Research Article

Cleaner Environment Approach by the Utilization of Low Calcium Wood Ash in Geopolymer Concrete

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Abstract
The waste disposal issues were the most severe problems that could cause global warming, which depletes the environment. The research hypothesis was to find the suitability and sustainability of utilizing the waste by-products in the invention of green geopolymer concrete to eliminate the tremendous effects caused by the wastes. Due to the increased demand for fly ash in recent years, the requirement of high alkaline activators, and elevated temperature for curing, there was a research gap to find an alternative binder. The novelty of this research was to utilize the waste wood ash, which is available plenty in nearby hotels and has an inbuilt composition of high potassium that can act as a self alkaline activator. Waste wood ash procured from the local hotels was replaced with fly ash by 0 to 100% at 10% intervals. The setting and mechanical characteristics were found on the prolonged ages to understand the influence of waste wood ash. Microstructural characterization was found using Scanning Electron Microscope and X-Ray Diffraction Analysis to define the impact of waste wood ash in the microstructure. The research findings showed that replacing 30% waste wood ash with fly ash attained better performance in setting properties and all mechanical parameters. The obtained optimum mix could provide the best alternative for fly ash in geopolymer to eliminate the economic thrust by the requirement of alkaline activators and deploy the environmental impact caused by the waste wood ash.

Keywords: Waste wood ash, Green geopolymer concrete, Dynamic modulus of elasticity, K_2O, SEM

1 Introduction

Environmental impact due to cement production has been grown, and the global emission rate has also increased in recent years [1]. One ton of cement production has released 1 ton of CO_2 into the atmosphere [2]. The clinker production process was the major emitter of CO_2 in the overall cement production process [3]. The 1 ton of clinker production needs 4GJ of energy which could employ to depletes the natural resources [4]. The researchers had already taken initiatives to reduce the environmental impact caused by cement production

[5]. The cement has been replaced by industrial byproducts and supplementary cementitious materials [6]. However, the replacement levels have been limited to 25% to 50%, which could not significantly reduce global CO_2 emission [7]. The waste disposal issues were the most severe problems that could cause global warming, which depletes the environment [8]–[11]. The utilization of industrial byproducts instead of cement will have been resulted in eliminating the CO_2 emission by the cement production [12]. Davidovits [13] found the cement-like material formed by activating the industrial by-products with alkaline activators. Production of geopolymer concrete using industrial by-products could be an alternative for reducing the environmental impact caused by the cement industry [12]. The invention of Geopolymer Concrete (GPC) using fly ash as an aluminosilicate binder has been studied [14]. The fly ash-based GPC requires high alkaline activators for the dissolution of Alumina (Al) and Silica (Si) [15]. The FA-based GPC has required an elevated temperature curing to attain the maximum characteristic strength and requires prolonged time for setting [16], [17]. On the other hand, the demand for fly ash increased in recent years due to plenty of advantages and awareness [18]. Hence, the researchers focused on finding an alternate binder for fly ash in GPC [19].

Ground Granulated Blast furnace Slag (GGBS) ash has been used as an alternate binder in GPC, and it eliminated the prolonged setting time required by the fly ash. However, high calcium in GGBS reacts with an alkaline solution early and promotes early age strength [8], [20]. Besides, the high calcium disrupts the geopolymeric reaction and left the Al and Si unreacted [21]. Geopolymer contains high calcium has rapid setting time, and limited workability [22]. Geopolymer concrete made with the Rice Husk Ash (RHA) contains less calcium, and high silica has been investigated [23]. The increased amount of silica particles in RHA requires a high alkaline solution to develop the geopolymerization reaction at later ages [24]. The excess amount of silica decreased the strength attainment and left many unreacted silica particles [25]. Palm Oil Fuel Ash-based GPC achieved the maximum strength while blended with GGBS or Fly ash [26]. Besides, the compressive strength and geopolymerization were enhanced with the Na_2SiO_3 to NaOH ratio [19]. Bio-Medical Waste Ash has been used as the alternate for GGBS in GPC to reduce the setting time of mix [27]. Modified Sludge Ash (MSA) has been used to replace fly ash in GPC [16]. The addition of MSA has decreased the initial water absorption, and it allows to cure of the specimens at ambient temperature. Volcanic ash has been used to synthesize GPC to reduce the efflorescence and setting time [9], [28]. Volcanic Ash has performed weakly in the alkaline medium, which requires high alkaline activators. The probability of utilizing the Oil Shale Ash for the replacement of GGBS in GPC has been found [29]. Olive Biomass Ash has been used as an alternate binder in GPC, and it does not achieve the reaction of geopolymerization in later ages [30].

