformation, (c) binder with 15% limestone (l/b=0.24), showing shape instability, and (d) binder with 30% limestone (l/b=0.27) showing satisfactory printability and buildability.

In addition to the binary fly ash – limestone systems discussed earlier, slag or OPC were also used as components of the activated binders to develop ternary blend systems. In such cases, the fly ash content was fixed at 50% (mass-based). The fly ash – OPC – limestone system was activated by a combination of sodium sulfate and NaOH so as to reduce the overall alkalinity of the activator and ensure easier handling. It has been shown that Na₂SO₄ (a neutral salt) activation of high volume fly ash mixtures result in 28-day compressive strengths of ~30 MPa when cured at ambient temperatures [38]. The addition of 1% NaOH enhanced the cohesiveness of this system. The fly ash – slag – limestone system was activated using NaOH or a combination of NaOH and sodium silicate to provide a Na₂O-to-powder ratio (n) of 0.05 and SiO₂-to-Na₂O ratio of the activator (Mₙ) of 0.50. In the latter system, 1% Al powder was used to delay the setting time of the mixture. The chosen mixtures were mixed at 200 rpm for 30 seconds, followed by 1200 rpm for 90 seconds to obtain a homogenous mixture. Table 2 lists the selected binders used for further studies. Note that the letter (F, L etc.) corresponds to the ingredients (see Table 1), and the number in the subscript refers to the mass fraction of the ingredient in the starting binder blend. The median particle sizes of
blends are also listed in the table to indicate how the use of minor ingredients change $d_{50}$ of the composite mixture. This is significant since yield stress is known to be well related to the square of $d_{50}$ [20,35].

Table 2: Binder proportions and the median particle sizes ($d_{50}$) for the final printable mixtures

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>FFA (%)</th>
<th>Slag (%)</th>
<th>OPC (%)</th>
<th>LS (%)</th>
<th>Al powder (%)</th>
<th>Alkali activator (%)</th>
<th>Liquid/powder ratio</th>
<th>$d_{50}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{85}L_{15}$</td>
<td>85</td>
<td>15</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td>0.27</td>
<td>15.20</td>
</tr>
<tr>
<td>$F_{70}L_{30}$</td>
<td>70</td>
<td>30</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td>0.27</td>
<td>10.37</td>
</tr>
<tr>
<td>$F_{50}C_{30}L_{20}$</td>
<td>50</td>
<td>30</td>
<td>20</td>
<td>1</td>
<td>2</td>
<td></td>
<td>0.30</td>
<td>11.32</td>
</tr>
<tr>
<td>$F_{50}S_{30}L_{20}$</td>
<td>50</td>
<td>30</td>
<td>20</td>
<td>5</td>
<td></td>
<td></td>
<td>0.35</td>
<td>8.79</td>
</tr>
<tr>
<td>$F_{50}S_{30}L_{19}A_{1}$</td>
<td>50</td>
<td>30</td>
<td>19</td>
<td>1</td>
<td>n=0.05* , $M_s=0.5$**</td>
<td></td>
<td>0.30</td>
<td>8.71</td>
</tr>
</tbody>
</table>

* $n$ = Na$_2$O/total powder (mass based); NaOH is the source of Na$_2$O.

