Eco-Friendly Geopolymer Composites Prepared from Agro-Industrial Wastes: A State-of-the-Art Review

Asiya Alawi 1, Abdalrhman Milad 1,*, Diego Barbieri 2, Moad Alosta 1, George Uwadiegwu Alaneme 3 and Qadir Bux alias Imran Latif 1,*

1 Department of Civil and Environmental Engineering, College of Engineering, University of Nizwa, P.O. Box 33, Nizwa 616, Oman
2 Department of Civil and Environmental Engineering, Norwegian University of Science and Technology, Høgskoleringen 7A, Trondheim, 7491 Trondheim, Norway
3 Department of Civil Engineering, Kampala International University, Kampala 20000, Uganda
* Correspondence: a.milad@unizwa.edu.om (A.M.); qadir.omran@unizwa.edu.om (Q.B.a.I.L.)

Abstract: Portland cement (PC) is a common material used in civil infrastructure engineering. Cement production emits roughly 2.2 billion tons of CO$_2$ per year, contributing 8% of global emissions in 2016. This contributes to almost half of the calcination process, and together with thermal combustion, clinker generation could be responsible for 90% of the sector’s emissions. One effective technique for dealing with these industrial by-product wastes is to employ them to make cement replacements such as concrete and mortar, which can be used in a variety of applications. As a result, the purpose of this research is to review the current advancements, challenges, and future perspectives on the utilization of agro-industrial waste (AIW) produced around the world in cement-based products. Geopolymers (GPs), on the other hand, reduce carbon dioxide emissions and have the potential to be a complete or partial replacement for PC in the construction sector. The GP technology enables the use of AIW in combination with an alumina–silicate (A–S) phase with minimal environmental impact. GP-cement is mostly produced by activating alkali silicates or alkali sols with secondary raw materials such as calcined clays, fly ash (FA), zeolite, metakaolin, etc. Mixing various resource materials, including additives, A–S, and alkali sols, alkali concentrations, optimizing the curing temperature, the SiO$_2$/Na$_2$O ratio, microstructural behavior, and other factors, results in GP-cement with outstanding mechanical and durability characteristics. The review concludes that AIW-based geopolymer composites have shown promising results in terms of their mechanical properties, durability, and environmental sustainability, which makes them emerge as promising future building materials with applications in a wide range of industries.

Keywords: GP; waste-derived materials; sustainable; eco-friendly; mechanical and durability properties

1. Introduction

Geopolymer (GP) is an inorganic material usually produced from aluminosilicates or ceramics that creates non-crystalline or amorphous, long-range, covalently bonded networks with its temperature-dependent microstructure when mixed with an alkaline activator solution. It can be considered as a green cement that has superb mechanical characteristics, low energy in its production, and releases less carbon dioxide for the life cycle global warming intensity of concrete [1]. Furthermore, applications of GP may be used for coatings and adhesives, high-temp ceramics, medicinal applications, geotechnical for the purpose of soil stabilization, the construction of asphalt pavement, and new types of cement for concrete [2–4]. GP usage has more advantages than the ordinary PC since it can protect the environment and provide materials that can save energy used for construction works, which include wastes as a sustainable resource that allows the reuse and recycling of agricultural and industrial waste and its by-products, for instance as biomass ash, FA, cement kiln, and mine tailings [5]. GP contains superb characteristics, such as corrosion and fire resistance to chemical...
Concrete is a composite material that combines aggregates and binders to form a versatile building material that is used in many structural construction projects and has a global consumption of around 30 billion tons per year. Hence, there is a reduction in the amount of PC that is used as a fundamental binder to create conventional concrete [8]. Furthermore, the production of PC is related to harmful environmental issues such as carbon dioxide emissions and the severe usage of natural resources [9]. A cumulative amount of 1.5 tons of raw materials is needed to mix with approximately 1 ton of PC to generate 0.55 tons of carbon gases, with the burning fuel producing approximately 0.4 tons of CO\textsubscript{2} that sum up from 0.85 to 1.1 tons of carbon gas emissions [10]. Moreover, industrial cement production is related to burning approximately 12 to 15 percent of fossil fuels in the kiln or furnace, decarbonation of limestone, and using electrical energy. Since the past decade, there has been an increase in awareness related to environmental issues due to the production of PCs [11,12]. As a result, professionals and researchers in the construction industry have been searching for viable alternative approaches to generating sustainable green materials for construction in order to achieve zero carbon emissions by recycling solid wastes and their by-products by replacing conventional concrete materials [13]. The principal advantage of using GP-cement is low fuel usage and decreasing the emission of carbon dioxide since chemical procedures produce zero carbon dioxide and can cause an 80% to 90% reduction in carbon dioxide emissions. Other benefits are shown in Figure 1. First of all, the low carbon footprint of geopolymer cement has a lower carbon footprint than traditional Portland cement, making it an environmentally friendly choice for construction projects. Secondly, the durability of geopolymer cement is highly durable and can withstand extreme weather conditions. Third, the cost-effectiveness of geopolymer cement is higher than that of traditional cement, as it requires less energy and materials to produce. Forth is strength. Geopolymer cement is stronger than traditional Portland cement and can withstand higher temperatures and pressures. Moreover, geopolymer cement has a higher fire resistance than traditional cement, making it an ideal choice for construction projects that need to be more fire-resistant. Hence, geopolymer cement requires less maintenance than traditional cement, making it easier and more cost-effective to maintain. Finally, geopolymer cement can be used in a wide range of construction projects, from roads to bridges to buildings [3].

