3DPC literature review on the effects of mixture composition on constructability

by

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Abstract

The advent of 3D printing technology offers an alternative building method to the construction industry by offering innovative solutions for complex and sustainable building designs. This research paper explores the critical aspects of 3D printed concrete mixture design and its applicability in constructing robust and efficient structures. The study reviews concrete mixtures explicitly tailored for 3D-printing, considering both fresh and hardened properties, and printability. Breaking down the individual mixture components and their effects on the concrete properties is critical to developing a proper mixture design.

The influence of various parameters, such as binder composition, water ratios, aggregate size/quantity, chemical admixtures, and fiber reinforcement, on the mechanical properties, durability, and workability of 3D-printed concrete is investigated.

Case studies testing the effects of concrete mixture components on the fundamental rheological (flow) properties needed to achieve printability and the mechanical properties needed for structural design are given. Additionally, examples of housing, infrastructure, and specialized architectural elements using 3D-printed concrete is presented.

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Chapter 1: Introduction

Three-dimensional printing is a recent technological advancement that has proven to have many applications to solve real-world problems. 3D Printers have been developed to manufacture objects with precision, following a scripted two-dimensional path for each layer of the object, which may require thousands of layers until completed. Printing applications use many materials, most commonly plastics and, more recently, metals, for smaller printers, but larger applications are being developed with printable concrete for structures. For the last 15 years, research on three-Dimensional Printable Concrete (3DPC) has focused in improving the practice (Buswell, et al., 2018). This construction method, additive manufacturing (AM), deposits concrete layers on top of each other in a cementitious paste. The nozzle shape forms these extruded layers supplied by a continuous supply of fresh concrete mixture. Unlike traditional concrete, no initial manual labor or formwork is required to construct these layers, designed to form load-bearing concrete walls.

Two types of concrete printing currently exist: powder-based and extrusion-based printing (Li, et al., 2020). The extrusion of printable cementitious materials layer by layer in filaments or paste from a nozzle mounted on a robotic control system, extrusion-based printing, is the focus of this report. The robotic control system varies between projects. Figure 1 shows examples of robotic control systems. Extrusion-based 3DPC offers design freedom, allowing curved or complex geometries that traditional methods would struggle to create. Additionally, 3DPC sections can also be printed offsite and transported to the construction site, similar to precast concrete. This method does not require formwork, which has a number of benefits. The first is that formwork accounts for 35-54% of the concrete construction cost and consumes 50-

75% of the total construction time (Paul S. C., 2018). Figure 2 shows examples of printed structures and components.

Using 3DPC requires a specific mixture design for the material to be correctly printed. The ability for concrete to be printed is known as its printability. For a traditional concrete mixture to be printable, it must be altered. The contents of this literature review detail the

Figure 1: Examples 3D concrete printer setups
(Molitch-Hou, 2021), (Link, 2015), (HANNAH, 2022)

required mixture components for concrete to meet printability requirements. The required fresh properties of pumpability, extrudability, buildability, and printability are reviewed in Chapter 2, as well as desired characteristics of the concrete. Hardened material properties such as compressive strength, tensile strength, flexural strength, and modulus of elasticity are discussed

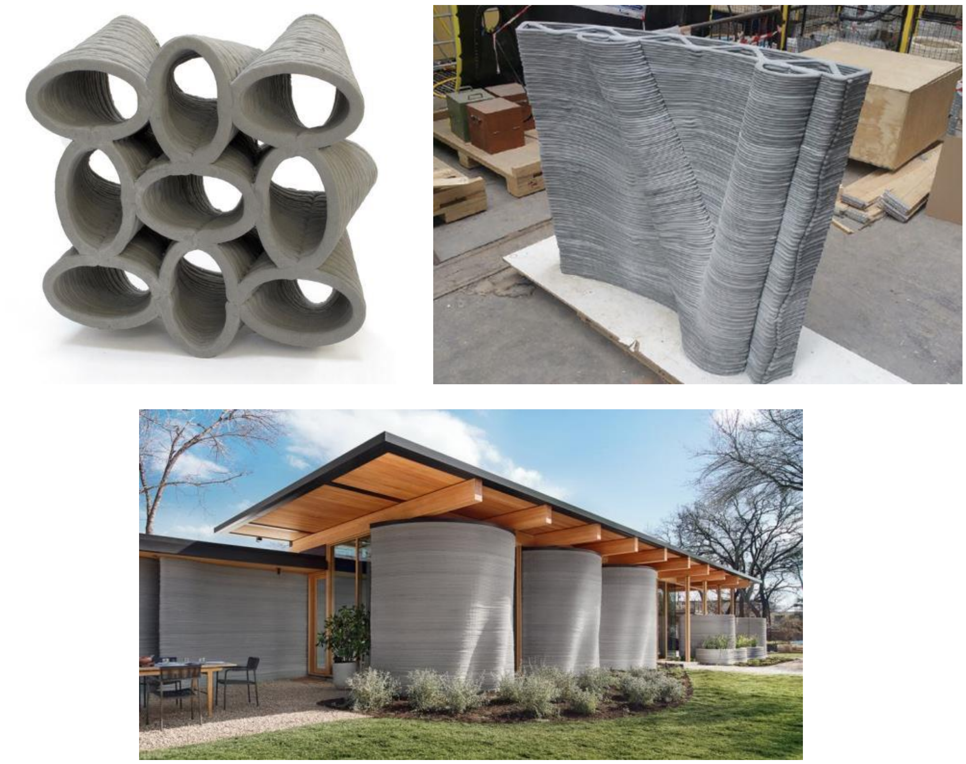

Figure 2: Examples of complex geometry made possible through 3D concrete printing

Figures from: (Gosselin, et al., 2016), (ICON, 2024)

in Chapter 3. The individual components needed for 3DPC are discussed in Chapter 4, accounting for the cementitious materials, water-to-binder ratio, aggregates, chemical admixtures, and finer reinforcement. Recent research studies, focusing on creating mixture designs, and their comparisons are discussed in Chapter 5. Using these studies, the effects of the different mixture components are presented and compared to determine the beneficial materials for proper concrete printing. This extensive literature review analyzes the effect the mixture composition has on the fresh and hardened properties of 3DPC.

Chapter 2: Fresh Properties

Three-Dimensional Printable Concrete (3DPC) is an innovative material with distinct characteristics that differentiate it from traditional concrete. It necessitates a delicate balance between fluidity for seamless flow through a dispensing tube, and rapid hardening and load-bearing capacity once dispensed, all without the need for additional support structures (formwork). Achieving these crucial attributes hinges on the specific fresh properties of the material, which will be discussed in this section. These encompass rheological properties, workability, printability, and extrudability, collectively governing the behavior of 3DPC from its initial mixing stage to its ultimate placement. This introduction serves as a prelude to a comprehensive exploration of the intricate features and requirements of 3DPC within the context of additive manufacturing technologies.

2.1: Rheology

More commonly known as workability, rheology is the science of flow and deformation of matter, and investigates the relationship between stress, shear rate and time (Chen, et al., 2018). A standard method to test the workability of fresh concrete is the slump test under ASTM (American Society for Testing Materials) C143 (Gelardi, 2016). This test, however, is inadequate for testing the required flow properties for a concrete mixture that is 3D printed. Two mixtures with different flow behaviors can have the same slump, so a deeper analysis of the fundamental rheological properties is needed. These properties are thixotropy, viscosity, and yield stress. A perfect balance of these flow properties to match the printer device allows 3DPC to perform at the highest capacity.

Rheology is a science at the intersection of solid and fluid mechanics, and the best way to properly represent 3DPC is in this context and by classifying it with the Bingham model

(Gelardi, 2016). The Bingham model is the most commonly used method for identifying the relationship between shear stress and shear rate for concrete mixtures. Newtonian fluids have a linear relationship between shear stress and shear rate, representing a constant viscosity. Examples of Newtonian fluids are water or oils, and they follow Newton's model given by Equation 1:

$$\tau = \eta\dot{\gamma} \qquad \text{Eq'n 1}$$

Where τ represents shear stress, $\dot{\gamma}$ represents the shear rate, and the slope η represents viscosity. Concrete has a specific shear stress, called yield stress represented by τ_0 it must reach before flow can occur, thus classifying it as a non-Newtonian fluid, specifically a Bingham fluid. Below the yield stress, the material is stationary, even under the effects of gravity. The yield stress is due to the attraction of cement particles within the mixture and can be influenced by the amount of aggregate present (Gelardi, 2016). The plastic viscosity is also a factor that influences the performance of a mixture as the shear rate increases. The viscosity decreases rapidly as the shear rate increases, causing the mixture to increasingly act like a Newtonian fluid. The equation for a Bingham fluid differs from a Newtonian fluid, with plastic viscosity represented by μ_p in Equation 2:

$$\tau = \tau_0 + \mu_p\dot{\gamma} \qquad \text{Eq'n 2}$$

Figure 3 illustrates the relationship between Newtonian fluids and Bingham Plastics. The mixture design of concrete impacts this equation, and a mixture optimized to a printer will yield suitable paste for 3D printing concrete extrusion.

The findings from studies provide crucial insights into the rheological properties required for successful 3D printing of concrete mixtures. For example, (Zhang, et al., 2019) established that having values of viscosity beyond 3.8 to 4.5 Pa*s, yield stresses exceeding 178.5 to 359.8 Pa, and thixotropy values surpassing 6284.5 Pa/s rendered the mixture impractical for printing for that printer and mixtures parameters. When these values did not meet these requirements, the

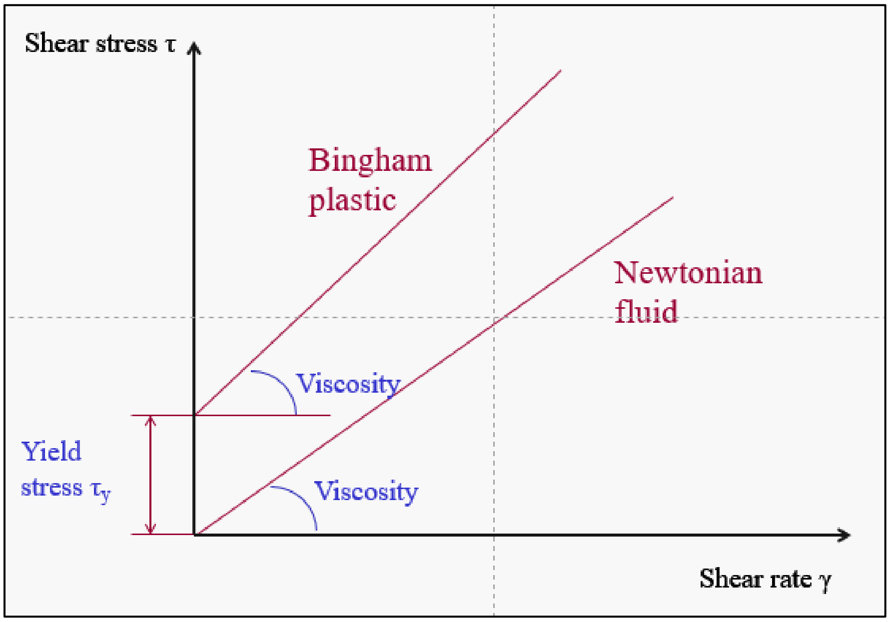

Figure 3: Graph of Newtonian fluid and Bingham plastic (Concrete Society, n.d.)

paste would fail pumpability, extrudability, and buildability requirements.

(Chen, et al., 2018) emphasizes the significance of maintaining specific rheological parameters for optimal printing. Chen et al (2018) noted apparent viscosity under a constant shear rate of 100 s^{-1} ideally falls within the range of 5.5 to 7.5 Pa*s. The plastic viscosity and yield stress should also be controlled within the ranges of 1.650 to 2.538 Pa/s and 390 to 542 Pa, respectively. These values differ from Zhang's due to the different mixture composition and printer traits.

Furthermore, Buswell et al. (2018) refines the criteria for suitable mixtures. For mixtures containing CEM I and Fly Ash, plastic viscosity, and yield stress values of 38.7 ± 4.5 Pa*s and

0.59 ± 0.08 kPa were identified as conducive to pumping and extrusion. Likewise, mixes incorporating CEM I and Limestone filler demonstrated suitability for these processes with plastic viscosity and yield stress values of 21.1 ± 2.4 Pa*s and 0.27 ± 0.03 kPa, respectively. Similarly to the studies previously presented, these conclusions differ depending on the mixture design. When optimizing 3DPC many variables exist, such as varying printer types and dimensions. Ensuring the analysis remains broad enough to be applicable across various printing parameters is crucial when developing an optimized blend. Regardless, these findings collectively provide valuable benchmarks for formulating 3D-printable concrete mixtures with precise rheological properties.

2.1.1: Thixotropy

Thixotropy denotes a material's ability to break down, or become less viscous, under shear flow and restructure itself at rest. For fresh concrete, thixotropy is time-dependent due to irreversible structural breakdown and hydration occurring, slowly solidifying the mixture, and ensuring that after being broken down it cannot fully recover its yield stress (Gelardi, 2016). The rate at which hydration occurs can be increased or decreased by altering the mix composition, namely by using admixtures to prevent loss of yield stress. Thixotropy can be related to green strength, which is the initial strength of the concrete paste shortly after extrusion. With high thixotropy, the material can rebuild its structure quickly and have sufficient strength to hold itself and additional layers deposited above it (Zhang, et al., 2018). When concrete is analyzed using the Bingham model, the degree of thixotropy is subject to alteration based on component ratios and the inclusion of specific additives. The proper ratio of fine aggregate to cement and the ratio of water-to-cement are primary influencers. However, thixotropy can also be affected by using admixtures, aggregate gradation, temperature, and open time (Gelardi, 2016). An optimal blend of these factors will yield the ideal conditions needed to satisfy the rheological requirements for the mixture.

2.1.2: Viscosity

Viscosity is the amount of resistance to flow due to a fluid's internal friction has, with a higher viscosity having more friction. Typical examples are water, milk, and oil, which have low viscosity, while soap, honey or concrete have much higher viscosity. Viscosity is an essential parameter for 3DPC due to its relation to yield stress and thixotropy, as it is directly influenced by shear stress. When the concrete mixture is pumped, the pump applies a shearing force that turns the mix less viscous and, therefore, able to flow and deform easily to be transported to the extruder. When not being pumped and the mixture turns into paste, the shearing stress is relieved, and the mix becomes much more viscous, almost to a solid state. Due to having characteristics of a Bingham fluid, concrete can be said to have plastic viscosity (Li, et al., 2020).

The viscosity should change throughout the printing process, and the mixture should be tuned for the correct viscosity at each stage. For instance, the mixture should have low viscosity during pumping so particles stay as a paste and the hydraulic conductivity does not reach critical levels. A similarly low viscosity is desired during extrusion for a continuous paste. For buildability, however, a high value of viscosity is needed for shape retention and for stiff, sticky layers to be formed for proper bonding and low vertical deflection (Zhang, et al., 2021).

2.1.3: Yield Stress

Yield stress is the minimum amount of shear stress required to initiate flow for a material, a critical component for 3DPC mixtures. Low yield stress values cause the structure to collapse during the printing process and very high yield stress makes the mixture too stiff to be printable.

Similar to viscosity, a dynamic yield stress is desired for 3DPC mixtures because at different stages of printing the optimal yield stress value changes. A moderate amount of yield stress is desired during pumping, an optimum amount during extrusion, and a high value after being printed (Zhang, et al., 2021). Factors that impact the yield stress include the w/c ratio, the fineness of cement, and the coarse aggregate content (Gelardi, 2016) presented in Chapter 4.

2.2: Printability

Printability is a critical determinant for the successful operation of the 3D printing process and is related to the workability of concrete in a printing system. The material's ability to perform optimally within a 3D printing system is collectively known as printability, and is intricately tied to several key attributes, namely pumpability, extrudability, and buildability (Zhang, et al., 2021). These properties are contingent upon the rheological behavior of the mixture, which is influenced by factors such as slump and shear stress, collectively working in concert to achieve an adequate level of printability. Understanding and optimizing these aspects are pivotal in ensuring the seamless execution of 3D concrete printing.

2.2.1: Pumpability

Pumpability is a crucial property that addresses the concrete mixture's capacity to be efficiently transported and pumped to the 3D-printing nozzle or extrusion system without clogging, segregation, or other flow-related issues. These 3DPCs must have optimized flow properties so the printer can continuously print without interruption. This attribute is paramount significance for 3DPC machines, enabling uninterrupted and continuous printing operations. As previously discussed, the mixture exhibits favorable flow characteristics when its viscosity is lower. However, the mixture tends to adhere to the walls at lower viscosities, resulting in the central section becoming enriched with aggregates.

