INVESTIGATION ON FEASIBILITY OF UTILIZING COFFEE-HUSK ASH AS AN ALKALINE ACTIVATOR IN GEOPOLYMER CONCRETE

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Abstract. Cement production is the major source of global warming which induces 7% of total greenhouse gas emissions. Reducing the use of cement in construction industry needs to be adopted by any of the alternates. One of the best alternates to reduce the impact caused by the cement production process is geopolymer concrete which can completely replace the usage of cement. Geopolymer is trending technology which possess numerous advantages than ordinary Portland cement concrete technology. Geopolymer is produced by the mixing of solid precursor and monomer. Most widely used solid precursors are waste industrial byproducts such as fly ash, GGBS, metakaolin etc., and monomers are alkaline activators like sodium hydroxide and Na2SiO3. Meanwhile, the properties of geopolymer concrete are decided by the various parameters such as quantity of aluminosilicate source in precursor, ratio of Na2O/SiO2, SiO2/Al2O3, NaOH/Na2SiO3, solution to binder ratio, concentration of NaOH etc., The alkaline activators mostly used are chemical activators which is harmful to humans. Hence, there is a need of finding an alternate for chemical activators in the geopolymer concrete. In this proposed methodology, the chemical alkaline activators have been completely replaced by the waste residue product named coffee husk. Coffee husk is a residue produced from the coffee powder production industry. A total of 18.29 MMT of coffee husk ash has been produced every year. Coffee husk has an inbuilt composition of potassium which is one of the alkaline activators. However, the coffee husk ash needs to be calcinated by the use of oven before to use. In this research, an attempt has been made to utilize the Coffee husk ash (CA), as an alkaline activator and efficient activation mechanism of CA will be examined.

Keywords. Alkaline activator, Mechanical properties, Geopolymer concrete, Flyash, Coffee husk ash.

1. Introduction

Sustainability-related issues have been receiving more and more attention presently. An additional indication of this concern is the rise in research aimed at enhancing sustainability across several domains. This explains why a wide range of studies carried out especially in

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the construction industry are evident, primarily in the field of building materials. These studies focus mostly on concrete and its constituent parts. Around the world and in construction projects, concrete is the material of choice. The following components make up the majority of this building material: Portland cement, water, aggregates, both fine and coarse, and occasionally other fibres, admixtures, etc. Portland cement is the primary ingredient in concrete out of all of these substances since it improves the compounds' ability to bind together [1]. Clinker, gypsum, and maybe more minerals combine to form Portland cement, a mineral binder. Nevertheless, the production of Portland cement carries some environmental risk, particularly in the form of clinker [2]. In order to generate one tonne of clinker, about 2.8 tonnes of limestone and clay must be obtained from non-renewable mineral sources. Additionally, the manufacturing of clinker emits a significant amount of carbon dioxide (0.9 tonnes) into the atmosphere. The last two issues arise from the following: (i) using fuel to maintain the rotary kiln operating at temperature near to 1450 °C; and (ii) converting limestone (CaCO₃) to calcium oxide (CaO) in order to create the clinker's calcium silicates and calcium aluminates. Therefore, in order to reduce the detrimental impacts of building on the environment, a number of research projects are looking into alternatives which reduces the dependence on Portland cement, namely the usage of clinker. One such alternative is alkali-activated binder (geopolymer), which is environmentally friendly since it employs renewable energy sources, emits less CO₂, and consumes less energy [3,4]. Concrete made of geopolymer is becoming more and more popular as an environmentally friendly alternative to traditional cement-based concrete. Based on a novel binder technology, it forms a strong matrix by activating industrial or natural byproducts with alkaline solutions [5,6]. By cutting carbon dioxide emissions throughout the concrete manufacturing process, this approach minimises the environmental effect of ordinary cement. In geopolymer, water is mixed with an alkaline activator that has an alkali source and a solid precursor, which is often an amorphous aluminosilicate material [7]. A substance containing hydrated Portland cement might be produced from this combination. A classic two-step mixing process involves first mixing the solid precursor with an activator solution prepared by dissolve an alkaline activator in the water. However, recent studies [8–10] have reduced the hazards associated with high alkali concentration and streamlined production by adopting a one-part geopolymer mixing process. Mineral sources such as metakaolin and calcined clays, industrial wastes like fly ash and blast furnace slag, and agricultural byproducts can also provide solid precursors [11,12]. Alkaline activators affect the combination's pH and have an impact on the reaction's speed.