** $M_s$ = SiO$_2$/Na$_2$O (molar based), Sodium silicate solution is the source of SiO$_2$.

2.4 Test Methods

2.4.1 Rheological characterization

A mini slump cone with a bottom diameter of 38 mm, top diameter of 19 mm, and a height of 57 mm was used to determine the shape stability of the printable binders. The paste was loaded in the mini-slump cone and then slowly lifted to determine the slump value. A dynamic shear rheometer (TA Instruments AR 2000EX) was used to carry out the rheological studies using a parallel plate geometry to determine the shear stress ($\tau$) of the printable pastes as a function of shear rate ($\dot{\gamma}$). The upper and lower plates were serrated at depths of 1 mm and 0.15 mm respectively to prevent paste slip on the shearing surface. The bottom plate contained Peltier elements, and was conditioned to a temperature of 25 ± 0.1 °C. The volume of paste sample was calculated for a plate gap of 2 mm and evenly put on the bottom plate to avoid an overfilled state while testing. The sequence of steps employed in rotational parallel plate rheology includes: (i) a stepped ramp up pre-shear phase for approximately 80 s to homogenize the paste, (ii) a stepped ramp-up, and (iii) a stepped ramp-down, as shown in Figure 4(a) [36,39]. The data was collected from only the down-ramp phase. Shear stress and shear rate data were extracted using TA Instruments’ TRIOS software package. The range of the shear rate used in this test were from 5-to-100 s$^{-1}$, and the Bingham model was used to extract the apparent yield stress from the relationship between shear stress and shear strain rate. In addition to shear rheology, the parallel plate test set up was also used for the tack test. The tack test indicates the adhesive properties and cohesion of the paste mixtures. These properties are important to ensure that the pastes adhere well to surfaces, which influences the
interface properties [40]. The paste was placed on the bottom plate and a gap of 2 mm was set between the plates. A pre-shear phase similar to the one shown in Figure 4(a) was used to homogenize the paste. The top plate was set to rise at a constant velocity of 10 μm/s until the sample was completely separated from the plates. The normal force experienced by the top plate was recorded as a function of plate separation.

A 4.45 kN servo-controlled MTS machine was used to carry out the extrusion rheology studies of alkali activated printable pastes. The paste sample was filled in the extruder immediately after mixing, ensuring that no air voids are entrapped in the paste. The plunger was placed inside the barrel in direct contact with the compacted paste. The assembly was placed in a specially fabricated holder to allow the upper platen of the test machine to axially compress the plunger. A multi-speed extrusion test with ram velocities ranging from 150 mm/min to 10 mm/min was used. Figure 4(b) shows the experimental procedure used for the extrusion rheology tests. The nozzle (die) diameters used for the extrusion test were 4 mm and 6 mm, and the corresponding nozzle lengths were 35 mm and 20 mm respectively. The extrusion velocity is calculated from the ram velocity using flow equivalence, given as:

$$D_b^2 V_{ram} = D_d^2 V_{ext}$$

where \(V_{ram}\) is the ram velocity and \(V_{ext}\) is the extrusion velocity, and \(D_b\) and \(D_d\) are the barrel and die diameters respectively.

![Figure 4: Experimental procedure used for: (a) parallel plate rheology, (b) extrusion test.](image)

2.4.2 Pore structure and mechanical properties

The setting times of the selected mixtures were determined in accordance with ASTM C 191-18a [41], with a time gap between each penetration reading of 15 minutes. Mercury intrusion porosimetry (MIP)
was used to investigate the porosity and critical pore sizes of the different layers of the printed pastes.

Small samples carefully obtained from different printed layers were placed in the low-pressure chamber of the porosimeter (Quantachrome Instruments Pore Master). The sample was pressurized with mercury from an ambient pressure to 345 KPa (60 psi). This is followed by intrusion of mercury in a high-pressure chamber where the pressure was increased to 414 MPa (60,000 psi). The pore diameter (d) as a function of the intrusion pressure can be obtained from the Washburn equation as:

\[
d = \frac{-4 \sigma \cos \theta}{\Delta P}
\]

where \(\Delta P\) is the difference in the pressure between successive steps (MPa), \(\theta\) is the contact angle between mercury and the cylindrical pore (130° in this study) [42–44], and \(\sigma\) is the surface tension between mercury and the pore walls (485 mN/m).

The specific gravities of the paste samples were determined using a gas pycnometer (Ultrapyc 1200e, Quantachrome Instruments). The compressive strengths of the printed pastes were determined on printed cubes of 40 mm side length. The flexural strength of the printed pastes was determined using a three-point-bending test. A displacement rate of 0.5 mm/min was used for the tests [45]. Three replicate specimens 21 mm x 21 mm x 120 mm in size were tested for each mixture listed in Table 2.