Most of the source material discussed above has required a high alkaline solution to enhance the strength parameters by the dissolution of silica and alumina [15]. The excess amount of Si and Al existing in the binder also requires a high alkaline solution for dissolution. Besides, minimizing the setting time has also an essential parameter for using the GPC in real-time applications. Increasing in either silica (Si) or alumina (Al) content helps in reducing the setting time of high calcium-based geopolymer [31]. However, maintaining the silica and alumina ratio is much tricky. Eliminating the high calcium present in the binder or utilizing the source material with less calcium and high K_2O content can solve the problem mentioned above [32]. The availability of source material in the manufacture of geopolymer concrete for real-time applications has been relatively minor. Based on the different parameters reviewed, the feasibility of the production of GPC was less than 7% in global [33]. The unfeasibility was mainly due to the less availability of alkaline activators and the higher sodium silicate cost. Here there is a need for the research to reduce the requirement of independent alkaline activators to associate the above statement.

Biomass Wood Ash (BWA) has been used in the hybrid geopolymer concrete made using GGBS, Pulverized Fly ash [34]. The inclusion of BWA reduced alkaline solution requirement by lowering the molarity to 10 [20]. High calcium present in the binder results in disruption of geopolymerization reaction at later ages, leading to a reduction in strength attainment [35]. The self-activating mechanism of High Calcium Wood Ash (HCWA) on geopolymer concrete was studied [36]. 50–60% replacement of HCWA enhanced the

mechanical and durability performance at an early age due to the combination of geopolymerization and pozzolanic reaction [11], [37]. However, geopolymerization was not occurred at later ages due to calcium, which utilized the alkaline solution for dissolution at an early age itself [38]. The utilization of source material with high alkaline has also explored the problems such as rapid setting, later age geopolymerization, and unreacted Al and Si. Hence there is a need for aluminosilicate source material that contains less calcium and activating medium (i.e.) high potassium oxide for the production of GPC and to attain later age strength by maintaining geopolymerization reaction.

The research hypothesis has to find the suitability and sustainability of utilizing the waste by-products in the invention of green geopolymer concrete to eliminate the tremendous effects caused by the wastes. The novelty of this research has to utilize the Low Calcium Waste Wood Ash (LCWWA), which is available plenty in nearby hotels and has an inbuilt composition of high potassium that can act as a self alkaline activator. The study aims to produce the Low Calcium Geopolymer Concrete (LCGPC) at lower molarity using LCWWA. Thus, in the current study, low calcium wood ash was replaced by 0–100% at 10% interval in fly ash-based GPC. Setting characteristics like consistency, setting time in initial and final were carried out in this study. Mechanical features like dynamic modulus of elasticity, flexural and compressive strength, mainly focusing on later ages, were studied. In addition, microstructural and mineralogical characterization of LCGPC made up of FA and LCWWA is also to be assessed by SEM/EDX for the process of geopolymerization.

2 Material Properties

2.1 *Materials*

2.1.1 Fly Ash (FA)

Physical characteristics of FA used in this study were found as sp. gravity of 2.82, LOI (loss of ignition) of 1.79%, and surface area of 325 m^2/kg [39]. In compliance with ASTM C618 [40], the class F Fly ash could be used as a binder in this research to produce GPC. Based on the chemical compounds analyzed using EDX, the FA would describe as more minor in calcium [41].

2.1.2 Low Calcium Waste Wood Ash (LCWWA)

A waste by-product resulting from locally available hotels is Low Calcium Waste Wood Ash (LCWWA) [41]. To remove massive agglomerate particles and carbonaceous constituents from the consequent geopolymer mixtures earlier, the LCWWA was sieved through 90 μm. The physical characters such as surface area and sp. gravity of LCWWA were 567 m^2/kg and 2.43 [42]. Table 1 illustrates the chemical compositions of LCWWA and FA, which were confirmed by the XRD analyzer.