Figure 1. Advantages of GP-cement usage for sustainable constructions.
The deployment of eco-friendly and sustainable practices in the development of agro-industrial waste-based geopolymers has significant environmental, social, and economic benefits. By utilizing waste materials as a resource, we can reduce waste, conserve natural resources, and reduce greenhouse gas emissions while also creating new economic opportunities [14].

Foregoing research has demonstrated that the use of industrial residues and their derivatives for substituting PC, for instance, ground-granulated blast-furnace slag (GGBFS) and FA, can minimize the emission of greenhouse gases caused by the production of cement by about 10% to 20% [15,16]. The usage of alkali-activated (AA) binders in the construction sector has gained considerable attention in the past decades as excellent binders that can be developed without PC. AA binder systems are useful for managing waste as they can integrate and recycle industrial agro-waste and its products, namely palm bunch, residual ashes from rice husk, thermal power plants (FA), slag from steel plants, wood wastes, and bagasse [17]. In 2016, Assi et al. [18] carried out research on the initial and final compressive strengths improved by FA-based GP concrete at room temp. However, the results show that compressive strength obtained without external heat could be enhanced through PC usage as a partial ratio of FA. Moreover, the permeable void ratio is influenced by the PC ratio, which increases due to the significant reduction [19].

Additionally, in 2018, Reddy et al. [20] carried out investigative research that showed that GP-cement is more homogeneous and well bonded to the aggregate, notably with less surface failure than PC. Based on that, long-term durability and corrosion-based enhanced-crack resistance are achieved using GP-cement. The influence of age on GP strengths of the GP mixtures varies from those of PC. The GP-cements have higher compressive strengths, ranging from 29.7 MPa (8 M) to 56.2 MPa (14 M) on the 7th day and from 40 MPa (8 M) to 60.2 MPa (14 M) on the 28th day, while for the concrete mixture with PC, the values were 22 at 7 days and 33 MP at 28 days. These findings denote an increase in strength between the 7 and 28 days, with 15% (8 M) and 7% (14 M) for the GP-cements. As for PC, there was an increase of 33% from the 7 to 28 days. GP-cement has consistently higher splitting-tensile strength compared to PC. Furthermore, in their experimental studies, Zerfu and Jaya [21] noted that GP concrete using FA has significant engineering, environmental, and economic benefits compared to conventional PC concrete. The literature review noted that GP has better compressive strength and is more economical compared to PC concrete, for instance, in terms of resistance to corrosion and environmental pollution. This review aimed to investigate the usage of an agro-industrial by-product, for instance, FA, rice-husk ash, saw dust ash, etc., as a resource material that contains A–Ss to produce green GP concrete by utilizing metallic alkali activators. The information obtained from this review will provide the required knowledge to integrate and recycle waste that is generally disposed into the environment to obtain eco-friendly and sustainable materials for construction. Moreover, to assess the effect of industrial agro-waste on the performance of AA binders according to mechanical strength and durability, green concrete is created using various molar concentrations and kinds of activators. Furthermore, this review will explore the latest research on the synthesis and properties of geopolymer composites derived from agro-industrial wastes, with a particular focus on their potential applications in sustainable construction materials [22].