In addition, the production of one part GPC is better off using weak acid salts as alkaline activators rather than caustic sources, which can cause exothermic reactions and burns on the skin when combined with water. Previously, for example, commercial Na₂CO₃ (containing 10% Na₂O) was used as an alkali activator in combination with a mixture of fly ash and blast-furnace slag as solid predecessors [13]. After 28 days at ambient temperature, the resultant concrete demonstrated a compressive strength of 60 MPa [14]. Studies using ash from sugarcane straw, biomasses high in potassium, ash from almond shells, and ash from olive stones have shown that agricultural waste can also be used to create alkaline activators [8,15,16]. Examining alternative materials as alkaline activators is a significant field of study for geopolymer concrete researchers. The objective is to analyse the impacts of coffee husk ash on the characteristics and functionality of geopolymer concrete. Thus, the objective of this work is to use coffee husk ash (CA) as an alkaline activator. Given that coffee husk ash mostly consists of K₂O, it is suitable for this use. Coffee husks, a byproduct of the production of both dry and wet coffee, can be used as bioenergy for generating electrical power.

Despite the fact that the process of manufacturing coffee produces a huge amount of wastes, previous research on the use of coffee husk ash in geopolymer has not been
thoroughly examined, and there is little data available on coffee waste in this type of binder. Discarded coffee grounds, an insoluble consequence of producing coffee beverages, stand out among these wastes. Fly ash, blast-furnace slag, and wasted coffee grounds were combined as a solid precursor in a research that employed a combination of NaOH and Na$_2$SiO$_3$ alkaline activator. The results showed that mixes containing higher percentages of blast-furnace slag outperformed fly ash mixes due to the slag's calcium oxide (CaO) concentration, which increases the initial strength and requires less alkaline activator. Despite all of the strengths being less than 2 MPa, not a single sample demonstrated any meaningful strength for structural uses. In a further study, spent coffee grounds were combined with rice husk ash and the blast-furnace slag as reliable predecessors. In another study, spent coffee grounds were combined with the ashes of rice husks and blast-furnace slag as solid predecessors. Even with the finest mechanical performance, applications in road subsoils can make use of a compressive strength of less than 2 MPa. The study investigated various alkaline activator proportions ranging from 0 to 15% of K$_2$CO$_3$ in relation to BFS mass [17]. Through an examination of mortars' mechanical and physical characteristics and microstructural investigations of pastes, the possibilities and impacts of CA as an alkaline activator in OP-GPC were assessed. Effectively employing CA as an alkaline activator might possibly give a valuable solution for waste generation, as it would produce a less hazardous GPC with suitable properties and increased sustainability for use in the civil engineering construction applications.

2. Materials

Coffee husk was collected and burned for 10 hrs at 1000°C in a muffle furnace in order to obtain coffee husk ash, as specified. GGBS is the waste product obtained from blast furnace used in iron industry [18]. It is a cementitious component that has numerous applications in concrete. These materials are mostly silicates and calcium aluminates, and they are non-metallic. It requires only ambient curing. When compared to alternative binder materials like fly ash and wood ash, it offers a higher compressive strength. Natural sand from a river that had a highest particle size of 4.75 mm is collected and used as a filler. To verify that the mix design conforms with the ASTM C33 standard, the average fineness modulus had been calculated by using particle size distribution data. Physical characteristics and the particle size distribution of fine aggregates in the experiments are shown below in Table 2 and Figure 2.

<table>
<thead>
<tr>
<th>PROPERTIES</th>
<th>RESULT</th>
<th>ASTM C33 limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (Kg/m$^3$)</td>
<td>15788</td>
<td></td>
</tr>
<tr>
<td>Bulk specific gravity</td>
<td>2.58</td>
<td>2.4 – 2.9</td>
</tr>
<tr>
<td>Apparent specific gravity</td>
<td>2.47</td>
<td>2.35 – 2.9</td>
</tr>
<tr>
<td>Particle size</td>
<td>9.5 – 0.14</td>
<td>9.5 - 0.15</td>
</tr>
<tr>
<td>Water absorption capacity</td>
<td>1.32</td>
<td>0 – 4%</td>
</tr>
<tr>
<td>Silt content (%)</td>
<td>4.2</td>
<td>&lt;5.0</td>
</tr>
<tr>
<td>Free surface moisture</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Particle size distribution curve