3. Results and Discussions

3.1 Mini-Slump Flow and Initial Setting Times

The workability of the pastes and their setting times are important parameters in the qualification of 3D printable binders. Sufficiently long initial setting time is necessary to avoid premature stiffening while the mixture is being extruded and printed. Figure 5(a) shows the mini slump values and Figure 5(b) shows the needle penetration as a function of time for the selected paste mixtures. It is desirable to have a cohesive mixture demonstrating minimal slump to obtain a stable print with little or no deformation while maintaining extrudability. The maximum mini-slump value recorded was less than 9 mm which allowed consistent extrusion while being able to retain the shape during and after printing. The initial setting time ranged between 1.5 to 6.0 hours, which is generally attributed to the low reactivity of fly ash at ambient temperatures. For the mixtures \((F_{85}L_{15})\) and \((F_{70}L_{30})\), the setting time of \((F_{70}L_{30})\) was apparently delayed, attributable to increased alkaline activator (10% of NaOH) used in this mixture compared to (5% of NaOH) used in \((F_{85}L_{15})\). The increased NaOH decreased silica polymerization resulting in delayed setting time as reported in [46]. For the slag or OPC containing mixtures \((F_{50}S_{30}L_{20})\) and \((F_{50}C_{30}L_{20})\), the rapid setting was
attributed to the presence of slag [47] and OPC which helped accelerate the setting time at ambient temperature. However, the mixture containing slag along with alumina (F_{50}S_{30}L_{19}A_{1}) showed the longest setting time of approximately 6 hours due to the presence of alumina that delayed the setting time as proved in literature [48]. The cohesiveness of the mixtures, attained through improved packing of particles [24,49] (Section 2.3), ensured that the printed shapes were stable.

Figure 5: (a) Slump values and (b) initial setting times of the printable pastes.

### 3.2 Rheological Characterization of Fresh Pastes

#### 3.2.1 Yield stress from parallel plate rheology and its relation to printability

The yield stress of the pastes is influenced by the composition of the binders, and the type and amount of activators. Figure 6(a) shows the effect of mixture composition on the yield stress and plastic viscosity of the selected binders. The F_{70}L_{30} mixture shows the lowest yield stress due to the higher amount of NaOH (10%) which acts like a superplasticizing admixture [37]. The yield stress of the F_{85}L_{15} mixture is higher because of the lower water content in this mixture and the lower amount of NaOH. For mixtures containing 50% of fly ash, the yield stress and plastic viscosity are higher when OPC is present in the mixture than when slag is present. From the particle size distributions shown in Figure 1, it appears that OPC has a higher fraction of finer particles (0.5 to 5 \mu m) than slag, which could explain this behavior from a particle packing point of view. This is consistent with the inverse size dependence on yield stress shown in several studies (e.g. [50]). It is also conceivable that the surface charges in OPC that influence flocculation, and the effects of particle shapes might also play a role in this behavior. The yield stresses vary between 150 Pa and 500 Pa for all the mixtures evaluated, which is very similar to the extrudable and
printable OPC-based binders evaluated in a companion study [20]. As suggested earlier, this range depends on the printing parameters also.

It is instructive to understand the influence of the activating agents on the yield stress of suspensions. Hence the yield stress of the printable binders shown in Figure 6(a) are compared to those obtained when water is used as the dispersing medium instead of the alkaline solution. The results are shown in Figure 6(b). The decrease in yield stress when alkaline activators are used as dispersing media can be attributed to the fact that alkaline solutions act in a manner similar to that of superplasticizers [37]. The higher the alkalinity of the activator, the larger the decrease in yield stress.

Figure 6: (a) Yield stress and plastic viscosity of the printable binders, and (b) effect of alkali activators on yield stress of design printable fresh pastes.

Figure 7(a) shows the mini slump test on an extrudable fly ash-water paste at an l/b of 0.25, while Figure 7(b) shows an extrudable fly ash-water-NaOH paste at an l/b of 0.20. It can be seen that, in addition to decreasing the yield stress (even at a lower l/b ratio), alkaline solutions also resulted in enhanced cohesiveness of the pastes and better shape retention.