2. GP Elements (Composition)

Geo polymerization is an advancement in technology that alters pozzolanic materials that contain A–S by a chemical procedure using the alkaline solution to create beneficial GP materials, as displayed in Equation (1). It is vital to ensure this procedure takes place at either room or slightly raised temp. [23].

\[
\text{Alumina-silicate} + \text{Alkali (NaOH or KOH)} = \text{GP Paste} \quad (1)
\]
During the geo polymerization process, the following two basic procedures are observed: First, use sodium–hydroxide to dissolve the A–Ss obtained from the pozzolanic ash materials to get small ions of reactive silica and alumina. Next, the polycondensation process forms amorphous to semi-crystalline polymers [24]. Inorganic materials containing A–S will react chemically with alkaline sols, which leads to the polycondensation process to create GPs that have three basic structures depending on the ratio of alumina to silica [25]. The three basic structures are namely poly (sialate), poly (sialate–silox), and poly (si-alate–disiloxo), as shown in Figure 2.

![Figure 2. Structure of polysialates.](image)

Due to the activation of alkali in the aluminosilicates in FA industrial residue, GP, which is an inorganic polymer, is obtained with the chemical structure presented in Equation (2) [26].

\[ M_k \left\{ \frac{-(SiO_2)_q - AlO_2}{k} \right\} \]

where M denotes the alkali cation, k denotes the polycondensation degree, and q denotes the alumina-to-silica ratio. Under alkaline conditions, a 3-D polymeric chain structure is generated during the chemical process, whereby inorganic synthetic GP is obtained. The microstructural and mechanical characteristics of the developed GP are influenced by the composition of the raw materials and the alkaline solution concentration [27]. Generally, GPs are produced by mixing source pozzolanic materials and alkaline sols. These A–S materials are mixed with a suitable molarity concentration of metallic hydroxide alkalis solution to produce sodium silicates and GPs [28]. Figure 3 displays what takes place throughout the FA polymerization process.
The AA is usually milled together and reduced to fine-grain mixture particles that are similar to PC. This mixture is created using different amounts of water, as displayed in Figure 4 [29].

Geo polymerization of FA and alkali solution, which serves as the resource material for A–S, produces a chainlike structure and 3-D polymeric ring with Si-O-Al-O bonds that are produced in ambient temp. and is an energy-efficient cleaning procedure. Firstly, the geo-polymerization process involves dissolving Si and Al atoms using hydroxide ions. Next, the source material ions will be converted into monomers. Finally, the developed

![Diagram of Geo polymerization process of fly ash (FA).](image)

Figure 3. Geo polymerization process of fly ash (FA).

![Diagram of Dry mixing geo polymerization.](image)

Figure 4. Dry mixing geo polymerization.
monomers will go through polycondensation into polymeric structures [30,31]. These stages of geo-polymerization might take place simultaneously or in an overlapping manner. During the second stage of polymerization, water is eliminated, but water is consumed during PC hydration. Furthermore, due to the varying sizes and densities of the ionic charges, different cations from the alkali solution affect the growth and nucleation of A–S chains in different ways. Hence, the rate and extent of polymerization that takes place change. For example, potassium cation (1.33 Å), which is larger in size and possesses a lower density charge compared to sodium cation (0.97 Å), generates a GP matrix with a much higher level of polymerization [32].

2.1. Fly Ash FA

FA, also known as flue ash, is a spherical and glassy element that forms grey powder and is generated by steam-generating plants and coal-fired power stations’ waste. It has pozzolanic characteristics that denote the rich presence of aluminum and silicate oxides, referred to as supplementary cement-based materials. Additionally, FA as an IW is very suitable for various engineering apps, for example, landfills, mines, flowable fills, and GP concrete [33]. Generally, FA is described as a by-product of coal power plant combustion that forms fine particles that soar upwards with flue gases, but the bottom ash will not rise. It is a heterogeneous material that has a chemical composition made of mainly Al₂O₃, ferric oxide, and silicon [34]. FA is a common ingredient used in the production of geopolymer concrete, which is a sustainable alternative to traditional Portland cement-based concrete. However, the quality of FA can significantly impact the performance and properties of the resulting geopolymer concrete, such as improving its mechanical and workability behavior while reducing shrinkage, environmental impact, and the risk of alkali–silica reaction (ASR) [35,36]. Overall, using high-quality FA in geopolymer concrete can lead to a more durable, workable, and sustainable construction material. Careful selection and testing of FA can ensure that geopolymer concrete meets the necessary standards and specifications for a reliable and long-lasting building material [37].

