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Escuela de Ciencias Físicas e Ingeniería

Review of 3D printing technology for cementitious materials

Trabajo de integración curricular presentado como requisito para la obtención del titulo de Ingeniero en Nanotecnología.

Autor:

Quillupangui Cadena Julio Alejandro

Tutor:

PhD - González Vázquez Gema

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Abstract

3D printing is a helpful technology that demonstrates advances with all industries. However, it is still at the beginning of its development in the construction industry. The main objective of this thesis project is to review all the new advances presented today in this technology. The importance of every part that conforms 3D printing will be discussed here. This review analyzes the motors' significance and the different configurations of printers exist today. This review presents the new advances in materials and improvements that these materials have along with the mixture. The mixture is the most crucial part of the 3D concrete printer because its composition affects its properties. In traditional construction, each material has a specific function on the building, how the properties can increase to an ideal range. However, in 3D concrete printing, every material affects all the properties, making it harder than conventional. Therefore, there should be more research about materials and how to improve them with new techniques, methodologies, and extrusion technologies. In 3D concrete printing, cement hydration and the thixotropic behavior of the material drive the extrusion system. Mechanical properties have crucial importance in construction. However, in 3D printing, there are techniques to enhance the reinforcement and all the mechanical properties.

Key Words: 3D Printing, Concrete, Cementitious, Nanotechnology, Clay, Technology.

Resumen

La impresión 3D es una tecnología útil que demuestra avances en todas las industrias. Sin embargo, aún se encuentra al comienzo de su desarrollo en la industria de la construcción. El objetivo principal de este proyecto de tesis es revisar todos los nuevos avances que se presentan hoy en día en esta tecnología. Aquí se discutirá la importancia de cada parte que conforma la impresión 3D. Esta revisión analiza la importancia de los motores y las diferentes configuraciones de impresoras que existen en la actualidad. Esta revisión presenta los nuevos avances en materiales y las mejoras que estos materiales tienen junto con la mezcla. La mezcla es la parte más crucial de la impresora 3D de hormigón porque su composición afecta a sus propiedades. En la construcción tradicional, cada material tiene una función específica en el edificio, cómo las propiedades pueden aumentar a un rango ideal. Sin embargo, en la impresión 3D de hormigón, cada material afecta a todas las propiedades, lo que lo hace más duro que el convencional. Por lo tanto, debería haber más investigación sobre los materiales y cómo mejorarlos con nuevas técnicas, metodologías y tecnologías de extrusión. En la impresión 3D de hormigón, la hidratación del cemento y el comportamiento tixotrópico del material impulsan el sistema de extrusión. Las propiedades mecánicas tienen una importancia crucial en la construcción. Sin embargo, en la impresión 3D existen técnicas para potenciar el refuerzo y todas las propiedades mecánicas.

Palabras Clave: Impresion 3D, Concreto, Cemento, Arcilla, Tecnología, Tecnología.

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Chapter 1

Introduction

Designing prototypes for industries has a is crucial and critical importance development of new technologies, patents or processes.[27] Therefore, the main aim of the different industrial sectors has been focused on the automation of their process, making it a success in its notable industrialization. As a result, the cost production decreases, and that made it more accessible and cheaper the product developed. Automated production ideas have existed since the '80s by Charles Hull invented stereolithography.[28] 3D printing, also known as Rapid Prototyping (RP) and Additive Manufacturing (AM), refers to the process that sequentially deposits materials in a layer-by-layer way to build 3D digital object product as per Computer-Aided Design (CAD).[29] Around the same time as Hull[29], Carl Deckard, an undergraduate student of Texas University, developed the Selective Laser Sintering (SLS) process, such a process as hall's patent.[30] Many diverse 3D printing technologies can manufacture objects using various materials, from polymers, ceramics and metals, capable of fulfilling most engineering and design needs. Nowadays, the 3D printing technology is increasingly getting better results, more accurate prints, and reducing all the different extrusion problems in some materials used. The current trend of 3D printing in Building and construction research demonstrates a increase on interest and, therefore, the publication also increased. According to Yi Wei (2021)[31] from 1997 to 2012, there were 42 publications. However from 2013 to 2016, there 73 publications were being the double on just 3 years in comparison with 16 years passed before as the figure 1.1 Today, there is a lot of new researches about 3D printing and new materials and technologies.

Early applications of 3D Printing (3DP) were for prototyping and designing purposes, but due to continuous research in material science, it has since been used in many industrial applications such as the automobile, aerospace, military and medical sectors Over the years, the construction industry has been responsible for 7% of the total global CO_2 emissions on regular Portland cement (RPC) production.[30]

In addition, RPC have an environmental pollution caused by dust and the enormous energy consumption required from having a plasticity temperature of over 1300[30] C. For all these reasons, construction industry have increases its controls on RPC developing and using more materials. The construction industry has not developed at all the industrialization overall of its processes. On the other hand, in the last years, the traditional mixing and cost-production have remained the same, avoiding any novel process to build along with the World. Nowadays, in

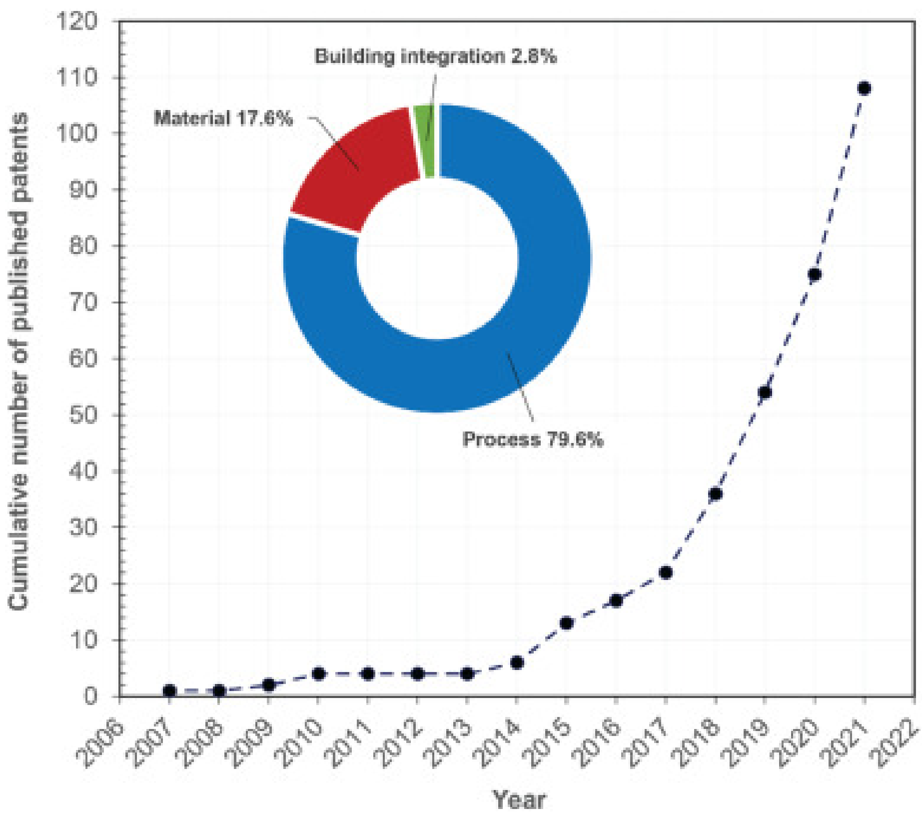

Figure 1.1: Trend of publication about 3D Concrete Printing. 1997 - 2021.[1]

some countries, new technologies exist, increasing the value added to the house and new mixing and pre-fabricated structures.[32] The main problem with these new technologies is the high-cost assembly production of the powerful and giant machines used. The first attempt at the automated process in construction industry appeared around the '80s by the Japanese researchers. First robots on construction were used for concrete floor finishing, spray painting, tile inspection, and materials handling. These new methodologies of construction improve the presentation and the accuracy in the ending details. The Figure 1.2 shows the initial tries of the construction process automated.

Nevertheless, the construction sector can obtain many benefits by automating more processes than they do. Proper research and development of 3D Concrete Printing would increase the free framework construction reducing at the exact time cost with a free digital design due to the 3D printing process. Actually, New novel fully automated robots on construction process improve building production, and 3D concrete structures creating free novel design civil structures, and new reinforcement materials[3] as Figure 1.3 shows.

On 3D Concrete printing (3DCP)[2], the extrusion and the mixing aim to research all the problems. A simple material as concrete brings diverse, complicated technologies that must be analyzed, avoiding blockages or ruptures on post-printing. The extrusion technology works according to the paste of cement used on the printers. The

Figure 1.2: Robots used on construction such as floor finishing, spray painting and materials handling.[2]

configuration printer depends on the project focus and the field where the house will build.

The major problem is the production of simple Portland cement being the main factor in CO2 contamination and emissions. On the other hand, 3D Printing has the main advantages of using new materials such as natural retarders, clays, and nanomaterials, which improve concrete quality and reduce contamination rate. There are many researches about concrete making houses biodegradable. In addition, the emission has been reduced by 30% using nano-clays and biopolymers. Some researchers use cells to improve the reduction of CO2, using the CO2 emitted as a feed of the bioparticles.

3D Printing in Ecuador is still beginning on polymers. There is some research about new materials but not in the construction automation sector. 3D concrete Printing will develop the research around construction materials, the buildings will enhance their structures, and the contamination will reduce as most as the technologies on substantial increases.

This thesis project extensively reviews all 3D printing technologies, evolution, and the new 3D printing concrete process. The new advantages that 3D concrete Printing brings around the World. It also analyzes the primary Importance and function of the leading materials used in this technology. The main objective is to bring a complete and extensive explanation of how 3D concrete Printing works and to bring new ideas about future research needed to enhance this technology. The following chapters will define the basic definition of 3D Printing. The Importance of each part of the Printing. The function and how to affect each part with the final results. Also, the chapter on materials explains the Importance of each material and how the properties affect 3D concrete printing. It also explains the main difference between traditional construction and 3D concrete printing and how new materials are used to improve the properties. Moreover, how are nanomaterials used to improve new properties of 3D concrete Printing?

Figure 1.3: Different Reinforcement structures used, analyzed and developed on 3D Concrete Printing.[3]

Chapter 2

Theoretical Background

2.1 Automation on industries.

At the past, industries created its products in diverse ways. Little by little, the research and development were increasing in order to search new methodologies and technologies that led to the industry decrease of the production cost, and also, increase the manufacture amount reducing the time production. However, the main limitations were the facilities of the industry, and the speed that human can traditionally manufacture the product. If the human manufacture were increased, the precision on object development decreases by the high speeds production. Along the time, the industries developed the procedures that involved the automation of different process. The first movement that rises the industrialization was the industrial revolution in the last 200 years ago. The set-up, operation and control of machine tools came to be operated automatically rather than by skilled workers. This word changed to 'automation' after the Second World War, though originated in 1936 by D.S. Harder. The development of machine tools has contributed to the modernization of manufacturing.[33] So, Developments in electronics and control engineering advanced the tendency towards automatizing generating low-cost mass production without increasing human manufacture.

2.1.1 History of 3D Printing, and technologies behind.

Along the time, in industries, the object manufacture changed to accomplish new low cost-production objectives. They have developed new methodologies, new robots and new process production to increase their speed and quality without increasing cost, to enhance the mass production. The term robots, machines, prototyping, and computed design were appearing along the needing to control the new automated process. The objects, products were developing on computers and new process were appearing to designate the new process to develop a product before distributed it along the world.

Rapid prototyping (RP) also called solid free-form fabrication (SFF)[27] is a combination of techniques and processes used to construct solid model of part directly with the assistance of computer. The software aided design

(CAD)[33] software. On 3D printer, the first machine using this technology was commercialized in the 1980s, which used the stereolithography (SLA) process created by Charles Hall. This method uses a photosensitive polymer that endure under the excitation of certain lights with specific wavelengths.[34]

A 3D printer manufactures these objects by filling (entirely or in a porous fashion) the space enclosed by each such surface with a solid material. The solid material is created by energy deposition, for example, by melting a solid and selectively laying it in the region enclosed by that surface, or by a chemical reaction, for example, by solidifying a liquid selectively in the locations enclosed by that surface.

According to Chang (2015; pp 746)[34], RP, 3DP, Additive Manufacture technology develops five principal steps to complete the prototyping-analysis process. CAD solid modelling, model conversion to STL, STL model slicing, model fabrication, and post-processing, resulting in a physical prototype.

1. The first step is creating CAD files by designers, prototyping, artists, architects, engineers, and others developing its 3D objects. Some research defines CAD format as Computer-aided design (CAD), also known as computer-aided design and drafting (CADD), uses computer technology for design and documentation. Computer-aided drafting describes the process of drafting with a computer.[35] It is used in many different areas such as crime scene drafting, dental prototyping, engineering object design, house description and design, and many other uses which represent in three-dimensional and digital the objects which are developing.

2. The second step is slicing 3D objects into STL files to make a cross-sectional layer with different thicknesses, depending on user needs. A standard file format to define these surfaces is the Standard Tessellation Language or, as also commonly referred to, the stereolithography file format, abbreviated as "STL." The STL format defines surfaces as a collection of triangles (called facets) that perfectly fit together without gaps, like a puzzle.

3. The third step is using Software to build the layer one by one to make the 3D object and final printing algorithm for 3D Printing. Inside the software the there are some algorithms running to obtain the best printing path. The first analysis is that the algorithm needs to develop the 2D slices on the software and give the STL file commands. The properties can change on software. The properties that are possible to changes are the Thickness of the wall and the layer, The pattern in which the printer will print the wall or the object, The speed that the object will be printed; The temperature, the width, the orientation, the infill of the object; all these properties can change the physical, mechanical characteristics on the object.

4. The next step is Printing digital Objects using an STL file previously created by a 3D printer. This process may vary depending on the material used on prints. For example, FDM printing has a melting process; the SLA process requires led with specific wavelength enduring layer by layer the material; Concrete Printing requires continuous mixing to have a correct density and fluidity paste printing.

5. The last step is the post-processing technologies implying the cleaning and curing of the object.

Today, the Rapid Prototyping process has improved the product development cycle, making it easier, faster and cheaper.[36,37] In addition, industries are developing new technologies to make 3D Printing more accessible for education in schools, colleges, universities, and laboratories. Material is extruded in different ways depending the technology used. There are several types of RP technologies. All the technology depends about what material will be treated. The most important rapid prototyping technologies currently available or under research are shown in figure 2.1

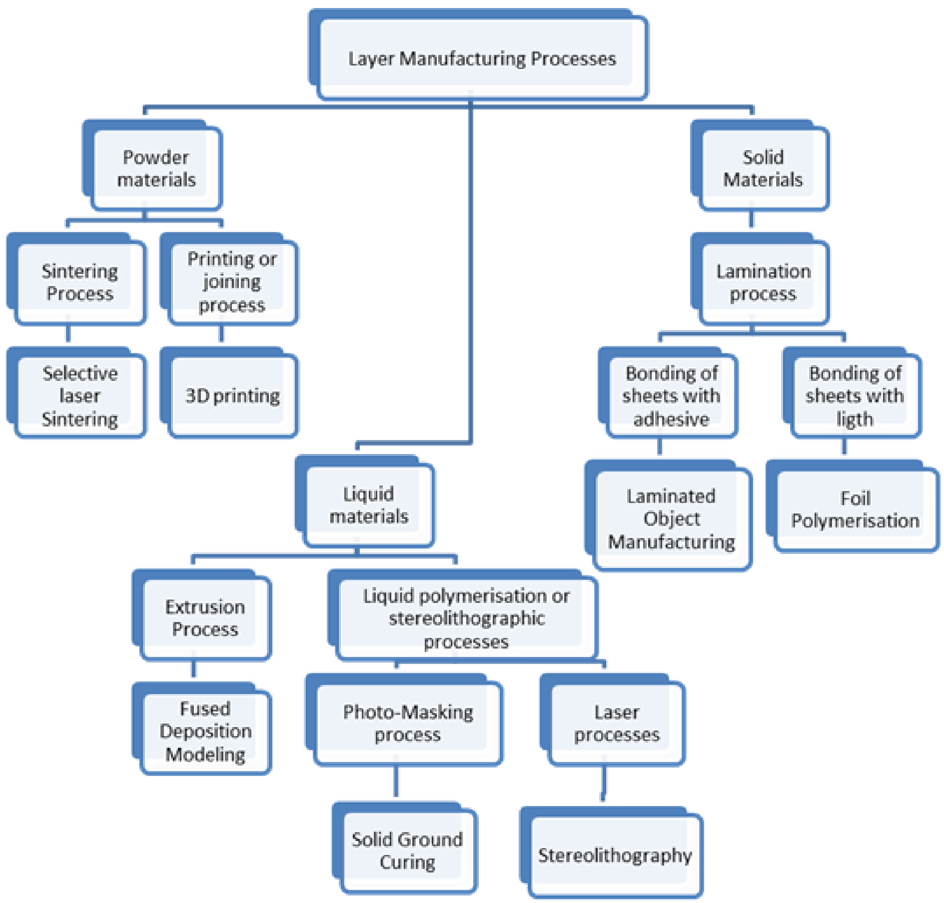

Figure 2.1: Classification of RP technologies.[4]

The most famous technologies are the Fused Deposition Modeling, Stereo-Lithography, Selective Laser Sistering. However, there are being developing new technologies according the challenges found or the necessities to produce a rapid prototyping machine to enhance.

