

A Study of Geopolymer Fresh Properties & Mechanical Properties in 3D Concrete Printing: A Review

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Abstract: Due to its enormous potential to reduce wastage, labor needs, construction costs and expand design freelancing, 3D concrete printing has become broadly applied in the construction and building areas. One of these is Geopolymer concrete (GPC) who has been found by researchers as the replacement of normal concrete. This report presents the general review of 3D printing by studying the usage of fly ash and blast furnace slag as material in geopolymer 3D concrete. There are 62% of the previous research studies of geopolymer in 3D construction. There are about 96% of the whole previous research used fly ash and 63% used ground blast furnace slag as the alkaline active binders in the geopolymer composition. It is found that activators is needed to enhance the compressive strength of geopolymer. There are 49% of the previous researchers used sodim hydroxide (NaOH) and sodium silicate (Na₂SiO₃) as the alkaline activators in the geopolymer composition. Molarity of the activators brings the effect on geopolymer compressive strength. There are about 64.5% of previous research used molarity between 10M to 14M. Fresh properties in geopolymer become one of the key factor to develop compressive strength. It is shows that 43.75% of previous research affected the buildability and flowability, 68.75% extrudability and 56.25% for the setting time. However, some areas such as the parameters of the flowability on using fly ash are rarely present by the researchers which is need more future investigations.

Keywords: Geopolymer, 3D Printing, Flowability, Extrudability, Buildability

1. Introduction

3D printing which is additive manufacturing has been widely used in the construction and building areas [1,2]. Geopolymer has been introduced after Ordinary Portland Cement (OPC) to reduce the greenhouse emission due to industrialized process such as cement binders, aggregates (coarse & fine), followed by the effect in cement hydration process [3]. Geopolymer is one of the efforts to reduce the uses of cement binders such as fly ash that undergoes procedure known as geo-polymerization involving reaction of aluminosilicates material with alkaline liquid benefiting in low carbon dioxide [5,6].

Materials for geopolymer concrete (GPC) needed to be focus on in order to complete the process to reduce the carbon emission. Researchers discovered five GPC mixtures in order to determine the amount of applications in 3D concrete printing which are fly ash (FA), ground granulated blast furnace slag (GGBFS), silica fume (SF), alkaline reagent, water and river sand. These materials have significant effect on compressive strength of GPC at 28 days with addition of alkaline activators [4].

The paper aim to perform a general review of 3D construction, the chemical composition of 3D concrete, fresh and mechanical properties of 3D concrete printing (3DCP). Previous studies by some researchers shows that materials in GPC with certain amounts of activators have the tendencies for extrusion in 3D concrete printing. By conducting the research review comprises the impact of using geopolymer to help in properties such as buildability, flowability, extrudability and setting time. An important feature of geopolymer is they accomplished the mechanical properties of compressive strength, flexural strength, tensile strength and yield strength. The understanding between correlation of mechanical properties and the application of alkaline activators is essential for engineering studies to interpret the results. To ensure compliance with regulations, two materials have been picked to incorporate between the cement binders and alkaline activators. The relations are greatly applied to verify the strength and workability of GPC in 3D printing.

2. Composition of Geopolymer in 3D Construction

GPC is such an emerging technology that has been used globally to create more sustainable development for lowering gas emissions where it was first introduced by Davidovits of France resulting technology in specialized industry [7,8]. This geopolymer is created from geologically sourced silicon and aluminium by production of FA with the similar chemical makeup of zeolite [9]. Polymerization include the process of Si-Al minerals in alkaline environment that form up a chain structure of Si-O-Al-O links. GPC has longer service life, zero carbon emission, reclaimed industrial waste, durable and high strength for its structural applicability [10].

Fly ash (FA) has several small components materials which are magnesium oxide (MgO), vanadium, manganese, phosphorus, germanium and gallium. It also categorized as Type F (low lime content) and Type C (20% higher lime content) with a shape of spherical-glass that has a density of 2.2 to 2.8 g/cm³. However, there are slightly difference between these two class where Type F fly ash need alkaline activators since the rate hardening is faster while Type C does not need any alkaline activators [13].