Many studies have been carried out to explore viable alternatives to minimize the dependence on PC in the civil construction field by developing sustainable green technologies by the use of FA [38]. GP concrete production using FA looks promising in providing materials that can substitute cement binders to reduce and stop carbon gas emissions [39]. These materials are vital components of AA green concrete because there are plenty of the required raw materials containing sufficient amounts of calcium, alumina, and SiO₂ in reactive form. Environmental pollution has become an issue since approximately 60 percent of FA is used haphazardly as a landfill [40]. Nuaklong et al. [41] have done a study on the mechanical and fire resistance characteristics of FA, which has a rich content of calcium oxides, to create an AA concrete mixture with rice-husk ash that is an eco-friendly and sustainable construction material. Their findings revealed that the compressive strength of GP at 28 days’ hydration was between 36 and 38.1 N/mm² because of the requirement for enhanced density and microstructure in the blended matrix. Moreover, adding rice-husk ash to silica had a negative influence on the residue’s fire resistance strength characteristic. Wong et al. [24] stated that FA, which is rich in calcium when mixed with brick powder, generated 44.21 N/mm² after being cured for 28 days. Furthermore, laboratory findings revealed that replacing the brick powder with more than 10 percent indicated an inhomogeneous microstructure in the concrete matrix. The chemical composition and relevant app of FA in the alkaline-activated binder are displayed in Tables 1 and 2.
### Table 1. The chemical composition of FA.

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>SO(_3)</th>
<th>TiO(_2)</th>
<th>K(_2)O</th>
<th>CaO</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>Na(_2)O</th>
<th>LOI FA (Class)</th>
<th>FA References</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.46</td>
<td>0.1</td>
<td>2.02</td>
<td>0.95</td>
<td>0.93</td>
<td>60.42</td>
<td>31.06</td>
<td>3.34</td>
<td>-</td>
<td>-</td>
<td>F</td>
<td>[42]</td>
</tr>
<tr>
<td>0.98</td>
<td>0.88</td>
<td>-</td>
<td>2.46</td>
<td>3.23</td>
<td>49.9</td>
<td>24</td>
<td>14.4</td>
<td>-</td>
<td>3.5</td>
<td>C</td>
<td>[43]</td>
</tr>
<tr>
<td>0.97</td>
<td>0.05</td>
<td>-</td>
<td>1</td>
<td>1.29</td>
<td>57.9</td>
<td>31.1</td>
<td>5.07</td>
<td>0.09</td>
<td>0.8</td>
<td>F</td>
<td>[44]</td>
</tr>
<tr>
<td>0.76</td>
<td>0.31</td>
<td>-</td>
<td>0.23</td>
<td>0.31</td>
<td>65.6</td>
<td>26.5</td>
<td>5.49</td>
<td>0.36</td>
<td>0.41</td>
<td>F</td>
<td>[45]</td>
</tr>
<tr>
<td>0.6</td>
<td>0.2</td>
<td>-</td>
<td>0.9</td>
<td>0.2</td>
<td>70.3</td>
<td>23.1</td>
<td>1.4</td>
<td>0.4</td>
<td>2</td>
<td>F</td>
<td>[46]</td>
</tr>
<tr>
<td>1</td>
<td>0.4</td>
<td>-</td>
<td>1</td>
<td>0.5</td>
<td>62.3</td>
<td>28.1</td>
<td>2.1</td>
<td>0.5</td>
<td>2.5</td>
<td>F</td>
<td>[47]</td>
</tr>
</tbody>
</table>

### Table 2. Relevant studies on the application of FA in alkaline activation materials.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Geo Polymerization Materials</th>
<th>GP Chemical Composition</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jiang et al. [48]</td>
<td>Na(_2)SiO(_3) and NaOH sols alkaline activators with Class F FA as source material.</td>
<td>NaOH of 8 M, sodium oxide of 8.3%, silica of 28.7%, and 63% water.</td>
<td>Improved thermal–mechanical property of produced GP.</td>
</tr>
<tr>
<td>Rahmadina and Ekaputri [49]</td>
<td>Na(_2)SiO(_3) and NaOH sols were the activators, while Class F FA was the source material.</td>
<td>NaOH of 8 M, sodium oxide of 18.5%, silica of 36.4%, and 45.1% water.</td>
<td>GP compressive strength increased up to 27%, and porosity has an effect on its mechanical property.</td>
</tr>
<tr>
<td>Payakaniti et al. [50]</td>
<td>NaOH and Na(_2)SiO(_3) sols alkaline activators with Class C calcium lignite FA as source material.</td>
<td>NaOH of 10 M, sodium silicate of 12.53% by sodium oxide weight, silica of 30.24%, and 57.23% water.</td>
<td>The mechanical behavior of GP paste improved due to the geopolymerization reaction.</td>
</tr>
</tbody>
</table>