The main factor varied in almost all the materials and technologies used on FDM is the extrusion of material. Depending the state and rheology of material. Many different materials can be extruded using 3D printing, such as polymers, clays, chocolate, cells and also concrete. On concrete 3D printing is fundamental to know FDM technologies where only changes the extrusion because the different state and rheology. Also, there are new more technical words along the correct development of concrete objects. On the other hand, there are other type of 3D printing that develops the uses of cement powder. Perhaps, Powder based printing has an increased advantaged on the quality and details factor, the main reason to not consider it as a total replacement on traditional construction is its size limitations. In addition, other factor that powder based 3D printing is the contamination that results at the end of each printing.

2.2 3D Printing Technologies

Most of the SFF techniques, so far, have been limited to low temperature materials such as papers, polymers, and waxes for fabricating prototypes.[27] Material is extruded in different ways depending on the technology used. Extrusion of polymer, also known as fused deposition modelling (FDM), represents the most widespread and economical 3D printing technology, especially non-medical applications. In addition, it is the most commonly used technology for home printers. The technology behind FDM is sintering process which involves the join of particles along the pressure increases.[38] There are many materials used sintering process such as ceramics and metals, however polymers needed new other process to improve that actual process before created.[38] Another process derived from sintering is two stage sintering. Two-stage sintering (TSS) is an effective way to achieve fine-grained micro-structured ceramics with high densification and relatively low cost. TSS method is successfully applied for all types of ceramics such as structural ceramics, bio-ceramics, ferrites, piezoelectric ceramics and electrolyte ceramics.[38] TSS consists of heating the samples in two stage such as Figure 2.2. The first stage have a higher temperature exposition than second letting the process managing a controlled grain growth.

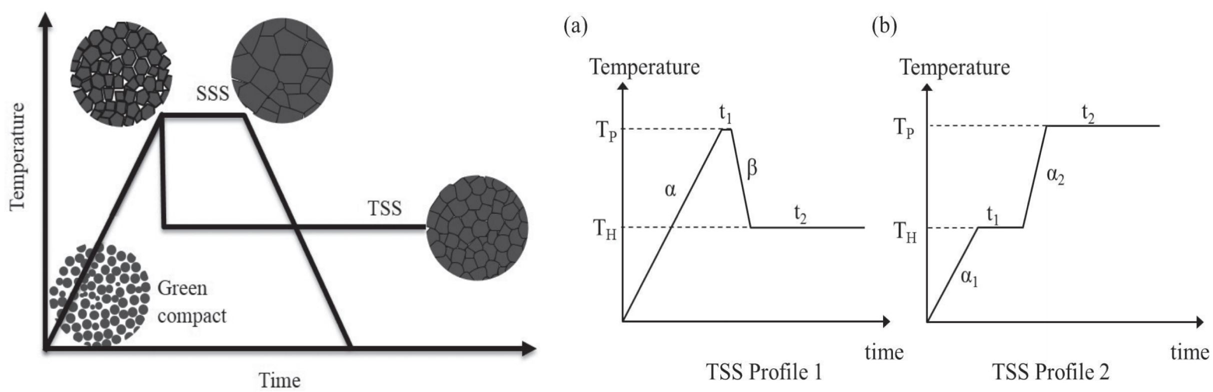

Figure 2.2: On the right side, the difference between normal (SSS) sintering and TSS. On the left side.Two different stages used on TSS to manage a controlled grain growth on ceramics.[4]

Fused deposition processing, whether FDM, FDC, or FDMet using a commercial FDM system, builds a 3D object layer by layer from a CAD design, just as other SFF techniques do.

In this technology, one or more heated extrusion head(s) melt the thermoplastic filament and deposit it selectively on the build tray in the shape of the printed layer of the object. The filament is heated electrically to a molten extruding it through a nozzle tip. Material filaments are moved in the X and Y coordinates, resulting in a material deposition before the base moves down in the Z-direction and the corresponding layer begins.[5]

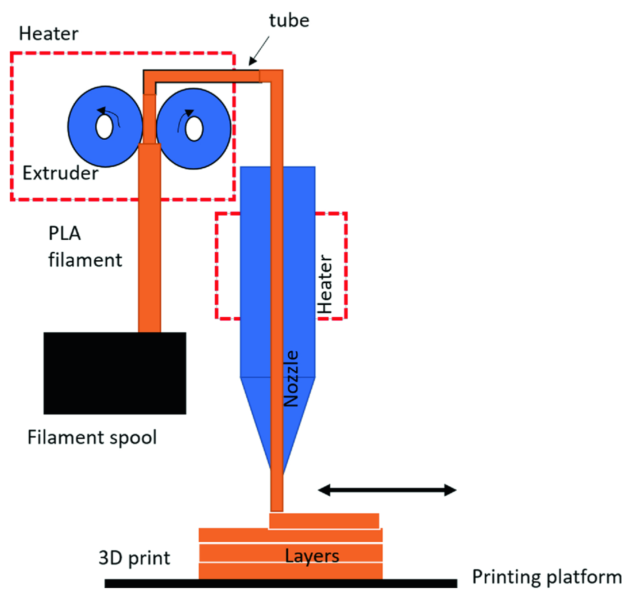

Figure 2.3: Fused deposition modelling system setup.[5]

A software moves the head that also provides a track for the nozzle to follow. The consumer breaks the support material away to manage the object printed. Then, the element is ready to use. Nowadays, the primary materials used in this process are polyamide, polycarbonate, polyethene, ABS, polypropylene and investment casting wax. This technique is a clean, effective and user-friendly 3D printing process. Usually, thermoplastic materials used in FDM have the form of filament. The material is an essential part of 3D Printing. It gives the properties to the 3D object. The printer fabricates materials with various combinations of orientation and layer thickness in an FDM machine that uses Acrylonitrile Butadiene Styrene (ABS) plastics, polylactic acid (PLA), Carbon Fiber (CF), and others. A platform keeps a constant temperature on filament extruded to avoid glue problems. Fused deposition modelling (FDM) is one of the most widely accepted methods in the industry due to its simplicity of operation and ability to fabricate parts with locally controlled properties. The significant advantage of the FDM process is its simplicity, reliability and cost-effectiveness. However, it exhibits an inferior surface finish of the fabricated part.

2.3 3D Printing procedures

The novel technologies behind 3D concrete printing (3DCP) gives the freedom to design, and manufacture non conventional and complex geometries. As mentioned before, the 3DPC processes have developed in three major categories named by their inventors as contour crafting (CC) by the similar procedures, D-shape , concrete printing[39].

In the same way, these three processes follows the same approaches on printing technologies such as extrusion and pumping concrete guided by a CAD file which contains the 3D designed object. On 3D concrete printing is used extrusion and pumping because the filament is not solid anymore as the figure 2.3 shows. Despite, it uses the same approaches to pump concrete by a nozzle. The CAD file is sliced into a STL (standard triangulation language) file collected from 3D object design. STL uses information in layer-by-layer section of the object. The process to divide 3D object into cad and make it readable for the printer into 2D layer by layer languages is called "slicing" which typically is done by specialized software. In traditional 3D printing of polymers, some of the software used are Cura Slicer based because its free license uses let to users slice and develop the 3D objects easily in addition of all its features. Another software used in the most home manufacture 3D printer is Octoprint software, which let us to move the printer in all the axis with a specific high details, using G-code Commands letting a freedom of movement. There appear also some features that 3D polymer printers have such as temperature of nozzle, bed temperatures, height of nozzle, speed, and many other characteristics giving a complete movement of the 3d printer. So, there are many other software with different focus to manage the printers being some free and some pay to use.

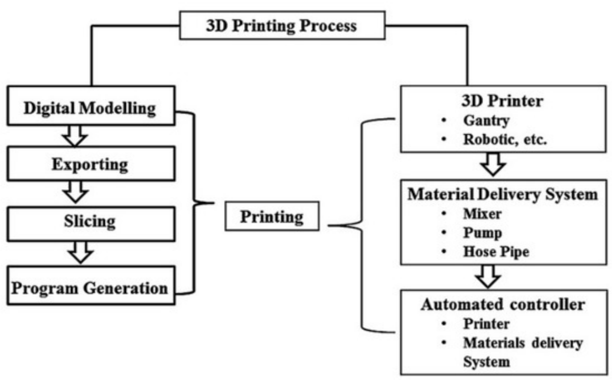

Figure 2.4: Slicer Software used on 3D printing to segment and manage printing features on 3D printers.[6]

The movement of the printer depends the type of 3D printer is used. Those are derived from Cartesian, Polar and hybrid of 2, created by the software before mentioned, also called "Slicer".[2] There is the obvious advantage of simplicity in computer numerical control on a horizontal plane.[40] In order to achieve better 3D printed objects, there must be a good combination of these elements in the system.[2] On 3D concrete printing, the default slice is not defined, because the developers prefer to build and set up their own software using technology based on slicers before mentioned.[41] And also, the parameters will change depending the numbers of axis that printer have, the nozzle size, the path followed by head printing, the buildability, and printability of the paste cement.

2.3.1 Traditional construction vs 3D concrete printer.

On Building, there are several factors to consider as toxic production. Cement production contaminates at least 5% of the global anthropogenic CO2 emission, adding 7% of fuel consumption's worldwide. Actually, concrete contains between 10% - 12% of cement by volume[42]. So, the cement and construction industry is an important polluter on Co2 emission, being necessary to reduce and create new technologies to involve new green building products.

Significant changes have occurred in the construction industry and the architectural/engineering procedures on the promotion of environmentally responsible buildings[35]. The new Green Building attempts to efficiently use materials such as water, land, energy, and materials. Also, the buildings have a healthy environment compared with the past traditional structures built. Construction with 3D printing technologies has no design limits, contrary to typical construction for some complex designs. On 3CPC, the design is done on 3D software, which develops all the 3D printers' steps. This step is critical to avoid all the possible challenges that print will have. The pattern the printer will follow is critical to know because the infill, reinforcement, buildability, extrudability, and some other properties change the strength of the structure.

With a design performed, the next step to consider is the material for construction and the techniques used to build it. Usually, typical construction uses bricks of clay or concrete. The methodology used to build houses and some structures, such as domed, was unique in some countries and also replied worldwide. The technique and the ratio used are crucial to developing the Building correctly.
Improper mortars and materials were used during the restoration of historical buildings. They were done without examining the materials' physical, mechanical, and chemical properties. These unfair practices increased the deterioration rate and resulted in severe material losses and physical damages. The lack of information on traditional manufacturing techniques and brick masonry systems used in vaults and domes has caused irreversible consequences.[43]

There is crucial importance on the water-cement ratio to obtain correct strength properties. The essential components of ordinary concrete are cement, water, sand, and stones. Generally, the amount of sand and stone accounts for above 70% of the total volume, functioning as the frame, so they are respectively called fine aggregate and coarse aggregate. On 3DPC, the water-cement ratio is also crucial because the mechanical properties made printability the cement by the head printing, and at the end, in the nozzle. Without an excellent rheological property, printing may not be possible because there will be shrinkage, rupture, and fracture. The Fresh state on concrete refers to the time between the mixing and the extrusion of the cement paste.[2]

The significant advantages of 3D printing are potential high-speed construction, formwork-free, minimal labor, and, importantly, increased freedom to design complex geometries and shapes. Also, with the 3D printing philosophy of additive construction instead of subtractive construction, materials waste can be eliminated or reduced significantly.

The reinforcement solves some structural problems against the pressure on walls and structures on constructions. However, on 3D printing, the reinforcement is still in research. Nowadays, several types of research are tried with fibers, clays, and rods still. For example, the rod could be parallel to layer by layer printing side or a vertical setup, as Fig. shows. It depends on the printer's time or the nozzle setup installed. Also, the reinforcement could be handly added, which has demonstrated an increase in structural strength in some projects.[41]

2.4 3D concrete printer setup

Nowadays, there exist 3 different types of 3D concrete system printing and some derived from them. The main used 3D concrete printers are gantry, robotic, and crane system. The approach to use one of those depends on different factors such as quality of printer, complex designs printings, mobility, size of house and also cost of printer able to build or buy. The Gantry and crane systems use the same configuration sharing the same main advantage of the easy scalable in size against robotic which needs a complex configuration to get a bigger scale printer. On the other hand, arm robotic printer has more accuracy by its 6 axis robot than crane and gantry which only have 4 axis movement. Therefore, if the printing needs more details, gantry and crane is the correct configuration to use by its low cost[41] For example, there are some laboratories in universities using a gantry printer with a printing size around 40 m x 10 m x 6 m (length, width, height) size which is usually used to print large scale building components.[31,41] There are some projects of 3D printing house that some universities have been developed and created. In some cases, the printer has been moved to the plain where the house will be built. On the other hand, some universities have adopted the printing of some building components on their labs to move them to the place of construction. This focus lets to Assembly the house as pre-fabricated structures. One example is the Technical University of Eindhoven in Netherlands with its gantry 4-axis printer gaining a total printing size of 11 m x 6 m x 4 m. Win sun has another 3D gantry printer that already has printed multiple houses like a five-story apartment block and also an 1100 m2 mansion[2].

2.4.1 Types of printers

1. Arm Robotic Printer

   The Arm Robotic configuration has many advantages on mobility. It has less axis restrictions than Delta and Cartesian printers. However, The technology used is too expensive on industrial situation. This technology used many motors that Cartesian and Delta Printers depending the configuration and the innovation used. The software to develop these technologies usually uses RepRap. Usually, RepRap configurations uses special circuits hard to obtain and configure, however RepRap mainboards are the main used on 3D new developed printers. Arm Robotic are designed by the needed to avoid supports. In addition, the more axis movement, 8 or 6 axes, let to develop more accurate, and stronger objects by the head printing movement. This type of printers, erase the restrictions of some 3 patterns presented on Cartesian printers.[40,44]

2. Delta Printer

   There are many 3D concrete printers that uses Delta configurations. A delta 3D printer, hence delta printer, is a type of parallel robot that uses geometric algorithms to position each of three vertical axes simultaneously to move the nozzle to any position in a cylindrical build area. There are two disadvantages against Cartesian which they are the complexity simultaneous movement of 3 o 4 motors at the same time which increase the printer cost. There are some algorithms used to calculate and calibrate Delta printers.[45] The other disadvantage is the spherical limits range on distance because the mobility wont let the base to move along the 3D object printing. The Printers are more exact than the two other configurations by its more exact coordinates steps,

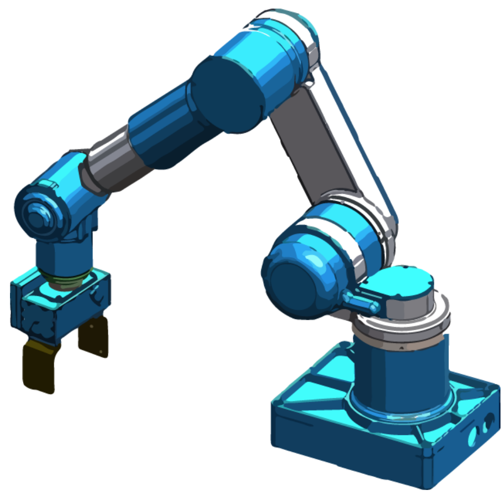

Figure 2.5: Arm robotic base 6 axis movement.

but the smaller size of its printers limits the design able for this printer such as Fig. 2.6.[40] Delta printers move more complexly, they possibly present some advantages over Cartesian ones, such as rapid speed and building capacity, higher production volume, less inertia of the extrusion assembly, less moving parts, easier enclosure and better temperature control.[46]

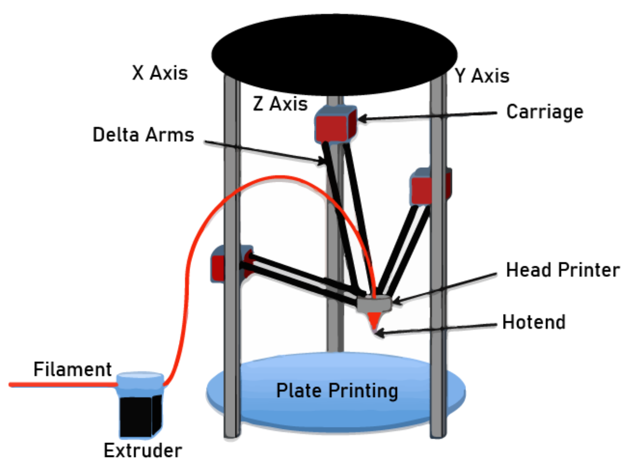

Figure 2.6: Delta 3D FDM Printer and Parts.