Printability is defined as the ability of a mixture to extrude (extrudability) and maintain the structural integrity when built in layers (buildability) [51], as explained earlier. Yield stress is an important rheological parameter that influences printability. It is also well known that slump of a cementitious mixture is related to its yield stress [52,53]. Thus, the use of mini slump values and the yield stress obtained from rotational rheology are synergistically considered to arrive at bounds for printability of the paste mixtures. Here, in addition to the alkali-activated binders considered in this paper, data from a companion work on OPC-
Based binders [20] are also used. Figure 8 depicts the yield stress and slump of a range of mixtures considered, both printable and non-printable. All the considered mixtures were extrudable. A lower mini slump value and a higher yield stress are generally found to be the requirements for a printable mixture.

Figure 7: Mini slump of 100% fly ash paste mixed with: (a) only water, and (b) water with 10% of NaOH showing the effect of alkaline activator on paste slump and its cohesiveness.

Figure 8: Yield stress vs. slump value of printable and non-printable mixtures (Data for stable mixes (OPC) labelled in the graph was obtained from our previous study [20].

The evolution of yield stress with time provides useful indications on the window of printability. For all the selected mixtures, yield stress was determined using the parallel plate geometry after maintaining the paste at rest different periods of time, as shown in Figure 9(a). The time interval between two measurements were determined based on the setting time of the pastes (Figure 9(b)). For the pastes that set faster (i.e., the 50% fly ash mixtures containing slag or OPC), the yield stress was measured after a rest period of 30 minutes, while for the other mixtures, the first rest period was 60 minutes. Corresponding to every time interval of yield stress measurement, a single filament was extruded and printed at different times after initial mixing. An example is shown in Figure 9(b) for the F85L15 mixture. The yield stress of the mixture corresponding to the final time beyond which it cannot be extruded and printed is designated as
the upper bound of yield stress. For all the mixtures evaluated here, the yield stress limit of extrudability and printability was around 700 Pa (limited by the printer’s capacity used in this study). In Figure 9(b), it is shown that, at 60 minutes (the time of first yield stress measurement for the F85L15 paste), remixing was done for 30 s before printing the filament again. This is to simulate the homogenization that happens during the pre-shear phase in the yield stress measurement method. The time from initial mixing to the time when the yield stress reaches approximately 700 Pa is termed as the printability window. Based on the above analysis, the F70L30 and F50S30L15A1 mixtures showed the longest printability window (3h) while the F50S30L20 mixture showed the shortest window (1h). The printability window is found to scale relatively well with the initial setting time of the pastes, indicating that the setting time could be used as a surrogate parameter to estimate the printability window. This finding assumes significance since it shows that a simple test such as the setting time can be a useful indicator of an important process parameter, i.e., printability window, relating to 3D printing. It is also important to note that this result has been arrived at based on the few selected mixtures from this study and extensive investigations are needed to ensure that the relationship is valid over a wide range of mixture compositions.

Figure 9: (a) Yield stress of printable mixtures with time showing the printability zone, and (b) extruded filaments of F85L15 mixture as a function of time after mixing. (R: remixing for 30 s after 60 min from initial mixing time).

3.2.2 Tack test (extensional rheology)

Extensional rheology can be used to quantify the adhesive and cohesive nature of the pastes, which are influential in 3D printing. Cohesion is defined as the internal strength of the material at rest while adherence is defined as the tendency of the material to stick to a surface [54]. These properties influence
the interlayer bonding in layered manufacturing, which plays an important role in the mechanical properties of the printed components.