In contrast, a significant portion of the mixture is left behind. The diameter of the pumping tube, the pressure at which the mixture is pumped, and the fundamental rheological properties must be considered to transport the mixture properly. To maintain uniformity and counteract segregation, it becomes imperative for the mix design to withstand the rigors of high pumping pressures (Zhang, et al., 2021). One effective strategy in mitigating these challenges is the incorporation of positive displacement pumps, which introduce a lubricant within the pump tubes, ensuring uninterrupted pumping without the risk of clogging (Buswell, et al., 2018). The desired characteristics for pumpability are shared by extrudability, and when satisfying the requirements for one the requirements for the other is met.

2.2.2: Extrudability

Extrudability refers to the ability of a concrete mixture to be extruded or pushed through the nozzle of a 3D printing system in a controlled and consistent manner. This property is different from pumpability due to the performance hinging on the smooth deposition of intact paste layers (Li, et al., 2020). This property is heavily contingent on the rheological attributes of the mixture, emphasizing its ability to flow through the extruder during the printing process. Achieving optimal extrudability necessitates a thorough analysis of the interplay between factors such as the extrusion rate of the fresh paste and the printing speed (Ma, et al., 2018). As discussed in pumpability, maintaining an acceptable pumping speed depends on the flow characteristics of the mixture, which directly translates into the extrusion rate.

Furthermore, the composition and flow properties of the mixture must be precisely tailored by the size and shape of the nozzle to ensure accurate printing. The hydraulic conductivity of the mixture is an important factor. The mixture should not have a higher hydraulic conductivity than the speed of extrusion (Zhang, et al., 2021). If the mixture's hydraulic conductivity surpasses the extrusion rate, the liquid component of the mixture will flow more readily compared to the cement and aggregate particles (Li, et al., 2020). This discrepancy can lead to non-uniformity in the printed layers at best, and at worst, result in clogging and solidification within the extruder. Important ASTMs for flow must be met to ensure continuous extrusion and clogging do not occur. ASTM C1437 for hydraulic cement mortar and ASTM C230/C230M display tables the mixture must adhere to for proper pumpability and extrudability (Marchment, et al., 2019). Thus, meticulous attention to extrudability is paramount in achieving successful and consistent 3D concrete printing.

Layers inevitably will have gaps between them, usually in the corners of the layer between the adjacent layers and layers above and below. Minimizing or eliminating these voids allows for a homogenous mixture and thus an increased mechanical strength. Using rectangular nozzles allows for greater laminar flow when compared to circular nozzles, decreasing the deformation of the paste, and allowing for increased surface area for bonding (Li, et al., 2020). Rectangular nozzles, however, lack the geometric freedom circular nozzles offer. The nozzle type selected must be considered in the design due to the possibility of voids forming in sections of the structure.

2.2.3: Buildability

Buildability refers to the suitability and ease with which a concrete mixture can construct the desired 3D-printed structure. As successive layers are added, a natural tendency for the previously printed layers to undergo deformation exists. In the absence of formwork typically used in conventional concrete construction, the concrete must possess the capacity to support its weight and the load imposed by subsequent layers, without compromising structural integrity. To avert the risk of collapse, the mixture must exhibit sufficient initial green strength, enabling it to withstand the imposition of additional layers without deformation (Zhang, et al., 2021). High viscosity, yield stress, and proper thixotropic properties are required for adequate green strength. These properties and sufficient open time must be precise for the window of strength to be met shortly after extrusion. Open time, in this context, denotes the duration from the initiation of the chemical reaction after the water is added to the concrete mixture to when the material is deemed printable (Li, et al., 2020).

Robust interlayer bonding, a pivotal factor in buildability, ensures the stability and structural integrity of the constructed form. Failure to establish proper bonding can result in the formation of cold joints. Numerous variables come into play in achieving buildability, mirroring considerations for other material properties. However, the foundational requirement for buildability lies in endowing the mixture with sufficient strength and the necessary time to attain that strength between successive layers, ultimately safeguarding the stability and structural integrity of the constructed form.

In a comprehensive study, tests were conducted with copper tailings as a replacement for fine aggregate to demonstrate the importance of buildability and the contributing factors to consider. Copper tailings are solid metal scrap left over after purifying copper ore and are damaging to the environment when not disposed of properly. The tailings are usually difficult to dispose of, so being able to incorporate them into a concrete mixture would be beneficial. Ma et al. (2018) tested six mixtures with copper tailing replacement of 0% to 50% to observe the effects of the fresh and hardened properties. Twenty layers were printed to observe the buildability and the stability of each paste, with an open time of 10-minutes used. Copper tailings, with their finer particles than sand, showed interesting results. Increasing the replacement increased flowability but decreased the stiffness of the extruded paste. As the replacement increased, the buildability of the layers decreased, eventually representing a clump of paste for the 50% replacement while the 10% replacement has the lowest vertical displacement and the most consistent layers. Ma et al. (2018) reasoned that the stiffer mixtures, such as ones with larger aggregate particles, had better buildability at the expense of flow. When analyzed further, printing with open time in consideration can yield better results. Ma et al. (2018) found extrudability becomes impossible around the 90-minute mark after hydration, and good flowability exists from the start of hydration to the 30-minute mark. The time between 30 minutes and 90 minutes yields the optimal buildability window for the mixture to be stiff enough for buildability and fluid enough for extrudability. After taking the open time into account and increasing it, the higher copper tailing replacement mixtures were able to achieve excellent buildability.

2.3: Characteristics of 3DPC

Fresh property characteristics of 3DPC that contribute to the hardened concrete properties discussed in this section are the open time, setting time, and green strength. These attributes, originating from the fresh composition of the mixture, play a fundamental role in shaping the final properties of the solidified concrete. These traits are pivotal for the concrete mixture to attain optimal qualities necessary for the construction of a high-quality structure.

2.3.1: Open time/Setting time

Open time refers to the duration from when water is first introduced into the concrete mixture to the point at which the layers are being printed or deposited. This is a critical period where bonding occurs between deposited layers. More open time poses a risk of more concrete particles forming between the layers due to chemical reactions occurring and stiffening due to hydration. With a considerably short open time, concrete may start to solidify prior to the extrusion process, leading to blockage or clogging of the printing nozzle. On the other hand, excessive open time may result in inadequate green strength, causing the concrete to lack the necessary support for itself and subsequent layers. This lack of green strength could lead to layer depreciation, causing the structure to lose the precision of the printer geometry and could lead to structural failure.

The setting time for the mixture is the duration of time from being initially printed to when the maximum strength is achieved. Within the setting time is when the green strength is important for the buildability of the mixture. The green strength must be sufficiently strong to support consecutive layers of 3DPC. The open and setting times depend on the moisture content of the concrete mixture and its thixotropic properties (Sanjayan, et al., 2018). As with all components, it is a balancing act to have the right amount for the maximum performance of the materials. A lengthier open time benefits for continuous extrusion and interlayer bonding but may negatively impact the buildability by compromising the concrete's shape stability (Li, et al., 2020). The way open time affects interlayer bonding is critical to the mechanical properties of 3DPC, presented in Chapter 3. Sufficient open time allows the many layers of paste to bond into a monolithic wall, and with an ideal mixture, have isotropic properties. An open time that gives sufficient bonding between layers ensures that this method of additive manufacturing has the necessary mechanical properties to function as a structural member.

2.3.2: Green Strength

Green strength pertains to the early strength or initial mechanical properties displayed by recently printed concrete. Green strength is closely related to the thixotropy of a mixture, so the better the mixture is at rebuilding its structure after extrusion, the higher the green strength will be. The strength manifests soon after hydration occurs and shear stress is removed from the paste, and before the concrete undergoes complete curing to attain its ultimate strength. If the concrete shortly after extrusion is a stiff, sticky paste, the high viscosity and thixotropy properties are showing, and are contributing to the green strength. This is an important property regarding the buildability of the 3DPC mixture and is correlated to the yield strength obtained from the thixotropic properties. Green strength over time has been observed to follow a pattern similar to that of yield strength (Zhang, et al., 2021). Lacking the essential green strength would result in the inability to support successive layers, leading to the collapse of the structure. This is a critical property for additive manufacturing (AM) as it enables the structure to continually build upon itself. Figure 4 illustrates the necessary green strength gain for proper buildability of a structure.

Green strength is not just the ability to support sequential layers, it impacts the measure of vertical displacement from its self-weight and from the sequential layers. (Li, et al., 2020). Vertical displacement is critical for the buildability of this material and is tied to the yield strength the mixture possesses. If the vertical displacement or initial slump is excessive, the structure may move too far away from the extruding nozzle, resulting in print failure. Deformation greater than what is designed for will inevitably result in a failure due to the geometric accuracy of printed material being disrupted, causing unstable or weak layers to form, and inevitable collapse.

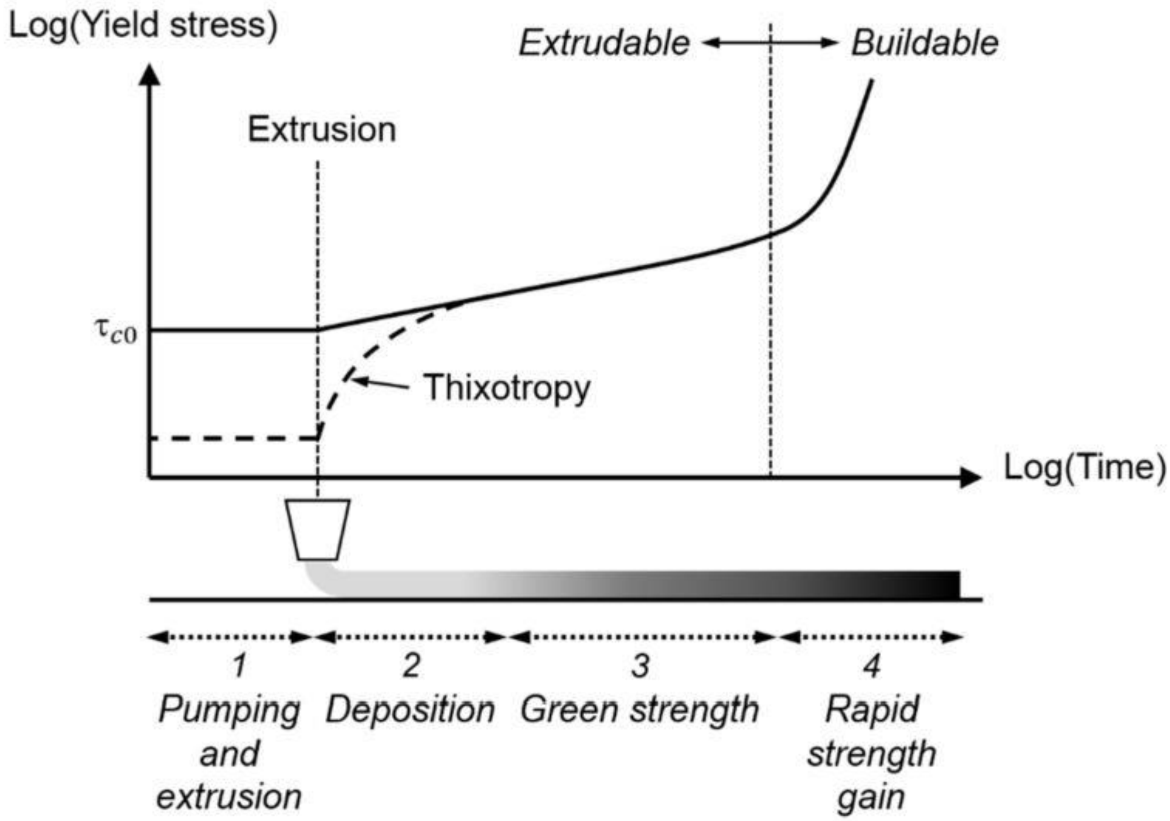

Figure 4: Evolution of yield stress and strength for 3DPC materials (Li, et al., 2020)

Chapter 3: Hardened Properties

Once the fresh states of 3DPC achieve optimal conditions, they significantly influence the characteristics of the hardened concrete. These attributes denote the mixture's strength through various parameters, including inter-layer bonding strength, compressive strength, flexural strength, and modulus of elasticity. These properties hold an important role for commercial application and for this material to be viable in the design for structures. Ensuring the reliable and consistent determination of these properties for any 3DPC mixture is imperative for standardizing mixtures. Having predictable hardened properties will facilitate the implementation of this building material into building codes that can be used for designing structures.

3.1: Inter-Layer Bonding Strength

Proper concrete bonding between layers occurs when the concrete mixture is freshly printed. The strength is achieved after the concrete mixture hardens and depends on the bond between printed layers. Numerous studies indicate that the inter-layer bond between layers is crucial to the material’s structural integrity and strength requirements (Paul, et al., 2018). This is primarily because without proper bonding, individual layers will remain separate, lacking collective strength. Each layer of the 3DPC mixture must form a homogenous bond to achieve the desired strength. Influencing the mixture properties to prevent hydration from occurring too quickly while maintaining high viscosity maintains moisture content and stability for fresh paste, allowing for a proper bond to form. (Sanjayan, et al., 2018) found that the moisture level at the surface between the layers had a significant impact on bond strength. Marchment et al. (2019) found that CCAs used to increase viscosity and particle dispersion significantly increased the effective bond area material properties. Therefore, selecting the proper ratios of mixture components can increase the bonding strength by changing the flow properties for the most effective bond. The component of bonding strength is unique to additive manufacturing; due to the automated process, the mixture must achieve an appropriate bond strength autonomously without outside interference.

When the bond between layers does not occur, cold joints are formed, and lack a proper connection between the layers. Cold joints are formed from the mixture setting too fast, not allowing the mixture to become homogenous between layers. These cold joints usually have gaps, voids, or air bubbles between the concrete layers to varying degrees that decrease the overall strength of the bond. They can also be formed from low printing speeds and longer time gaps between printed layers (Li, et al., 2020). Because of this, a long open time is desired for the printed mixture. The bond strength is highly dependent on the adhesion of the layers, which is a function of the time between extrusions (Le, et al., 2012) and relates to the moisture of the layers and the open time.

Marchment et al. (2019) tested the adequate compressive and inter-laying bond strength for different mixtures, the spread diameter of printed paste and the overall effective bond area. The only variable that changed was the addition of different rheological altering admixtures, the effect of changing the flow properties on inter-layer bonding was observed. The bonding was affected in three ways: by increasing the open time, the viscosity, and the dispersion of cement particles between the layers. Large sections for each mixture were printed and several test samples were extracted for testing. Tensile strength tests were used to determine the bond strength of each mixture and it was found that the effective bonding area was increased in all cases. The increased open time allowed moisture to persist between the layer surfaces and created a stronger bond after hydration occurred. When the viscosity was increased, it similarly increased water retention and decreased the surface drying effect, again increasing the bonding strength. With an increase to the dispersion of cement particles between layers, the effective anchorage area between the layers increased and allowed for a stronger, more homogenous bond to be formed. Marchment concludes that the higher the flow characteristics of a mixture are, the stronger the bond between layers can be.

Zhang et al. (2019) indicated that the sand-to-cement ratio or the sand-to-binder ratio (S/B) had a significant impact on the bonding strength of the mixture. A large S/B ratio can make the mixture too stiff, decreasing the effectiveness of the bond. At a high S/B ratio, approximately 1.5, the material was not able to be extruded. At lower S/B ratios, such as 0.6 or 0.8, the mixtures had higher flow, and larger slump values. With high flowability, the mixtures also had low yield stress and viscosity. The only S/B ratios that were used to determine the compressive strength for the mixtures were the 1.0 and 1.2 mixtures, which demonstrated excellent bonding between layers for proper strength.

The addition of fibers for reinforcing the concrete mixture, detailed in Chapter 4, may cause issues with the material bonding due to the fibers being unevenly distributed in the extruded paste, preventing proper adhesion from occurring. Consideration of these fibers in the mix design may increase the tensile strength of the mix but will decrease the potential bonding strength, as well as cause protrusions out of the mix (Zhang, et al., 2019). As long as bond strength is adequate and cold joints are not formed, the mixture should form a continuous and homogenous wall structure that can be analyzed for compressive and flexural strengths for use in structural design.

The presence of weak interlayer joints poses a significant durability issue. These weak joints facilitate the capillary ingress of water and other detrimental fluids deep into the structural components, potentially compromising the durability of the printed concrete and protective role concerning steel reinforcement if reinforcing is present. The susceptibility of layer-to-layer interfaces to serve as convenient pathways for external fluids is frequently observed in 3D-printed elements, and prevention is critical (Zhang, et al., 2021).