3. Cartesian Printer

   The Cartesian printer can have a rail as a guide of one on its axis, in which the printer can move independently. It moves to develop new continuous 3D printings. The most widely 3D printer configuration is the cartesian, meaning that the printing movements happen on the X, Y and Z orthogonal axes. 2.7[45] One of the disadvantages was the limit on one of its axis. Because One should keep constant to obtain and maintain the precision on the printing, the main reason to choose this configuration is that it can develop an arm robotic if the mobility of the head printer is a problem, eliminating a possible inaccurate printing. Some comparative studies shows that 3D Cartesian printers are at least 10% faster than Delta Printer. However, the Cartesian printer gives lower surface finish than Delta and Arm Robotic Printer.[45]

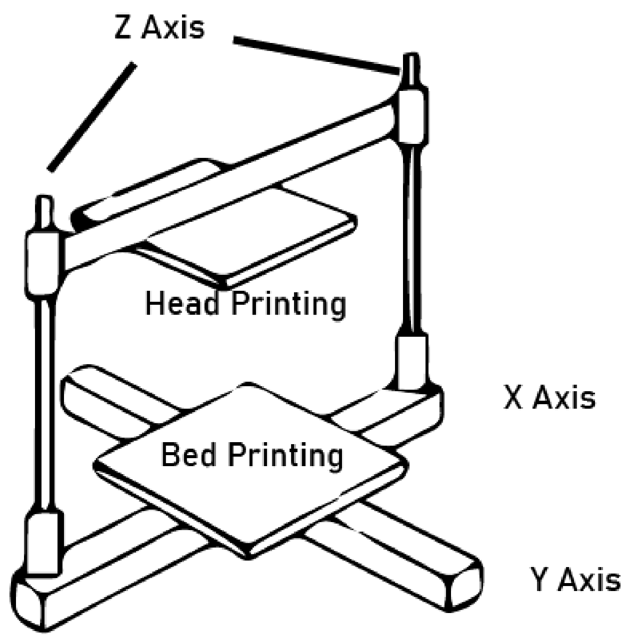

Figure 2.7: Schematic Cartesian 3D Printer. The Head Printer, and Extruder changes depending the material or filament used.

2.4.2 Motors and configurations

3D printing uses 2 different types of motors to have the most possible control on each movement. Motors used on 3D regular Printing or educational robots are the step motors[47]. Depends the material treated to choose one for the printer. These motors have been used along the time on older printer by its exact accuracy movement. But also, there are new motors used on automation, especially on arm robotic system. The Servomotors are known by the free movement and its freedom on more axis than step motors before mentioned. Therefore, the cost is higher. They are preferred by new automation machines. The step motor or servomotors movements are regulated by the same principle. The essential property of the stepping motor is its ability to translate switched electrical excitation changes into precisely defined increments of rotor position.[48] Stepper motors are a kind of electromagnetic mechanical devices which can transform discrete electric impulses (typically square wave pulses) into linear or angular displacement.[49]

These increments are defined as "steps", which are little angle increments depending the motor. The speed of the motor is directly proportional to the pulses done, and the angular increment is directly proportional to the number of the stimulation done. The force, the speed and the accuracy depend on the motor, usually for 3D printing the motor required high torque to move without complexities the structure along the axis.

The stepper motors are useful for applications that need high torque with exact precision. There are also some motors, with higher torque than other using a gearbox, increasing also the number of steps, which is better on quality and precision. But it also depend on uses, because it make it slower. The precision increases if the number of steps is higher. on 3D Printing, is crucial to have precision because in some cases, the detail needed are around 1 [um] movements which could be done by a motor with 0.9 step angle. There is some type of stepper motors. Bipolar stepper motors have a single winding per phase and unipolar stepper motor has one winding with center tap per phase. The stepper motors need a driver to send them the pulses, and control it correctly. The driver motor traduces the pulses into movement, there are also new technologies increasing on drivers, making the movement more exact. The motor uses the specific electrical pulse to move correctly, doing the movement silence without wasted of energy. The consumption is important to avoid any overheat on motors.

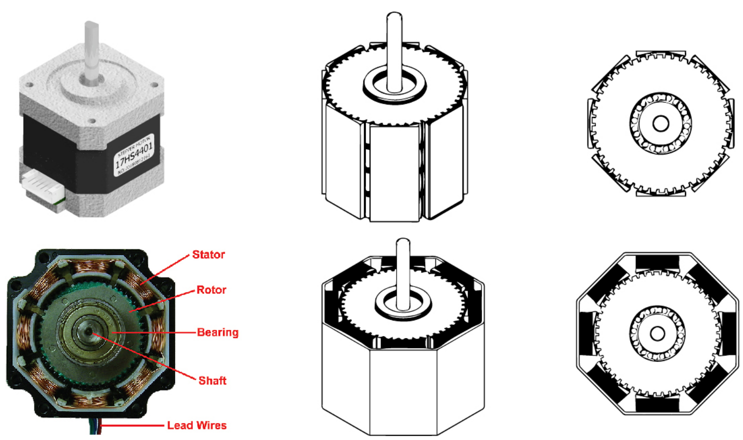

Figure 2.8: Stepper Motor schematic parts

2.4.3 Extrusion system and delivery mortar process

The extrusion system begins after the mixing of the mortar. All the materials are mixed to form the concrete, then it is pumped along the system and extruded by the nozzle following a layer by layer pattern to form the final object. The material is not solid, as regular polymers on 3DP;

Researches have demonstrated that extrusion material or the flow of fresh concrete on 3D printing is defined in two important procedures to:

1. The pre-casting concrete, being the transportation of the concrete, from the mixing to the nozzle or head printing.

2. The post mixing Extrusion process, involving the layer by layer addition, and the structural construction.

On 3D concrete printing and 3D clay printing, the material used has particular rheology, due to its thixotropic behavior, and properties to achieve which should be able to form a line of concrete without problems, and no deformations. Because if the material has not consistency, dosage and configuration, the printer can get in damage and also the house will be weaker than regulars due to voids. Some properties are still a challenge which are still studied. To have a correct performance from extruder we need to think of 3 main specifications.[50]

1. The shape and the size of the nozzle orifice (Fig.2.9-B,C).
2. Shape, mechanism, and number of trowels.
3. The Flow and its mechanism. (Fig.2.9-A)

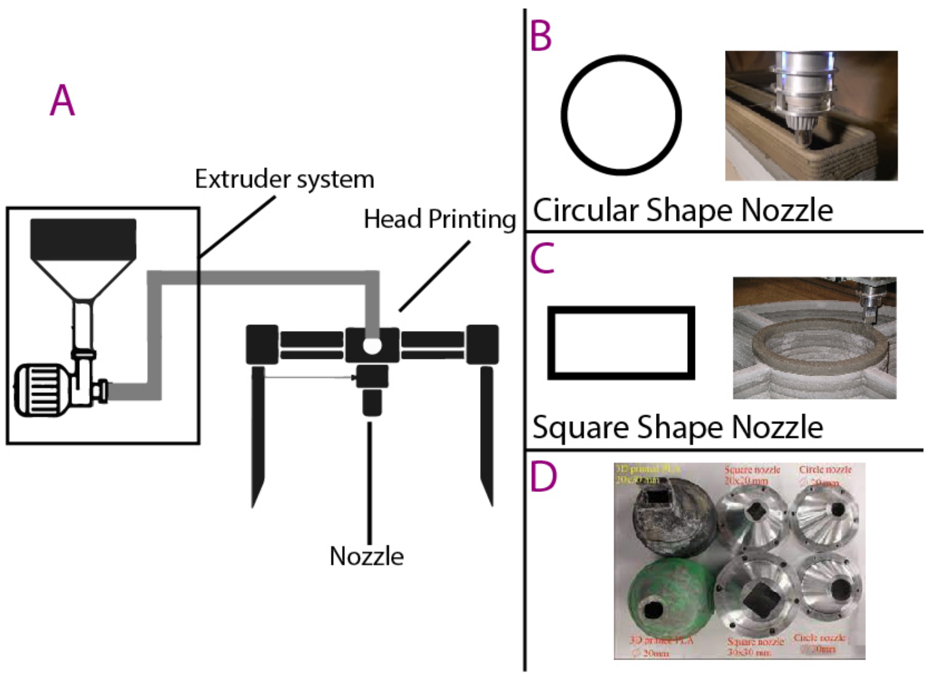

Figure 2.9: A) Schematic definition of a 3D concrete Printing. B) Circular nozzle used for 3D printing.[7] C)Square Nozzle shape used on 3D printing to enhance the quality of Printing and increase the slump.[8] .D)Different Examples of nozzle used on 3D printing. The size can change if the quality, speed, or pattern requires change.

The orientation of the nozzle should remain tangent to the tool path to prevent twisting and displacement of the fresh layer.[7]

The displacement of layers would create instability on upper layers, making the next steps printing impossible. Diverse projects used different nozzle shapes such as circular, rectangular, square, and elliptical, getting different results. Also, using side trowels to get better surface results. The side trowels also have possible different shapes depending the results wanted. The advantage of using a circular shape is the freedom of movement on printing because there is no need to turn on edges or change angles in printing. However, the circular extrusion gives the lower contact surface ending in low layer bonding. On the other hand, square shapes lose the freedom of movement, and the head must turn on every edge. However, the main advantage is the high contact surfaces, and also, the final results do not need more manufacture.[2,51] Inside the head printing is a screw mechanism which push increasing the pressure on concrete and giving the final mixing and texture before it goes along nozzle Fig.2.7-A. Though, the head printing could not have the screw depending the mixing done before pumping.

The nozzle orifice size depends on the size of the object printed, the design of the object, and also, in 3D regular printing, the quality aimed of surface. On regular printing, the nozzle is changeable to accomplish the correct distribution of time, material and surfaces finishes. Usually, as bigger is the object the nozzle orifice size are also bigger because there is a time reduction. But, as bigger is the size layer, higher will be the material used. Nowadays, the orifice sizes used on 3DCP are between the ranges of 9 x 6mm, and also, 38 x 15mm of rectangular orifices, which is not default options[52], with a printing of speed around 75mm/s and a time game of 30 seconds.[53] On the other hand. circular orifice size are around 22mm. With this nozzle the pumping speed reached are between 0.04L/s - 0.09L/s, However, a comparative with analogous extrusion processes of concrete the speed should be 2L/s which is realistic speed for 3DCP. The principle to change the nozzle is to have a wider layer line which reduce the times of repetitions of the head printing passing by.

The three main parameters that define the speed printing is:

1. Orifice size and shape.
2. Concrete fresh time setup.
3. Time loop repetition.

Orifice will bring the material depending the size of orifice. The Fresh time concrete will limit the time between extrusion and mixing. And finally, time loop repletion will used to avoid fractures, or spilling because the concrete could be too fresh or too dried when the loop begins again.

The pumping and the extrusion of many other materials can be calculated simulating because the behavior is predictable or at least easier.

2.5 Materials

The transformation of a product is variable and depends on its material characteristics, which create different behavior patterns when passing through specific processes. Therefore, a complete understanding of the properties allows a better selection of materials. In addition, it serves as a guide to follow the most appropriate procedure to arrive at the desired mechanical and physical property. It is essential to consider all the materials behind a substantial and how each one develops it. Some industries have developed a complete understanding about materials creating new technologies behind this knowledge. However, concrete is still a not well researched material. There

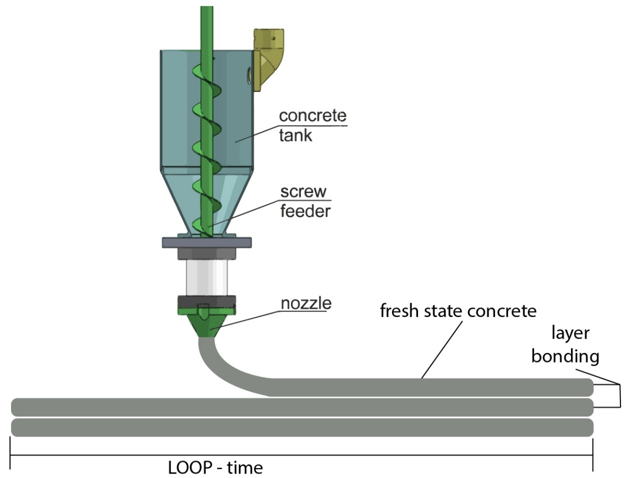

Figure 2.10: The extrusion of concrete by the orifice of the nozzle. A schematic representation of line-over-line printing.

are several tries to achieve new measuring methods to enhance cementitious materials, and also, to develop 3D printing on construction industry. Concrete/mortar fluid is the most used material globally, around 10 billion tons per year. However, it does not necessarily mean that all its mechanical properties are known well. An example of the research on Concrete is how it evolved by increasing its shear strength of concrete between 15 - 20 MPa, used in 1979, to 100 - 120 MPa used today in skyscrapers[54]. This increase is due to innovation in reinforcements, such as fiber reinforcement, gradation of aggregates, clays and much more. In addition to new concrete materials, self-compacting concrete, nanomaterials, chemical reagents, etc...[55,56] Once, the new procedures and techniques enhance construction since efficiency has improved. However, Cement is still highly needed, contaminating the ambient by its production, emitting CO2, and also, there is not possible reducing the amount of waste created. Wasted 3D printing is also conveniently used to perform a new concrete with the waste that every construction done. This a methodology improvement for a bio-construction.

Today, among studies done about concrete 3D printing increases the knowledge about these new technologies. An examples are show on Fig 2.11, the research at the University of Loughborough[57] and at University of Eindhoven[58], which make a comparison about Contour Crafting, 3D Printing, D-Shape remarking the main differences and also the such new aims with 3D printing. However, Despite its rapid growth, there is still limited understanding of the material about methodology and there is not default procedures to conclude mortar is well developed.