Figure 10(a) shows the normal force as a function of plate displacement for the printable alkali-activated fly ash-based pastes, and Figure 10(b) shows the peak force and the gap displacement corresponding to the peak load. The adhesive and cohesive properties of the paste can be evaluated by the absolute value of the peak force and resistance of the paste to elastic failure [55]. An elastic increase in the normal force until the peak is demonstrated by all the mixtures. The peak load (corresponding to critical gap displacement) corresponds to the cohesion of the mixture beyond which rupture occurs and force starts to decay under a combination of viscous effects in adhesion and intrinsic cohesion. A higher peak force is reported to correspond to a higher adhesive capacity [55]. Figure 10(c) depicts the adhesion energy of the selected pastes, defined as the area under the force-displacement curve. The energy required to separate the paste under a normal tensile force is indicative of the influence of material composition on the bonding capacity, which influences interface properties of the 3D-printed structure.
Figure 10: Tack test results showing: (a) absolute normal force as a function of plate displacement, (b) peak force and corresponding gap displacement for the selected pastes, and (c) adhesion energy of the design printable pastes.

The average peak forces of the selected pastes were between 6 N and 10 N whereas the total displacement (at complete separation) ranged between 2 to 9 mm (excluding the initial gap of 2 mm). The peak forces and the corresponding gap displacements shown in Figure 10(b) indicate that the paste containing OPC demonstrate the lowest gap displacement at peak force. This is corroborated by the lowest adhesive energy showed by this paste as shown in Figure 10(c). The lower gap displacement and the faster force decay after rupture indicates lower cohesive forces in the system containing OPC as compared to other mixtures evaluated. This can also be attributed to the lower alkalinity of the paste containing OPC – the higher viscosity of NaOH combined with its higher concentration in the other systems contributing to increased cohesive stresses in the fresh state. Further, the paste containing the highest amount of NaOH ($F_{70L_{30}}$) showed the highest adhesive energy among the mixture studied, once again emphasizing the influence of the activating agent characteristics on early age adhesive and cohesive forces. The adhesion energy of the alkali-activated fly ash-based pastes reported here are 1.2 to 2 times higher than that of the OPC-based pastes reported in our previous work [20]. While much of this is attributed to the activator characteristics as mentioned earlier, this has implications in interlayer properties when a wet-on-wet layer construction scheme is implemented, as is the case with 3D-printed cementitious structural elements. Also, higher modulus can result in a reduction of inter-layer bond strength [56] which is related to lower adhesive energy of the mixes.

3.3 Influence of the Extrusion Process on the Rheology of the Printed Material
The rheological response of fresh binder mixtures was reported in the preceding sections, and criteria that could be used to infer important characteristics such as printability window, yield stress bounds, and adhesive characteristics discussed. However, extrusion involves application of pressure on the fluid paste at a certain velocity, and the rheological characteristics are highly sensitive to pressure and speed of extrusion. Analytical models and numerical models to evaluate the behavior of a yield stress fluid under pressure have been reported [57–61]. However, for ease of analysis and interpretation, we carry out extrusion rheology and implement a phenomenological Benbow-Bridgewater model [61] to analyze paste extrusion and infer the rheological characteristics of the extruded and printed material. The Benbow-Bridgewater model employs a plasticity approach to analyze the extrusion rheology of dense ceramic suspensions [62].

Figure 11 shows the extrusion force-displacement relationship for a selected alkali-activated fly ash-based paste (F70L30) subjected to different ram velocities, for different L_d/D_d ratios (9 and 3.33). An instantaneous increase in force is experienced because of the upsetting of the paste before its exit through the die. The pressure drops correspond to the changes in ram velocity, and the force plateau for each ram velocity is considered to be the corresponding extrusion force. The significant influence of L_d/D_d ratio on the extrusion force is shown in Figure 11, which can be used to glean the importance of the extruder geometry for desirable extrusion-related parameters.

Figure 11: Force vs. ram displacement for a printable paste in a syringe extruder subjected to different ram velocities.