3.2: Compressive Strength

One of the most critical tests for concrete is the compression test, which is performed to determine if the concrete mixture has adequate strength to be loadbearing. This is a standard test for concrete. A cylinder tested following ASTM C39 or a cube compression test following ASTM C109 is typically used to determine its design strength, but others, such as European standard EN 12390–2, can also be used (Aramburu, et al., 2022). Both tests have been used in determining the compressive strength of specimens, and the values can be related with a 0.65-0.90 cylinder-to-cube strength ratio (Elwell & Fu, 1995). This range depends on the compressive strength of the concrete, and high strengths have higher ratios. For simplicity, a cylinder to cube strength ratio of 0.8 will be used. When cubes are used for compressive strength tests, they are evaluated in all directions to determine their strength. Since AM results in the concrete being anisotropic, or more specifically orthotropic for this material, each axis should be tested for compressive strength. A coordinate system is typically used for describing the orientation of the tested block, as shown in Figure 5. They are denoted as a) Perpendicular b) longitudinal, and c) layer-to-layer orientation and are marked on an XYZ axis. The X- and Z-axis are parallel to the printing path (dashed lines) and the gravitational direction (the height

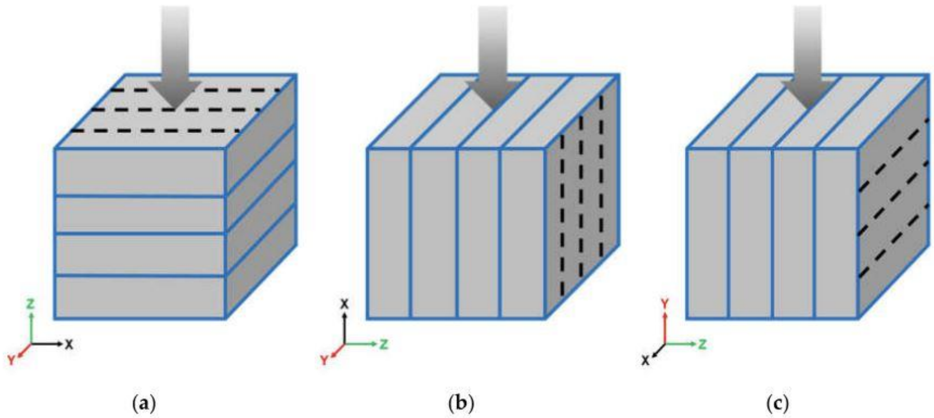

Figure 5. Cubes specimens from the printed mixture are tested in compression in each direction (Li, et al., 2020).

during the printing process), respectively. Printed layers are located in the X-Y plane (Li, et al., 2020).

Le et al. (2012) experimented with a high-performance concrete mixture and its uses for 3DPC. Several trials were performed to achieve printability before an optimal mixture was found and could be used for testing. This mixture has a 60:40 sand to binder ratio and a water-to-binder ratio of 0.26, with the addition of a superplasticizer and a retarder to achieve proper printability. After developing the mixture, printed specimens were formed and cast specimens were cured to compare the mechanical strengths. Standard cube tests were used for the compressive strength tests and the developed strength was observed over time. For both the mold cast specimens and the printed specimens, the specimens with higher dosages of superplasticizer (1-2% compared to 0.5%) had higher compressive strengths compared to the smaller superplasticizer dosage after 7 and 28 days. Implementation of the 1.5-2% retarder resulted in the specimens having no measurable compressive strength at the 1- and 7-day marks, but it did not impact the compressive strength when compared to the other mixtures after 28 days. Both the cast and printed specimens had high compressive strength values of approximately 100 MPa (14.5 ksi), with the printed specimens having a 15% strength reduction when tested in planes parallel to the extruded layers. Le et al. (2012) contributes the lower strength to be from the anisotropy that occurs with 3DPC specimens, and remarks that a decrease in voids between layers would decrease the strength reduction that occurs due to the testing orientation.

(Panda, et al., 2017) performed experiments using 27 cubes extracted from a printed slab for compression tests to be performed at 7-, 14-, and 28-day intervals and in each orientation. These results yielded average compressive strengths of approximately 22 MPa at 7 days, 31 MPa at 14 days, and 35 MPa at 28 days (2552 psi, 3597 psi, and 4061psi cylinder equivalent, respectfully). The longitudinal specimens were found to have a slightly larger strength than the rest. This matches the majority of the studies concluding that the longitudinal direction has the highest compressive strength of all orientations when voids are present from printing.

3.4: Modulus of Rupture

Referred to as the modulus of rupture, the flexural strength of a material indicates its capacity to withstand bending before yielding occurs and measures the tensile strength. Similar to compressive strength, the flexural strength varies in each direction, up to six possible directions. Figure 6 shows the six directions and the loading direction of each. Researchers commonly focus on evaluating the longitudinal direction, as the loading direction is commonly perpendicular to the extruded layer direction (Li, et al., 2020). When evaluating from other directions, such as when the layers are parallel to the loading direction, the main resisting force is the tensile bonding strength of the specimen (Nerella, et al., 2019). The strength of the material is influenced by the homogeneity of the bonding, with a more homogenous mixture resulting in greater strength. A homogenous bond is not always formed, so it is essential to test each direction for strength similar to compressive strength.

(Le, et al., 2012) conducted reasearch for a high performance fiber-reinforced mixture that could be used for 3PDC applications, and tested it against a typical concrete mixture to compare mechanical properties. In addition to the compressive strength tests, Le perfromed tests for the modulus of rupture, and found the printed specimens had higher strength than the cast specimens did. The cast specimens had 11 MPa (1.6 ksi) average flexural strength and the cast specimens had 16 and 13 MPa (2.3 and 1.9 ksi) average flexural strength for the two longitudinal loading directions. Le noted that the tests for the other orientations yielded a much lower average flexural strength of 7 MPa (1 ksi). This is conributed to the anisotropy resulting from the printing process where the flexural strength for those orientations is highly dependent on the inter-layer bond strength.

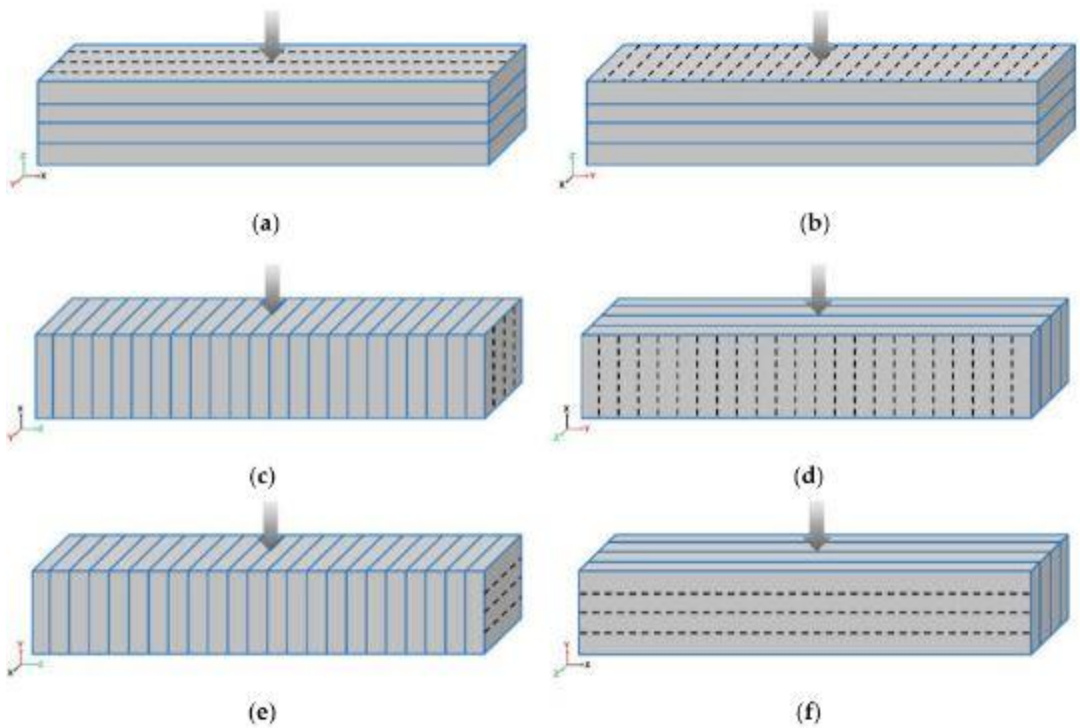

Figure 6: **<u>Flexural specimens from the printed mixture with each testing direction</u> (Li, et al., 2020).**

(Panda, et al., 2017) investigated the mechanical properties of 3DPC specimens when fly ash is used as the primary binder instead of portland cement (PC) in search of a better and greener binder for additive construction. Within his research, Panda et al. (2017) determined the different strengths for each orientation of the material in compression and flexture. Results of the 28-day, 3-point bending test found an average flexural strength of approximately 9 MPa (1.3 ksi) in the longitudinal directions and an average flexural strength of 4.4 MPa (0.64 ksi) in the direction that tensile forces govern. The drop of about half the flexural strength matches with the results found by Le et al. (2012), and Panda et al. (2017) similarly attributed the strength reduction to tensile force acting perpendicular to the layer direction.

(Nerella, et al., 2019) conducted mechanical strength tests for a 3DPC mixture that contained fly ash and silica fumes to replace a portion of the PC. Another mixture contained only PC as the binder to function as the control and the mechanical properties of both mixtures were compared. Another variable tested was the open time between layers, and how varying this affected the tensile strength and flexural strength. Nerella et al. (2019) concluded, similar to Le et al. (2012) and Panda et al. (2017), that the specimens tested in the non-longitudinal direction had significantly less strength than the longitudinally tested specimens. When increasing open time for the specimens, the tensile bond strength was directly reduced, and caused the flexural strength for the tested specimens to be reduced. The decrease was pronounced for the mixture containing only PC as a binder, while the mixture with fly ash and micro silica fumes showed a less signifigant drop of strength. Further details about the mixture content is presented in Chapter 4.

3.5: Modulus of Elasticity

The modulus of elasticity, E, is a critical property in analysis: for the estimation of the deformation of buildings and members, and used for determining the modular ratio. For 3DPC, this parameter plays a vital role in assuming the safe range of elastic deformation of the material and allows comparison with the modulus of traditional concrete. Stiffness and the stress-strain relationship are both determined from the modulus of elasticity and are crucial properties to know when designing with any building material.

(Seo, et al., 2023) performed a study to perfect a 3DPC mix containing polypropylene fibers that could be used in both air and underwater environments. In this study, Seo evaluated the mechanical properties of all the specimens to determine the average modulus of elasticity of each 3DPC speciman. The stress-strain relationship was found for each cylinder specimen to determine the elastic modulus following ASTM C469. The average modulus identified for the printed sample proved to be 35.1 GPa (5090 ksi) equivalent to approximately 55 MPa (8000 psi) concrete compressive strength if using $Ec = 4700\sqrt{f'c}$ (or $Ec = 57000\sqrt{f'c}\ imperial$). This a higher value than traditional concrete typically has, meaning the 3DPC mixture has higher compressive strength and elasticity limit values than cast concrete.

(Zhang, et al., 2019) performed an earlier study that tested several mixes for the rheological and hardend properties of the high-thixotropy 3D printing concrete. Flowability, or the rheological properties such as: viscosity, yield stress, thixotropy, open time, and wet properties were all considered to control the printable properties. The best performing mixture for printability was then evaluated for mechanical properties and used to build large scale components for further testing. When testing for the modulus of elasticity, Zhang concluded an average value of 36.6 GPa (5308 ksi) and that the value, as well as the values for the axial compressive strength and Poisson’s ratio, were similar to conventional concrete values.

Chapter 4: Mixture Composition

Composition is the most critical aspect of concrete mixture design, as it determines the strength and material properties. For purposes of 3DPC, the mixture must be viscous enough to flow through a tube to the printer head and have enough strength to support its weight and other sequential layers. For the mixture to achieve these conditions, a traditional mixture of concrete is not sufficient, and other components must be added to make the paste printable. A typical concrete mixture consists of water, cement, coarse aggregate, and fine aggregate at the most basic level. Retarders, water reducers, and other chemical admixtures can also be used to change concrete's properties depending on the desired performance or environmental factors. Examples of contributing factors to add these to the mixture could be the temperature of where the concrete is being placed, the moisture of the area, and set time. Similar to these factors, 3DPC desired properties that are attained by the use of admixtures. A comparison of different studies and similar trends for mixture design is presented in Chapter 5. This chapter addresses the critical components considered for 3DPC, such as the water-to-binder ratio, aggregate, fly ash, silica fumes, chemical concrete admixtures, and fiber reinforcement.

4.1: Cementing materials

In order for concrete to form, an active binder material is required to chemically react with water during hydration to harden and bind the materials together. The binder is the most active component of concrete with that usually being cement, which usually has the greatest unit cost (Levy, 2012) but many 3DPC mixtures have other active materials used for bonding. Supplementary cementing materials (SCM) are used to alter the properties of the mixture: reducing the heat of hydration, improving workability, and improving mechanical strength. Both Portland cement (PC) and SCMs are comprised of minerals having varied physical and chemical properties that impact the performance of the concrete. Coal fly ash (FA), silica fume (SF), granulated blast furnace slag (GBFS), and metakaolin (MK) are the most commonly used SCMs for 3DPC applications (Nodehi, et al., 2022). These pozzolanic materials contain calcium oxide (CaO), aluminum oxide (Al_2O_3), and silicon dioxide (SiO_2) at varying amounts as shown in Figure 7. Binder materials have varying amounts of these minerals which influences their effects on concrete formation. Used to optimize 3DPC mixtures, the chemical composition of these SCMs affect the hydration process and influence the fresh, mechanical, and transport properties of concrete (Panesar, 2019). PC is the typical primary binder for concrete mixtures. FA and SF are the most commonly used SCMs that are detailed and compared for their advantageous properties in 3DPC herein.

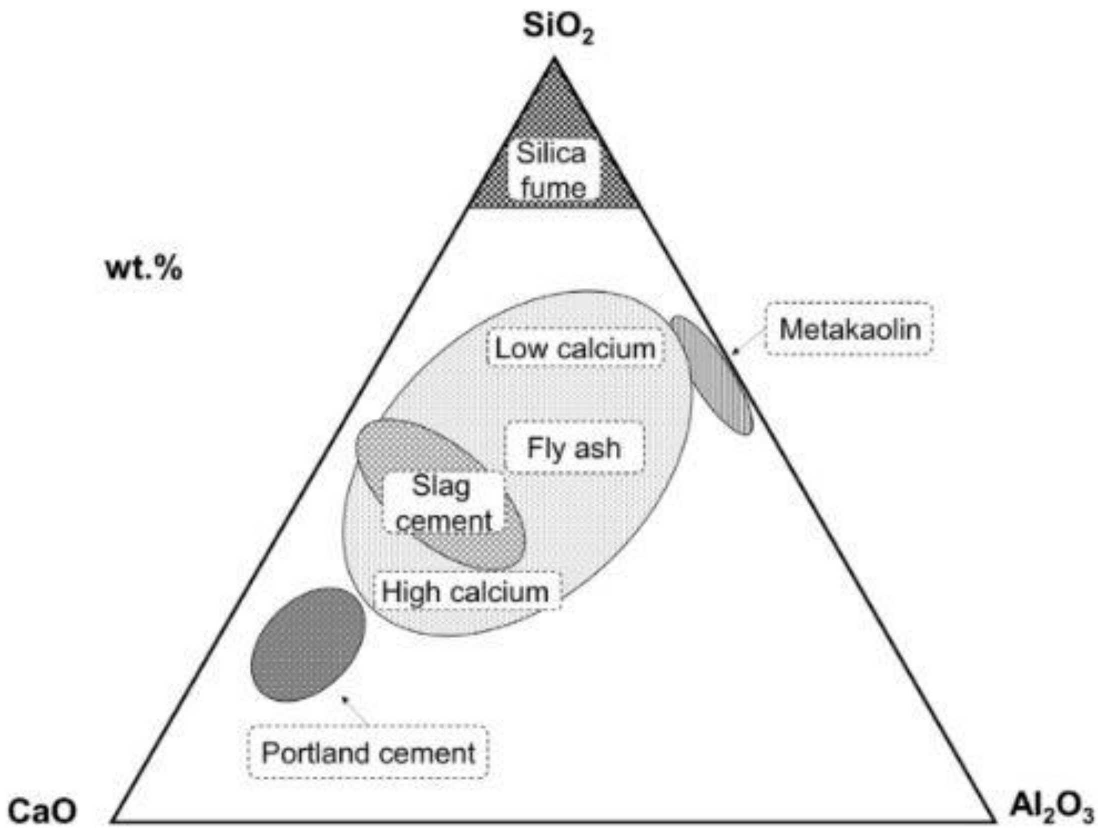

Figure 7: Ternary diagram of SCM from (Panesar, 2019)

4.1.1: Portland Cement

Portland Cement (PC) is specified as one of ten types in ASTM C150 and defined in ASTM C219-20a as “a hydraulic cement produced by pulverizing clinker, consisting essentially of crystalline hydraulic calcium silicates, and usually containing one or more of the following: water, calcium sulfate, up to 5% limestone, and processing additions.” The type of PC is specified by its: chemical composition, air content by percent volume, fineness modulus, compressive strength, heat of hydration, and time of setting. PC Type 1 is a general-purpose cement, used when special conditions or requirements are not needed and is evaluated in this report. PC generally has particle sizes of range between 1-50 micrometers (μm) depending on the gradation (Osborne, 2023). The fineness of PC affects the rate of hydration, as the finer particles have more surface area and is able to react with more water, allowing for more early strength and generating more heat (Levy, 2012). In addition to CaO, Al_2O_3, and SiO_2; Fe_2O_3 is also present in PC along with minor oxides at low percentages that can still influence the cement properties (Gelardi, 2016). These chemical compounds along with added gypsum form the silicates C_3S and C_2S (C = CaO, S = SiO_2) and the aluminates C_3A and C_4AF (A = Al_2O_3, F = Fe_2O_3). C_3S, tricalcium silicate, is the most prevalent and important component, comprising 50-70% of the PC and reacts with water to form calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) during the hydration process (Gelardi, 2016), creating what we know as concrete over time.