In Concrete 3D printing, there are continuous material control due to anisotropic material behavior which appears by interlayer bonding, one of the main problems on 3D printing. Therefore, high-performance materials are used, reducing errors and enhancing their properties, such as nano-clays to perform better the gradation and nucleation of concrete. First at all, on extrusion, concrete should behave as liquid with low viscosity while is inside the pump. However, outside the behavior is totally different like solid being able to resist deformation. So, The most important

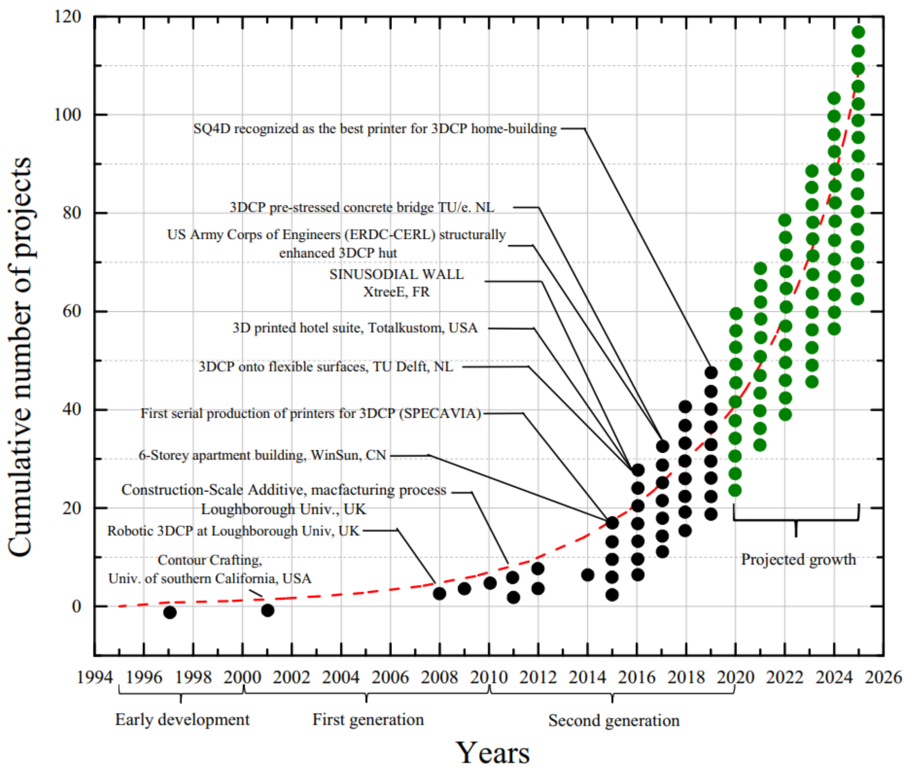

Figure 2.11: History and achievements of 3D printing since the concept in 1997.[9]

factor to consider on concrete is its yield stress. The yield stress defines as the minimum stress that a material needs to perform a complete change on its behavior, passing from a classic rigid solid material to a viscoelastic material being able to pump, or extruded.

The First step is the mixing all the materials. There has been used clays, aggregates, . The material will be mixed by some minutes. Some researches as Le *et al.*[59] describe the mixing time around 2 to 10 minutes. But it also depends about the mixing proportions. The mixing can also involve high speed mixing and also low speed, the main objective is to obtain a nearly homogeneous mixing. However, by the aggregates, the mixing will not be fully compacted. Where the density should have the correct measurement is on nozzle where the pressure also is different.

Pump will exerts enough pressure, achieving concrete dynamic yield stress, causing the changes to a manageable and with high flowability concrete being pumping along the system by its new properties, until the pressure goes down below its yield stress. Once the concrete is pumped the, the high static yield stress allows the material to resist more deformation and being harder to flow. There is the moment where buildability takes importance.[56] After extruded, time gets importance by hydration of concrete by its irreversible structural changes, and also, the reversible physical changes in the structure due to thixotropy.

The material with thixotropic behavior changes the viscosity concerning the limit of effort. Since the high density of stable material, it transforms into a material of low viscosity under the excitation of tension or flocculation exerted on it such as Fig. 2.12.[60] That's the ideal behavior of material.

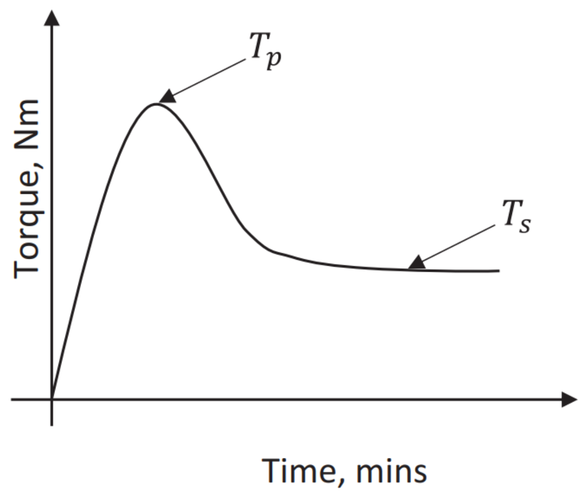

Figure 2.12: Typical decay of yield stress when the speed mixing increase[10]. This is the thixotropic behaviour of 3D printable concrete

The size of grain distribution on 3D printing is important to avoid voids, and also an increasing of pressure on pumping. That is why the size grain used is the maximum 2mm.[50,56]. According with Kuder and Shah[61], Srinivasan *et al.*[62] the presence of nanoclay enhance extrusion and the fresh state properties of stiff cementitious materials due to the different size of grain. The voids created inside by a homogeneous size grain could be filled by grains with different size

The Properties related with extrusion are the Extrudability (extrusion capacity) and pumpability or flowability. These are related with the ease of pumping concrete through pipes and nozzles. As was mentioned before, the mixing will determine how homogeneous is and how high will be the pressure needed to create a constant flow of concrete. To predict and create a knowledge and model prediction there should be a simulation which considered all the factors along the flow of concrete. The pumping model prediction of Newtonian fluids such as water or oil are well described, and simulated. Concrete, on the other hand, being a not newtonian fluid there are several models used to describe its flow because it is a viscoelastic fluid[63].

When pumping, the mortar must have layers without deformation or zero slumps to increase the contact area between layers improving adhesion. It must have a low viscosity, controlled by using chemical admixtures such as accelerators, retarders or superplasticizers in the printer's nozzle[64]. A production of zero slumps also needs care on fine aggregates due to voids, and consistency of mortar.

Yield Stress on 3D concrete Printing

Yield stress has been used to describe cementitious materials which originates from the interaction van der Waals force of different particles and the colloidal microstructure of hydration products.[65,66] For cement, due to the large complexity of the material, no values for the Hamaker constant have been measured. However, the data published are just assumptions for concrete. There should be more studies about force interactions.[65] The interaction force and colloidal microstructure sustains a certain amount of stress to resist the paste deformation before the cement paste begins to flow.

There is an optimum range of yield stress in which the material is both extrudable, with the correct proportion of size grain, temperature, water ratio, chemical reagents, and also with enough effort to achieve the acceptable dynamic yield stress, and an acceptable buildability. Once it is extruded the obtaining high static yield stress is the main objective to support above layers, achieving around zero deformation and the self-weight support. However, the pump type system, the shape and size of nozzle, the extrusion speed, and some other factors are important to consider.[11]

As mentioned before some studies demonstrate that exist two yield stress. The static yield stress and the dynamic yield stress. The dynamic yield stress and plastic viscosity can be obtained by the Bingham mode. So, the relationship of shear stress, dynamic yield stress and plastic viscosity can be expressed by Eq.2.1

$$\tau = \tau_d + \mu(\frac{d\gamma}{dt}) \tag{2.1}$$

where τ and τ_d represent the shear stress and dynamic yield stress, respectively; μ is the plastic viscosity, and it represents the ability to resist the paste flow once static yield stress is exceeded; $\frac{d\gamma}{dt}$ is the shear rate.

The static yield stress is an important index to evaluate the structural build-up of 3D-printed paste, and it corresponds to an undisturbed, well-connected microstructure related to the structure stability[67] Chen *et al.* [11] done research to calculated the static yield stress doing a low constant shear rate applied and held for some time to test the shear stress of paste. Fig. 2.13 shows the shear stress evolution of 3D-printed Mortar cement paste with rest time, and it indicates that shear stress increases firstly to a peak value and then decreases until it reaches the equilibrium value. The reason is that cement paste will produce many flocculation structures once the mortar contacts with water, which can resist the deformation during the shear process. Therefore, the shear stress increases with time before breaking the flocculation structure, and the paste presents the solid elastic behavior. At this time, the deformation can recover to its original state. However, when the stress broke the flocculation structure, the paste begins to flow and exhibits viscous liquid behavior. Once the shear stress exceeds a critical value in the linear viscoelastic region, the cement paste will start to flow, and this critical shear stress is called the static yield stress. After that, the shear stress increases significantly with the rest time, caused by the cement hydration and recovery of the microstructure. At this time, the bonding force of cement hydration products gradually increases, resulting in high shear stress.

Ideal behavior should look like Fig 2.12 shows and the Fig 2.13 apparently simulates well how the paste behaves under a shear stress.

Unlike the paste stacking process, paste extrusion is a flowing process. The 3D-printed paste flows through the pipe and pumps it throw the extrusion nozzle. The dynamic yield stress corresponds to the breaking down of

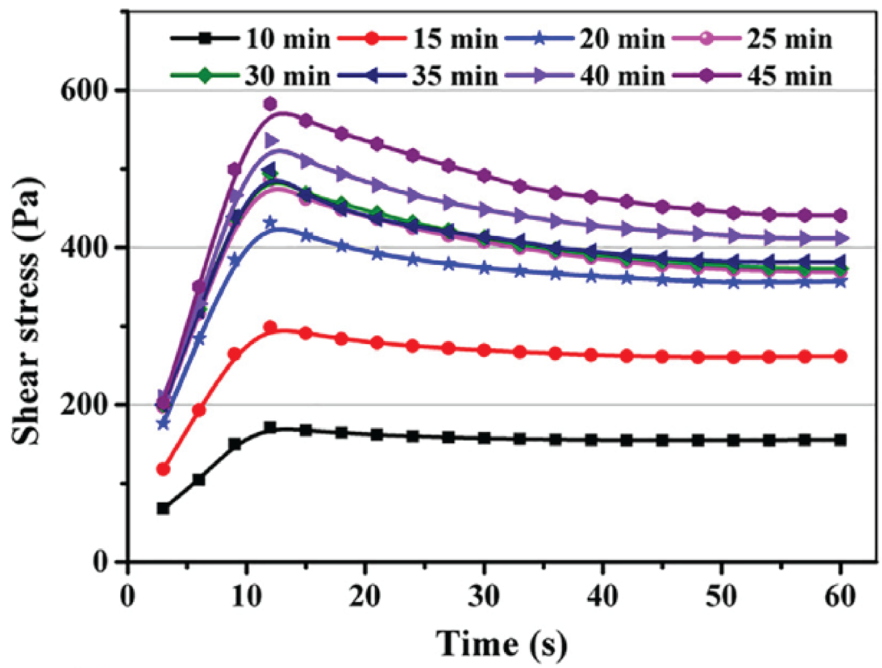

Figure 2.13: Shear stress evolution of paste on Chen *et al.*[11] with rest time. Looks similar as Fig. 2.12. Also there is observed the evolution with metakaolin used on that research.

microstructure, affecting the pumpability of 3D-printed paste.[68] Therefore, the low dynamic yield stress is of great importance for the printing quality of 3D-printed structures, which is related to the pumpability. Fig. 2.14 shows the shear stress evolution of 3D concrete printing done by Chen *et al.*[11] composites with time under the four-step test program. The first interval is the pre-shear stage under the constant shear rate of 100 s_{-1} , aiming to obtain a uniform paste. Notice how 100 Hz is enough to break the paste structure and keep the paste flowing. Then, Chen *et al.*[11] remove the shear stress. The third and fourth intervals tested present the shear thinning behavior. Once the shear rate exceeds a critical value, the paste structure breaks nucleation, and the shear stress increases linearly.

The purpose of the three-stage curve was to observe the apparent viscosity recovery after the paste structure breaks down, which reflected the thixotropy significantly. The relationship between shear stress and apparent viscosity is on by Eq. 2.2, and the recovery degree could be by Eq. 2.3

$$\tau = \eta(\frac{d\gamma}{dt}) \tag{2.2}$$

$$R = (\frac{\eta_1}{\eta_0})100\% \tag{2.3}$$

where η is the apparent viscosity; η_1 and η_0 represent the initial and recovery apparent viscosity; R represents

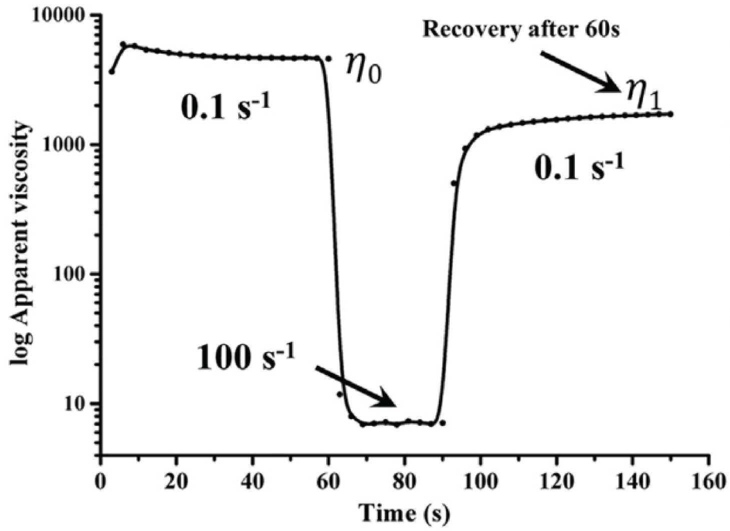

Figure 2.14: The thixotropic behavior of mortar on 3D concrete extrusion. There are 3 stages presented.[11]

the recovery degree.

Pumpability

In general, concrete pumpability is the capacity of concrete under pressure to flow while maintaining its initial properties.[69,70]

These are related to the ease of pumping the concrete through pipes and nozzles. The pumping prediction of Newtonian fluids such as water or oil is well described and simulated. Concrete, on the other hand, is a viscoelastic fluid[63] making it harder for the simulations by all the factors to consider.

Two methods of improving pumpability are. 1.- including sufficient paste content and enough grout to form a thin smearing boundary layer on particles. 2.- suitable grout consistency and structure between aggregate grains to hinder forced or pressurized bleeding during high-pressure pumping. More advanced concrete testing devices such as rheometers and viscometers can be used to estimate both parameters of the Bingham model and are, therefore, more suitable for estimating the pumpability of fresh concrete. In this case, the Dynamic yield stress (viscosity) will be measured and calculated.[11,65] However, there are more techniques to measure pumpability, for example, the Sliding Pipe Rheometer. In this method, the pumpability is tested by filling the pipe placed in the topmost position with fresh concrete and eventually letting the pipe slide downwards under the force of the weights attached to the pipe. While the pipe moves, the concrete body remains in the initial position, pressing against a pressure sensor positioned at the head of the metal piston along which the pipe slides down.[63,71] On extrusion the compressing of mortar when it passes along the tubes and pipes. In 3D concrete printing, this is changed by the requirement of pumping the fresh material over appropriate distances depending on the printer (gantry, robot or crane) size and working volume (length, width and height).[72]

Buildability

Buildability is another critical parameter to evaluate the printable performance of concrete materials. Buildability, which combines properties of printed layers being self-supportive and shape retention, refers to the ability of the bedding layers to hold the subsequent layers on top of them without collapsing or deforming. On traditional construction there is not problem about buildability because concrete fills a mold and is supported by framework. On 3D printing, Its crucial to have an excellent buidability to built up layer by layer correctly without any deformation. There are some ways to enhanhe buildability.

- Changing the nozzle type. Therefore, the nozzle could be squared shape which some research as demonstrated well defined lines.
- Increasing the number of adjacent filament layers. The buildability will stable if there ares more printing lines to support at its sides.
- Creating a cellular-type structure can also be used to improve the buildability. The infill of the wall can also helps to keep the shape of the walls, instead, the buildability will be better.
- Enhance the rheology properties of the material predicting and simulating the behavior of the extrusion.

There are models developed by Perrot *et al.*[13] to indicate if the layered structure is able to sustain its own weight and able to predict the failure time when the structure is going to collapse. In the case of the wall, conforming the wall height increases, the load on the initial and below layers will also increase. Perrot *et al.*[13] defines a vertical rate construction as R. Then the Vertical load or effort that the first layer will support defines by this equation:

$$\sigma_v = \rho g h(t) = \rho g R h(t) \tag{2.4}$$

where ρ is the specific weight of the concrete, t is the age of the first deposited layer (which starts with its deposition) and h is the height of the vertical structure located above the first deposited layer.[13]

The stability of the first layer can be tested by comparing the vertical stress given by Eq. 2.4 with a critic failure stress, which is linearly linked to the yield stress of the first deposited material:

$$\sigma_c(t) = \alpha_{geom}.\tau_0(t) \tag{2.5}$$

where $\tau_{0,0}$ is the yield stress of the first deposited material and α_{geom} is a geometric factor which depends of the form of the built structure.