The Benbow-Bridgewater model can be expressed as:
\[ P_{\text{ext}} = P_1 + P_2 = (\sigma_0 + \alpha V_{\text{ext}}^m) \ln \left( \frac{A_b}{A_d} \right) + \frac{ML}{A_d} (\tau_0 + \beta V_{\text{ext}}^n) = \sigma_Y \ln \left( \frac{A_b}{A_d} \right) + \frac{ML}{A_d} \tau_w \]  

where \( P_{\text{ext}} \) is the total extrusion pressure, \( P_1 \) is the die entry pressure (the pressure required to extrude the paste from the barrel through the die entry), and \( P_2 \) is the die land pressure (which allows the paste to flow through the die under pure shear conditions). \( V_{\text{ext}} \) is the extrusion velocity, \( \alpha \) and \( \beta \) are velocity multipliers, and \( m \) and \( n \) are velocity exponents. \( \sigma_0 \) is the extrusion yield stress (as opposed to pure shear yield stress, since the confinement effects of the barrel and the compressional effects of the ram influence yielding) at the die entry, \( \sigma_Y \) is the apparent velocity-dependent extrusion yield stress of the plastic material, \( \tau_0 \) is the slip yield stress, and \( \tau_w \) is the velocity-dependent shear stress experienced by the paste due to its interaction with the die wall. The geometrical parameters include \( M, L, A_b \) and \( A_d \) which are the perimeter of the die, length of the die, barrel area, and die area respectively. The exponents \( m \) and \( n \) are taken as 1 (i.e., the extrusion pressure-velocity relationship is taken as linear, which was observed here, as well as in [20]), and thus the equation is reduced to a four-parameter model.

The Benbow-Bridgewater equation was derived based on a uniform die diameter. However, the die geometry used in this study is the frustum of a cone (\( D_{\text{entry}} \neq D_d \)). In this case, the area of die is a function of length of the die and the second term corresponding to the die in Equation 3 is modified suitably [20] as:

\[ P_2 = P_{\text{ext}} - P_1 = \frac{ML}{A_d} (\tau_0 + \beta V_{\text{ext}}^n) = \sum_{i=0}^{n} \frac{M_i}{A_i} L_i (\tau_w) \]  

\( M_i L_i \) is the surface area of the individual cylinder that forms part of the frustum, and \( A_i \) is the cross-sectional area of the cylinder. \( L_i \) is taken as 1 mm.

To determine the Benbow-Bridgewater parameters, the extrusion force is plotted as a function of \( L_d/D_d \) ratios for different ram velocities. The linear relationship between \( L_d/D_d \) and the extrusion force for different velocities is extrapolated back to the Y-axis to give the force at \( L_d/D_d = 0 \), from which the die entry pressure \( P_1 \) for different velocities are calculated. \( P_1 \), along with the barrel and die areas, is used to calculate the velocity-dependent yield stress \( \sigma_Y \). The wall shear stress \( \tau_w \) is determined from Equation 4.

Figure 12 depicts the extrusion yield stress (\( \sigma_Y \)) and the wall shear stress (\( \tau_w \)) predicted by Benbow-Bridgewater model, which can be considered as the extrusion process-related parameters since they are dependent on extrusion velocity. The size of the error bars in this figure show the stresses corresponding to the highest and lowest extrusion velocities (which are deduced from ram velocities) used. The extrusion yield stresses predicted from the model range from 75-to-162 KPa while the shear yield stresses extracted...
through parallel plate rheology ranged from 155-to-520 Pa. Shear yield stress of 50-to-200 Pa measured through rotational rheology has been correlated to yield stress in the 3-to-40 kPa range from extrusion experiments [63]. The influence of the extrusion process on rheological response of pastes are thus evident. To achieve shape stability, it has been reported that the yield stress of extruded paste should be greater than 20 kPa [64]. All the alkali-activated fly ash-based pastes satisfy this criterion.

Wall slip shear stress is an important parameter in 3D printing of binders since this stress must be surmounted to ensure flow out of the nozzle. The wall shear stress, which is also pressure dependent as is known for other concentrated suspensions [65–67], depends on the $L_d/D_d$ ratio as can be noticed from Figure 12, showing that it is. It is seen from this figure that the $F_{70L_{30}}$ mixture shows a higher wall shear stress not withstanding a smaller extrusion yield stress. This could potentially be due significant changes in the paste during the extrusion process (e.g., liquid phase migration) leading to inhomogeneous particle distribution in the die. The consequence is a higher energy need for extrusion and printing, likely resulting in further phase separation and inhomogeneous print quality. Extensional and wall stresses predicted through models thus serve as important tools in the apriori determination of the effectiveness of chosen mixture compositions and extruder geometry in ensuring efficient extrudability and printability.