2.1.3 Alkaline solution

The invention of GPC requires two base alkaline activators, such as hydroxide and silicate. In this research, NaOH pellets are having 1.47 specific gravity were used. For the silicate-based activator, Na_2SiO_3 (sodium silicate) having 1.70 specific gravity was used. The amount of water needed for the dissolution of NaOH pellets was determined [43].

2.1.4 Fine aggregate and coarse aggregate

Local Natural River sand with an sp. gravity of 2.62 was used during the study as fine aggregates, a maximum aggregate size of 1.18 mm, and a fineness modulus of 2.42. The fine aggregate has been left to dry in a dried surface condition before use. In this study, a 10 mm-sized coarse aggregate with fineness modulus and sp. gravity of 7.59 and 2.89 was utilized. Water was used to get soluble sodium hydroxide. The amount of water required to get the soluble NaOH was calculated from the study [44].

Table 1: Fly ash and LCWWA Chemical Compounds in % by Mass [41]

Chemical compound	CaO	SiO_2	Al_2O_3	MgO	K_2O	P_2O_5	MnO	C	Gd	TiO_2	Fe_2O_3
FA	2.53	48.63	32.41	0.90	0.11	-	-	7.10	-	1.78	3.10
LCWWA	2.61	38.25	22.23	2.95	15.51	2.96	-	10.22	0.48	1.22	2.97

2.2 *Methods*

2.2.1 Mix proportioning and curing

While the manufacture of GPC, the ratio of FA: LCWWA was optimized by 0 to 100%, with 10% step incremental. In the previous study, the authors found the optimized ratio for alkaline/binder ratio and molarity of NaOH [42]. Therefore, 0.45 and 2.50 were made constant for the ratio of activators to binder and silicate to hydroxide ratio. Meanwhile, the optimum molarity of Sodium hydroxide was determined as 10 M [41]. The ratio of sand to binder was set at 2.50. The design mix was followed by the modified guidelines of Indian standards for geopolymer concrete [45]. Mixing water was calculated based on the research done in [44]. The exact mixture proportion of the geopolymer concrete for optimizing fly ash/LCWA ratio is shown in Table 2. The quantity of materials such as NaOH, Na_2SiO_3, fine aggregate, and coarse aggregate was calculated as 110.21 kg/m^3, 275.58 kg/m^3, 666.62 kg/m^3, and 993.11 kg/m^3 [42]. The standard mixing procedure was followed to achieve the homogenous mix. The specimens were kept for curing under room temperature before acquiring the testing ages.

Table 2: Mix proportioning in kg/m^3 [42]

Mix id	FA %	LCWWA %	FA	LCWWA
GC	100	0	550.00	0.00
GCW10	90	10	495.98	32.11
GCW20	80	20	440.88	64.22
GCW30	70	30	385.66	96.34
GCW40	60	40	330.64	128.46
GCW50	50	50	275.62	160.50
GCW60	40	60	220.39	192.61
GCW70	30	70	165.27	224.73
GCW80	20	80	110.15	256.85
GCW90	10	90	55.03	288.97
GCW100	0	100	0.00	321.99

2.2.2 Setting and mechanical characterization

Using the Vicat needle apparatus, the setting characteristics such as consistency, initial and final setting time, and standard consistency of LCGPC mixtures were measured in compliance with BS EN 196-3:2005 [46]. Compressive strength of the LCGPC mix was found using Standard Test Method for Compressive Strength of Hydraulic Cement Mortars given by ASTM C109 [47]. A total of 165 numbers of cubical specimens with size 150 × 150 × 150 mm (Figure 1) was used to perform the compressive strength. 165 numbers of standard prism specimen of size 500 × 100 × 100 mm was casted to found the flexural strength of LCGPC mixes (Figure 2). The flexural strength test was performed as per the standard test procedure given in ASTM-C293 [48]. Modulus of elasticity test (Figure 3) was performed in the cylindrical specimen of size 500 × 100 mm by following the standard test procedure given by ASTM C215 [49]. A total of 165 numbers of cylindrical specimens were casted to perform the modulus of elasticity test. For each test, three specimens were tested for all testing ages, and mean values were considered. The microstructure analysis of the selected mixtures of the LCGPC was assessed in terms of morphological and elemental composition changes

Figure 1: Compressive strength of the LCGPC cubical specimens.