The hydration process undergoes five phases before fully curing into concrete. Phase one occurs within just a few minutes, with ettringite precipitating due to the high reactivity of the aluminates and the availability of calcium sulfate (Gelardi, 2016). Phase two, also called the induction period, is the open time in which reactions are slowed and workability is possible.

Phase three, also called the acceleration period, is when rapid formulation of C-S-H and CH occurs and takes place over several hours, allowing the concrete to cure and gain strength. During the fourth phase, the amount of heat decreases and reactions slow, with the concrete continuing to cure. The fifth phase is the continuation of curing over time as the concrete slowly gains more strength.

4.1.2: Fly Ash

Fly ash (FA) possesses pozzolanic properties similar to naturally occurring pozzolans of volcanic and sedimentary origin. ASTM C618 defines fly ash as finely divided residue that results from the process of combustion of ground or powdered coal and that is transported by flue gases. FA is a byproduct of coal-fired electric and steam generating plants, with a large production of FA in the United States and Canada due to increased use of pulverized coal (Tikalsky, et al., 2002). Even with the 62 million metric tons of fly ash produced in the United States in 2001, only about 32% was used (Pavements, 2017). The waste is due to the high amounts of carbon from “scrubbers” that reduce air pollutants in most of the ash and expensive transport costs. To meet demand, FA is often imported from other countries (Henderson, 2016). Freshly produced FA straight can be harmful to the skin or to inhale due to the metallic elements in its chemical makeup, such as mercury, arsenic, or copper (Coal Ash, 2018). This makes FA an attractive building material since it is otherwise toxic for the environment and has few other uses (Dale, 2023).

FA is deemed an active binding agent for concrete as it shares a chemical composition similar to PC and undergoes a reaction with water to form concrete. During combustion, the coal impurities fuse with the exhaust gas to form amorphous, spherical fly ash particles with sizes ranging from 2-74μm (Panesar, 2019). Types of FA are separated into two main classes depending on the chemical composition, class F and class C. Similar to PC, fly ash has the same chemical components including CaO, SiO_2, Al_2O_3, and Fe_2O_3 with the 60-90% being amorphous phases (Panesar, 2019). Class F FA is produced from burning anthracite or bituminous coal and must have a chemical composition requirement of $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70\%$ and has a high amount of amorphous silica that controls the pozzolanic activity. Class C FA is produced from burning lignite or subbituminous coal and must have a chemical composition requirement of $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 50\%$. The CaO content is therefore greater in Class C compared to Class F, and they are sometimes classified by high-calcium or low-calcium fly ash (Tikalsky, et al., 2002). The hydration reaction with FA follows the same principle, but Class F FA tends to create a denser and more gel-like product compared to PC. The addition of FA to the binder changes the flow behavior of cement paste due to the spherical particles shape. The smooth glass particles allow water to flow easier, causing the mixture to require less water for the same workability. For a given slump, the water demand is reduced when fly ash is used. For 20% replacement of cement for fly ash, 10% less water is needed (Pavements, 2017). The particle shape also decreases friction within the mixture when flowing, allowing for better pumpability and a more cohesive mixture due to the small particle size (Tikalsky, et al., 2002). FA also extends the setting time, consequently causing a reduction in early compressive strength and yielding a less viscous mixture (Thomas, 2007).

(Nayak, et al., 2022) compiled studies testing the use of fly ash as a replacement binder in concrete to determine the potential benefits. Nayak found that fly ash particles absorb on the surfaces of oppositely charged cement particles, preventing them from flocculating. As a result, a large amount of water is released, thus lowering the water demand for a particular workability.

FA was found to have reduced initial compressive strength for the mixtures tested but had higher overall strength when tested after a 28-day curing period.

(Nerella, et al., 2019) performed mechanical strength tests with two mixtures, one with PC as the only binder and one with 30% fly ash and 15% silica fume partially replacing the PC binder to study the different properties. Specimens were extracted from printed mixtures at varying open times to compare the flexural and compressive strengths. When comparing flexural strength after 28 days, the specimens containing only PC were found stronger than the specimens containing fly ash replacement in all cases except for when tested in the nonlongitudinal direction. This indicates replacement binder increased the tensile strength but reduced the flexural strength. Nerella et al. (2019) remarked that the specimens with binder replacement had a noticeably better homogenous microstructure between each layer. When comparing these specimens for compressive strength after 28 days, the mixture containing only PC were found weaker than the mixture with fly ash replacement in all cases, indicating the replacement binder decreases compressive strength. A decrease of 28.2 MPa (4.1 ksi) or 33.6% strength reduction is observed, going from 100 MPa (14.5 ksi) to 71.8 MPa (10.4 ksi). While this is a large difference in strength, the base mixture has a similar composition to a high-performance concrete mixture, so this strength reduction will not restrict its use in design since no more than 34 MPa (5 ksi) strength is typically needed. Due to the binder with replacement still having a strong compressive strength, Nerella et al. (2019) concludes partially replacing PC with fly ash and silica fumes showed superior performance overall from homogeneity and multidirectional loading when compared to a mixture only containing PC.

(Panda, et al., 2017) studied the use of fly ash as the primary binder for a 3DPC mixture. Panda et al. (2017) used 85% of the binder as fly ash, 10% as silica fumes, and 5% as slag

(GGBS). The mixture also had approximately 50% of the dry materials as sand for aggregate with a maximum particle diameter of 2 mm. Since the use of fly ash reduces the amount of water needed for a concrete mixture, using fly ash as the primary binder results in low water content, resulting in a low water-to-binder ratio of 0.126 when compared to the typical 0.3-0.4 water-to-binder ratios. Because of this low ratio, higher pressures were required for pumping and Panda et al. (2017) speculates this led to a higher density print of 2250 kg/m^3 (140.5 pcf) compared to the cast specimen of 2150 kg/m^3 (134 pcf). Panda et al. (2017) observed that the mixture was a non-Newtonian fluid and had thixotropic properties. These properties are ideal for 3DPC due to the high yield stress and low viscosity, allowing extrusion without losing stability. The average compressive strength of the printed specimens was slightly lower than the cast specimens after 28 days. Chapter 3 contains the overview of the other mechanical properties for Panda et al. (2017) study.

4.1.3: Silica Fume

Another type of pozzolanic material used is silica fume (SF), which can be included as a useful binder material in the formation of concrete. ASTM C3534 defines silica fume as a very fine pozzolanic material, composed mostly of amorphous silica produced by electric arc furnaces as a by-product of the production of elemental silicon or ferro-silicon alloys. Particles of SF are spherical and extremely fine, with average sizes of 0.1-0.3μm (Panesar, 2019). The extreme fineness means SF is a highly reactive binder and causes much more heat to be produced during the hydration process (Holland, et al., 2000). Similar to PC and FA, SF has a chemical composition of CaO, SiO_2, Al_2O_3, and Fe_2O_3, but with over 90% of the composition being SiO_2 (Holland, et al., 2000). When hydration occurs in a mixture and CH crystals are formed, they usually form parallel to the aggregate surface, which are weak and easily broken. With the addition of SF, a stronger bond of CH crystals between the cement paste and the aggregate is made, making a denser structure even with small (2-5%) additions (Holland, et al., 2000). Silica fume addition typically increases the water demand for a mixture, so the use of chemical concrete admixtures, water reducers or superplasticizers, are often used in conjunction and enable adequate dispersion of the particles. SF tends to reduce bleeding and allows for greater cohesiveness in the mixture, but binder replacement of over 10% can present workability challenges and increases the brittleness of the concrete (Panesar, 2019). With reduced bleeding and increased heat of hydration, water near the surface of the concrete is evaporated quickly, and without water to replace it plastic shrinking can occur, especially for concrete with high amounts of SF (Holland, et al., 2000).

(Zhang, et al., 2018) evaluated several mixes that had partial replacement of PC with nano clay and/or silica fumes to study the changes to the fresh properties of the mixture. Zhang et al. (2018) used only 2% partial replacement of each separately as the only differences for the mixture composition. Fine aggregates made up 50% of the mixture with a maximum particle size of 1mm (0.0394in) and several chemical concrete admixtures were used. Zhang et al. (2018) observed that the viscosity, yield stress and thixotropy of the mix remarkably increased for the mixture containing silica fume when compared to the fresh concrete without silica fume. As the setting time increased for the mixtures, the green strength of the silica fume mixture increased considerably compared to the base mixture, but not nearly as much as the mixture containing both silica fume and nano clay replacement. The mixture with silica fume exerted the most heat and at a faster rate than the other mixtures during the hydration process. This is likely due to how reactive silica fumes are from their extremely fine particle size.

(Kwon, et al., 2016) performed flow and printability experiments on various mixtures to evaluate the effect of SCMs and chemical concrete admixtures on fresh concrete. Tests for the pressure per unit length, size of aggregates, mineral admixtures, and superplasticizers were all compared to the same control mixture without the test additive. Of the mineral additives, fly ash and silica fume were both tested separately, and evaluated for their flow rates at increasing amounts of replacement. Kwon did not specify the contents of the mixture, only that the mixtures tested had already known compressive strength values of 50, 80, and 100 MPa (7.3, 11.6, and 14.5 ksi, respectively). Two types of silica fume were used for this experiment, regular SF, and zirconia silica fume (ZSF). Both types of SF have high percentages of silicon dioxide, approximately 95%, but ZSF contains zirconium dioxide at approximately 4% (Silica Trading, 2018). Kwon et al. (2016) calculated the flow rate for the control mixture and the SF mixtures for comparison and found that the addition of SF resulted in a substantial increase to flow. With a 10% addition, the flow rate increased slightly for the SF mixture and doubled for the ZSF mixture. With a 20% addition, the flow rate increased by approximately one and a half times for the SF mixture, and approximately four times the amount for the ZSF mixture. Kwon et al. (2018) concluded that the addition of SF enhances the pumping performance and ZSF doubles the performance when used.

4.2: Water-to-binder ratio

The workability and printability of concrete is dependent on a proper water-to-binder (W/B) ratio. ASTM C1602 defines this as the ratio of the mass of water, excluding water absorbed by the aggregates, to the mass of Portland cement in a cementitious mixture. Having a W/B ratio that is appropriate for the mixture is an essential aspect of concrete design. When water is added to the mixture, it reacts with the binders and starts an intricate chemical reaction known as cement hydration. This chemical reaction has initial strength that holds the mixture together and gets progressively stronger as the binder is hydrated. For typical concrete, a maximum W/B ratio of 0.4 to 0.5 is used (Levy, 2012) and changing this ratio directly impacts its slump, yield stress, and viscosity. The more water added to the mixture increases the workability, but also increases the porosity of the concrete, decreasing the strength of the concrete. Having a lower ratio of water increases the strength but decreases workability and can make the mixture too stiff to be able to print. According to (Gelardi, 2016) the increase of water content decreases both yield stress and plastic viscosity. The W/B ratio was adjusted with a trial-and-error process by (Zhang, et al., 2019) to obtain maximum buildability and yield strength. As the binder content increased and the aggregate content decreased, the water demand increased slightly, but the overall W/B ratio had a decreasing trend. Zhang et al. (2019) indicated that to maintain buildability for 3DPC, as the aggregate content decreases the W/B ratio should decrease as well.

Typically, less water means the mixture will have more strength and durability, but it is more difficult to place unless a water-reducing admixture is used. 3DPC paste performs better with a lower W/B ratio, closer to a 0.3 ratio (Zhang, et al., 2021), (Zhang, et al., 2019), (Paul, et al., 2018). The compressive strength of concrete, which depends on the W/B ratio, is used for engineering design purposes. The compressive strength of the concrete increases quickly over time until the maximum strength is attained around 28 days after the water and binder reaction occurs as explained in the compressive strength section in Chapter 3. When the required compressive strength is determined, the required binder content is then calculated based on the selected W/B ratio (Levy, 2012).

To ensure good printability for the mixture, the desired yield stress for flow is required. Yield stress is the critical shear stress above which flow initiates and is a factor in the amount of slump a mixture has (Wallevik, 2006). The yield stress must be low for fluidity to occur, so the mixture can easily flow through pumping and out the nozzle. However, a high yield stress is desired after extrusion occurs, so the paste does not deform from the force of gravity or sequential layers. With the right water-to-binder ratio and mixture, the paste should behave as a Bingham fluid and have an ideal amount of yield stress to accommodate both parameters. The amount of water in the mixture determines the flowability of the mix, which alters the yield stress and printability.

4.3: Aggregate

Coarse and fine aggregate, which comprise of approximately 60% of traditional concrete volume, are fundamental components of concrete. Aggregate is specified by ASTM C33 as granular material, such as sand, gravel, crushed stone, or iron blast-furnace slag, used with a cementing medium to form hydraulic-cement or mortar. ASTM C33 specifies that coarse aggregate has a predominant portion resting in the 4.75mm (No. 4) sieve and is determined by the fineness modulus of the material. Coarse aggregate improves the performance of concrete by reducing the shrinkage and cracking, increasing the density for durability, reducing the amount required cementitious material (Mahajan, 2023). Coarse aggregates are an essential component of typical concrete mixtures, and combined with cementitious materials and fine aggregates it provides concrete with strength and durability. Fine aggregates consisting of sand fill in gaps and voids around the coarse aggregates, allowing the concrete to flow well and distribute its strength evenly. The size of fine aggregates must have a predominant portion resting in the 75μm (No. 200) sieve and not be larger than the 9.5mm (3/8in sieve) according to ASTM C33.

Coarse and fine aggregates combined are approximately 60-75% of the mixture and allow the cement substance to effectively bond to and create a strong concrete mix (Wood, 2023). For 3DPC mixtures, the printing nozzle and tube mandate a maximum size of aggregate that can be used. The desired fresh 3DPC properties can also restrict the size and amount of aggregate. The use of coarse aggregate is limited and sometimes eliminated due to aggregate size restraint.

(Cheikh, et al., 2017) assessed how the ratio of nozzle diameter to aggregate size affected printability and extrudability of the 3DPC. Cheikh et al. (2017) found a minimum nozzle to aggregate ratio of 4.25 that allows the paste to extrude homogenously and without clogging the printer. As long as coarse aggregate exceeds this ratio, the mixture will not have any blockage when it is extruded out the nozzle. Knowing the maximum particle size is critical for mixtures, even though they tend to consist primarily of fine aggregate for increased printability and flow properties. (Le, et al., 2012) had a maximum aggregate diameter of 2mm due to the nozzle having a diameter of 9mm. While the reasoning for this is not as extensive, it fits into the 4.25 maximum ratio found by Cheikh et al. (2017). Most studies observed did not evaluate the ratio of aggregate size to nozzle diameter for varying reasons such as the particle size being considerably smaller than the nozzle diameter, or simply because after multiple tests the aggregate selected has the best performance without clogging.