Figure 12: Velocity-dependent extrusion yield stress and wall shear stress (at two $L_d/D_d$ ratios) for the printable pastes. The error bars relate to the range of stresses corresponding to the range of extrusion velocities.
Figure 13(a) depicts the relationship between the extrusion yield stress and the shear yield stress determined from parallel plate rheology and the peak force from tack test. For the selected mixtures, the extrusion yield stress from extrusion rheology and the shear yield stress from parallel plate rheology are well correlated, indicating that the determination of simple shear yield stress indeed can be used to infer the behavior of the paste under extrusion. The tack force and the extrusion yield stress are also well correlated. It can be postulated that the adhesive forces because of the viscous nature of the mixture in the presence of activators (as explained earlier) keeps the particles closer together, which consequently results in an increased extrusion yield stress for the mixtures exhibiting higher tack force. Figure 13(b) depicts the relationship between the shear yield stress from parallel plate rheology and the extrusion force required. The extrusion force is taken as the force corresponding to the highest point in the force-displacement relationship shown in Figure 11. These relationships can be useful in understanding the extrusion response of these binder systems from straightforward laboratory tests.

3.4 Compressive and Flexural Strengths of 3D-Printed Binders

The compressive and flexural strengths of the alkali-activated fly ash-based 3D printed cubes and beams were evaluated after the respective curing regimes. In the first curing regime, all the samples were cured in a moist chamber (23 ± 1°C, > 98% RH) until 28 days. In the second regime, all the samples except the mixture containing OPC (F50C30L20) were exposed to heat curing (at 70°C) for two different durations (24 h and 48 h). Figure 14 shows the test directions. Three companion specimens were used for compressive and flexural strength testing.
Figure 15 depicts the compressive and flexural strengths of the selected binders. When moist cured, the compressive strength increases with reducing amount of fly ash in the binder, as expected. The compressive strength of the paste containing OPC is the highest. Similar strengths have been attained for mixtures containing high volumes of fly ash, activated using alkali sulfates [38]. The 28-day compressive strength the F_{50}S_{30}L_{20} mixture activated using NaOH was lower than that of F_{50}S_{30}L_{19}A_{1} mixture activated using sodium silicate, owing to the presence of reactive silica from the sodium silicate leading to enhancement in the reaction product volume and constitution. The fly ash-limestone specimens (F_{85}L_{15} and F_{70}L_{30}) cured at (23 ± 1°C, > 98% RH) and tested at 28-day showed the lowest compressive strength among the test specimens. The compressive strengths of the F_{85}L_{15} and F_{70}L_{30} mixtures activated using NaOH improved when cured at 70°C, with a longer curing duration providing better strengths. The compressive strength results of 3D printed binders shown here suggest that the trends are similar to the compressive strengths of binders cast in a conventional manner [38,68].

Figure 15(b) depicts the flexural strength of the 3D printed alkali activated fly ash-based binders. For the F_{85}L_{15} and F_{70}L_{30} mixtures, the heat treatment improved the flexural strength when compared to the moist curing regime. However, the heat treatment was found to cause extensive microcracking in the F_{50}S_{30}L_{20} and F_{50}S_{30}L_{19}A_{1} mixtures due to the high shrinkage of slag-containing alkali activated binders [69,70], thereby leading to poor flexural strength (microcracking influences flexural strength more than the compressive strength). The slag-containing specimens moist-cured at ambient temperatures showed the highest flexural strengths. When shrinkage is countered through moist curing, and the reaction of slag is facilitated, better strengths are obtained. The flexural strength of the OPC-containing mixture was also found to be lower since the interfacial strength of this mixture (as evidenced from tack test results) likely is lower, resulting in interlayer failure at relatively lower flexural stresses. Also, F_{85}L_{15} and F_{50}C_{30}L_{20} showed...
a higher modulus (peak force to displacement ratio) from the tack test and relatively lower flexural strengths. This complements previous observations where higher modulus resulted in lower inter-layer bond strength [56]. More studies on this aspect is ongoing.