Figure 2: Flexural strength of LCGPC prism specimens.

Figure 3: Dynamic modulus of elasticity of LCGPC concrete mixes.

by Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-Ray (EDX) functionality.

3 Results and Discussion

3.1 *Setting characterization*

3.1.1 Standard consistency

Figure 4 established the standard consistency values of different mixes. The mix GC attains its consistency at a w/b (water/binder) ratio of 0.35, whereas mix GCW100 grasps the same at a w/b ratio of 0.48. Due to its large specific surface area of 558 m^2/kg, the inclusion of LCWWA in GPC had a significant effect on the increasing demand for water to obtain normal consistency. The specific surface area of the binder material should influence in need for water for achieving its consistency [50]. The inclusion of LCWWA between 30 to 50% shows less water requirement than the mix with 100% LCWWA [41]. That less water requirement is because of the high amount of fly ash with a less specific surface area of 324 m^2/kg [21]. In the range of 10% to 70%, the presence of fly ash resulted in decreasing the water demand by 17.77%.

The water required to reach the standard consistency has been reduced by adding spherical fly ash, whereas LCWWA was formed by angular particles requiring more water [51]. The water needed to reach the standard consistency has been reduced by adding fly ash [33] with a spherical shape, whereas LCWWA was formed

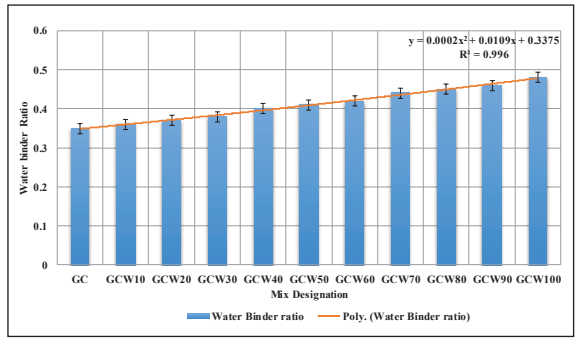

Figure 4: Standard consistency of LCGPC.

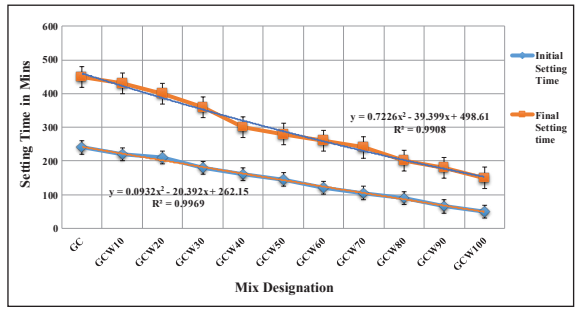

Figure 5: Setting time of LCGPC.

by angular particles requiring more water. Moreover, due to the lubrication effect of alkaline solutions, inner-particle friction has been developed [52].

3.1.2 Initial and final setting time

Graphical representation of time taken by each mix of low calcium GPC for its initial and final set was illustrated in Figure 5. The inclusion of fly ash [53] and LCWWA in the geopolymer mixture increased both the setting times. The time taken by the control mixture GC for the initial setting was found out to be 240 min, and the final setting time was 450 min [54]. While the mix with 100% LCWWA attains the initial setting at the time of 50 min and the final set at 150 min which is the least compared to all mixes. The decrease in setting time is due to calcium content in the mixture full of LCWWA [52]. Both the aluminosilicate source materials contain less calcium, which leads to a delay in the setting time. It was inferred that the addition of wood ash with high calcium rapids the setting time [55]. High calcium in the source material leads to a quick setting of the mortar [56].

The replacement of 100% LCWWA with fly ash, the initial and final setting times have reduced to the range of 50 to 150 min because of the marginal presence of calcium in the mixture compared to the control mixture [57]. Meanwhile, the increased setting times were observed based on the curing of the mixture at room temperature. While the mixes have been cured at a high temperature, the initial and final setting time of the entire LCGPC mixture has been improved [39]. Further, mix with 80% of LCWWA sets quickly at room temperature than other mixtures due to increased calcium [57].