(Zhang, et al., 2019) evaluated multiple mixes to determine factors that influence the flowability of 3DPC, one of which evaluated the effect of different binder-to-aggregate ratios. After constant successful prints were made using 50% aggregate in the dry mixture, a mixture with 5% less aggregate was printed for comparison. This specimen had considerably more slump and significantly less yield stress than the 50% mixture did under the same shear rate. Zhang et al. (2019) further tested the difference of aggregate size and the effect it had on the mixtures, creating a mixture using 4.75mm (0.187in) aggregate against one with 1.18mm (0.0465in) aggregate. Zhang et al. (2019) found that aggregate size did not have a significant effect on the flowability performance of the mixture, and that the percentage of aggregate in the mixture by mass was the most critical parameter for 3DPC flow properties.

(Wang, et al., 2022) evaluated the effect of varying the amount of coarse aggregate included in the mixture. The performance of 3DPC in regard to yield stress and mechanical strength properties were observed and compared. Four varying amounts of coarse aggregate of size 5-10mm replaced sand aggregate that had a fineness modulus of 2.6 from 50-80% and was compared to a base mixture with no coarse aggregate and cast specimens of the same mixture. All mixtures had a 0.3 water-to-cement ratio, 50% aggregate to binder, and had admixtures included for optimized printing performance of the base mixture. A direct relationship of increasing yield stress was found with the increase of coarse aggregate replacement, and also with the plastic viscosity of the mixture. When testing for the hardened properties, the increase of coarse aggregate also increased the 28-day compressive strength for the first two mixtures (50% and 60% replacement) but decreased back down with the 70% and 80% replacement mixtures, where Wang et al. (2022) indicates there is an optimum dosage for compressive strength. A similar trend to compressive strength was found for the flexural strength tests, with 60% replacement having the most strength, and more strength than even the cast specimens. When compared for the splitting tensile strength, the 60% replacement mixture once again dominated for strength, but the mixtures having the lowest values were the 70% and 80% replacement mixtures. Wang concludes the study by stating the mechanical properties of 3DPC is more sensitive to aggregate size than casted concrete was shown to be.

4.4: Chemical concrete admixtures

Chemical concrete admixtures (CCA) modify the properties of fresh or hardened concrete. CCAs can be divided into five types: accelerating, retarding, water reducing/plasticizing, air entraining, and water proofers (Jianxia, 2012). Accelerators and retarders modify the rate of cement hydration. Superplasticizers, water reducers, and viscosity-modifying admixtures modify the rheological behavior of fresh concrete. Air entrainers and shrinkage reducers enhance the durability of hardened concrete (Gelardi, 2016). Similar to SCMs, CCAs are a beneficial addition for 3DPC mixtures due to their ability to alter the performance of the fresh and hardened characteristics in an attempt to optimize the mixture. Retarders, superplasticizers, and viscosity modifying agents are discussed in this section since these CCAs are most beneficial for 3DPC mixtures.

(Marchment, et al., 2019) tested the effect of using retarders, superplasticizers, and viscosity modifying agents as the only variable to test flow and bonding properties for 3DPC. ASTM C439 defines an admixture as a material added to a cementitious mixture to modify its freshly mixed, setting, or hardened properties and that is added to the batch before or during mixing. Marchment had a control mix to test against the CCAs to observe differences in flow properties and bonding of the layers after extrusion. The first mix contained a retarder to delay the rate of hydration for the mixtures primarily by reducing the heat generated to avoid surface drying. The second mix contained a superplasticizer that was used to increase the particle dispersion between the printed layers, effectively increasing the bond area anchorage. A viscosity modifying agent (VMA) was used in the last mixture to thicken and increase the workability of the paste and keep particles from segregating. The mixtures were then printed and compared by testing the compressive and inter-layer bonding strengths. When compared to the control mixture, all mixtures containing CCA had a significant increase to the effective bond area, and a moderate increase to the mechanical strengths. Marchment notes that the retarder having extended setting time, the superplasticizer having high flowability, and VMA having high viscosity indicate the attributes important for improving the bond strength.

4.4.1: Retarders

Retarders are used to delay the setting time chemically or thermally for a concrete mixture. ASTM C494 defines retarders as an admixture that decreases the rate of reaction of Cementitious materials thus increasing setting time of concrete. Retarding a concrete mixture chemically involves delaying the setting time and preventing hydration from occurring. When a mixture is delayed thermally, liquid nitrogen or ice is used to reduce the reaction rate and temperature, slowing down the hydration process and increasing the open time (Gelardi, 2016). The use of retarders could be an essential component for 3DPC mixtures depending on the printing setup. If a larger structure is being printed and a long open time for bonding to take place is required, this would be a useful admixture. Retarders have been used in an effort to increase the open time of the mixture for flow properties and for increased bonding, but this can also delay the buildup process if the open time is too long for green strength to occur (Li, et al., 2020).

(Le, et al., 2012) evaluated a high-performance concrete mixture with a goal of optimizing it to be printed without formwork. The high-performance mixture had 70% cement, 20% fly ash, 10% silica fume and water-to-binder ratio of 0.26. Within this research, Le used a superplasticizer and a retarder formed by amino-tris, citric acid, and formaldehyde. The retarder was used between the amounts of 0.5% and 2% for the specimens and the compressive strength was assessed after 1, 7, 28, and 56 days. Le et al. (2012) noted that when over 1% retarder was used, it significantly reduced the compressive strengths measured at 1 and 7 days, and when over 1.5% compressive strength could not be measured due to the mixture still being fluid. All mixtures were still able to achieve a desired 100 MPa (14.5 ksi) compressive strength after 28-days, showing that the long-term mechanical properties were not impacted by this admixture. Le mentions in his concluding remarks that 0.5% was the optimum amount of retarder to use for a desired open time of 100 min. Research by Le et al. (2012) illustrates that a retarder is useful for 3DPC mixtures due to its ability to delay when hydration occurs, and that an excess is not necessarily detrimental to the printing process.

4.4.2: Superplasticizers

Plasticizers are added to concrete mixtures to increase the fluidity of the mixture without having to add additional water. ASTM C1017 specifies a plasticizing admixture as a chemical admixture which produces flowing concrete without further addition of water. Superplasticizers are much stronger plasticizers and are also called high range water reducers (HRWR), or water reducing agents (WRA). Superplasticizer molecules physically separate cement particles, making the concrete more workable and easier to place. This means the workability of concrete can be improved without having to alter the water-to-cementitious material (binder) ratio, which could compromise the durability and strength of concrete (Gelardi, 2016). Superplasticizers increase the workability of fresh concrete, making it a useful addition for transport, pumping, and pouring. These are all desirable traits looked at for 3DPC mixtures to aid in printability.

Water reducing agents such as plasticizers affect the concrete depending on the alkali content of the cementitious material. Cement compounds such as C_3A are impacted by these admixtures, which influence the setting time and early hydration. It has been shown that the compressive strength of concrete is improved with the addition of WRA when the alkali content is low (Levy, 2012).

(Rahul, et al., 2019) performed printability tests for a 3DPC mixture to determine the effects of admixtures on the mixture's performance. Using a standard mixture containing 80% PC, 20% fly ash, 60% fine aggregate, and 0.32 water-to-binder ratio, Rahul et al. (2019) evaluated the effect of increasing the percentage of a liquid superplasticizer in the mixture. Five tests of increasing the dosage failed due to blockage of the nozzle, effectively making printing impossible. The sixth test had a dosage of 0.09% superplasticizer and was able to briefly extrude from the nozzle before blockage occurred, but extrusion was thin, and the layers did not conform to the required dimensions, so the test was therefore considered a failure. When the dosage was increased to 0.10% superplasticizer, the paste extruded continuously with good flow and without blockage occurring. The mixture also was extruded at the correct dimensions and without deformations occurring after sequential layers were printed, making this dosage pass the extrudability and buildability tests. At a dosage of 0.11% superplasticizer, the mixture extruded well, but with slight deformations occurring on the initial layers after sequential layers were added on, causing a buildability failure. After evaluating all the mixtures, Rahul et al. (2019) found that mixtures with too low of a superplasticizer dosage had too high yield stress and viscosity to allow extrusion. With too much superplasticizer added, the yield stress was too low, and the required shear stress was therefore too low to meet the buildability requirements. This study reinforces the importance of using admixtures for 3DPC to satisfy the specific printing requirements to achieve buildability.

4.4.4: Viscosity Modifying Agents

Viscosity modifying agents (VMA) are used to control the stability and cohesion of concrete mixtures. ASTM C494 recognizes VMAs as a specific performing admixture used for viscosity modification, and it is typically used for self-consolidating concrete (Phelan, et al., 2010). VMAs are used to provide stability for fresh concrete, making a more robust mixture and reducing water loss from capillary suction or evaporation. Many different types of VMAs can be used for concrete, most being natural organic compounds such as cellulose-ether derivatives or starch but can also be inorganic compounds such as nano-silica (Gelardi, 2016). VMAs have an influence on many different fresh properties, including plastic viscosity, yield stress, shear thinning behavior, and thixotropy. Using the right VMA can optimize 3DPC mixtures to have the desired fresh properties for printing.

(Kruger, et al., 2019) evaluated the physical and chemical influences on the microstructure of 3DPC when admixtures are added to a base mixture. Kruger et al. (2019) used a mixture containing 70% PC, 20% silica fume, 10% fly ash, approximately 60% fine aggregate by weight and a water-to-binder ratio of 0.32. Added to this mixture was a superplasticizer, the VMA, and nanoparticles with one removed or altered for seven total mixture variations, including the control. The mixtures were compared for fresh and hardened properties when printing circular hollow columns until failure occurred. When Kruger et al. (2019) compared the mixture with the VMA to the mixture without the VMA, it was noted that the VMA mixture seemed more cohesive and stickier but had similar workability properties. Kruger et al. (2019) also noted that the mixture without the VMA had higher dynamic and static shear stresses in all cases when compared to the mixture with the VMA added. While not the main focus of his research, Kruger et al. (2019) demonstrated how the addition of a VMA increased the flow resistance of the mixture and created a more comprehensive mixture.

4.5: Fiber reinforcement

A popular addition to 3DPC is the use of small material fibers to enhance the mechanical properties of the mixture after hardening. ASTM C1116 details fiber reinforcing requirements for concrete and defines them as slender filaments which may be discrete or in the form of bundles, networks, or strands of natural or manufactured materials that can be distributed uniformly throughout a fresh cementitious mixture. Fibers such as steel, glass, synthetic, and natural are used to reinforce concrete (Daniel, et al., 2002). Fibers are generally not added to increase the strength, though they have shown improvements if implemented correctly. These fibers are added primarily to bridge across the matrix cracks that develop as concrete is loaded (Panesar, 2019). Implementing tensile reinforcement is a challenge for 3DPC due to the printing configuration and the limitations of extrusion. These fibers must be able to be printed without clogging the extruding nozzle and be able to spread between layers for maximum performance. Figure 8 illustrates the typical path these fibers take when being extruded, which is parallel to the printed layers. As discussed in Chapter 3, one of the most important factors for mechanical strength is the tensile bond strength of a mixture. Unlike conventional concrete with formwork, rebar and tensile reinforcement cannot easily be included in an automated system like 3D printing. To combat this disadvantage, researchers have been testing how steel, polypropylene, nylon, and other material fibers integrated in the mixture can affect the mechanical properties as well as increase the performance of 3DPC.

(Seo, et al., 2023) evaluated the use of polypropylene fibers for 3DPC mixtures used in underwater and air environments. The study by Seo et al. (2023) was used to determine the modulus of elasticity for these mixtures. The addition of the polypropylene fibers had some influence on the stress-strain relationship of the mixtures after the yield point was reached, young's modulus was not affected. Splitting tensile strength tests were performed for each specimen, and it was found that the fiber-reinforced specimens had an increased strength when compared to the specimens without fibers included in the mixture.

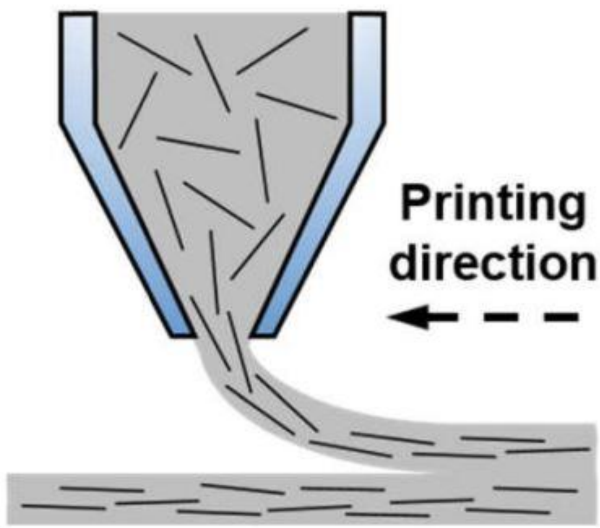

Figure 8: Illustration of fiber reinforcement extrusion (Li, et al., 2020)

(Hambach & Volkmer, 2017) assessed how integrating several types and lengths of fibers can impact the compressive and flexural strengths of a 3DPC mixture. The reinforcing fibers were carbon-, glass- or basalt material with an average length varying from 3-6 mm (0.118-0.236 in). The alignment of these fibers was forced due to extrusion through a small nozzle of 2 mm (0.0787 in) diameter, and they are capable of achieving high values of flexural strength, up to 120 MPa (17.4 ksi). A water reducing agent was also used to produce a low enough viscosity for adequate flow to be achieved without blocking occurring. An amount of 1% by volume of fibers was used for each fiber along with a control specimen, and they were printed with one of two different print paths. The first print path was typical for most studies and had longitudinally placed layers circling around to the center, while the second path was a crosshatching pattern. When the specimens were compared for flexural strength, Hambach & Volkmer (2017) found that 1% by volume of carbon fibers provided a considerable amount of strength increase when compared to the other fibers. The cross-hatching pattern yielded the lowest strength for all of the fibers tested, and all samples had an average flexural strength less than 15 MPa (2.2 ksi) while the longitudinally printed carbon fibers specimen had a strength of nearly 30 MPa (4.4 ksi). The fibers displayed little to no effect on the compressive strength of the mixtures for all cases. Hambach & Volkmer (2017) concluded that the carbon fibers were the only ones shown to improve the flexural strength considerably, and also contributed it to the fibers being orientated in the longitudinal direction from the printing path.

Chapter 5: Discussion

To effectively compare different 3D printed concrete mixtures for purposes of optimizing their mixture design, the essential focus lies with the fundamental rheological properties. These properties influence the workability, printability, extrudability, and buildability to ensure printing is possible and stable. Among these, thixotropy, viscosity, and yield stress stand out as pivotal considerations. Thixotropy, a property intrinsic to concrete, describes the reversible gel-like behavior exhibited when subjected to shear stress. This characteristic is particularly relevant in 3D printed concrete, as it influences the material's ability to maintain shape during printing while allowing for ease of flow through the nozzle. Viscosity dictates the material's resistance to flow and is influenced by shear forces due to concrete acting as a Bingham fluid. In the context of 3D printing, optimal viscosity is essential for ensuring smooth extrusion and accurate deposition of layers, ultimately affecting the dimensional accuracy and surface finish of printed structures. Yield stress, often associated with materials exhibiting both solid and fluid-like behavior, represents the minimum stress required to initiate flow. In 3D printing, this property influences the material's ability to support its own weight without slumping or sagging during deposition, thereby contributing to the structural integrity of printed layers. Comparing different 3D printed concrete mixtures based on thixotropy, yield stress, and viscosity entails a detailed examination of their rheological profiles and how it is affected by the mixture composition. By evaluating these fresh properties comprehensively, we can gain insights into the material's performance and inform optimal mixture compositions for additive construction applications. Due to these properties being essential for printed concrete to perform appropriately, it is always considered and most often the primary topic of interest when evaluating 3DPC.

Unlike traditional concrete, 3DPC demands a delicate equilibrium between fluidity for seamless extrusion through a dispensing tube and rapid hardening and load-bearing capacity upon deposition, all without the need for additional support structures. Achieving this balance requires understanding and optimization of the fundamental rheological properties such as thixotropy, yield stress, and viscosity. Satisfying parameters such as pumpability, extrudability, and buildability complicate the optimization process, as each has their own unique requirements that must be satisfied and are impacted by the printed components. Characteristics such as open time/setting time and green strength must be meticulously controlled to ensure proper layer adhesion and dimensional stability during construction. The composition of the mixture, including the water-to-binder ratio, choice of aggregates, supplementary cementing materials, chemical concrete admixtures, and fiber reinforcement all must be considered for the optimization process. Balancing these numerous variables requires a comprehensive testing and analysis of various mixtures to determine how each mixture component affects the individual fresh properties as well as hardened properties after a printable solution is found.