Blast furnace slag (BFS) is non-metallic product consisting essentially of silicates and aluminosilicates with iron blast furnace made up of 95% constituents (silicon, calcium, aluminium, magnesium and oxygen) [8]. Extensive cooling and freezing turns molten slag to fine aggregates smaller than 4.75 mm No.4 sieve in crystallization. The blast furnace is made up of iron oxide (ore, pellets, sinter), fluxing stone (limestone or dolomite) and fuel (coke) in terms of BFS components [9].

Geopolymers binders made up of alkaline activators and additives are added to promote rapid development of GPC strength. Some of the alkaline activators used are SiO₂, Al₂O₃, Fe₂O₃, CaO, MnO, TiO₂, P₂O₅, Na₂O₃, K₂O, SO₃ and MgO as illustrated in Figure 2.1. The chart data reveals that SiO₂, Al₂O₃, Fe₂O₃, CaO and MgO are commonly used activator which shows higher than 10% studies from previous researchers. The previous experimental studies of geopolymer mixture materials can be seen in Figure 2.2. It is very clear that most researchers used FA binders in the mixture design for geopolymer concrete. In addition, due to the spherical shape particle of FA and high content of FA allows for lower binder ratio which facilitates better extrudability.

Moisture exposure helps pozzolan interacts chemically with calcium hydroxide to generate compounds with cementitious characteristics at ordinary temperatures according to American Society for Testing and Materials (ASTM). Identification that Class F fly ash that contains 15% low lime quantities possessed greater combination of silica, alumina and iron (greater than 70%) than FA Class C [10]. Higher lime content (30%) gives the fly ash self-hardening which applies in the study where materials used is for demonstrating the strain hardening of geopolymer concrete (SHGC). Sodium based

(Na-based) with 8 molarity of NaOH and sodium silicate solution ($\text{SiO}_2= 29.4\%$ and $\text{Na}_2\text{O}= 14.7\%$) while potassium based (K-based) made up of 8 molarity ($\text{SiO}_2= 24.8\%$ and $\text{Na}_2\text{O}= 11.2\%$) and oil coated PVA fibers with 1.2 wt.% oil content is used for developing compressive strength of SHGC [11]. Sodium silicate has been used by many researchers as activator with different composition of materials (SiO_2 , Na_2O , water) [1,12]. The use of fibres helps to increase the flowable state of geopolymer and increase the compressive strength of up to 41% higher due to air entrapped in the structure. Percentage of 0.0056 wt.% poly-propylene fibers as activators is added to avoid shrinkage in geopolymer mixtures [1,11]. But some researchers focused on the addition of 1% fibers by mass to increase the flexural strength of concrete. Previous research has established that the molarity in concentration produced better strength in geopolymer concrete. Superplasticizers has been widely used in production of fly ash-based geopolymer to increase flowability of mixtures. It is because superplasticizer contains materials that can hold water in the geopolymer paste that provides better extrusion during printing [13].

According to investigation on the impact of GPC, the used of FA Class F causes binder temperature to be increased. It comprises 70% of SiO_2 , Al_2O_3 , Fe_2O_3 with less than or equal to 5% CaO. NaOH and Na_2SiO_3 are the alkaline activators used with NaOH pellets accounting for 98% of the total [14]. The pellets have a SiO content of 34.64%, Na_2O content of 16.27% and water content of 49.09%. fine aggregate with a 0.88% water absorption rate is used in Naphthalene superplasticizer to improve the workability of the mixture of 40%. Therefore, a superplasticizer content for 0 to 2.5 wt.% is added to obtain sufficient of workability. Moreover, the use of SP resulted in increased of 136% relative slump and N-based SP reduced the activator slag ratio caused an improvement in mechanical strength [2].

The 8.0 M concentrations gives positive impact on compressive strength with FA-based geopolymer activated only by NaOH solution and Naphthalene-based SP [11]. While the usage combination of NaOH with sodium silicate solution with the molarity of 10 and molarity of 12 (12M) is used in development of alkali activated slag [13,15]. The replacement of GGBS with Sugarcane bagasse ash (SCBA) shows consistency of compressive strength for 3,7 and 28 days when the concentration of SP is increased to 14M with amount 6 kg/m³ [16].