3. Mix Design and Methodology

The mortar mix for mechanical performance study was prepared with the mortar ratio of 1:3 [19]. The processes described in ASTM were adhered to in the preparation and casting of the specimens. For each of the test specimens, three layers of casting were used, and each layer was manually compacted using a steel tamping rod that was struck 25 times. Every component was measured using a weighing system to ensure uniform proportions and prepared in accordance with its weighted proportion before being combined. Before adding water, GGBS and CA were first mixed dry. This process was repeated a short while later. All test specimens underwent a 10-minute blending process with a steady 30-rpm spinning speed. The study was conducted by three phases viz., CA production and BFS/CA physicochemical analysis, mechanical and physical testing of OP-GPC mortars based on BFS, Microstructural analysis of OP-GPC pastes based on BFS.

3.1. CA production and BFS/CA physiochemical analysis

The physiochemical characteristics of CA were determined and analysed in the first part of the investigation. To find the ideal calcination period, coffee husk waste was first calcined for several duration of time—2, 4, 6, 8, 10, and 12 hours—in a laboratory furnace set at 1000°C. To achieve uniform particle dispersion, the resultant CA was calcined, cooled, and then milled. After that, the ash's chemical composition, alkali concentration, XRD, FTIR, CA production efficiency, pH, and water solubility were all analysed. Based on optimum results, samples that were burnt for ten hours at 1000°C were chosen for additional examination. To find the pH and water solubility of CA, a variety of experiments were run on it after it was calcined for varying amounts of time.

3.2. Mechanical and physical testing of OP-GPC mortars based on BFS

In order to investigate the effects of using CA as an alkaline activator, mortars were tested for strength using consistent ratios of water to blast-furnace slag and natural siliceous sand to the blast-furnace slag. The reference alkaline activator, C-PC, was also used, and various percentages of K₂CO₃ with respect to blast-furnace slag mass were tested for both CA and
C-PC. The CA was derived from coffee husk waste after being calcinated for 10 hours, which was found to be the ideal production time.

3.3. Microstructural analysis of OP-GPC pastes based on BFS

The paste were made in the third stage of the research for looking at the microstructure and reaction process. With the exception of the inclusion of sand, these pastes were made by manually using the same process as the mortars and were exposed to the same curing conditions. For C-PC-15% and CA-15%, XRD testing was performed after 7 days, and for C-PC-10%, C-PC-10%, CA-10%, and CA-20%, it was done after 28 days. After 28 days of curing, fractured samples of K$_2$CO$_3$-20%, K$_2$CO$_3$-10%, CA-10%, and CA-20% were examined for SEM analysis [20].

4. RESULTS AND DISCUSSIONS

4.1. BFS/CA Physicochemical Characterization

The CA contains K$_2$O of 61.78 percent of weight, which is made from coffee husk waste and is calcined for 10 hours. Other oxides including CaO, MgO, and Fe$_2$O$_3$ are present in trace amounts. There are particles of unburned organic matter present in CA due to the high loss on ignition (LOI) of 19.08 weight percent upon calcination up to 950°C. At 0.0121 ± 0.0002 mol per gramme, CA shows a total alkali concentration that suggests it could be used as an alkaline activator. High amounts of potassium compounds were found in a variety of biomass ashes, including wasted coffee grounds (43.10 weight percent K$_2$O), almond-shell biomass ash (46.98 weight percent K$_2$O), and olive-stone biomass ash (32.16% K$_2$O), according to some earlier research. Out of all the biomass ashes, CA has the greatest K$_2$O content [21,22].

Similar results to those in CA were found in previous studies on biomass ash from almond shells and olive stones, where potassium carbonate was found to be a major component. Additional crystalline phases, including calcite, gypsum, fairchildite and arkanite were discovered in the biomass ash analysis of almond shells. Analogously, crystalline phases such as portlandite, calcite, anorthite, quartz, kalinicite and gismondine are observed in the analysis of biomass ash from olive stones. Remarkably, BFS did not show any crystalline phases in the material. However, an amorphous phase is indicated by the BFS diffractogram with a shift from the base line.
The aforementioned graph shows the solubility of ash in distilled water, the pH levels in distilled water, and the efficiency of CA formation. Longer calcination times—up to 10 hours—generally result in higher CA production efficiency, solubility in distilled water and pH. But calcining the ash for longer than ten hours doesn't make it any better. Notably, CA generated after 10 and 12 hours have almost comparable solubility, pH, and efficiency values. In particular, the pH of distilled water is 14 and the CA production efficiency approaches 99.9% after 10 hours of calcination. Additional extended calcination does not result in a discernible decrease in the amount of organic materials in the ash. Since K₂O is very soluble in carbonates, which contribute to the ash's alkaline character, it can be used as an alkaline activator.