3.2 *Mechanical characterization*

3.2.1 Compressive strength test

In Figure 6, the compressive strengths of low-calcium geopolymer concrete cube specimens cured at 3, 7, 28, 56, and 90 days are presented. The obtained results found that the replacement of LCWWA up to 30% at any curing period produces a substantial effect on enhancing strength in compression [58]. Meanwhile, beyond 30% addition of LCWWA influenced significant strength reduction [41]. This could be due to the effect of unreacted particles of fly ash [59].

Already mentioned in the previous literature [60], the unreacted particles of Al and Si due to the higher presence of calcium in the source material could be minimized in this LCGPC geopolymer mixture [61]. The incorporation of LCWWA induces to enhance the compactness of the geopolymer structure and early age strength [37]. The strength gains at an early age were influenced by the precipitation of polysialate phase and the monumental dissolution of the amorphous phase of source materials [62]. There is a continuity in strength attainment of LCGPC on long-term curing durations of 28, 56, and 90 days. The strength attainment in the later age was gradual due to the perfect performance of geopolymerization reaction [63]. The optimum GCW30 attained the compressive strength of 21.68, 28.98, 38.9, 41.63, and 44.25MPa at 3, 7, 28, 56, and 90 days of concrete curing. This strength attainment was due to the lowest calcium presence and less alkaline solution for dissolution [64]. Meanwhile, on prolonged curing of 90 days, the compressive strength of the optimum mix was increased by 16.45% compared to the mixture without LCWWA content.

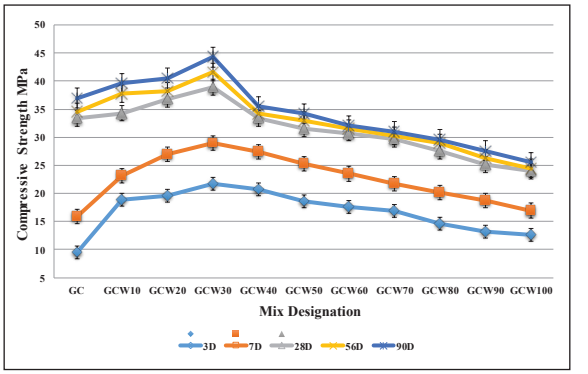

Figure 6: Compressive strength of LCGPC.

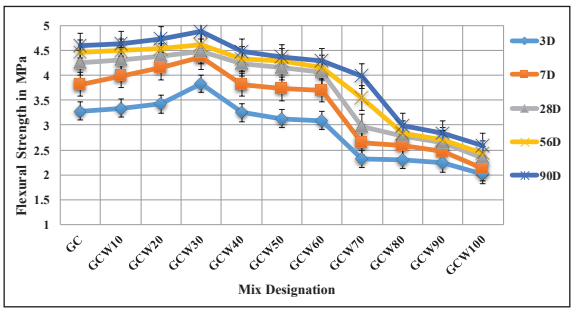

Figure 7: Flexural strength of LCGPC.

3.2.2 Flexural strength test

Figure 7 illustrates the flexural strength for LCGPC prism specimens with various LCWWA content at 3, 7, 28, 56, and 90 days of curing duration. Like the strength achieved in compression, the replacement of LCWWA up to a replacement level of 30% at all ages of curing time has significantly influenced the increase of flexural strength in LCGPC [58]. Furthermore, a decrease in strength attainment was noticed while the inclusion of LCWWA exceeded 30% and above [41]. The highest flexural strength has been observed in the mix with 30% LCWWA content in all curing ages [38].

The bonding strength could be enlarged to resist the flexural loading by enhancing the interfacial zones of concrete [65]. Meanwhile, the formation of C-S-H gel due to the geopolymerization reaction enhanced the pore filling ability of the geopolymeric gel matrix. It helps to achieve better performance in the flexural strength at all ages of curing [52]. Compared to control mixtures, mixtures beyond 30% LCWWA replacement decreased the flexural strength at any age of concrete

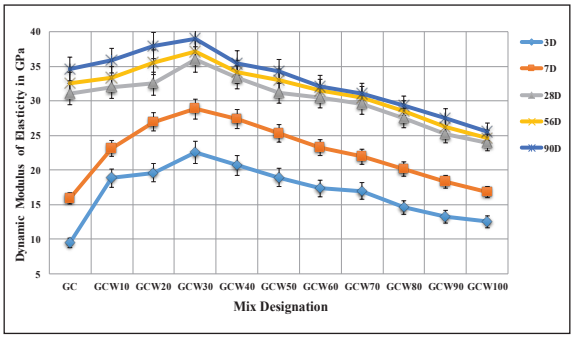

Figure 8: Dynamic elastic modulus of LCGPC.