On the other hand, yield stress is commonly considered to be linear during the dormant period this formula. The rate of formation of $C - S - H$ bridges is constant because the heat of hydration is constant during the so-called *dormant* period. So, all the interactions and the formation of CSH bridges have to consider on the formula. So, To describe a non linear model by all the exponential creation of CSH bridges, Perrot *et al.*[13] propose there should be a not negligible increase in yield stress, as an exponential grow. So, to describe the complete nucleation of concrete with respect to time should follow the next formula.

$$\tau_0(t) = A_{thix} t_c (\exp \frac{t_{rest}}{t_{t_c}} - 1) + \tau_{0,0} \tag{2.6}$$

where τ_c is a characteristic time, the value of which is adjusted to obtain the best fit with experimental values, A_{thix} as the constant rate of increase in yield stress over the time with rest. [16]

Properties of shear stress, viscosity, open time and green strength of concrete material are also very important since they relate to pumpability, buildability and interlayer adhesion. [11]

Open time refers to how long the mortar is manageable without any hardened property. And also, can be defined as the time between the mixing and the extruded first line. There depends the effort done on mortar. The green strength of 3DPC is related to its fracture on the surface when load is exerted on top of the bed layer as fig 2.16

To calculate the Open time or Critical failure time, the minimum time between printing of layers to allow the bedding layer to develop enough strength, follows the Eq.2.7.

$$t_f = \frac{\tau_{0,0}}{\rho g R \alpha_{geom} - A_{thix}} \tag{2.7}$$

$$\alpha_{geom} = 2(1 + \frac{D}{2\sqrt{3}h}) \tag{2.8}$$

where: $\tau_{0,0}$ is the yield stress of first deposited material, A_{thix} is the constant rate of increase of yield stress over the time, t_c is the characteristic time (a value which is adjusted to obtained the best fit curve of experimental values), t_{rest} is the time at rest, i.e. $t_{rest} = 0$, ρ is the specific. weight of concrete, g is the gravitational acceleration, R is a constant that depends on the rate of construction and ranges from 1.1 to 6.2 [m/h], α_{geom} is a geometrical factor which depends on the form of building structure, D is the diameter of the structure, and h is the height of vertical structure on the first deposited layer. [13]

The yield stress (τ_c) of concrete can be estimated from slump flow test results as follows:

$$\tau_c = \frac{\rho g(h_0 + h(R_0))}{\sqrt{3}} \tag{2.9}$$

where: h_0, h and R_0 are obtained from the slump flow test as shown in Fig. 2.15.

To enhance the buildability, the deformation that concrete will have by the load of the upper layers is important to measure. It should be measured accurately. As shows the Fig. 2.16[73]

For testing deformability, a small slump cone of diameter $d_0 = 100mm$ is used. In the slump tests, no external vibration is applied to consolidate the fresh concrete. The maximum diameter of the spread d1 and the diameter perpendicular to it d_2 are then measured. The deformability (Γ) is then calculated as follows

$$\Gamma = \frac{d_1 d_2 - d_0^2}{d_0^2} \tag{2.10}$$

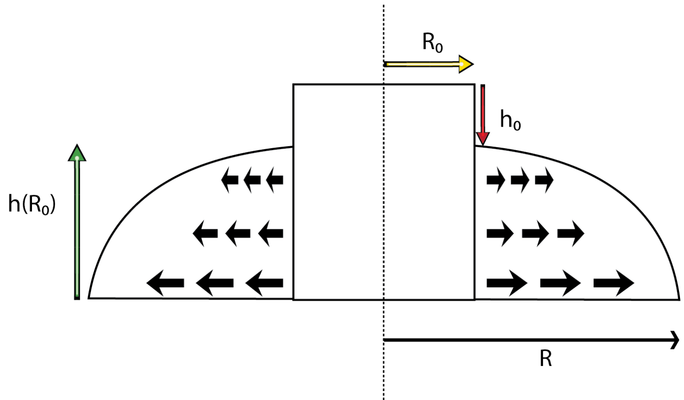

Figure 2.15: schematic of the behavior of mortar specimen creating slump and spread on its shape due to rheological properties.[12]

Typically, a quick reduction in deformability is required after printing for shape retention. Alternatively, a more direct measure is the plastic viscosity of the fresh concrete. The variation of plastic viscosity with time can be expressed as follows:[73]

$$\mu_m(t) = \mu_m(0, T) + \Delta.\mu_{eq}.(\frac{t}{t_f}) \tag{2.11}$$

where: $\mu_m(0, T)$ is the initial plastic viscosity at the test temperature, $\Delta\mu_{eq}$ is the slope of the linear regression, t_f is the final elapsed time.[74]

2.5.1 Construction materials

In order to achieve a well process 3D printing on concrete, the properties on every stage should be accurately considered and studied. On table 2.2 are mentioned some of the researches done. the composition changes depending the analysis done.

On traditional construction the main materials are the binder mix, water, thicker aggregates, and fine aggregates. In some cases, there is used admixtures and chemical reagents to increases the join, with the correct hydration time. Also, in some cases the mix already pumped is put on vibration to enhance the gradation, and therefore, the nucleation of the mixture. On the other hand, if we analyze the material used on 3D concrete printing, the material are almost the same with a little difference. The water binder ratio will be different because, as mentioned on sections above, the rheology of the material should be different as traditional construction. And also, the other difference is the size of grain used. This is changed by the possible obstruction on pipes, tubes or extrusion system of the 3D printer. The uses of high radius grain should income into blockage, and also the self-weight support of the line concrete could be impossible to resist. On construction when the mixture does not uses thicker aggregates it takes the name of mortar.

So, sand, cement, and fine aggregates should have as maximum of 2 mm grain radius as uses on the studies of

Material Composition									
Authors	Cement	Fly Ash	Silica fume	Fine Aggr.	Water	Chem. Reagent	Fibre	NanoClay	Additional
Nerella *et al.* [75]	430	170	180	1240	180	10	-	-	-
Le *et al.* [59]	579	165	83	1241	232	16.5	1.2 (PP)	-	-
Perrot *et al.* [13]	Binder content expressed as a weight: Cement 50%, limestone filler 25%, kaolin 25%, w/c = 0.41,SP/cement = 0.3%								
Al-Qutaifi *et al.* [76]	-	100	26	100	-	-	1% (SF) or 0.5% (PP)	-	-
Malaeb *et al.* [77]	125	-	-	160	w/r:0.39	0.5-1 ml	-	-	-
Weng *et al.* [78] (weight proportion)	1	1	0.1	0.5	0.3	1.3	-	-	-
Zhang *et al.* [79]	864	-	18	900	0.35	0.0125	-	18	-
Ye *et al.* [80]	655	604	118	246	363	-	-	-	-
Rahul *et al.* [56]	663	165.7	-	372.9	265	1.08	1.8	-	Quartz powder - 497
Chen *et al.* [11]	100	-	-	100	35	0.30	-	0.15 TA - 0.40 HPMC	-
W/R= Wright Ratio, PP = Polypropilene, HPMC = hydroxypropyl methyl cellulose, WRA = water reducing agent, TA= Tartaric Acid, SF = Steel Fiber,									

Table 2.1: Different mixtures on 3D concrete printing research to enhance rheological properties.

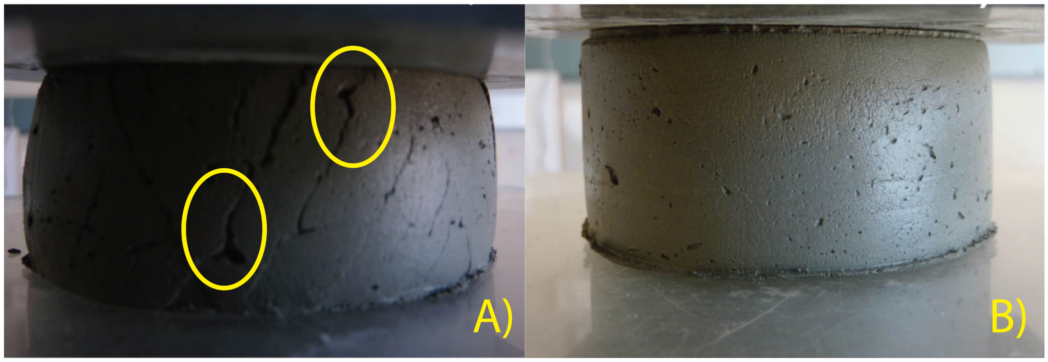

Figure 2.16: Perrot *et al.*[13] analyzing the green strength putting a load above a cylindrical concrete. A) There are fractures by the load. Deformability is measured by the difference of the shape using 2.10 B) The initial condition before the load is higher than green strength.

Perrot *et al.*[13], Le *et al.*[59], Nerella *et al.*[75], Al-Qutaifi *et al.*[76]. On the other hand. there is also the possibility to change sand by other type of fine aggregates as Rahul *et al.*[56] done. They use a fine quartz powder as aggregates, and also uses a quartz sand. This is possible due some developers create a smashed powder to have a fine aggregate. So, the mixture takes a composition and behavior as a paste. But that not means is another type of fluid. As explained before, the mixtures still are taking in count as cementetious material which behaves as a yield stress fluid by the thixotropy behavior. Therefore, the material changes depending on 3D printer requirements, the temperature, and also, the country where the research is done. That is the main reason about the uses of several materials. The high radius grain are used to have a well gradation on construction as the Fig. 2.18 shows. The gradation helps with the increasing of density on concrete making it better on stress strain resistance. That is why is used clays, cement, nanoparticles, fibers, and also some powder aggregates to achieve a correct gradation Fig. 2.17

Cementitious materials

The concrete mix usually consists of binder and fine sand aggregates and some mineral admixtures or additives, also called the dry mix. Ordinary Portland Cement (OPC), fly ash (FA), granulated blast furnace slag, silica fume (SF), and nano-silica (NS) are usually used in different proportions to form a binder, depending on the composition of each of these materials.[81] These materials provide significant technical benefits to concrete, including improved flowability, strength, durability performance, dimensional stability, and lower heat of hydration.[18] In general, the helpful addition of this fine-grounded admixtures can improve the fluidity, stability, and early-stage strength of concrete due to their fine particles and high pozzolanic reactivity. Those are potentially exhibiting pozzolanic reactivity, that is, react with calcium hydroxide (CH) to form additional cementitious compounds, calcium (alumino) silicates hydrate (C-A/S-H).[82] On cement, the main interaction is with water when occurs the hydration. The interaction between water and cement will generate heat. Ordinary Portland cement (OPC) is hydraulic cement and composed primarily of four kinds of minerals: “alite (C_3S), belite (C_2S), aluminate (C_3A), and aluminoferrite

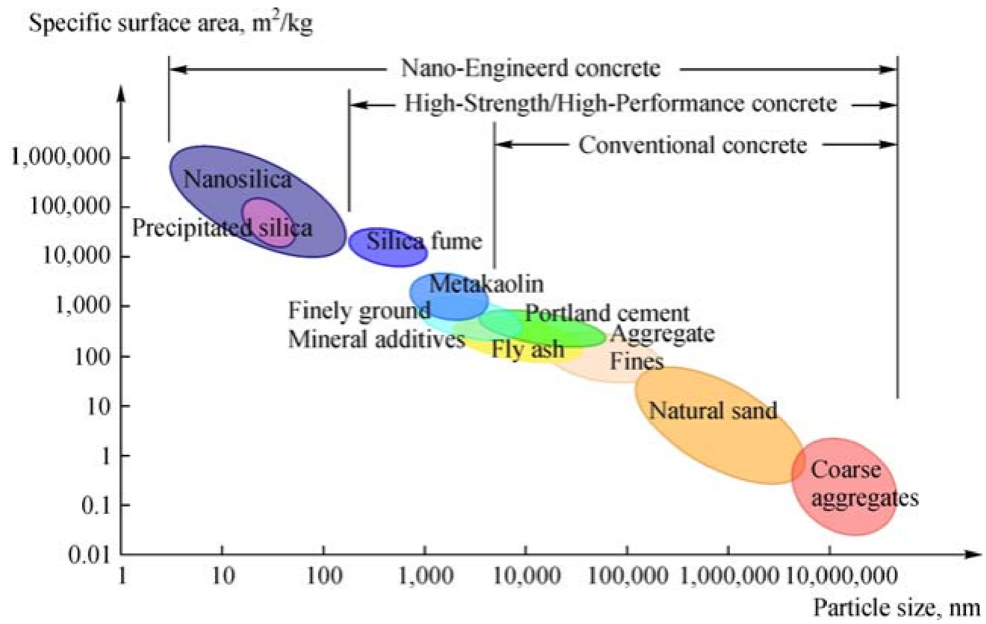

Figure 2.17: Particle size and specific surface area related to concrete materials.[14]

(C_4AF)". These four fundamental compounds specify the hydraulic characteristics of the cement because they assimilate for over 90 % of Portland cement.[82] So,the main Hydration products on cement are calcium silicate hydrate ($C-S-H$) and calcium hydroxide as the equations below. Therefore, $C-S-H$ represents the role of a binder of the cement paste and ultimately influences the strength and durability of concrete.[82]

$$2C_3S + 11H \rightarrow C_3S_2H_8(C-S-H) + 3CH(calcium-hidroxide) \tag{2.12}$$

$$2C_2S + 9H \rightarrow C_3S_2H_8(C-S-H) + CH(calcium-hidroxide) \tag{2.13}$$

For this interaction the cement hydration is a highly exothermal reaction that occurs in a certain phases.

1. Speedy primary processes
2. Dormant (recumbent) period
3. Precipitation (acceleration) period
4. Delay (retardation) period
5. Long-range reactions

There are also some characteristics which influenced the heat hydration of cement. That is why the correct dosage is required to have a good pumpability, a thixotropy behavior will let also have a correct extrudability. Plastic viscosity is the resistance of a fluid to flow when the fluid is flowing[78]. The behavior and the rheological properties are attributed by the inter-particle forces (C-S-H).[13,83,84] On 3D printing, some research define the second yield stress is due to the C-S-H interaction on pre-mixing stage. The first is due to elastic resistance of material. C-S-H forms up to about 60% of the hydration products in hardened cement paste and is primarily responsible for some of its principal properties such as strength, shrinkage, and for its durability. An electron micrograph of the products formed in hydrated Portland cement is shown in Aali Alizadeh[15] on Fig.2.18.

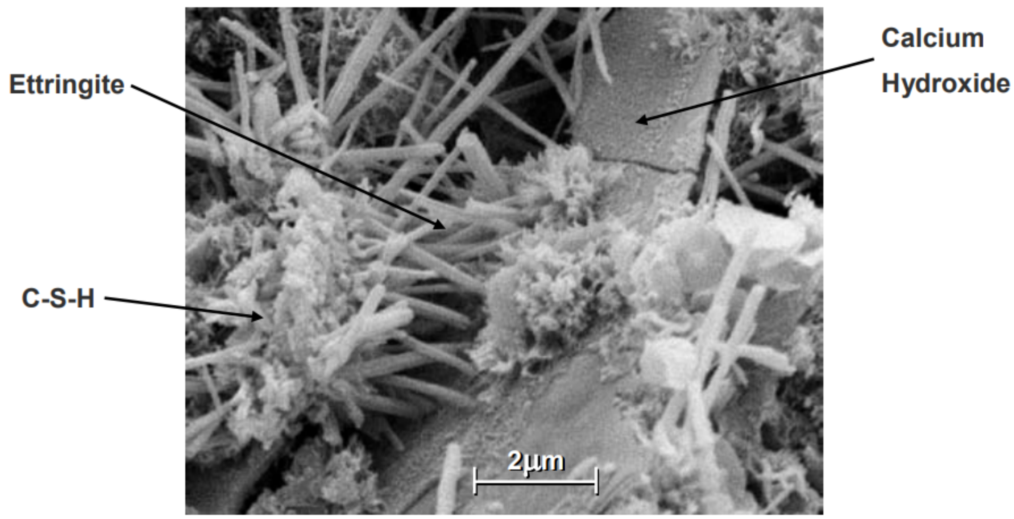

Figure 2.18: An electron microscope image of Portland cement hydration products.[15]

Ordinary Portland cement changes depending the place where it is produced.[84] There are several types and it can improve some properties, but also can be chosen depending temperature, or which admixtures have. Because, the heat reduction of cement hydration is the aim on several researches to enhances and increase open time, and also, workability.