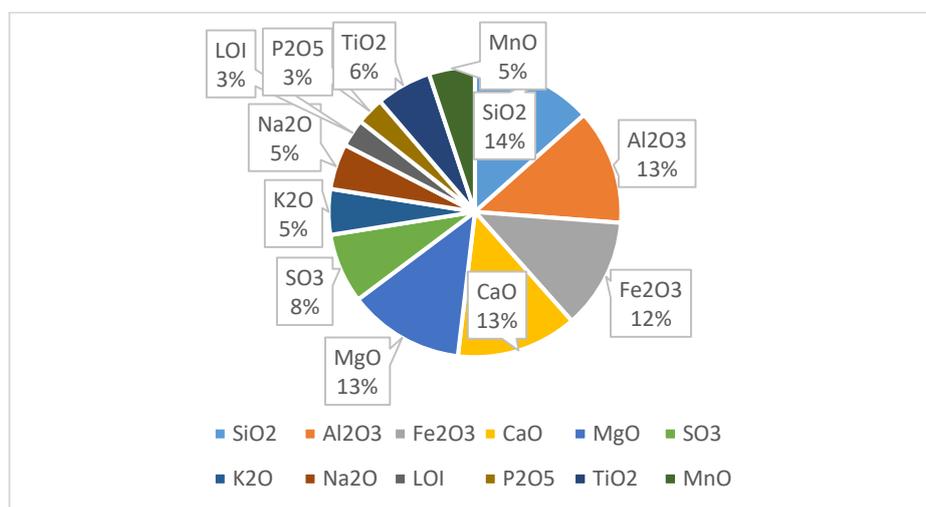


Figure 1: Previous studies of chemical compounds used for geopolymer mixtures

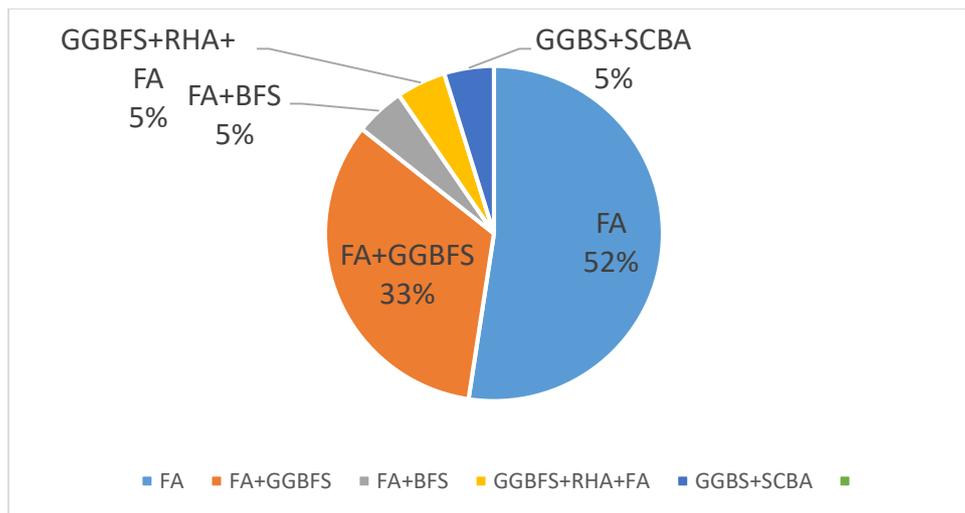


Figure 2: Materials mixtures of geopolymer concrete

3. Mechanical Properties

One of the important criteria in mechanical properties is strength and the strength is determined by various of laboratory test of geopolymer 3D printing. Recent research on geopolymer concrete found that the production process, curing period and curing temperature all have significant impact on the compressive strength of the material [17].

3.1 Compressive Strength

A few factors that affect the compressive strength in geopolymer concrete are specimen's size, material used, the molarity of concentration, curing condition and temperature. There are two types of curing for geopolymer which is ambient curing and oven dried curing. The dissolution of sodium hydroxide (NaOH) shows lower value for slump than sodium silicate [14,17]. It is found that the aluminosilicate materials resulted in maximum value of compressive strength (18 MPa) which is useful for geopolymer mixtures. However, geopolymer compressive strength can be increased up to 42.5 MPa (20%) by using the concentration of NaOH(14M) for 7 days [19]. One of the researchers reviewed that the polymerization process has increased the compressive strength with longer curing periods which is more than 24 hours as can be seen in Figure 3 [18].