[57]. Most likely due to the absence of CaO compounds, Calcium-Alumino-Silica-Hydrate gel and Ca-polysialate frames can be produced [60]. With a longer duration of 90 days, the bending strength of 4.89 MPa was significantly improved, while the mixture has 30% LCWA compared with that of the control mixture 4.59MPa.

3.2.3 Dynamic modulus of elasticity

The modulus of elasticity of all LCGPC specimens at all curing ages has illustrated in Figure 8. Compared to the control mixture, the replacement of LCWWA up to 30% established an increasing trend in the dynamic modulus of elasticity [22]. Meanwhile, at the all-ages of curing, beyond 30% inclusion of LCWWA showed 24.64–35.48% of a substantial drop in elastic modulus compared to the control mixture [41]. Compared to other curing ages, the dynamic modulus of elasticity of LCGPC at an early age was higher. In 3 days of curing, the dynamic modulus of elasticity has increased by 24.64–58.07% compared to the control mixture [41]. There was a trend in the increment of up to 44.93% in dynamic modulus of low calcium geopolymer concrete at 7 days of curing. The increment was due to the early age easy dissolution of the aluminosilicate source material [53]. Furthermore, the increment rate on elastic modulus in later ages was lesser than the earlier age increment rate [20].

The LCGPC contain 30% LCWWA exhibited the highest elastic modulus compared to all other mixtures. Due to the low calcium level, the overall pore volume and pore connections decreased the geopolymeric reaction also improves pore filling in the interfacial transition region up to the later years [66]. GCW30

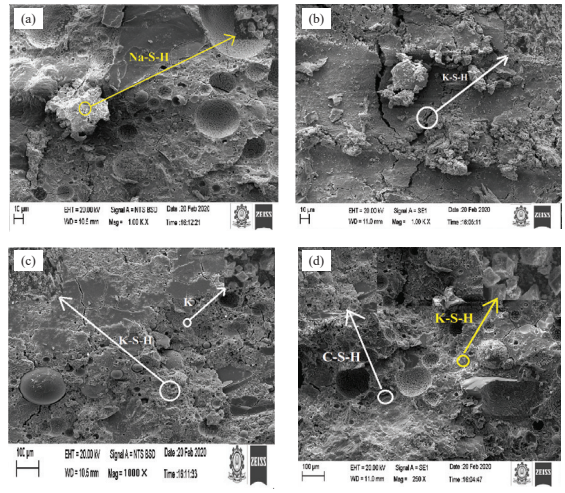

Figure 9: Microstructure analysis of LCGPC mixes (a) GCW0 (b) GCW100 (c) GCW10 (d) GCW30.

with dynamic modulus values of 22.54, 28.82, 35.98, 37.13, and 38.94 MPa was the optimal combination of 3, 7, 28, 5, and 90 days. The result of a higher LCWWA material has been attributed to the rising numbers of amorphous monomers, leading to further production of polysial networks at room temperature curing [62].

3.3 *Microstructural characterization*

3.3.1 Scanning electron microscope

The microstructural analysis of LCGPC specimens was done with Scanning Electron Microscope (SEM) and illustrated in Figure 9(a)–(d). The formation of Sodium Silicate Hydrate (Na-S-H) gel due to low calcium fly ash dilution is revealed by Figure 9(a). The micrograph of GCW30 displays a heterogeneous and cracked matrix with unremoved solvent while curing and ageing. These findings indicate that the coexistence between reacted and unreacted microspheres produces a more substantial connection [59]. Nonetheless, it is the result of the particle pore bridging. Compared to a mixture of 100% fly ash, the GCW10 and GCW30 mixtures have increased homogeneity and density of gel matrices, particularly with the GCW30 mixture. It also noted that the portion of the unreacted or partially reacted FA microspheres of mixtures GCW10 and GCW100 is relatively lower than that of the control mixture [63]. That means higher dissolution rates of FA particles in