Another binder material is the Fly Ash (FA) which comes from the coal-fired power plant as a residue. FA of class F contains greater than 70% silica content while FA of class C contains 15 to 30% CaO.[81]There are two types of fly ash. Class F fly ash comes from burning anthracite or bituminous coal, low in CaO and high in SiO2 around its 70%. Class C fly ash comes from the burning of sub-bituminous coal and lignite, with higher CaO content which range is between 15%–30%. Elevated CaO gives class C fly ash unique self-hardening characteristics. Moreover, adding fly ash to concrete can densify the cement matrix by filling pores and improving mechanical strength.

Due to higher CaO content, FA of class C shows self-hardening characteristics. SF is the bi-product obtained from the smelting industry and contains about 61% to 98% silica. The two major physical features of silica fume are its high content of amorphous SiO2 and extreme fineness. SiO2 content varies from 61% to 98% based on the type of alloy being produced. Silica fume consists of spherical particles with particle diameters around 0.1–0.5 mm, and its Blaine fineness is in the range of 13,000–30,000 m2/kg More than 95% of silica fume particles are finer than 1 m. Aali Alizadeh [85], Siddique [86] on his study demonstrated that addition of 10% silica fume in a lean concrete (100 kg/m3) of cement reduced the water demand. [86] On hardened properties, Mazloom *et al.* [87] found that when concrete mixes incorporating higher silica fume content tended to require higher dosages of superplasticizer to enhance the workability. However, with Silica fume due to the grain size the porosity decreases according with Rossignolo [88].

Most authors used several trial mixes before choosing the best mix composition. A significant amount of fine particles were used in all mixes. However, the uses of fine particles such as SF or FA does not mean all the properties will be enhanced. To use a binder material there should be a research about the property needed on concrete mixtures. Because, some enhance the porosity increasing the manageable of concrete. However, SF decreases and there is needed a superplasticizer to have an acceptable workability. The composition can also affect to the properties of mortar.

On fine aggregates, there is Limestone, a filler, a product obtained from the fine grinding of Limestone. It is another notably used mineral admixture taken as cement replacement material. It contains a high degree of calcium carbonate ($Ca2CO3$). Substitution of limestone fillers in concrete has grown because it is cheaper and well-adapted and can present several advantages over ordinary cement.

The yield stress as mentioned before is also important on cement hydration, and therefore, on the properties of workability, extrudability, and finally buildability of the material. The first stage where the yield stress appears is on mixing, there appear the flocculation, the nucleation, hydration and colloidal process. Once the mixing finishes and the stress on concrete is over, the nucleation due CSH interaction appear as Fig.2.19 This nucleation turns locally the soft colloidal interactions between cement particles into CSH bridges. As a consequence, at the macroscopic scale, the elastic modulus increases. [16]

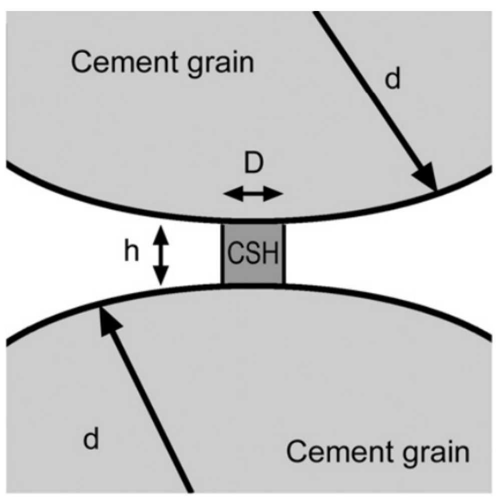

Figure 2.19: Calcium silicate hydrate interaction between two cement grains. [16]

So, according with Roussel *et al.* [16], the first seconds after the main problem is to avoid hydration exerting a force there. Because, at the end of mixing phase, cement particles are dispersed.Fig.2.20A) Because, Hydration is the origin of workability, pumpability loss as soon as the available mixing power becomes insufficient to break these inter-particle connections.[83] Then, due to colloidal attractive forces, cement particles flocculate the first seconds and form a network of interacting particles able to resist stress and displaying an elastic modulus as Fig. 2.20B) Finally, there comes from an increase of the size or numbers of CSH bridges between percolated cement particles.Fig. 2.20C), D)

The next stage is the flowability of concrete along pipes and tubes, it occurs until it achieves to the nozzle. Passing by all the system will increases the pressure and the nucleation will be higher. On this stage, there is not a mixing stress on the concrete so the pressure or the shear stress by the pump should keep the concrete on its dynamic yield stress to flow without problems. Also, once the concrete is pumped the size of grain is important to avoid blockage. Is important to mention that the pressure on nozzle will be higher than the rest of the system. This is because nozzle have a cross-section smaller than the rest of the pipe. So, concrete will be pushed out with a high level of density increasing the buildability. However, If the proportion of water are overpass the needed level, on nozzle, concrete could behave as a sponge, swelling all the water out and decreasing quality of concrete. Therefore, the distribution of the material, the water radio, and a correct dosage of materials takes a crucial importance on the selection on materials because the nucleation defines the porosity, the interaction between particles, the density and the strength of the structure. Roussel *et al.* [16]

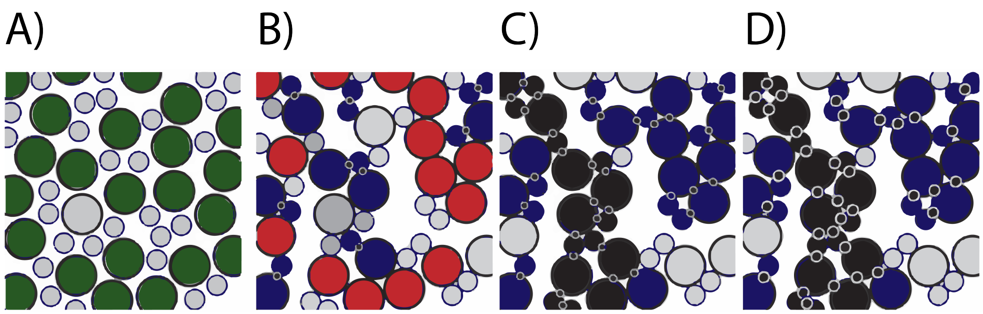

Figure 2.20: A) At the begging the particles dispersed. B) The flocculation initiates and the bridges of CSH appears, increasing the elastic modulus. C) A colloidal path appears and the increasing of elastic modulus. A percolated particles appears. D) The CSH bridges, and percolated path of particles increases in size creating and closing voids, involving in a complete interaction.

Researches demonstrate how the thixotropic behavior appears when a pressure, stress is done on it. Once it achieves the limit of yield stress, the behavior also changes and the flow should be constant. For that stage, the flocculation, nucleation, distribution size grain, and the pressure is considered. The importance to know how to calculate the open time which let concrete to flow without any problem along the extruder. The aim about a high density of concrete to achieve an almost zero deformation or zero slump on concrete. Most authors used several trial mixes before choosing the best mix composition for its objectives. On size distribution to fill voids, a solution is to use materials with smaller size distribution. Güneyisi *et al.* [89] uses Nano-silica (NS) with a size of 14 nm, and demonstrated with 4% have strong effect on the fresh characteristics and compressing strength. The use of powder materials does not always improve the flowability, despite an increase in the packing density of the granular skeleton. Güneyisi *et al.* [89] also demonstrates that Fly Ash (FA) with NS increases the slump and decreases the elastic strength of the mortar. Increasing NS content from 0% to 4% resulted in 16.7%, 23.9%, 27.1%, and 71.1% increment of the compressive strength[39]. The incorporation of silica fume, fly ash, or other supplementary cementitious components in concretes exerts a very strong influence in reducing permeation capacity.[90]

Quanji *et al.* [91] used a nano-clay with 3 nm grain size. In that research demonstrated how magnesium alumino silicate clay had a significant effect on the rate of change of thixotropy of the pastes. However, they recommend to use between 0.5 to 1% because above this percentages the change on thixotropy decays. Some research have used superplasticizers to improve the buildability and the extrudability of concrete.[11,66,77–79] Also, The addition of nanoclays have demonstrated to enhance the density of the mortar, and also increasing the greed strength of the walls.[11] Kazemian *et al.* [92] used attapulguita with an average particle length of 1.75μm and an average radius of 3nm.[92] found a considerable increase in viscosity and cohesion of mixture was observed as a result of small addition of Nano-clay.

Fibers

On the 3D printing mixture, the material to replace the thicker aggregate is the fibers and also the metallic reinforcement. Fiber are the replacement due to the help on b Synthetic high performance fibers like steel, glass or carbon fibers, have high tensile strengths, up to 6000 MPa. And also a Young's moduli around to 400 GPa. These fibers have proven a considerable potential for developing high tensile/flexural resistant cementitious materials on 3D Printing reinforcement.[17] Also, demonstrated how small fibers have an important role on small cracking, while longer fiber will help with larger cracking. Fibers behave as thicker aggregate which also have a singular behavior of order and distribution when they are pumped. Fig. 2.21

The research of Al-Qutaifi *et al.* [76] are used steel fiber which demonstrate to have an increasing on the green strength and the flexible strength. However, some researches found that fiber can also create a blockage or did not increase the strength. Therefore, there should be more research about steel fibers. Another study now using basalt fibers is presented by Ma *et al.* [93] where there find that 0.5% of basalt is enough to have a good extrudability. Also, they considered correct to print with 45 L/minute with 75 mm/s as the extrusion rate and speed respectively. On compressive load, the filaments parallel to the stress perform high resistance. splitting tensile, bending and shearing loading, the filaments perpendicular to the loading direction show better mechanical capacity than the parallel conditions. And, the direction aligned fibers contribute significantly to the resistance when exposed to tensile stress parallel to the filaments. The samples with identical materials perform distinct mechanical anisotropy. On another researched by Qian *et al.* [94], the alignment shows that the extrusion process plays an important role in aligning the fiber in desired direction. On that study the samples with less than 1% were more affected. On mechanical properties also increases and have a difference, Qian *et al.* [94] reported that tensile strengths have a big difference at parallel and transverse directions. Some research demonstrated there are two types on enhance with fibers. The first methods the above mentioned, the mixing should contain a certain percentage of fibers. Because, once mortar is extruded

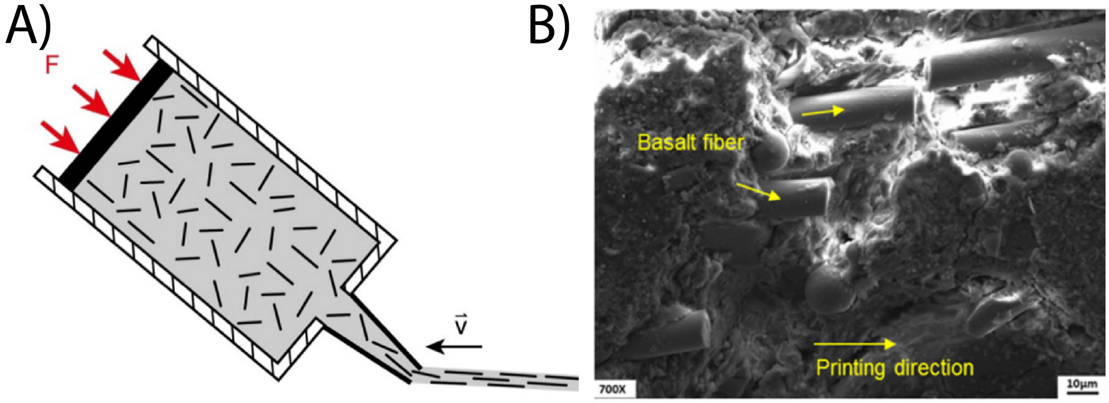

Figure 2.21: Fiber behavior against pressure and extrusion of the printer. A)Basalt Fiber alignment against pressure of the extruder.[17] B)SEM image where demonstrates the basalt fiber alignment done on a 3D printing samples.[18]

the fibers tends to align enhancing, flexural strength, compressive strength and shear resistance. The study done by Marchment and Sanjayan[19] the increasing moment strength in flexural by 170%–290%. They design a nozzle which advantage the alignment of fibers.

So, to also enhance mortar as reinforcement, on literature proposes and uses the fibers outside the mixing. Once the 3D printer passes the line and the cement begins to stay on its static yield stress, the fibers are used and dispersed along the line. This method enhanced the inter-layer bonding. Because according with Marchment and Sanjayan[19], fibers created links between layers and the printing has higher elastic modulus along the wall.

Chemical Reagents

Superplasticizers can reduce the water requirement while maintaining workability and improving strength. Fig. 2.23 illustrates the working mechanism of the superplasticizer. Cement particles are dispersed by a repulsive force generated by negatively charged superplasticizers, and the entrapped water is released. Therefore, the flow characteristics of concrete are improved. XRD and SEM analysis indicate that the addition of superplasticizer does not alter the types of hydration products but improves the degree of crystallinity and results in highly amorphous hydrates[20].

According with Chandra and Björnström[95] the most used superplasticizer is based on lignosulfonic acid (LS), melamine form-aldehyde sulfonic acid (SMF), naphthalene formaldehyde sulfonic acid (SNF) and polycarboxylic acid (CE). Their function on the flow characteristics, setting time, and yield strength changes considerably even from the same group. Due to, the different molecule's structure and chemical configuration chosen as superplasticizer.

On the other hand, accelerators are used on traditional and 3D printing. Those have a chemical composition which increases or accelerates the hydration of concrete, and also, the open time will decrease.[95] Concrete materials for 3D printing require a short setting time to promote the material to acquire enough early strength right after being deposited from nozzles. Setting accelerators are a class of admixtures commonly used for concrete to produce an

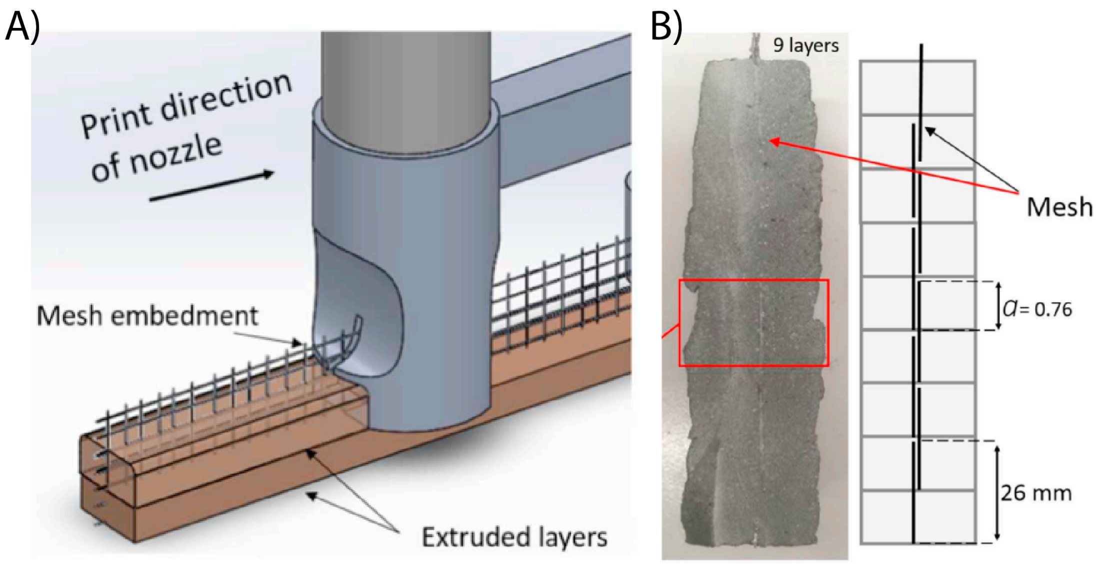

Figure 2.22: Design of nozzle to extrude fiber. A) The nozzle created by Marchment and Sanjayan [19]. B) The sample with the fiber dispersed parallel to the extruded layer.

immediate set.