5.1: Material ratios

No single material ratio will dictate the flow properties for a mixture, and so a comprehensive look at the material ratios will determine properties of 3DPC paste. The primary ratio that is fundamental to concrete is the water-to-binder (W/B) ratio, and the typical ratios and the effects on the mixture properties will be observed. Another material ratio is the aggregate-to-binder (A/B) ratio which largely affects the printability and is impacted not only by the amount, but the size of aggregates used. The combination of the aggregates to binder, or the dry ratio, and the wet ratio of the W/B are two of the most important parameters for concrete. Due to their importance, it is difficult to discuss these separately and they are compared together. The other material ratio of importance is the binder ratio. The chemical composition of the binder has a large impact on the properties of the mixture due to its effects on hydration. The time dependent properties are developed by this ratio and the active components within the binder. The material ratios of 26 different studies are tabulated and discussed throughout this chapter, and the values shown on the graphics are the average value of sometimes large quantities of mixture tests.

5.1.1: Dry/Wet mixture ratios

A comparison of W/B ratios used in several studies is shown in Figure 9. Several outliers are attributed to the study either from testing the effects of a higher ratio or the study did not require a large amount of water. The ratio is seen to be typically between a value of 0.25 to 0.45 for the majority of the studies analyzed, with an average value of 0.33. Figure 10 shows a comparison of aggregate-to-binder (A/B) ratio used across the same studies as the W/B ratios, with an average amount of 58% used. The data compiled accounts for all aggregate content used in the mixtures and is a measurement of aggregate present in the dry mixture before the addition of water or admixtures. Additionally, this is for fine and coarse aggregates due to the small number of studies that used and tested aggregates larger than 4.75mm (0.187in). Coarse aggregates have been found to increase mechanical strength and yield stress properties for 3DPC pastes (Wang, et al., 2022), but the addition of larger aggregate is limited by the nozzle size for extrudability to be possible.

The largest outlier for the W/B ratio (Panda, et al., 2017) can be attributed to the majority of the binder containing fly ash, which does not require nearly as much water for the same workability that can be attained with just Portland cement due to the material properties of FA. Another outlier (Tay, et al., 2019) where 23 different mixtures with varying W/B ratios and other material ratios were observed for fresh properties. (Zhang, et al., 2018), (Wang, et al., 2022),

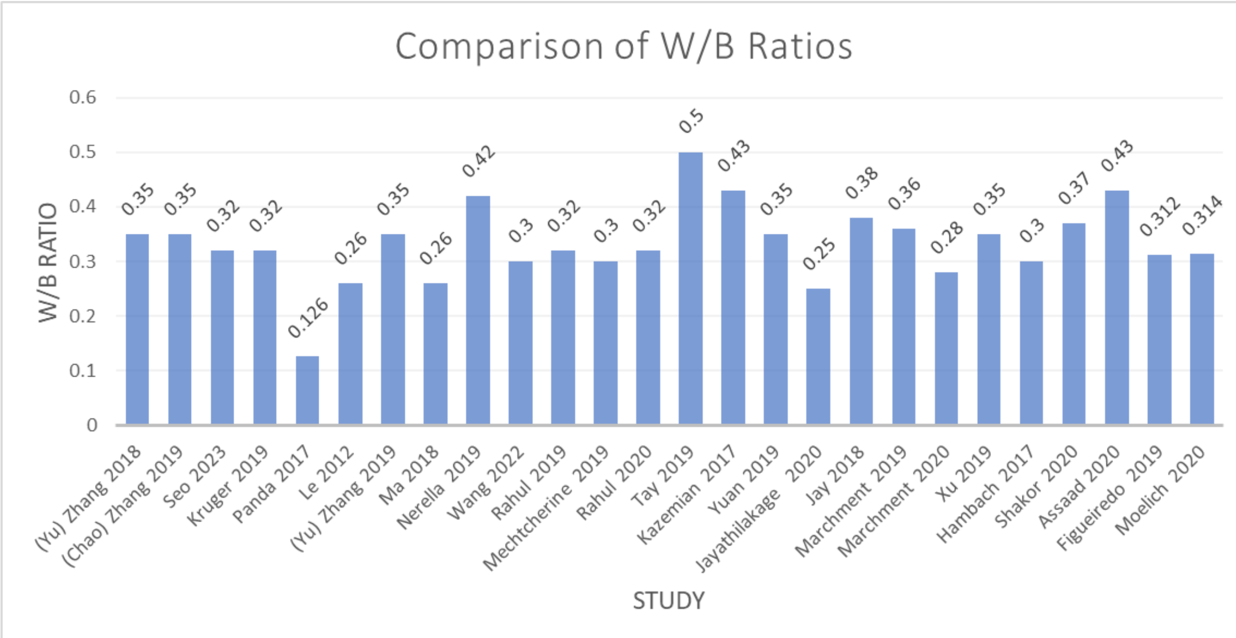

Figure 9: Comparison of W/B ratios

(Xu, et al., 2019) had an even 50% aggregate and binder used for the dry mixture and also had similar W/B ratios. (Zhang, et al., 2019) tested many mixtures to see the relationship between the W/B and A/B ratios, and 50% aggregate and 0.35 W/B ratio was the average value of the successfully printed mixtures. (Seo, et al., 2023) tested mixtures that could be printed for

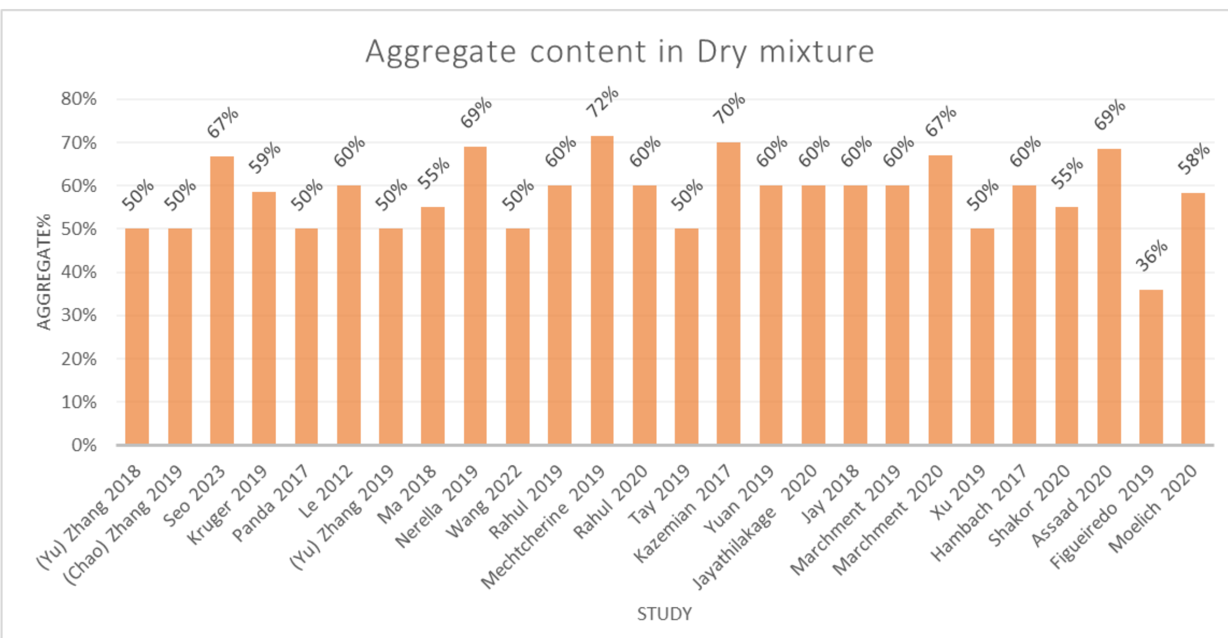

Figure 10: Comparison of dry mixture that contains aggregate

underwater environments to compare with above water ones and proportioned the mixture to have more aggregate and consequently a lower W/B ratio. (Kruger, et al., 2019) used the standard 3DPC mixture that is used at Stellenbosch University, which is a high-performance concrete mix with a water-to-cement ratio of 0.45 (W/B = 0.32 due to the use of fly ash and silica fume). (Le, et al., 2012) tested five starting mixtures with varying A/B and W/B ratios to achieve the best printability and found that a 60:40 ratio of the A/B and a 0.26 W/B ratio worked the best. (Zhang, et al., 2019) produced five mixtures with different sand-to-cement (S/C = A/B) ratios with the same W/B ratio of 0.35 to find an optimal mixture. Mixtures with the S/C ratio of 0.6 and 0.8 had such high flow properties they could not be properly printed, while the highest S/C ratio of 1.5 could not be printed due to the stiffness of the paste. When the last two mixtures with S/C ratios of 1.0 and 1.2 were compared for strength and rheological properties, the 1.0 ratio had slightly better performance. (Ma, et al., 2018) also tested five mixtures that all had the same aggregate percentages and W/B ratios of 55% and 0.27 respectively, with each mixture replacing a portion of the aggregate with copper tailing to see the effect. After adjusting for the open time, all mixtures were found to have sufficient buildability. Ma found that the increase of the finer copper tailing aggregate directly increased the flow and tended to increase the compressive strength. (Nerella, et al., 2019) tested two mixtures, one with only PC and one with SF and FA included in the binder but used the same W/B ratio. The A/B ratios varied slightly (69% for the PC mixture and 61% for the mixture with FA and SF), and the PC mixture's A/B ratio was used. (Rahul, et al., 2019) used 60% of the dry mixture as aggregate and a W/B ratio of 0.32 to test the effect of different additives to this base mixture. (Mechtcherine, et al., 2019) tested large scale printing with a large aggregate content of 72% of the dry mixture and a W/B ratio of 0.3. This study had one of the largest extruder nozzles used, approximately 150mm x

50mm (6in x 2in) for extrusion and is likely the reason for the higher aggregate content. (Lim, et al., 2012) used a high-performance cement-based mortar that was developed for 3D printing applications and was found to have the correct printability from 60% of the dry mixture being aggregate and approximately a 0.278 W/B ratio. (Rahul & Santhanam, 2020) tested lightweight aggregate replacement for use in 3DPC and used 60% of the dry mixture as aggregate and a W/B ratio of 0.32. Three mixtures as well as a control mixture were compared by testing for density, flow, extrudability, buildability, compressive strength, and modulus of elasticity. (Kazemian, et al., 2017) used the same A/B and W/B ratio for three test mixtures and a control to see the effects of adding SF, fibers, and nano clays to the mixtures. High ratios of 2.3 (70% dry mixture) for A/B and 0.43 for W/B were used. (Yuan, et al., 2019) tested four mixtures with the same A/B and W/B ratios of 1.5 (60% of the dry mixture) and 0.35 respectively, testing the effect of CCAs and sulphoaluminate cement (SAC) as a binder against a control mixture. (Jayathilakage, et al., 2020) used their mixture design to test the yield stress of 3DPC mixtures as well as the green strength needed for proper buildability. The mixture used had an aggregate content of 60% and W/B ratio of 0.25. (Sanjayan, et al., 2018) used a 1.5 A/B ratio and 0.38 W/B ratio to test how the open time, specifically the layer surface moisture, affects bonding between layers. Some of the same researchers in (Marchment, et al., 2019) and (Marchment & Sanjayan, 2020) tested the effective bond area after the addition of CCAs for a mixture and the practicality of using mesh reinforcing for tensile reinforcing in the respective studies, using similar material ratios. (Hambach & Volkmer, 2017) used their 3DPC mixture to test the effect of different tensile reinforcing materials using 60% fine aggregate in the dry mixture and a 0.3 W/B ratio. (Shakor, et al., 2020) used an A/B ratio of 1.2 (55% aggregate) and a 0.37 W/B ratio to test the effects of glass fibers on a 3DPC mixture. This test had a very Play-Doh-like paste that had large gaps between layers at higher velocities and turned more fluid at lower printing velocities, where the best printable extrusion speed was approximately 40mm/s (1.575in/s). (Assaad, et al., 2020) tested the effect of freezing and thawing 3D printed specimens using three mixtures in three different environments, (nine total tests) and the binder amount changed for each mixture. Since there are different ratios for each mixture, an average was taken for a W/B ratio of 0.43 and aggregate amount of 69%. (Figueiredo, et al., 2019) tested various (23) mixtures in a two series experiment for mixture performance. Each series used different binders with different ratios used, and different CCAs tested with. The first series, series X, had an average A/B ratio of 50% and a normal W/B ratio of 0.3. The other series, series Y, more closely matches with the mixture compositions it is compared to and is the one included in the discussion. Series Y had a normal W/B ratio of 0.312 but a lower-than-average aggregate amount of 36% of the dry mixture. Series Y consequentially had a much lower yield stress than series X due to the smaller proportion of aggregate. (Moelich, et al., 2020) looked at the contributing factors affecting plastic shrinkage cracking for 3DPC mixture and used a dry mixture containing 58% aggregate and used a W/B ratio of 0.314.

The research conducted by (Tay, et al., 2019) tested the effects of changing the W/B ratio, the A/B ratio, and the binder component ratios to explain the basic trends seem in all mixtures with regards to altering these ratios. Tay investigated the effects of altering mixture ratios on the slump and slump-flow of the mixture, and how these impact the pumpability and buildability. The W/B ratio was one of the primary factors that influenced the fluidity of the mixture, along with the A/B ratio. When conducting tests on various (23) mixtures, there was direct correlation between changing the amount of water and aggregate to the measurement of the slump and slump-flow values. Tay used the research to determine how significant changing the variables used in the mixture was to the impact of the slump measurements. From this test of variation, Tay found that the most significant components impacting the slump and slump-flow were the W/B ratio and the A/B ratio. Similar results are found from (Zhang, et al., 2019) where different W/B and A/B ratios were observed to directly impact the flowability of the mixtures. Zhang tested the impact of changing the W/B ratio to see a direct change in flowability, increasing steadily as the amount of water increased. Trial mixtures were used to analyze how the A/B and W/B ratios must change to maintain an optimal yield stress. As the A/B was decreased, the demand of water was forced to increase, but the overall W/B ratio was decreasing. It is important for trial mixtures to be used when developing 3DPC in order to find the best flow and setting properties. Once ratios for the A/B and W/B are found to produce favorable pumpability, extrudability, and buildability properties, further optimization can be done to improve upon the mixture design.

5.1.2: Binder ratios

The binder ratio is also an important parameter when selecting a mixture composition. The chemical components used as binder for hydration determine fresh and hardened properties of concrete and are essential to consider. Figure 11 displays the binder ratios used for the same studies discussed above. The amounts of Portland cement (PC), silica fume (SF), fly ash (FA) and other components are listed by percentage of the binder. Binders that are included in the study vary, with most being nano clay and some being blast furnace slag. Like with the W/B ratio, several studies stand out as outliers such as (Panda, et al., 2017) and (Figueiredo, et al., 2019) using a large amount of FA to replace PC as the dominant binder. A trend can be seen for most studies, as the average mixture composition appears to consist of mostly PC, a small amount of FA, and a smaller amount of Silica fume. The percentages of 70% PC, 20% FA, and

10% SF seem to be used for a typical mixture composition that includes SCMs. The primary goal is to balance fluidity, particle size, and chemical makeup to assure proper hydration and flow is attained for sufficient printability. All mixtures that used FA clarified it as being Class F, or low-calcium fly ash with the exception of (Mechtcherine, et al., 2019) (Ma, et al., 2018) not

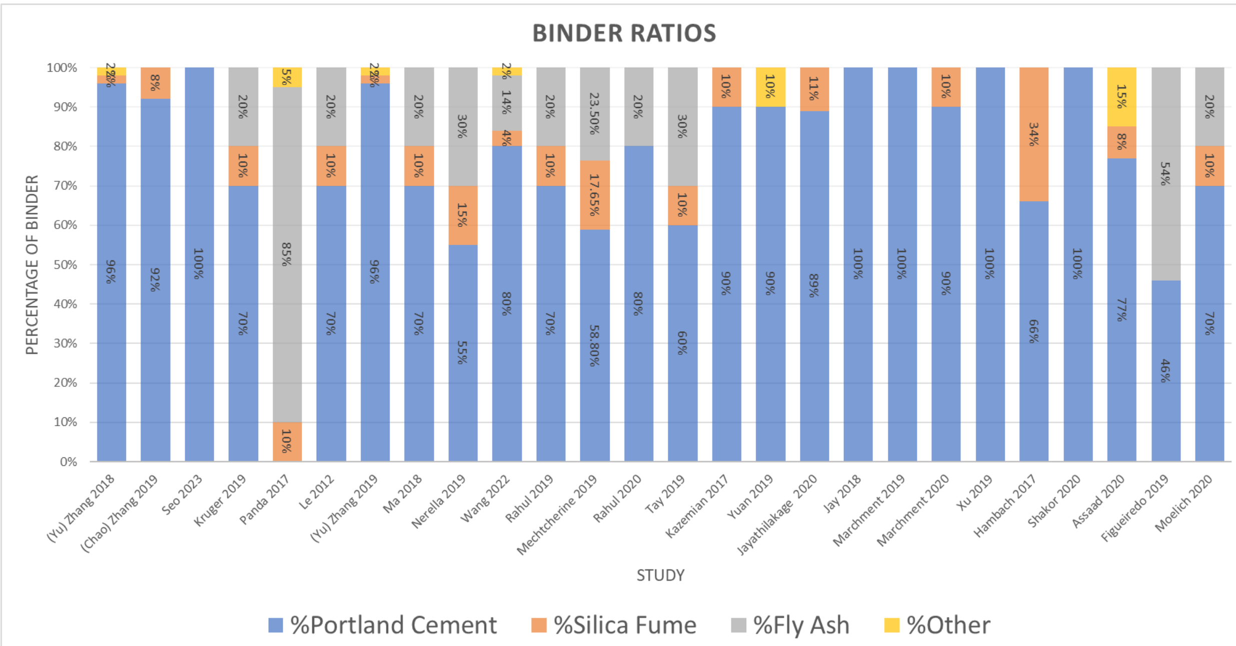

Figure 11: Comparison of Binder ratios

listing the chemical composition for the binder components.