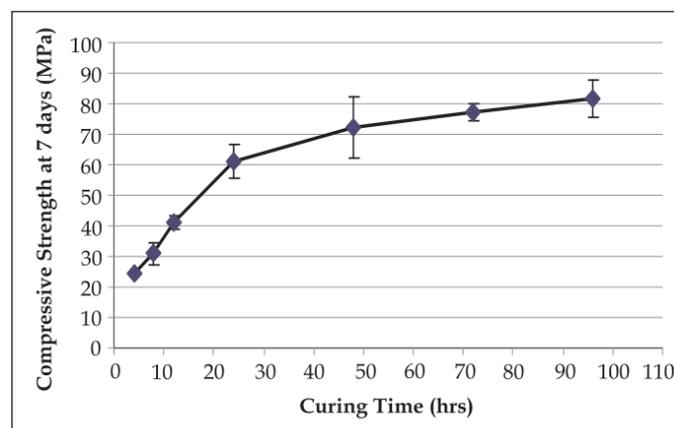


Figure 3: The effect of curing days on compressive strength of geopolymer concrete

3.2 Effect of chemical activators on compressive strength of Geopolymer Concrete

The compressive strength of geopolymers alter over time as a result of the mixture design which includes a variety of precursors, activators and variable ratios between them as well as water/solid ratios.

The usage of 1kg binders developed compressive strength with the curing period of 1,3,7 and 14 days depending on the Si to Al ratio [3,14]. This is because concrete gains its strength when moisture content retained within longer period of curing. An experimental study is carried out by using limestone and aggregate with water/binder ratio of 0.4 resulted in increased of compressive strength up to 70 MPa [2]. When cement is replaced with binders such as FA and ladle furnace slag (LFS), the compressive strength drops. The combination of GGBS and FA gives high bond strength causing the structure to be more compressible[15,20].The replacement of GGBS with SCBA increased up to 30% of the control mix because SCBA anticipates water demand. Other proportions where 5% replacement of GGBS shows changes in compressive strength but 15% replacement is much better for alkali activation [21]. Other than that, compressive strength shows relatively high (53.03 MPa) with higher amount of activators concentration (10 to 14M) in 28 days of curing periods [3]. Conversely, usage Palm Oil Fuel Ash (POFA) resulted in the rapid development of compressive strength 65.45% (7 days), 60.3% (14 days) and 62.7% (28 days). The effect of curing days on compressive strength of geopolymer concrete is illustrated in Figure 4 [7].