Finally, with the opposite function are the retarders which have the function to be adsorbed on the surface of cement particles to form an insoluble layer. This process delays the hydration of cement. The most used are based on Sodium gluconate (SG), tartaric acid (TA), citric acid (CA) which favorable results in some researches [95]

2.5.2 Mechanical properties

Compressive strength is the maximum compressive stress that, under a gradually applied load, a given solid material can sustain without fracture. Concrete compressive strength requirements can vary from 17 MPa for

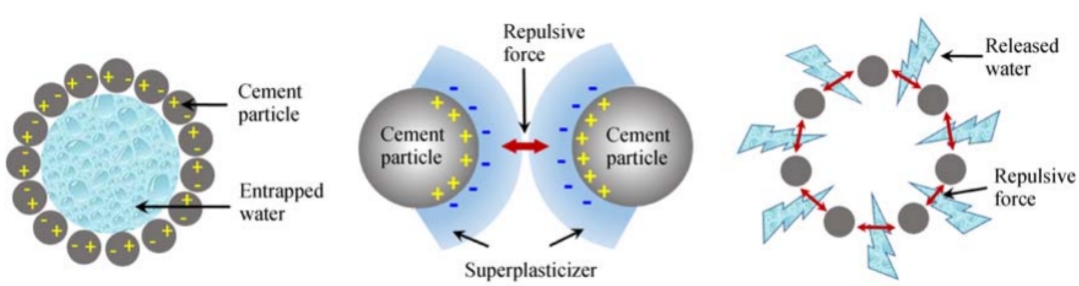

Figure 2.23: Action of superplasticizer on cement particles. [20]

residential concrete to 28 MPa and higher in commercial structures. Higher strengths up to and exceeding 70 MPa are specified for certain applications. Although the w/c ratio is dominant in determining concrete paste strength, studies find that air entertainment reduces strength significantly due to high porosity on the samples and insufficient heat concrete hydration. Strength is also influenced by curing, test direction relative to interlayer joints, as mentioned before, and in cases of fiber reinforcement, the fiber orientation. These factors affect and interpret compressive and flexural test results reported by various researchers. By high-pressure extrusion, air content is reduced, and strength increased, as shown in Fig. 2.24 With reduced air entertainment, the fiber alignment , and raw materials gradation significantly increases the flexural resistance and compressive Resistance.

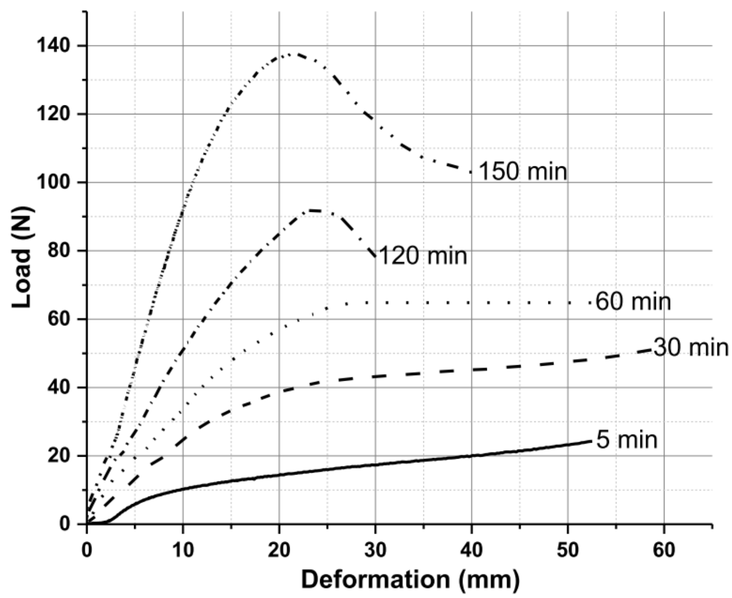

Figure 2.24: Stress vs strain figure of Flexural behavior of cast and extruded samples of fresh cement mortar age about time. 0 - 150min.[21]

By the anisotropic behavior on concrete samples. The load should measured along all the axis as fig. 2.25

This is because, depending the extruder and nozzle system, the layer could have a layer by layer path parallel or perpendicular from the load. This also converge into changes of the results. However, the unique results which demonstrate difference is the changing of dosage, using other materials, longer or shorter fibers, and also, a well developed nucleation due to a mixture with diverse size grain of materials. One study done by Paul *et al.*[2] demonstrated how a load by x, y and z direction can alter the stress vs strain diagram.

The influence of the position of the joints is clearer in the results of Paul *et al.*[2] compressive and flexural strengths were consistently the lowest in testing the direction a) of Fig.2.25

Various mechanisms could have led to these contradictory results, including reduced air content, segregation by printing non-optimized material, and curing conditions. Reduced air content could have led to the strengthening

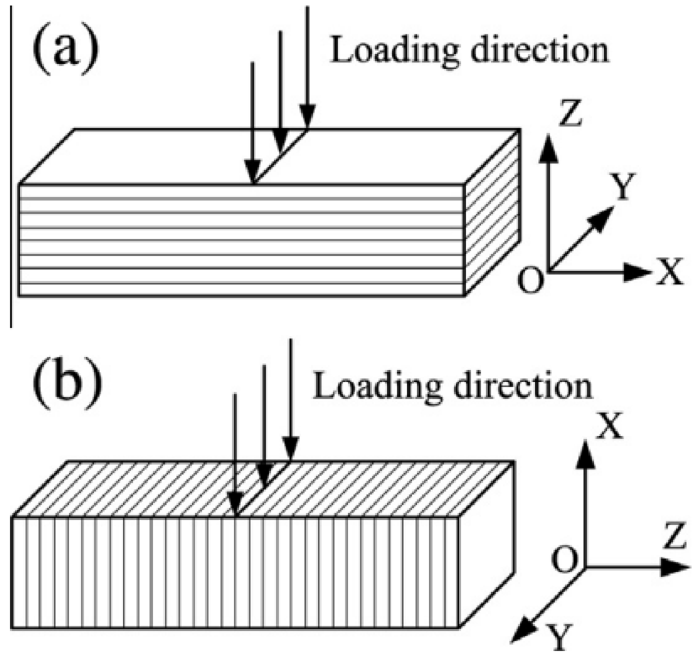

Figure 2.25: Due to the anisotropic behavior of the material, the Compressive strength changes along a different loading direction.[21]

in the specimens of Nerella *et al.*[75], Le *et al.*[59]. moist cured printed samples under damp hessian, while the cast specimens were cured at 20 C after stripping at the age of 1 day until the test age of 28 days, which could explain lower strength development in printed samples. However, flaws in the specimens due to segregation could also have caused lower strength of printed models

Flexural strength, considered on walls, will depend on the maximum bending stress's neutral point, directly proportional to the distance between the peak and the neutral point.[17]

Finally the quality also changes the results of the mechanical properties. If the layer is not well developed all the mechanical properties can fail. That is why At the beginning, the printing quality is considered to be good, but with time the hydration process accelerates and matrix becomes harder. So, the properties have to be analyzed along the time. On traditional concrete the development of this analysis is to enclose on a cylinder a mixture of concrete, and then the mechanical properties such as compressive strength, flexural strength and the young modulus will be measured. The cylinder is measured on 7 days, 14 days, and 28 days. The same process is developed on 3D printing, with the difference that the specimens are printed and analyzed. The analysis are also used on mixture of mortars, however those just determine how high is the density, and if the hydration of cement affects along the time.

In conclusion, In 3D concrete printing, direction and printing time significantly affect the overall load-bearing capacity of the printed objects. So, it is essential to consider the anisotropic properties of 3D printed objects and

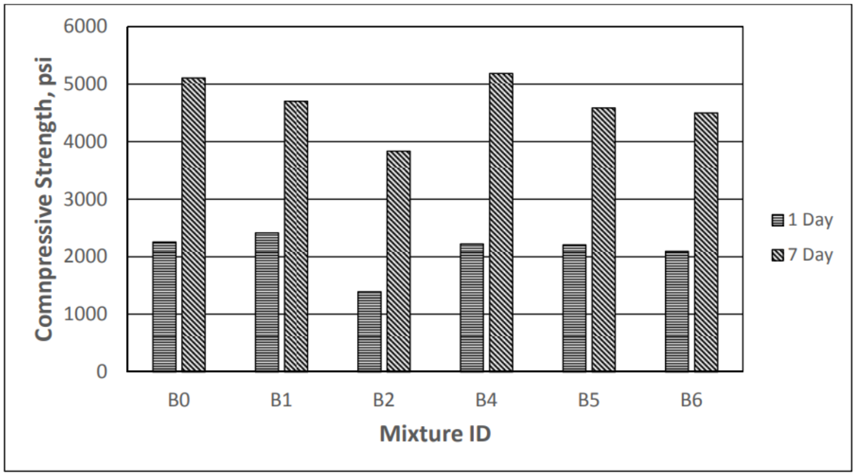

Figure 2.26: Compressive strength results along the time 1 and 7 days.[22]

proper printing speed when designing the structures.

2.6 Reinforcement

There are several tries of materials used on construction, and nowadays on 3D cementitious material printing. There are several reasons why to try many materials. As was mentioned above, some materials improve the gradation choosing them with a different size grain. Other materials where chosen also to increase the nucleation with stronger inner interaction. Finally, some were chosen to enhance the extrudability like retarders, super plasticizers. One concrete is outside the buildability. So the green strength and the compressive strength should be enough to support all the lines of concrete above, and also its self weight. Once everything was printed, the hydration, gradation, nucleation, and inner interaction takes the main importance, and will show how the mixture was correct. Some literature measures the progressive Resistance along 7 days, 14 days and finally at 28 days. there should be an increasing. which should have similar results as traditional results . Therefore, there should be an improvement on green, elastic and compressing strength. That is how 3D printing have many ways to improve the Resistance, by software or by partially manual job. The reinforcement enhances all the structural strength. Is like an additive on stress strain resistance. By software, 3D printing can be enhanced by the innovation

2.6.1 Infill Concrete printing setup.

The 3D concrete printing house process is similar to CC, an inner and outer wall is printed in layered fashion, as well as a cellular inner structure. This feature let printing to develop new infill technologies for houses. So, there are many possibilities such as new infill patterns as the fig 2.27 shows.

Also, engineering could find more rod reinforcement structures allowing a seismic Resistance building. The infill can also be filled with diverse types of natural and synthetic fibers, giving the well isolated houses against sound, temperature. The fibers can enhance mechanical properties and also can increasing the thermal remaining on the structure. Finally, infill can be also increase the material extruded perhaps the holes and space between walls will be less giving in certain cases and patterns and increase on strength properties, Fig2.27[96]

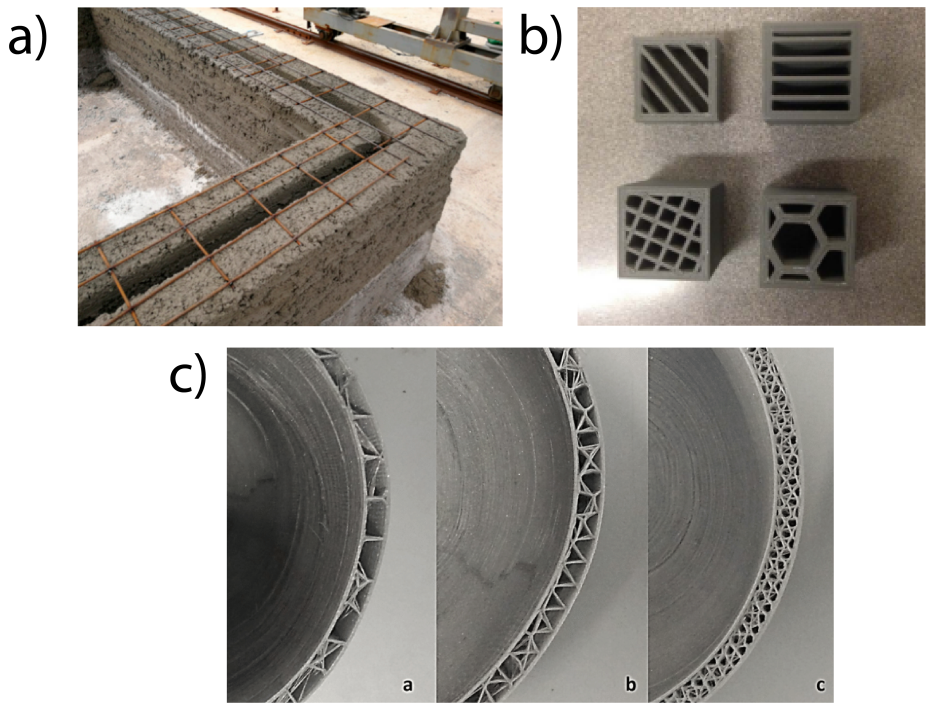

Figure 2.27: Different infill changes on 3D Concrete printing. A) A type of reinforcement with rod plate. B) Some patterns used on 3D printing. C) Different percentages of infill[6]

Nevertheless, the printer configuration used the material changes the properties looked for, the extruder used, the parameters to consider, and more other properties because the configuration does not change the movement of the head Printer. However, it changes how the filament or material is printed or pumped.

2.7 Nanotechnology on 3D concrete Printing

Nanotechnology is sub discipline of chemistry, engineering, or other fields. It represents the convergence of many areas.[25] Nanotechnology is a sub discipline of chemistry, engineering, or other fields. It represents the convergence of many areas. As science advances, many science brands become more specialized and accurate, leading to entirely new avenues of inquiry, even 3D printing. At the same time, the latest technologies and materials are also growing using nanotechnology. Nowadays, Researchers and enterprises prefer Nanotechnology due to all the advantages incoming on materials and how the enhancement increases properties of the material with low qualities such as the biomedical and electronic industries. Also, it improves productivity and quality while primarily reducing costs. Much research on nano-concrete has concentrated on the suitability of different nanoparticle types to enhance various concretes' features, their optimum dosages, price, and others.[97]

Science considers nanoparticles those with diameters less than 100 nm, which results in their behavior of interaction with atomic, molecular, and ionic behaviors. Due to these behaviors, nanoparticles are considered an option in high-performing technologies such as concrete development such as fig.2.28.[97] For instance, in building, some alternative binder materials such as fly ash, slag, silica fume, and some nano clays are used to replace cement partially in concrete due to decreasing cement consumption. Therefore, the construction industry could take a bio-friendly future.[98,99] The main characteristic of nanoparticles is that they have a high surface-area-to-volume ratio.[100] Chemical reactions at the interface mainly influence the behavior of such materials with a high surface area. Also, these nanoparticles can quickly form agglomerates if not distributed adequately into the mix. On the other hand, the higher surface area of the particles in cementitious composite requires more water to be wetted, resulting in less free dispersant water available in the mixture in aqueous systems.[25] The use of nanoparticles in concrete could modify the behavior in the fresh state of concrete, the hardened conditions, and the physical/mechanical and micro-structure development.

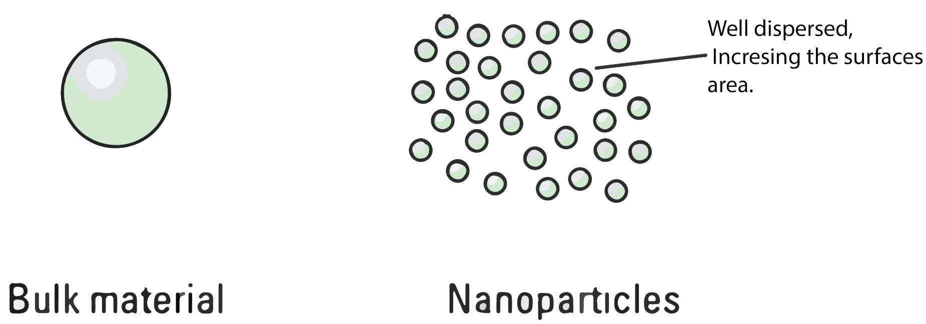

Figure 2.28: Main characteristic between bulk materials and nanomaterials.