(Zhang, et al., 2018) tested the replacement of small amounts (2%) of silica fume (SF) and nano clay (NC) for binder replacement. The type II PC predominantly consisted of CaO at 65% composition, and also had: 22% SiO_2, and approximately 5% of both Al_2O_3 and Fe_2O_3 in addition to small quantities of other compounds. The composition of the SF was predominantly SiO_2 at an amount of 95%. The NC used contained very few CaO compounds, approximately the same amount as SF (0.35% SF vs 0.52% NC) but contained a large portion (25%) of aluminum oxide (Al_2O_3) that the PC and SF lacked. The SF and NC also had similar specific surface areas, meaning their particle size and distribution were similar. Nano clay is seen in few studies but shows promising results for use in 3DPC mixtures. Both of these binders used showed significant improvement to the flow properties of the mixture and increased the heat generated from the heat of hydration by a significant amount. The mixture that contained both the SF and NC replacement had significantly increased green strength, yield stress, and layer height when compared to any of the other mixtures. This increase can be attributed to a high number of reactions occurring during the initial stages of hydration, causing early strength in the mixture. (Yuan, et al., 2019) performed a study similar to Zhang, et al. that alternatively used Sulphoaluminate cement (SAC) as a 10% binder replacement, which comprised of a large amount of CaO and SO3. With an additional addition of attapulgite (AG) for increased amounts of SiO2, this mixture also increased the yield stress and stiffness of the mixture as the additions increased. Mixtures that have sufficient amounts of chemical compounds to create the necessary silicates (C_3S and C_2S) and aluminates (C_3A and C_4AF) tend to be stiffer and yield more printable mixtures. (Marchment & Sanjayan, 2020) included the percentage of compounds in the final binder, listing the C_3S, C_2S, C_3A and C_4AF constituents of the OPC expressed as 57.59%, 14.87%, 4.10% and 13.94%, respectively. The binder used for this study only consisted of 10% replacement with SF other than PC, but this puts in perspective the compound ratios for hydration and the importance of having high amounts of CaO and SiO_2 in the mixture.

The study by (Panda, et al., 2017) performed experiments of 3DPC mixtures using fly ash (FA) as the primary binder make up 85%, as well as silica fume (SF) making up 10% and a small portion of Slag (GGBS). The slag is a unique binder addition compared to the other studies discussed, and has a sizable portion of CaO, which was 30-50% of its chemical makeup. Class F fly ash was used which contained only 1.2% CaO for the hydration reaction, so the addition of the slag was necessary for sufficient C_3S and C_2S to be formed for hydration to occur properly.

(Figueiredo, et al., 2019) tested two series of mixtures, with the first series containing 70% of blast furnace slag for the binder, and the second containing the mixture shown in the figure as 54% and 46% PC and FA respectively. The first series was not included due to slag not being a SCM analyzed in depth for this report, but it is noteworthy to mention the mixture also performed well for 3DPC applications. (Assaad, et al., 2020) used a unique supplementary binder of styrene-butadiene rubber (SBR) at 15% replacement to see its effects on the concrete material. Assaad, et al found that with 15% binder replacement of SBR, there was a slight decreased compressive strength, but slight increase to flexural and inter-layer bond strength. The strength changes are attributed to decreased porosity during cement hydration that improves inter-locking and monolithic bonding.

Across the studies observed, FA tended to reduce the viscosity, yield stress, and buildability, but increase the workability, green strength, and bond strength. SF tended to reduce the viscosity and workability, but increase the yield stress, green strength, and buildability.

5.2: Concrete admixtures

An admixture is anything added to the concrete mixture other than the binder, aggregate, and water that is used to alter the fresh or hardened properties. Additions such as chemical concrete admixtures and fiber reinforcement have significant impacts to the fresh and mechanical properties of concrete and are beneficial for 3DPC design. Small additions of CCAs or tensile fibers by mass can have large effects to the mixture's performance and properties. Table 1 has the mixture additives used for each study discussed, and just the addition is indicated since the dosage of all of these being a small percentage of the mixture. Plasticizers seem to be the most popularly used admixture for 3DPC, as they are used in nearly every study. (Xu, et al., 2019) and (Hambach & Volkmer, 2017) specified the use of water reducing agents (WRA), which share the same function as plasticizers in reducing the amount of water needed for increased workability. Other studies such as (Yuan, et al., 2019), (Zhang, et al., 2018), and (Seo, et al., 2023) specified the use of high range water reducers (HRWR) which have been classified as superplasticizers. Retarders are not used as much as the other admixtures but have still proved to be a useful addition for 3DPC properties. Viscosity modifying agents (VMA) are the second most popular admixture used for these studies, and have shown to have beneficial effects for the studies it has been used in. Studies such as with (Rahul, et al., 2019) and (Kazemian, et al.,

3DP Concrete Admixtures					
Study	Superplasticizer	Retarder	VMA	Other	Fibers
(Yu) Zhang 2018	X	X	X	-	-
(Chao) Zhang 2019	X	-	-	-	-
Seo 2023	X	-	X	-	X
Kruger 2019	X	-	X	-	-
Panda 2017	-	-	X	K2SiO3	-
Le 2012	X	X	-	-	X
(Yu) Zhang 2019	X	-	X	-	-
Ma 2018	X	-	-	-	X
Nerella 2019	X	-	-	-	-
Wang 2022	X	-	X	-	X
Rahul 2019	X	-	X	-	X
Mechtcherine 2019	X	-	-	-	-
Rahul 2020	X	-	X	-	X
Tay 2019	-	-	-	-	-
Kazemian 2017	X	-	X	-	X
Yuan 2019	X	-	X	-	-
Jayathilakage 2020	X	X	-	-	-
Jay 2018	-	-	-	-	-
Marchment 2019	X	X	X	-	-
Marchment 2020	X	-	X	-	Special
Xu 2019	-	-	X	WRA	-
Hambach 2017	-	-	X	WRA	X
Shakor 2020	X	X	-	Accelerator	X
Assaad 2020	X	-	-	AEA	-
Figueiredo 2019	X	-	X	-	X
Moelich 2020	X	-	-	-	-

Table 1: Comparison of Concrete Admixtures

2017) show viscosity improvements that increase the setting time and create is stiffer, thicker paste for printing. (Marchment, et al., 2019) tested the difference of using a plasticizer, retarder, and VMA on a control mixture. Different colored pastes were used to observe the bonding effectiveness and particle dispersion. The results of this found that the retarder and plasticizer had the greatest effect to improve the effective bonding area and the spread of the paste, directly increasing the inter-layer bond strength. The addition of VMA also showed improved bonding, but not to the extent of the other admixtures.

Unique admixtures compared to the rest of the studies have been used in (Shakor, et al., 2020) with the use of an accelerating agent, which is used to increase the early strength in concrete, and generally acts as the opposite of a retarder. Depending on the dosage, an accelerator can act as a retarder and a retarder can act as an accelerator. Shakor, et al used the specific combination of admixtures to dictate the opening and setting time of the mortar. Early shrinkage cracks occurred within this study and are attributed to the early setting time. (Marchment & Sanjayan, 2020) had a unique method for adding reinforcement to the printer, incorporating a vertical steel mesh between two concrete laying nozzles. This reinforcing was not a part of the mixture design but factors within the mixture such as hyperplasticizer and VMA contributed to the concrete bonding with this steel mesh. (Assaad, et al., 2020) incorporated the use of an air-entraining agent (AEA) that complied with ASTM C260 and was used to reduce the strength loss from freezing and thawing tests. The AEA reduced the overall compressive strength of the mixture by 12 MPa or 1.75 ksi (42.5 MPa to 30.6 MPa) compared to the specimens without use of the AEA. Despite this, the AEA reduced the drop in compressive strength and flexural strength due to freezing/thawing tests. (Panda, et al., 2017) included the use of Potassium Silicate (SiO_2 = 24.94%, K_2O = 19.09%, water = 55.97%) as an alkaline reagent. The alkali and calcium ions react with silica in the aggregate particles to form a gel, improving viscosity and yield stress for the mixture, with Panda, et al reporting a strong microstructure and binding of gels occurring.

The addition of tensile fibers being included in the mixtures is also prevalent for many of the studies. In every study except for (Hambach & Volkmer, 2017), (Shakor, et al., 2020), and (Figueiredo, et al., 2019) polypropylene fibers (PP) were used for tensile reinforcement. PP fibers are synthetic fibers that act like straw in mud to increase the tensile strength of the material. Studies such as (Rahul, et al., 2019) and (Le, et al., 2012) included the use of fibers in the mixtures to increase the buildability of the paste, and to reduce the plastic shrinkage after the concrete cured. (Seo, et al., 2023) reported an increase in splitting tensile strength with the addition of fibers, and no noticeable change to compressive strength with the addition of PP fibers. (Wang, et al., 2022) reported an increase to flexural strength for all the specimens when compared to the cast specimens due to the alignment of the PP fibers. When extruded through a printing nozzle, they become orientated in the direction of the layers, providing a bridging effect that acted as flexural reinforcement. (Hambach & Volkmer, 2017) tested three different material types of fibers for comparison, the materials being carbon, glass, and basalt. The results showed the use of glass and basalt fibers did not contribute to the strength properties to nearly the same extent as the carbon fibers did. The strength difference is attributed to the low modulus of elasticity of the glass and basalt fibers, being 72 and 93 GPa (10442 and 13488 ksi) respectively compared to the carbon's 230 GPa (33358 ksi).

5.3: Fresh and Hardened Properties

All mixtures had unique methods and components for testing their respective 3DPC mixtures. The most important aspect of these being the printability and mechanical strength they possess. Table 2 includes the known fundamental rheological properties and mechanical

3DP Concrete Properties						
Study	Compressive Strength (MPa)	Flexural Strength (MPa)	Bonding Strength (MPa)	Viscosity (Pa*s)	Thixotropy (Pa/s)	Yield Stress (Pa)
(Yu) Zhang 2018	-	-	-	3.8-4.3	8000-12000	180
(Chao) Zhang 2019	-	-	-	-	-	2459
Seo 2023	55	-	4.5	-	-	-
Kruger 2019	-	-	-	-	-	2000-3000
Panda 2017	35	7.5	1.4-0.4	-	-	-
Le 2012	75-102	11	3	-	-	-
(Yu) Zhang 2019	55	10	-	3.8-4.3	7500-11500	200
Ma 2018	53	7.8 (7 days)	-	-	-	-
Nerella 2019	100	8	-	-	-	-
Wang 2022	55	8	1.5	-	-	3568-7965
Rahul 2019	-	-	-	-	-	2500-4000
Mechtcherine 2019	50	6.75	-	-	-	-
Rahul 2020	-	-	-	-	-	-
Tay 2019	-	-	-	-	-	-
Kazemian 2017	46	-	-	-	-	-
Yuan 2019	-	-	-	-	-	1000-3500
Jayathilakage 2020	-	-	-	-	-	-
Jay 2018	20	7.5	0.5	-	-	-
Marchment 2019	34-53.4	-	1	-	-	-
Marchment 2020	22	-	-	-	-	-
Xu 2019	-	-	-	-	-	-
Hambach 2017	83	13.8-29.1	-	-	-	-
Shakor 2020	25-52	6.5-9	-	-	-	-
Assaad 2020	42.5	4.4	3.15	-	-	-
Figueiredo 2019	15	7	2	-	-	800-2500
Moelich 2020	-	-	-	-	-	-

Table 2: Comparison of Fresh and Hardened Properties

properties of each study discussed. It can be observed that some of the studies did not test these specific properties, but discussed traits of their 3DPC mixture that these properties correspond to. Studies that had none of the properties in Table 2 performed experiments to test buildability, flowability, or overall printability, which are difficult to quantify. The compressive strength was the most commonly recorded property of the studies, and an average value 48.6 MPa (7 ksi) was found between them. Yu Zhang, et al was the only study included that measured viscosity and thixotropy for the mixtures analyzed. Nearly every study mentions the importance of yield stress, viscosity and thixotropy for 3DPC applications, but few have measured it. Yield stress, however, was measured by several different studies and shows have values close to 3 kPa (0.435 psi) for most measured mixtures. Ranges of values are included due to several mixtures being tested, depending on the variable that was being assessed. (Wang, et al., 2022) had a large range of yield stress due to the study focusing on coarse aggregate replacement of fine aggregate and found much higher yield stress values as the percentage of replacement increased (3568 Pa to 7965 Pa). (Hambach & Volkmer, 2017) had a range of flexural strength values due to the different tensile fibers being used, with 13.8MPa (2ksi) strength with the basalt fibers and 29.1 MPa (4.22 ksi) strength with the carbon fibers.

(Rahul & Santhanam, 2020) was a study following up on the (Rahul, et al., 2019) study to expand upon what was found, using lightweight aggregate instead. Rahul, et al in 2019 tested the yield stress, flowability, penetration resistance, and heat generated from the three concrete mixtures evaluated. The study evolved a year later for Rahul & Santhanam when lightweight aggregates were tested instead with a focus on the modulus of elasticity and stress, as well as focusing on the buildability and deformation of the material. Compressive strength was used but only for early aged paste to determine the stress/strain relationship soon after extrusion. These studies are important to consider for the practicality application to ensure material stability and green strength are adequate for construction practices. The studies that do have fresh and hardened properties can be seen to have varying data. So many variables are changed between these mixtures and every study analyzes different properties of concrete. When analyzed individually, the strength and flow of these mixtures are justified. Studies that have higher compressive strength such as (Nerella, et al., 2019) and (Le, et al., 2012) used high-performance concrete mixtures with SCMs included for higher strength. Bonding strength was dependent on the opne time, which varied considerably by the study, which has a large effect on bond strength. The size and shape of the extruding nozzle, as well as the force of extrusion varied by study. Paste extruded through a large, angled nozzle with negligable pressure such as in (Marchment, et al., 2019) will have significantly differnet buildability parameters than a smaller nozzle extruding straight high extrusion rate. (Xu, et al., 2019) tested a nozzle that had an adjustable size and reported that it is imperative to balance nozzle travel speed, and material extrusion speed depending on the nozzle size and fluidity of the mixture. While these studies are difficult to analyze as a whole, close examiniation of their individual experiments can create an understanding for the proper mixture design needed to achieve printable concrete.