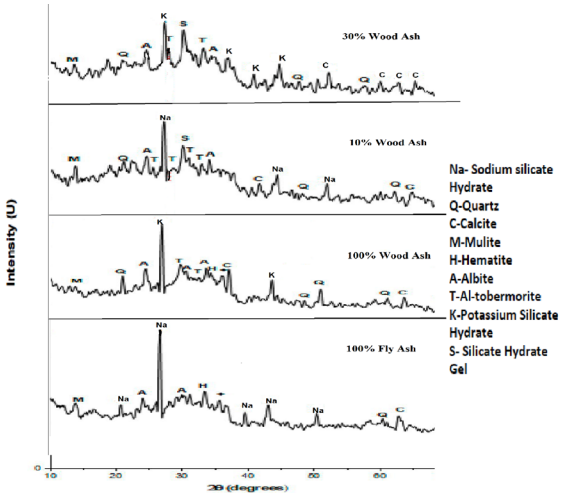

Figure 10: XRD Analysis of LCGPC Mixes.

mineral mixtures enhanced with LCWWA due to its alkaline nature.

3.3.2 X-Ray diffraction analysis

Figure 10 displays the accompanying XRD study of the LCGPC concrete. The XRD data showed a relatively high amplitude angle of 2θ degrees range between 28 and 30. This attribute is generally representative of the development of a geopolymer, with the assumption that a geopolymerization reaction occurred [67]. Mix with 100% FA produced a few amorphous zones, which were originally generated from FA, and also, the geopolymerization reaction created a new phase of Albite [68]. The partly-crystallized shape of Albite was classified as a relative of the sodium-polysialate gel band [69].

Compared to the control mix, the XRD diffracts of the mixes with various percentages of wood ash revealed many distinct variants of the crystalline structure [70]. Due to the dilution of LCWWA, the maximum crystal quartz peak was obtained and decreased the intensity with the decrease of LCWA [67]. This is due to the increase in the presence of calcium in the LCWWA. The development of this new phase of Altobermorite was considered to coexist with other phases [32]. The highest peak of intensity has been obtained with the mix of 100% FA. However, the formation of Na phases has decreased with the increase in the replacement percentage of LCWWA.

Meanwhile, the potassium silicate phase formation [71] was observed in the mixes with wood ash. The phase of potassium silicate formation was increased with increasing the replacement percentage of LCWWA due to the presence of K_2O in LCWWA [71]. The optimum mix GCW30 has found maximum high peaks in all the phase formations such as potassium silicate, calcite, mullite, Quartz, Silicate gel, and Albite [23]. This is the rationale behind the increased efficiency of the 30% wood ash blend in all its characteristics.

4 Conclusions

Efficient production of low calcium-based green geopolymer concrete using waste by-products to dispose of waste into an effective product has been investigated in this study. Further, the effect of low calcium waste wood ash on the setting and mechanical characters of LCGPC was studied in detail. The replacement of LCWWA has tremendous influences on the characteristics of LCGPC. The LCWWA replacement in GPC showed a significant effect on the increasing demand for water to obtain normal consistency because of its high specific surface area of 558 m^2/kg. LCWWA was formed by angular particles, which led to water demand. Moreover, due to the lubrication effect of alkaline solutions, inner-particle friction has been developed. Since the calcium is less abundant in fly ash than wood ash, the mix with 100% fly ash required a long time to set initial and final. However, LCWWA replacement increases the amount of calcium content and reaches a quick setting compared to the mix made only with fly ash. The replacement of up to 30% LCWWA replacement level has dramatically impacted the increase of compressive strength, flexural strength, and low calcium geopolymer concrete's dynamic elastic modulus. Increasing the replacement of waste wood ash beyond 30% resulted in decreasing in all strength parameters. Hence behind the consideration of effective waste disposal and resolving the problems in the fly ash-based GPC, the low calcium waste wood ash up to 30% replacement can be an effective alternate aluminosilicate source material. This low calcium green geopolymer concrete can be applied to real-time civil engineering products such as paver blocks, railway sleepers, bricks, etc. The research hypothesis has been proved that the low calcium waste wood ash could be an alternative binder material for the fly ash in GPC.

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