The addition of these nanoparticles to concrete enhances several properties, including rheology and thixotropy, mechanical strengths, and durability. An example is nano-silica. The aim of applying ultra-fine additives like nano-silica in cementitious enviroments is the improvement of characteristics of the plastic and hardened material. Micro and nano-scaled silica particles have a filler effect by filling up the voids between the cement grains.[23]

2.7.1 Nanoparticles Effects

Many researchers used different types of nanoparticles in concrete to enhance specific properties.

Nanomaterial	SiO_2	TiO_2	ZrO_2	Al_2O_3	Fe_2O_3	Nano fly ash	Graphene Oxide	CNF	CNT	Nanoclay	Zeolite Natural	Zeolite PWC
Heat of Hydration	✓	✓		✓					✓			
Rheology												
Slump reduction	✓	✓		✓	✓						✓	
Pressure on formwork										✓		
Green strength increased												
Reduced setting time	✓	✓								✓		
Viscosity and yield stress increased	✓									✓		
Mechanical	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Microstructure	✓						✓	✓	✓		✓	✓
Shrinkage												
Drying shrinkage											✓	✓
Autogeneous shrinkage									✓			
Durability												
Water absorption		✓	✓	✓	✓						✓	✓
Oxygen permeability												✓
Chloride ingress		✓									✓	✓
Corrosion rate									✓		✓	✓

Table 2.2: Nanoparticles and its enhancement on the different properties on 3D concrete Printing.[26]

Hydration cement

Hydration of cement and water is an exothermic chemical reaction. The temperature generated during the hydration process depends on the total heat evolved, the rate of evolution, and the system's thermal efficiency. Therefore, many different reactions often coincide in the hydration process. As the reactions continue, the products of the hydration process gradually bond together with the aggregates and other components of the concrete to form a solid mass as the fig. 2.20 and Fig.2.18. Typically, cement presents four types of minerals alite, belite, aluminate (C_3A), and tetra calcium alumina ferrite (C_4AF). The exothermic reaction occurs between tricalcium silicate (C_3S) and water as shown in the peak on the figure 2.29. This reaction indicates at what rate the minerals are reacting by monitoring the heat using a calorimeter. According to Zhang *et al.* [24], the peak is related to the precipitation of C–S–H gel, and CH corresponds to the acceleration or post-induction period. Nanoparticles help in growing further regions of the precipitation of C–S–H (form new peak) and induce growth of new regions of C–S–H gel. Also $nano-TiO_2$ changes the heat evolution of traditional heat flow. Nazari and Riahi [101] monitored the heat release in concrete with Al_2O_3 nanoparticles at different percentages of binder weight percentages 0.5%, 1%, 1.5%, and 2%. The total heat generated increases as the percentage of nanoparticles increases. However, the peak time decreases as the Al_2O_3 nanoparticles increase up to 1.5%. At 2%, the peak was similar to the control mix. However, all represents the same pattern flow, Though the total heat increases with time, the heat flow reduces after a certain time period.[25]

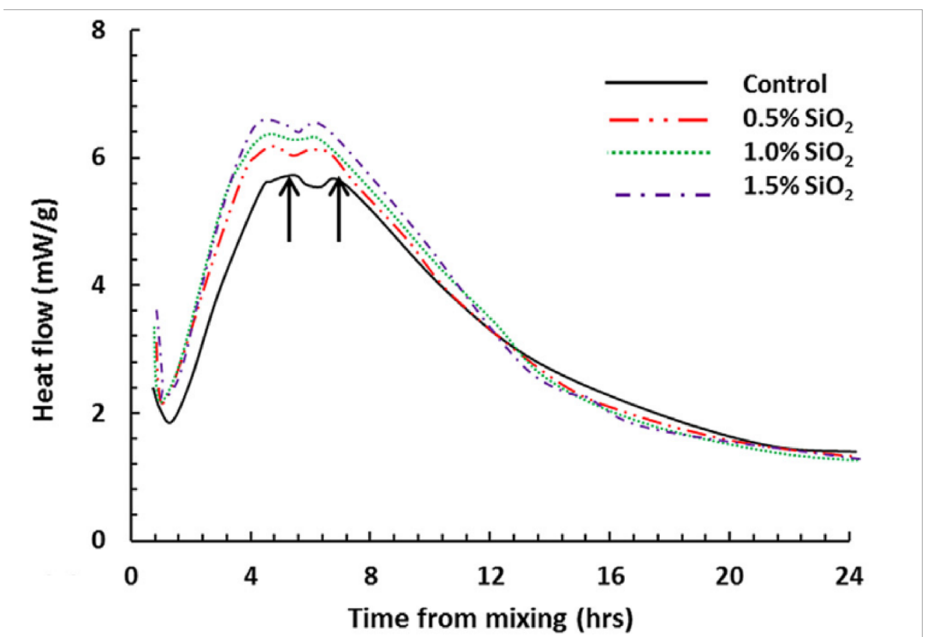

Figure 2.29: Influences of nano-SiO_2 addition on the heat of hydration of cement pastes.[23]

According with 106 [102], the pozzolanic reaction, silica and alumina react with calcium hydroxide to form additional hydrate phases, primarily C–S–H. Then, in cement pastes containing zeolite, lower calcium hydroxide content correlates with higher quantities of C–S–H, which increases the pozzolanic reactivity of zeolite in cement-based material. The inclusion of nano-size zeolites in cement-based materials swallows hydroxide calcium in the matrix, produces silica gel in the cement paste, and merges with the cations to form solid bonds and reduce the porosity of concrete. Zeolite reactions merge to reduce porosity along the time, increasing the packing and density of concrete.

Pozzolanic reactions of nanomaterials in 3D concrete Printing

The greater surface area of nanoparticles added to the binder may lead to higher chemical reactivity. Typically, nanoparticles reduce the number of nano-sized pores within C–S–Hs and strengthen the nanostructures of cement composites. The micropores around 50 nm or less are significant for drying shrinkage and creep, while the macropores bigger than 50 nm affect strength and permeability.[103] So, the uses of $nano - SiO_2$ should increase the interaction on cementitious materials and fill the pores, also increasing mechanical properties. Because C–S–H expands during hydration and adsorbs free water. According to with[104], Si is connected with four atoms of oxygen, creating a tetrahedron, the basic building block. The addition of nano-silica in cementitious materials increased the durability by increasing the stiffness of C–S–H, which is more resistant to calcium leaching.

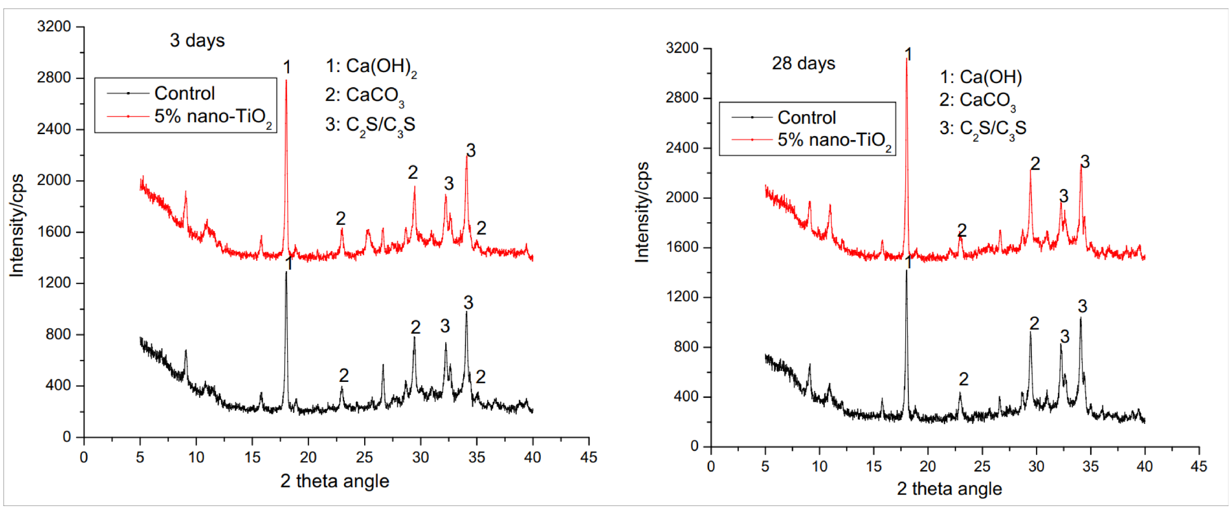

Figure 2.30: Influences of nano-TiO_2 addition on crystallization of cement pastes.[24]. XRD of 3 days and 28 days of cement before and after adittion of nano-TiO_2

The number of bonds done by the addition of $nano - TiO_2$ increases. The increase of C-S-H bonds demonstrates the increase in heat flow evolved on time discussed in the section before. The research done by Zhang *et al.*[24] shows the increase of the peaks on XRD. A comparison between $nano - SiO_2$, $nano - Al_2O_3$, $nano - TiO_2$, and $nano - ZnO$ done by Liu *et al.*[26] shows how $nano - SiO_2$ makes the microstructure of hardened paste more solid dense and accelerates the cement hydration process. Furthermore, the mechanical strength and flexural strength of mortar improve using the correct percentage of nanoparticles at different ages. An exceeded amount of nanoparticles created glomerates. According to with Liu *et al.*[26] the correct percentage to use on cementitious mixes is 3%. However, the uses of $nano - SiO_2$ result in performance degradation. The uses of $nano - Al_2O_3$ and $nano - TiO_2$ decrease compressive and flexural strength. Nazari and Riahi[101] concluded that the higher surface area of nano-silica produces more silica networks at the surface, which can, in turn, extend pozzolanic reactivity and also form a substantial amount of C–S–H.

Rheology with nanomaterials in 3D concrete Printing

The use of nanomaterials on concrete can also enhance the rheology properties. There are some nanomaterials used, such as nanoclay and $nano-SiO_2$ used in 3D printing. According to with Kim *et al.*[105], nanoclay improves the green strength of self-consolidating concrete (SCC). However, the flowability decreases due to the high consolidation of the cementitious materials with nanomaterials. Such high early green strength can significantly reduce pressure on the formwork. Also, the research found that it required less pressure (70%) with just 0.33% of nanoclay used on experimental tries.[106] Therefore, the green strength of concrete can be higher with the addition of nano-clay in concrete. The higher surface area of nanomaterials leads to higher water or chemical admixture demand. Thus, concrete viscosity and yield stress increase while workability decreases by the high packing range.[107]

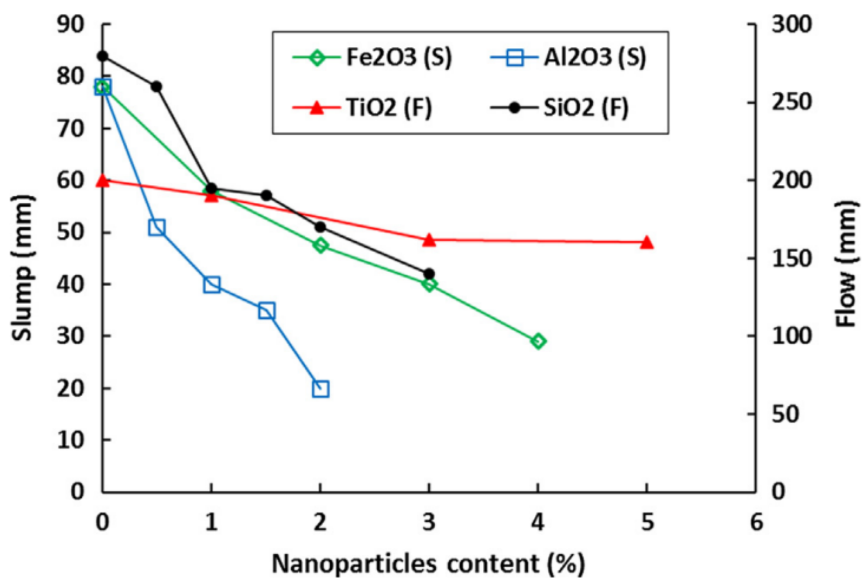

Figure 2.31: Influence of addition of different nanoparticles on slump and flowability of concrete.[24–26]

Nazari and Riahi[108] study the rheology of concrete mixing with nanomaterials and found that Slump values and L-box ratios decrease by 1.2–7.5% and 1.3–10.1% for the addition of 1% and 5% nano-TiO2 in the mixes. Due to the increase of interaction using nanomaterials, the slump decreases in the rheology properties. In both cases, the lower slump value of concrete explains by the rapid formation of C–S–H gel and the viscous behavior of fresh concrete. For the same reason, the setting time of concrete was shorter than for reference concrete

The effects of nano-clay on the compressive and tensile strength of mortar made from different sand-cement ratios where investigated by Nazari and Riahi [108]. In all mixes, significantly higher compressive and tensile strengths were observed in nano-clay mortar compared with the reference mortar.

Future with nanomaterials

Apart from the properties discussed above, different types of nanoparticles exist the researchers in cement-based materials in the areas such as thermal properties, self-healing, self-sensing, self-cleaning, electrical properties, energy storage capability, and others. One example is Magnetic iron oxide nanoparticles (IONs) can be used as the protective vehicle for bacteria to evaluate the self-healing performance in concrete environment. [109]

Chapter 3

Conclusions & Outlook

Concrete 3D printing has shown progress over the last year. This technology has developed new configurations of 3D printers to improve the quality of their products. The quality of its components has improved since the nozzles and extruders are a crucial part of having high-quality printing. In addition to that, new motors are also known to produce better printing results since they have greater freedom of movement and a more significant amount of torque in their configurations. Also, a new extrusion system has been developed, which combines the ability to use the fibers and gives a quality finish to the construction. The problem that persists in all 3D printing technologies is how the bond between layers decreases the different resistances of the material. The no bonding between layers is a problem since it gives the product anisotropic behavior, being more complex to analyze the mechanical properties in all directions. There should be more research on improving cement heat hydration interaction since it is crucial to have all suitable properties. Good knowledge of the cement's hydration temperature will help us have longer fresh times and greater manageability of the material and be able to have a more exact setting of the mortar. Finally, an almost null porosity already has a composition with high densities.

Today, different technologies and research dedicated to the production and improvement of 3D printing of concrete are known. One of the fundamental advances that have a current boom is nanomaterials. Since they replace the traditional materials and increase or improve mechanical properties demonstrated today in this review project. Likewise, it has been demonstrated how the number of nanoparticles used also varies the results of the mechanical and rheological properties. Therefore, it is essential to consider and mention that nanoparticles are essential and preferred for their high degree of the contact surface.

Furthermore, it helps the concrete mix have high degrees of compaction since it eliminates porosity. In addition, nano-silica has proven vital to having greater green strength in construction. Nanotechnology is still growing in this branch and presents incredible advances and discoveries in technology. However, there is still research that needs to be considered on 3D printing. There should be detailed research on how to increase the addition of layers. In addition to that, how to have greater manageability without much effort. More research should be on new materials that can replace cement and improve or achieve the same properties that this material provides. It is essential to mention that the future replacement of cement should be considered since the pollution exerted in its production continues to be one of the highest. Today, fly ash, silica fume, and gypsum are considered to replace cement. However, the production of this material is not cheaper than that of cement. Further research with nanoparticles is expected in the future since today, and there are ideas of self-compacting and self-regenerating concrete through bio-friendly systems. In addition, this technology does not exist in Ecuador and has a high clay capacity. The idea of the possible development of this technology in the country is presented. The low costs would be even higher due to the high quantity and variety of clays existing in Ecuador. The nano clay presents a significant contribution to this technology. We hope further progress will be made in the coming years.

Finally, to end this research project, this project is presented so that future projects can be rooted and generated in this country. Little research in the field of construction must end since the high environmental pollution generated either by waste or by the production of cement is not being considered. The most important thing for the realization of a project related to the 3D printing of concrete is to know adequate rheologies for a suitable extrusion and a good impression.

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