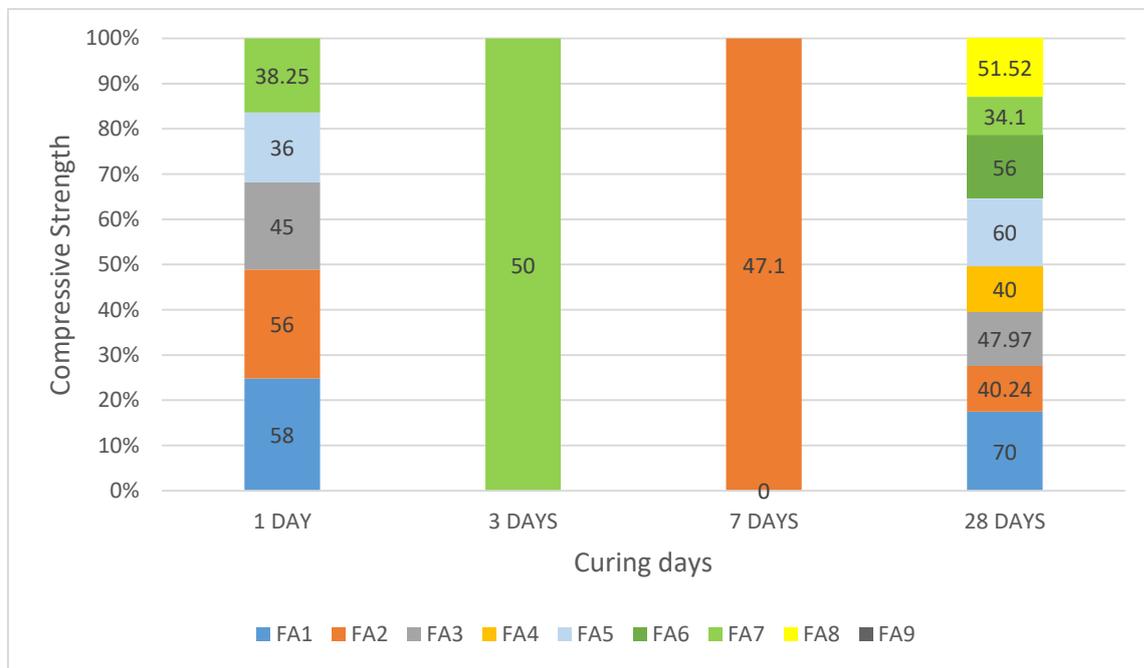


Figure 4: The effect of curing days on compressive strength of geopolymer concrete

Nevertheless, compressive strength decreased with multi-compound activators by using only NaOH solution but high compressive strength can be obtained if the multi compound activator ($\text{Na}_2\text{SiO}_3/\text{NaOH}$) amount used is 2.5. It is found that compressive strength of slag mortars activated by NaOH solution (4% and 5% Na_2O by mass of slag) were much lower than slag mortar activated by multi compound activator composed of 30% by mass of sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O}=3.4$) and 70% by mass of NaOH [26].

4. Fresh Properties of Geopolymer 3D printing

Flowability, extrudability, buildability and setting time are examined as the main features of printing materials in fresh condition in most extant literature. The contradictory demand is the ability of the materials to be fresh enough to be transported in construction-scale 3D printing [16].

4.1 Buildability

A study found that viscosity of geopolymer has recovery range from 20% to 25% because geopolymer does not have hydrodynamic (thixotropic) abilities and will cause breaking problems [24]. An experimental study by using microwave heating recover 100% accelerating polycondensation of initial recovery by heating filaments for 10 seconds allows the extrusion of geopolymer easily without deformation. The injection technology is better than casting method because of the less deformation when used injection method on plain samples [13].

4.2 Flowability

Lower yield stress resulted in better pumpability and flowability of geopolymer in 3D printing. Optimum yield stress which allows easier flow of geopolymer extrusion because low yield stress does not hold the shape after extrusion which results in collapsing and self-levelling [12]. Another important finding was that the evaluation of geopolymer flowability using flow table test [16]. In order to retain the plasticity, consistency and cohesion, 150 mm diameter of flow is used to be placed easily. Particle size distribution of 2 to 4 mm increased the flow of geopolymer paste rather than particle distribution with range 0 to 1mm which has lower geopolymer mortar flow. Binder flow rate become one of the factors to increase flowability. It is found that the flow rate is at least 170 mg/s with ratio 1:8 (metakaolin/sand ratio) to increase the printability of geopolymer paste [22].

4.3 Extrudability

Several experimental investigations of geopolymer concrete paste have been conducted based on extrusion abilities for 3D printing. Extrusion test with various parameters have been established. One of the parameters is particle distribution sand distribution which can caused blockage. A superplasticizer is used with amount of 0.3% due to increased surface area. Workability of geopolymer shows the correlation between the extrusion force and energy to produce better extrudability [25]. Geopolymer that has good printability properties have no voids and no dimensional variations for the mixture extrusion [2]. Another perspective has brought the method of reducing the material yield stress and viscosity in order to get better extrusion. However, it must depend on the geometry to be very specific flow system where shear localizes in narrow zone at the pipe or extrusion head. Both yield stress, viscosity and ability of lubrication layer gives radically changes with water content. For a typical layer of 1mm and 10 cm, the flocculation of the material after deposition must allow the initial yield stress between couple tens and couple thousands of Pa [9]. This is because the yield stress can reach value as high as hundreds of Pa where it affected the final deposited layers. This behavior relates to curvature of the layer deposited and has potentially causes tensile stresses. The small radius of curvature in the nozzle path may result in tearing or cracking at the outer edge of the material.

The prevention of blockage at the inside of pipe where yield stress zone needed to be in range of 0.3 kPa to 0.9 kPa. The mixtures with plastic viscosity of 38.7 kPa were suitable for pumping extrusion. To build vertical height, the extrusion must follow the finite path that positions of deposited material is repeated in every layer. Tool path of extrusion nozzle can only be linear and direction changes are inevitable. There are several factors that limit up the speed which is flow rate of the extruded material, limitations of the position apparatus and point to point interpolation issues with robotics. The distortion of the material is resulted from cycle time between layers that change material properties which affects the extrusion [23].