2.2. Acid-Based Agro-Industrial Waste-Based Geopolymer Concrete

Acid-based agro-industrial waste-based geopolymer concrete is a type of concrete that is made from agro-industrial waste materials and a mixture of acid and alkali solutions [51]. The acid-based approach involves using an acid, such as hydrochloric acid or sulfuric acid, to dissolve the silica and alumina from the agro-industrial waste material, which is then mixed with an alkali solution, such as sodium hydroxide or potassium hydroxide, to form a geopolymer binder [52]. The chemical reactions involved in the production of acid-based agro-industrial waste-based geopolymer concrete are complex and involve several steps [53]. The following is a simplified overview of the chemical reactions that occur during the production of geopolymer concrete using acid-based agro-industrial waste:

1. Activation of the waste material: The agro-industrial waste source materials are first activated using an acid solution, typically hydrochloric acid or sulfuric acid. The acid reacts with the silica and alumina in the waste material, forming soluble silicates and aluminates [54];

2. Formation of the geopolymer gel: The activated waste material is then mixed with an alkaline solution, typically sodium hydroxide or potassium hydroxide. This causes a chemical reaction between the soluble silicates and aluminates, resulting in the formation of a geopolymer gel. The gel binds together the waste particles, forming a solid material with cement-like properties [55];

3. Solidification of the geopolymer concrete: The geopolymer concrete is then cast into the desired shape and left to solidify. During this process, the geopolymer gel continues to harden and strengthen, resulting in a final product that is strong, durable, and resistant to acid and alkali attack [56].

The chemical reactions involved in the production of acid-based agro-industrial waste-based geopolymer concrete are similar to those involved in traditional cement-based concrete but with some notable differences [57]. Geopolymer concrete does not require the high-temperature kiln firing that is necessary for the production of cement-based concrete, which results in a significant reduction in carbon dioxide emissions. Additionally, the
use of waste materials as raw materials for geopolymer concrete promotes sustainability and helps to reduce waste sent to landfills [58]. The use of acid-based agro-industrial waste-based geopolymer concrete has several benefits, including:

i. Sustainable use of waste materials: The use of agro-industrial waste materials as raw materials for geopolymer concrete helps to reduce waste and promote sustainability. Agro-industrial waste materials such as rice-husk ash, sugarcane bagasse ash, and coconut shell ash can be used to make geopolymer concrete, which reduces the amount of waste that goes to landfills [59];

ii. Lower carbon footprint: The production of acid-based agro-industrial waste-based geopolymer concrete results in significantly lower carbon dioxide emissions compared to traditional cement production. This is because the production of geopolymer concrete does not require high-temperature kiln firing, which is responsible for a significant portion of the carbon dioxide emissions associated with cement production [60];

iii. Improved durability: Acid-based agro-industrial waste-based geopolymer concrete has been found to have better durability compared to traditional concrete. This is because geopolymer concrete has a higher resistance to acid and alkali attacks, as well as a lower permeability, which helps to prevent the penetration of water and other harmful substances [61];

iv. Cost-effective: The use of agro-industrial waste materials as raw materials for geopolymer concrete can be cost-effective, as these waste materials are often inexpensive and readily available. Additionally, the production of geopolymer concrete can help reduce costs associated with traditional cement production, as well as reduce energy and transportation costs associated with waste disposal [62].

Overall, acid-based agro-industrial waste-based geopolymer concrete is a sustainable and cost-effective alternative to traditional cement-based concrete. By utilizing waste materials as a resource and reducing the carbon footprint of the construction industry, acid-based agro-industrial waste-based geopolymer concrete can help promote environmental sustainability and economic development [63].