Figure 15: (a) Compressive strengths, and (b) flexural strengths of selected binders after subjecting to different curing regimes.

3.5 Effect of Extrusion and Overburden Pressure on Pore Structure

Layer-wise printing of cementitious composites can impact the pore structure (and thus the mechanical and durability properties) in multiple ways. The effect of extrusion (consolidation) is not uniform during the time the paste makes its way out of the extruder, resulting in differing particle concentrations and fluid contents (due to potential liquid phase migration). When printed in layers, the bottom layer is subjected to increased overburden pressure from the subsequently printed layers. The specific gravity, porosity, and critical pore size of the top and bottom layers of the printed cubes (layer dimensions of 6 mm x 3 mm; width x height) are compared in this section. Figure 16 depicts these pore structure parameters for the pastes studied. The variation in specific gravities between the top and bottom layers was less than 3% for all the pastes. It is observed that no significant difference exists in the porosity and critical pore size between the top and bottom layers for all the specimens. The bottom layer, which is printed first, is generally less influenced by the squeeze and consolidation effects because the material flows only a small distance before being extruded; however, the overburden pressure in this layer is higher. For the top layer, there is no overburden pressure, but the paste that constitutes this layer is
subjected to higher confinement effects in the barrel and gets subjected to pressure for a longer time while being extruded. It is thus likely that the net effect on the pastes is rather similar for the extruder geometry and mixture compositions evaluated here, resulting in insignificant changes in porosity between the top and bottom layers.

Figure 16: (a) Porosity and (b) critical pore sizes of top and bottom layers of the printed cubes.

4. Conclusions

The focus of this paper was on the material design and evaluation of 3D-printable binders based on alkali activation of fly ash-based blends. Using fly ash as the major ingredient, and limestone, slag, or OPC as minor ingredients, mixtures were proportioned so as to be extrudable and buildable (printable). When alkaline activators were used in lieu of water, the shear yield stress of the fresh pastes decreased, and the cohesiveness increased, similar to the use of a superplasticizer in conventional OPC systems. The yield stress was also found to depend on the particle sizes (and in turn particle packing in the suspension) of the constituents. The mini slump values and shear yield stresses determined on extrudable mixtures were synergistically used to arrive at bounds for printability of the paste mixtures. This study also defined a printability window based on concurrent measurement of time-dependent yield stress and extrusion printing of a filament of the paste. For the mixtures evaluated, a shear yield stress of 700 Pa (in parallel plate rheometry) indicated an upper limit of printability. This window was found to scale relatively well with the setting time of the pastes. The presence of alkaline activator also resulted in increased tack force and adhesive energy for these binders as compared to conventional cement-based binders.
The extrusion rheology experiments coupled with the Benbow-Bridgwater model facilitated the extraction of extrusion yield stress and die wall slip shear stress of alkali-activated fly ash-based binders, which are important process-related parameters in extrusion-based 3D printing. These parameters were shown to be related to shear yield stress and extensional (tack) properties of the virgin paste, thereby providing a means to understand the response of the extruded mixture from simple rheological experiments, and therefore could be used to link material design to the extrusion-based printing process. The compressive and flexural strength tests on the pastes showed that, in general, comparable mechanical properties as that of conventionally cast specimens can be obtained through layered printing. However, strength reduction likely due to microcracking (for mixtures containing slag, especially when heat cured) and weak inter-layer bonding (in mixtures containing portland cement) were observed, which requires careful material design and curing conditions to ensure long-term performance and durability. The study has shown that alkali activated fly ash-based binders can be successfully designed for beneficial properties.

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6. Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

7. References