### 4.2. Mechanical and physical characteristics of OP-AAB mortars based on BFS

**Table 2. CA / BFS Chemical Composition**

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>Fe₂O₃</th>
<th>LOI (950°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFS</td>
<td>46.05</td>
<td>30.78</td>
<td>12.13</td>
<td>4.56</td>
<td>0.67</td>
<td>0.58</td>
<td>2.01</td>
</tr>
<tr>
<td>CA</td>
<td>9.95</td>
<td>3.26</td>
<td>-</td>
<td>2.78</td>
<td>61.78</td>
<td>1.40</td>
<td>19.08</td>
</tr>
</tbody>
</table>

The chemical compositions of BFS and CA are shown in the table above. Insoluble contaminants such as carbonates and residual organic matter in the ash cause mortars utilising CA to have a lesser consistency than mortars employing C-PC. The increased concentration of CA, which lowers solubility and alters the mixture's water/solid ratio, is thought to be the
cause of this consistency decline. On the other hand, mortars with a higher consistency are produced by raising the C-PC content.

After the first seven days of curing, mortars' compressive strength gradually rose. In comparison to the results of 28 days, samples attained almost 57% of their compressive strength values after 7 days, with the exception of the CA-5% mortar, which displayed a distinct pattern. Potassium carbonate is present and speeds the hydration reaction, which is responsible for this early strength enhancement. The compressive strength of mortars is significantly influenced by the potassium carbonate content. Strength levels can rise when the alkaline activator content does. However, it was observed that in both the C-PC and CA cases, strength measurements tended to stabilise beyond a potassium carbonate level of 20%. Compressive strength did not significantly change after 28 days of cure [23].

![Figure 3. Compressive Strength of CA](image)

The compressive strength was also influenced by the source of the alkaline activator. CA has a beneficial effect on mortars based on BFS. There was a steady increase in relative compressive strength values above 75% for a range of potassium carbonate concentrations and curing durations. Significantly, with the exception of CA-5% after seven days of curing, CA with potassium carbonate contents between 5.0 and 10.0 weight percent consistently displayed similar values surpassing 100% throughout all curing times, reaching as high as 193%, suggesting a more beneficial impact of the waste in comparison with the commercial activator in these circumstances [23]. However, identical compressive strength values ranging between 76 and 87% in all curing durations were obtained using potassium carbonate content of 15 and 20 weight percent.
The less alkaline activator used in samples with CA and K$_2$CO$_3$ levels between 5.0 and 10.0 weight percent shows a lower degree of interaction between BFS and ash. Because insoluble carbonates from CA have physical impacts on the matrix, like fillers, heterogeneous nucleation, and lowering the water/solid ratio, their presence becomes important in increasing compressive strength. Because of the low degree of reactivity between the BFS and alkaline activator the range of 5.0–10.0 weight percent K$_2$CO$_3$, these physical effects in samples comprising CA can enhance the matrix density, leading to higher values of compressive strength than in samples containing C–K$_2$CO$_3$. Every physical impact has a unique mode of action. For example, heterogeneous nucleation sites might speed up the reaction early on and increase its strength. With reference to the latter physical effect, the effective water/solid ratio is lowered when insoluble carbonates are present, which lowers porosity and improves the behaviour of compressive strength. However, because of a chemical bond among solid precursor and the alkaline activator, which results in a denser matrix and enhances compressive strength, the physical consequences would be less pronounced at higher K$_2$CO$_3$ levels (15–20 wt%). Therefore, at 15–20 wt% K$_2$CO$_3$, extra impurities such as unburned organic matter from CA may hinder dissolving of BFS particle, which would diminish the development of compressive strength in CA-based samples compared to those containing C-PC. However, considering that CA is derived from the waste, and the relative compressive strength values in this area may be considered a positive result. Based on the results, it can be concluded that mortars made with CA have mechanical qualities similar to those made with C-PC, since both samples reach above 40 MPa after 28 days of curing. Because it comes from the manufacture of coffee, which is a renewable resource, and because it is a waste product, using CA as an alkaline activator has advantages that make the alkali-activated binder (AAB) system more sustainable. It's also noteworthy that mortars containing CA had a maximum strength of 40.9 MPa, which is comparable to the 45.2 MPa strengths samples from a study that used almond shell ash had [22]. Moreover, CA mortars performed better than samples from a study using used coffee grounds, in which 1.73 MPa of maximum strength was achieved.
4.3 Microstructural Analysis of OP-AAB Pastes Based on BFS