4.4 Setting Time

GGBS with FA and SF helps in rapid increase of mixtures setting time from 12 minutes to 47 minutes. Other than that, setting time presented the best performance in shape retention for the first layer height (7.5 mm). Optimum values in setting time 33 minutes and 20 minutes which contributes stabilizing the shape during the deposition of upper subsequent layers [4]. An experimental test is carried out to evaluate flow stress of cement paste containing limestone powder. The print changes with time when t is 0 when the cement and water first to contact. After 6 minutes of mixing, the yield stress of the mixture

is too low to support the structure of deposited layer. After it develops for 6 minutes, the materials went back to the state that able to support multiple deposited layers. The test is continued with the same mix found that the desirable behavior is maintained through 80 minutes until 99 minutes [23].

5. Conclusion

Geopolymer mixture proportions delivers the efficiency in terms of strength and fresh properties. Activators of NaOH, sodium silicate, silica fume, aluminosilicate brings the development in geopolymer fresh properties. The concentrations used in chemical mixtures builds up the structure, enhances the flowability and extrudability of geopolymer in 3D printing. There are some recommendations where the usage of small size aggregates (sand) upgrade the flowable in cementitious materials. The study of flowability geopolymer mixture paste in 3D printing should broadly discussed to develop 3D printing technology. In general, 3D printing with reinforced structure should be studied to develop 3D structures with better compressive since the 3D printing concrete is majorly non-reinforced.

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References

- [1] Guowei Ma et al., "Micro-cable reinforced geopolymer composite for extrusion-based 3D printing," *Materials Letters* no. 235, pp. 144-147, 2018, doi: 10.1016/j.matlet.2018.09.
- [2] M.Papachristoforou, V.Mitsopoulos, M. Stefanidou, "Evaluation of workability parameters in 3D printing concrete," in *Proc. Structural Integrity '10: 1st International Conference of the Greek Society of Experimental Mechanics of Materials*, 2018, pp. 155-162, doi: 10.1016/j.prostr.2018.09.023.
- [3] V.Keerthy, Y.Himath Kumar, "Experimental studies n properties of geopolymer concrete with GGBS and fly ash," *International Journal of Civil Engineering and Technology (IJCIET)*, Vol 8, no.1, January 2017. [Online]. Available: <http://www.iaeme.com/IJCIET/index.asp/>. [Accessed Dec 2, 2020].
- [4] Dong Van Dao et al., "Artificial Intelligence Approaches for Prediction of Compressive Strength of Geopolymer Concrete," *Materials* Vol.12 no.983, pp. 2-17, 2019, doi: 10.3390/ma12060983.
- [5] Kim Hung Mo et al., "Structural performance of reinforced geopolymer concrete members: A review," *Construction and Building Materials* no. 120, pp. 251-264, 2016, doi: 10.1016/j.conbuildmat.2016.05.088
- [6] S.Kumaravel, K.Girija, "Development of High-Strength Geopolymer Concrete," *Journal of Construction Engineering Technology and Management* vol.4, no.1, 2014. [Online]. Available: www.atmjournals.com [Accessed Dec.16, 2020].
- [7] Yanguang Wu et al., "Geopolymer, green alkali activated cementitious material: Synthesis, applications and challenges," *Construction and Building Materials* no.224, pp. 930-949, 2018, doi:10.1016/j.conbuildmat.2019.07.112.
- [8] Shaswat Kumar Das, Jyotirmoy Mishra, Syed Mohamed Mustakim, "An Overvoew of Current Research Trends in Geopolymer Concrete," *International Research Journal of Engineering and Technology (IRJET)*, vol.5, no.11, November 2018. [Online]. Available: www.irjet.net. [Accessed Nov.16, 2020].