(Tu, et al., 2023) also analyzed and compiled numerous studies to compare the components, ratios, and compressive strengths of 3DPC mixtures. Table 3 recreated the information found in the study, and the results are comparable to those found in this report. Tu et al. (2023) compared the studies by the amount of weight per cubic yard as opposed to the overall material ratio like this report. Compressive strengths are measured in MPa and have an average strength of approximately 41 MPa (6ksi), similar to the average compressive strength of the studies 26 observed at 48.6 MPa (7 ksi). The results in table 3 highlight the effect of changing the W/B and A/B ratios, and their effects on compressive strength. The mixtures vary greatly, and the values are not always consistent, meaning that more information for each study is required to fully understand how the material ratios impact the compressive strength. Tu et al. (2023) also discusses the use of supplementary cementitious materials (SCM) such as flay ash, silica fume, and slag for 3D printing. The article highlights large scale projects that use 3DPC and the benefits of using waste materials, specifically the effects to strength. Tu et al. (2023) also discussed the compressive and flexural strength ratios depending on specimen orientation. (Nodehi, et al., 2022) also complied numerous studies of 3DPC mixtures to review SCMs and their individual chemical makeups. Table 4 displays the mixture composition in ratios, where class F and C fly ash, metakaolin, blast furnace slag, and silica fume area all compared for their composition, but no strength or flow values are mentioned. The studies all were able to crease

Compressive Strength of 3D-Printed concrete prepared with various mix proportions										**Tu, et al., 2023**
Reference	**Cement (kg/m^3**	**Fine Aggregate (kg/m^3)**	**Water (kg/m^3)**	**W/C**	**Coarse Aggregate (kg/m^3)**	**Superplasticizer (kg/m^3)**	**Silica Fume (kg/m^3)**	**Fly ash (kg/m^3)**	**Slag (kg/m^3)**	**Compressive Strength at 28 days (Mpa)**
Meurer and Classen (2021)	550	1172	280	-	-	22	-	-	-	65.8
Alvarez-Fernandez (2021)	100	250	50	0.5	-	0.5	-	-	-	26.3
	100	250	46	0.46	-	1	-	-	-	28.7
	100	250	46	0.46	-	0.5	-	-	-	26.6
	100	250	46	0.46	-	0.5	-	-	-	27.2
Shakor et al. (2020)	300	360	112	0.37	-	1.499	-	-	-	50.82
Assaad et al. (2020)	615	1340	-	0.43	-	6.46	-	-	-	30.8
	-	-	-	-	-	-	-	-	-	26.9
Ding et al. (2020c)	300	300	105	-	-	0.83	-	-	-	31
	300	300	108.4	-	-	1.03	-	-	-	30
	300	300	81.75	-	-	1.25	-	-	-	24.5
	300	300	118.5	-	-	1.85	-	-	-	23.3
Joh et al. (2020)	576	1154	240	-	-	8.27	79	172	-	23.5
Dressler et al. (2020)	600	1258	270	-	-	1.8	-	-	-	31
Li et al. (2020)	259.2	864.1	345.6	-	-	17.3	-	-	-	44.09
	480.2	589.4	327.4	-	-	13	-	-	-	15
Hack et al. (2020)	500	1180	160	0.32	-	5	-	-	-	59.3
Shakor et al. (2019)	300	300	1000	3.33	-	2.5	-	-	-	59.7
	300	300	1032	3.44	-	3.33	-	-	-	59.7
	300	300	1032	3.44	100	2.5	-	-	-	59.7
Panda et al. (2019b)	300	1220	350	-	-	-	250	675	-	54
Lee, 2019, 2019b; lee et al. (2019c)	580	1146	232	-	-	8.29	83	166	-	66
Nerella and	627	1391	263.3	0.42	-	4.7	-	-	-	71.8
Mechtcherine (2019)	391	1260	164.2	0.42	-	7.82	-	-	-	99.9
Van Der Putten et al. (2019b)	620.5	1241	226.5	-	-	0.93	-	-	-	62
Ting et al. (2019)	300	514.29	197.2	-	-	-	43	86	-	30
Rushing et al. (2019)	300	690	-	0.47	300	975	-	-	-	40.5
Weng et al. (2018)	300	150	90	0.3	-	1.3	30	300	-	49.7
	-	-	-	-	-	-	-	83.55	-	-
Ting et al. (2018)	-	243	120	-	-	-	-	122.4	21.6	18.1
	138	221.7	906.9	-	-	-	12	-	-	23.1
Sanjayan et al. (2018)	300	450	114	0.38	-	-	-	-	-	13
	300	450	114	0.38	-	-	-	-	-	8
	300	450	114	0.38	-	-	-	-	-	16.8
	300	450	114	0.38	-	-	-	-	-	16
	300	450	114	0.38	-	-	-	-	-	13.9
	300	450	114	0.38	-	-	-	-	-	22.8
	300	450	114	0.38	-	-	-	-	-	14.5
	300	450	114	0.38	-	-	-	-	-	10.6
	300	450	114	0.38	-	-	-	-	-	19
Ma et al. (2018b)	300	514.29	115.7	-	-	1.243	-	-	-	43.1
	300	514.29	115.7	-	-	1.243	-	-	-	41
	300	514.29	115.7	-	-	1.243	-	-	-	41
	300	514.29	115.7	-	-	1.243	-	-	-	43
	300	514.29	115.7	-	-	1.243	-	-	-	53
	300	514.29	115.7	-	-	1.243	-	-	-	42
Papachristoforou et al. (2018)	37.5	48	144	-	-	0	-	-	-	40.6
	37.5	48	126	-	-	0.15	-	-	-	41.5
	37.5	48	117	-	-	0.3	-	-	-	42.3
	37.5	48	114	-	-	0.33	-	-	-	43.5
	37.5	48	108	-	-	0.39	-	-	-	55.4
Panda et al. (2018c)	-	1219.74	144.1	-	-	10.05	101.86	572.34	35.52	36
Panda et al. (2017b)	-	148.65	124.8	-	-	2.64	10.08	-	5.04	35
Khalil et al. (2017)	682.75	850	236.3	-	-	1.76	-	-	-	87
	675	800	236.3	-	-	1.76	-	-	-	86
Kazemian et al. (2017)	600	1379	259	0.43	-	0.3	-	-	-	44.7
	540	1357	259	0.43	-	0.864	-	-	-	49.9
	600	1379	259	0.43	-	0.36	-	-	-	45.1
	600	1379	259	0.43	-	0.9	-	-	-	45.9
Le et al. (2012a)	300	642.86	111	-	-	3	-	-	-	102
									Average:	40.87

Table 3: Comparison of studies by (Tu, et al., 2023)

printable mixtures for analysis and the ratios used are comparable to the ratios found in this report. An average of 30% FA replacement, and 9% SF replacement, and 0.34 W/B ratio are very similar to the 20% FA, 10% SF and 0.33 W/B ratio found. An analysis of tensile fibers,

Mix design ingredients of 3D printed concrete (3DPC) containing supplementary cementitous materials (SCMs) without alkaline activator

Nodehi, et al., 2022

Reference	FA/b	SF/b	GBFS/b	a/b	w/b	HRWR	VMA	NC (%)	Fiber (%)	MA (mm)
Kazemain et al.	-	0.09	-	2.10	0.43	X	X	0.30	PP (0.1)	2.4
ASTM-C619	0.20	0.10	-	1.20-3.0	0.28	X	-	-	PP (0.1)	2.0
Di Carlo	0.20-0.40	-	-	0.80-1.40	-	X	-	-	-	0.5
Jeon et al.	0.18	0.06	0.18	-	0.35-0.40	X	X	-	Nylon	0.6
Nylund et al.	0.22	0.04	-	1.30	0.35	X	-	-	-	2.0
Rubia et al.	0.20	0.10	-	1.4-2.0	0.50	X	X	0.10	PP (0.25-1.0)	1.2
Weng et al.	0.45	0.05	-	0.30	0.30	X	-	-	-	1.2
Ma et al.	0.20	0.10	-	0.6-1.2	0.26	X	-	-	PP (0.1)	1.1
Soltan and Li	0.20-0.50	0.10	-	0.40	0.26-0.40	X	-	0.70	PVA (2.0)	0.8
Paul et al.	0.40	0.20	-	1.70	0.40	-	-	-	-	1.0
Ogura et al.	0.10	0.15	-	0.90	0.24	-	-	-	PE(0.3-1.5)	1.2
Weng et al.	0.50	0.02	-	0.30	0.28	X	-	-	PVA (1.0)	2.5
Li et al.	0.20	0.10	-	0.70	0.27	X	-	-	PP (0.1)	0.4
Ma et al.	0.20	0.10	-	0.70	0.27	X	-	-	PP (0.1)	0.4
Ma et al.	-	0.12	-	0.90	0.25	X	X	-	Basalt	0.4
Weng et al.	0.50	0.02	-	0.30	0.30	NR	-	-	PVA (1.0)	1.0
Lu et al.	0.30	0.03	-	0.30	0.40	X	-	-	-	2.0
Hager et al.	0.20	0.10	-	1.50	0.23	X	-	-	-	2.0
Ting et al.	0.20	0.10	-	1.00	0.46	-	-	-	-	2.0
Nerella and Mechtcherine	0.20	0.20	-	1.70	0.23	X	-	-	-	2.0
Tay et al.	0.20	0.10	-	1.00	0.46	-	-	-	-	2.0
Nerella et al.	0.30	0.15	-	1.00	0.42	X	-	-	-	2.0
Liu et al.	0.60	0.05	-	0.50	0.23	NR	-	-	-	2.5
Weng et al.	0.50	0.05	-	0.20	0.28	X	-	-	PVA (1.0)	2.5
Rahul et al.	0.45	0.11	-	0.80	0.32	X	X	0.1-0.3	PP (0.2)	1.1
Tay et al.	0.20	0.10	-	1.70	0.50	-	-	-	-	2.4
Panda et al.	0.60	0.02	-	0.80	0.30	-	-	0.50	-	1.2
Nair et al.	0.20	0.03-0.1	-	NR	0.30-0.46	X	-	-	-	NR
Zhang et al.	-	0.02	-	0.60-1.50	0.35	X	X	0.20	-	1.0
Ma et al.	0.20	0.10	-	1.20	0.38	X	-	-	Basalt (0.1-0.7)	0.4
Nerella et al.	0.30	0.15	-	1.80	0.42	X	-	-	-	2.0
Chaves et al.	-	-	0.35	1.00	0.40	X	X	-	-	NR
Chaves et al.	0.55	-	-	1.40	0.30	X	X	-	-	1.0
Aghdasi et al.	0.20	0.20	0.2	0.80	0.25	X	-	-	PE (2.0)	0.5
Aghdasi et al.	-	0.20	-	0.70	0.26	X	-	-	PP (NR)	0.5
Tay et al.	0.08-0.25	0.07-0.10	-	1.30-1.60	0.45-0.55	-	-	-	-	2.0
Ting et al.	0.20	0.10	-	1.20	0.46	-	-	-	-	1.7
Kruger et al.	0.20	0.10	-	1.40	0.30	X	-	-	-	4.8
Sharanova et al.	0.20	-	0.10 (MK)	0.50	0.45	X	-	-	PP (0.1)	3.0
Panda et al.	0.18	0.02	-	1.00	0.35	-	-	0.50	-	2.0
Panda et al.	0.70	-	-	0.30	0.45	-	-	0.50	-	2.0
Panda et al.	0.50-0.80	0.03	-	0.30	0.45	-	-	-	-	2.0
Weng et al.	0.55	0.10	-	0.50	0.30	-	-	-	-	2.5
Chen et al.	-	-	-	2.70	0.30	X	X	0.35	-	2.0
Averages:	0.31	0.09	0.24	0.97	0.34			0.39		1.61

FA: fly ash; b: binder; SF: silica fume; GBFS: granulated blast furnace slag; a: aggregate; w: water; HRWR: high-range water reducer; VMA: Viscosity modifying admixture; NC: nano clay; MA: nominal maximum aggregate size; PP: polypropylene; PVA: polyvinyl alcohol; PE: polyethylene; NR: Not reported; X: Included

Table 4: Comparison of studies by (Nodehi, et al., 2022)

several admixtures, and aggregate sizes were some of the parameters that were also compared. Nodehi et al. (2022) indicates that the use of a HRWR, or superplasticizer, was a common addition for these printed mixtures in order for proper flow characteristics to be met. The inclusion of these two large studies increases the amount of printable concrete mixtures observed that can be compared, and aids in checking mixture design trends for what works well. Despite some of these studies overlapping, increasing the number of observed studies aids in identifying an optimal concrete mixture design that can be used.

Summary and Conclusions

The testing of 3DPC mixtures is a critical aspect of optimizing concrete mixture designs for additive manufacturing applications. Repetitive testing of different mixture components on the effects to rheological, fresh, and mechanical properties can be used to systematically identify components that can be used to achieve improved printability. By using specific ratios of these components, desired flow and performance properties can be measured to study the effects of these components on printability parameters. Values for the fundamental rheological properties of thixotropy, viscosity, and yield strength can be obtained by balancing W/B, A/B, and binder ratio. These ratios also are needed to meet target strength requirements so the mixture can be suitable for structural design. The individual effects of these components are beginning to have sufficient research to understand their effects on the fresh and hardened properties, as established by this report, but the interaction between different components must be analyzed further.

The desired characteristics of pumpability, extrudability, buildability, and overall printability were examined as a result of altering the mixture components and ratios. High fluidity, low yield strength, and a long open time are desired when the concrete is in the pumpability and extrudability stages. After extrusion, high thixotropic and viscosity values, as well as high yield stress and green strength are desired for the concrete to form structured layers that are stable during buildability. The continued placement and stiffness of these layers without displacement achieves proper printability for concrete.

From analyzing the mixture compositions of the studies observed, there are clear trends that should be followed for establishing a printable concrete mixture that is successful for use as a construction material. A water-to-binder ratio of 0.3 +/-0.05 should be used to ensure sufficient flowability and strength can be achieved. No less than 50% and no more than 65% of the dry mixture should consist of fine aggregate so the mixture can be extruded as a stiff, thick paste. The fine aggregate selected should be small enough that blocking of the nozzle will not occur, using the nozzle to aggregate ratio of 4.25 developed by (Cheikh, et al., 2017). Before printing, printability tests should be performed similar to (Tay, et al., 2019) to ensure a small initial slump, but a higher slump-flow when shear stress is applied to satisfy rheological properties. The binder composition should consist of a 20% +/-5% partial replacement of Portland cement with Fly ash, and 10% replacement with Silica Fume. The addition of FA will create a denser, more buildable mixture with higher green strength. The small addition of SF will make the mixture stickier for binding and create a more cohesive mixture overall. A high range water reducer or superplasticizer should be used, with the exact amount to be verified through testing. If a large structure is being printed where the nozzle head must travel far distances, a retarder may be recommended to ensure proper bonding occurs throughout the structure. The addition of fiber reinforcing will depend on the specific structural requirements, such as if higher strengths are needed for specially reinforced walls for high lateral forces, or if specific regions will see large amounts of flexure. Evaluating this mixture for the 3D-printer used is important to ensure the mixture fits and works well, otherwise alterations to the mixture must be made. Once the concrete is deemed printable, strength tests should be performed to ensure the strength is sufficient and as much as designed for.

Despite a general mixture design can be identified, a great deal of testing is still required before 3DPC can be used as a construction material. Testing of this mixture or ones similar to it must have the proper flow characteristics to be printable to create a cohesive structure. Once this can be completed, testing of the mechanical strengths, not just with samples, but with build walls and supports must be done. The testing of structural elements instead of samples by ASTM material strength tests will aid in identifying how this material behaves in an actual structure as well as with its interactions with other structural components. Testing of the long-term strengths and serviceability, the impact of the environmental factors, and life-cycle cost analysis must be performed extensively before 3DPC can become a more common method of construction. This recommended testing only considers the mixture design and the factors that will affect the structural design and performance and does not consider standardizing the 3D-printer itself or the process of construction that follows with it. Like all construction methods and building materials, once sufficient research is published 3DPC may become a more commonly used method of construction seen across the globe.

The extensive factors that must be considered when developing a 3DPC mixture restrict the development of this construction method and material. Proper attention to the material ratios, the admixtures used, and the printing parameters all must be considered. Studying the effects of the individual components and ratios is the first step in developing an optimized concrete mixture for printing and is the purpose of this report.

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Sincerely,
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____
Zhanzhao Li, Ph.D. Candidate
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Fri 3/15/2024 2:29 PM

Hello Dr. Li,

I am a student at Kansas State University writing my masters report over 3DPC mixture design, and have read and used your "Fresh and Hardened Properties of Extrusion-Based 3D-Printed Cementitious Materials: A Review" as a source.

I was hoping to get your permission to use several figures you used in my own paper.

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Glossary of Terms

3DPC – Three Dimensionally Printed Concrete

AM – Additive Manufacturing

SCM – Supplementary Cementitious Material

PC – Portland Cement

FA – Fly Ash

SF – Silica Fume

ZSF – Zirconia Silica Fume

W/B – Water-to-Binder

A/B – Aggregate-to-Binder

CCA – Chemical Concrete Admixture

HRWR – High-Range Water Reducer

WRA – Water Reducing Agent

VMA – Viscosity Modifying Admixture

PP - Polypropylene Fibers

AEA - Air-Entraining Agent

SAC - Sulphoaluminate Cement

S/C – Sand-to-Cement

GBFS – Granulated Blast Furnace Slag

MK – Metakaolin