The production of Alkali-Activated Binders (AAB) based on blast furnace slag (BFS) was tested, and the effects of adding calcium hydroxide (CA) were examined through tests utilising scanning electron microscopy (SEM) and X-ray diffraction (XRD) on the pastes. All pastes exhibit crystalline phases consistent with a C-S-H-like structure and hydrotalcite, which are features of BFS-based AAB, regardless of the curing duration and activator utilised. There was also evidence of calcite. Mostly from unreacted BFS particles or reaction products, an amorphous phase was seen. Certain crystalline phases were absent when CA was present, indicating that it was dissolved in the mixture and contributed to the creation of reaction products, which improved the development of compressive strength. To examine the broken samples of pastes C-PC15%, CA 15% energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) were used.

Each paste that was examined had both reaction products and unreacted solid precursor particles. The only things that marked these components apart were their shape and atomic composition. A few large, unreacted BFS particles and porous features impair the sample's mechanical properties. Figure 5 displays SEM micrographs of the broken sample from the 15% C-PC paste. The two main structures seen were a poorly compacted and layered structure (Point 1) and a compacted and continuous structure (Point 2). In terms of quality, the continuous and compacted structure is controlling. The addition of potassium carbonate acted mostly as a catalyst for the BFS reaction. Consequently, there were fewer unreacted BFS areas and a denser structure of the reaction products in the C-PC-15% paste. The C-PC-15% sample exhibited greater compressive strength values compared to the C-PC-10% sample, as a result of this behavior [20].

![Figure 5. SEM Micrographs of C-PC 15](image-url)
Fig. 6 shows the microstructure of CA-15%. Point A and Point B, the two primary structures seen in the CA-15% sample, were similar to those seen in the C-PC15% paste (Fig 5). Point A was a poorly compacted and layered structure. Occasional observations of porous structures in the paste are possible; one example is the pore of CA-15% (Point C). The C-PC 15% paste is richer in calcium than the CA-15% paste, according to a comparison between the two. Nevertheless, CA-15% paste showed K values that were comparable to those of C-PC-15% paste, indicating that the CA concentration in this paste had attained the K level that could be included in the reaction products. The most significant mechanical characteristics among the CA-based samples may have resulted from the denser structure and low unreacted BFS content of CA-15%.

5. CONCLUSIONS

Coffee husk ash (CA) was utilised as an alkaline activator in blast-furnace slag (BFS)-based one-part alkali-activated binders (OP-GPC). The CA produced for 10 hours at 1000°C demonstrated the maximum production efficiency when compared to other test times. The ash formed by this manufacturing process was mostly carbonates, notably K₂CO₃, with a high K₂O concentration (61.78 wt%), high solubility, and pH in distilled water (DW) of 2.5:6.0 and 14.0, respectively. The K₂CO₃ levels (%K₂CO₃ relative to BFS mass) that were utilised in the production of OP-AAB samples ranged from 0 to 15%. Commercial K₂CO₃ (C-PC) was also used to make reference mortars, all within the same range of carbonate concentration. The physical property findings show that as the amount of CA rose, the consistency of the mortar decreased. Mechanical properties showed that C-PC-15% had a compressive strength of 47.0 MPa and CA-15% had a compressive strength of 40.9 MPa following 28 days of curing at a moisture content greater than 95%. As a result, the mechanical properties of CA-mortars and C-PC-mortars were comparable. A thick, compact microstructure matching pastes created with C-PC was produced by the full reaction of CA and BFS, according to the findings of microstructural examinations of the pastes. Therefore, CA proved the most effective alkaline activator in OP-GPC, according to BFS. This application may lead to a unique, safer, and more sustainable AAB in comparison to earlier processes, in addition to giving coffee waste a valuable purpose.
References