- [9] Tu.T. Nguyen, Durability of Structure Report of Geopolymer Concrete Green Concrete, December 2009.
- [10] Lahiba Imtiaz et al., "A Review of Recent Developments and Advances in Eco-Friendly Geopolymer Concrete," Applied Science vol.10, no.7838, pp. 1-56, 2020, doi: 10.3390/app10217838.
- [11] Behzad Nehmatollahi et al., "Microscale investigation of fiber-matrix interface properties of strain-hardening geopolymer composite," Ceramics International, no. 43, pp. 15616-15625, 2017, doi: 10.1016/j.ceramint.2017.08.118.
- [12] A.Kashani and T.D.Ngo, 35th International Symposium on Automation and Robotics in Construction, ISARC. Australia, 2018.
- [13] K.Korniejenko, M.Lach, SY.Chou, WT.Lin, J.Mikula,D.Mierzwinski, A.Cheng and M.Hebda, "A comparative Study of Mechanical Properties of Fly Ash-Based Geopolymer Made by casted and 3D Printing Method," 660:012005 Int. Conf. Materials Science and Engineering, 2019, pp. 3-8, doi: 10.1088/1757-899X/660/1/012005.
- [14] Benny Joseph, "Behaviour of Geopolymer Concrete Exposed to Elevated Temperatures," PhD dissertation, Dept. Civil Eng. Cochin University, Kochi, 2015.
- [15] Parthiban Karthivel et al., "Effect of Partial Replacement of Ground Granulated Blast Furnace Slag with Sugarcane Bagasse Ash as Source Material in the Production of Geopolymer Concrete," Materials Science vol. 26, no.4, pp. 1-5, 2020, doi: 10.5755/j01.ms26.4.23602.
- [16] S.E Wallah and B.V.Rangan," Low Calcium Fly Ash-Based Geopolymer Concrete: Long Term Properties," PhD dissertation, Dept. Eng Technology, Curtin University, Perth, Australia, 2006.
- [17] Vemundla Ramesh and Dr.Koniki Srikanth, "Mechanical Properties and Mix Design of Geopolymer concrete- A Review," 184:ICMED ES3 Web of Conferences, 2020, pp. 1-5, doi: 10.1051/e3sconf.202018401091.
- [18] B.Vijaya Rangan, "Geopolymer concrete for environmental protection," Dept. Civil Eng. Science and Engineering., Univ. Perth, Australia, Technical Paper, April 2014.
- [19] Amir Ali Shahmansouri et al., "Compressive strength prediction of eco-efficient GGBS-based geopolymer concrete using GEP method," Journal of Building Engineering letter no.31, pp.1-11, 2020, doi: 10.1016/j.job.2020.101326.
- [20] Mateusz Sitarz et al., "Rheology and Mechanical properties of Fly Ash- Based Geopolymer Mortars with Ground Granulated Blast Furnace Slag Addition," Energies vol. 13, no.2639, pp. 2-12, 2020, doi: 10.3390/en13102639
- [21] Yamini J.Patel and Niraj Shah, "Development of self-compacting geopolymer concrete as a sustainable construction material," Sustainable Environment Research, Vol. 1 no. 28, August 2018.[Online].Available, www.journals.elsevier.com/sustainable-environment-research/. [Accessed Dec 8, 2020].
- [22] Asif Ur Rehman & Vincenzo M.Sglavo, "3D Printing of Geopolymer Based Concrete for Building Applications," Dept. of Industrial Engineering, Univ. of Trento, Italy, Technical Paper, August 2020.
- [23] Qais Frayyeh et al., "Mechanical Properties of fly ash geopolymer mortar reinforced with carbon fibers," MATEC Web Conferences no. 162, pp.1-6, 2017, doi: 10.1051/mateconf/201816202028.

- [24] Biranchi Panda et al., “The Effect of Material Fresh Properties and Process Parameters on Buildability and Interlayer Adhesion of 3D Printed Concrete,” *Materials* vol.12, no.1249, 2019, doi: 10.3390/ma12132149
- [25] Jonathan Thomas Kuchem, “Development of test methods for characterizing extrudability of cement-based materials for use in 3D Printing,” PhD dissertation, Dept, Eng, Missouri Univ., Missouri, 2019.
- [26] Behzad Nehmatollahi et al., “Effect of different superplasticizers and activator combination on workability and strength of fly ash based geopolymer,” *Materials and Design* no.57, pp. 667-672, 2014, doi: 10.1016/j.matdes.2014.01.064.