3. Methodology

This literature review aimed to examine the ability of various industrial agro-waste and their derivatives (ash) in the production of AA binder concrete to create eco-friendly and cost-effective construction materials [64]. The use of agro-industrial waste-based geopolymer composites has gained significant attention due to their potential to reduce waste and create sustainable materials. However, the literature on this topic is scattered, making it difficult to obtain a comprehensive understanding of the current state of research. This systematic review aims to synthesize the existing research on agro-industrial waste-based geopolymer composites using the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines [65,66]. A systematic search was carried out in four electronic databases (Scopus, Web of Science, ScienceDirect, and PubMed) to identify relevant studies published from 1995 to 2022, as shown in Figure 5. The search was performed using a combination of keywords related to agro-industrial waste-based geopolymer composites. Studies that met the inclusion criteria were evaluated for their quality using the Bias tool [67,68]. The initial search yielded 1455 studies, of which 135 were considered eligible for inclusion in this review. The studies were published between 2001 and 2022, and the majority of them were experimental and review studies. The studies investigated the effects of various parameters, such as the composition of the waste, the alkaline activator used, and curing conditions, on the microstructural durability and mechanical behavior of the composites. The schematic diagram of this methodological process is shown in Figure 6. In line with the foregoing, related and relevant literature studies on industrial agro-waste ashes, for instance, FA, sugarcane bagasse ash (SBA), palm oil fuel ash (POA), rice-husk ash (RH–SiO₂), sawdust (SA), and GGBFS, were discovered in this search and screening process [69,70]. Suitable keywords or subjects, for instance, A–Ss
and geopolymORIZATION, alkalis, AA binder, material science, potassium–hydroxide (KOH), sodium–carbonates (Na$_2$CO$_3$), sodium silicates (SS) and sodium–hydroxide (NaOH) were utilized to search in the research databases [71,72].

![Graph showing the number of publications from 1995 to 2022](Image)

**Figure 5.** Significant research materials published since 1995.

**Figure 6.** Overview of article search and screening procedure using PRISMA.

### 4. Geo Polymerization Overview

In 1978, the idea of GP was introduced by Davidovits to include A–S materials created by SiO$_2$ (silica) and amorphous Al$_2$O$_3$; dissolved in a highly AA medium at room temp. Furthermore, strong alkalis such as sodium and potassium-hydroxide are very suitable for dissolving SiO$_2$ and Al$_2$O$_3$; to produce A–S items [73]. This chemical reaction is highly influenced by the characteristics of the raw materials, the duration, and temp. of curing, and the concentration of AA. Several studies have revealed that silica and Al$_2$O$_3$; sources are found in abundance in agricultural waste materials and their by-products, whereas
alkalis can be obtained from the industrial chemical market [74]. Moreover, many industries, for instance, power plants, steel, aluminum, and biomass, have different ways to save their waste and by-products. Cement and steel manufacturing IW contain plenty of calcium and silica minerals that can be utilized for formulating different types of calcium silicates, while the IW used in the aluminum manufacturing sector, for example, red mud, kaolinite, and laterite kondalite, contains chemical content that is suitable for geo polymerization [75]. Additionally, agricultural waste biomass, namely bagasse, cassava peels, rice husk, palm bunch, and Bambara nutshe, contain approximately 80–90% SiO\(_2\) in amorphous form and are used as a GP process cost-cutter [76–79]. Moreover, residue from power plants, for instance, FA and bottom ash, contains good pozzolanic features that can be utilized in the production of concrete to partially reduce the usage of PC by up to 30% by weight. On the other hand, 100% of geo polymerization FA is utilized as construction material. This method of replacing cement with industrial or agricultural residues is a synergistic approach that encourages waste recycling to obtain sustainable construction materials and minimizes emissions of greenhouse gases [80,81]. The mechanical characteristics of GP binder depend upon the cement-supplementary cement-based materials replacement ratio, type and mineralogical composition of waste materials, and mixture design methodology [82]. Moreover, in terms of GP-embodied energy, the FA GP mixture requires approximately 40% energy in comparison to PC-based concrete material. Nevertheless, the alkaline activator chemical components used approximately 39% energy for sodium-hydroxide but 49% energy for sodium silicates. Hence, finding alkaline alternatives for liquid residue is necessary to produce a more economical GP. Therefore, a low-cost solution for the production of GP is required to provide AAs through an industrial liquid residue [83,84]. The Bayer liquid solution acquired from Al\(_2\)O\(_3\); offers a cost-effective solution since it contains a sufficient amount of A–S needed to create GP source material. Besides the availability of raw materials and construction materials for the new green building, the waste management and control mechanisms render GP crucial for accomplishing sustainable and eco-efficient infrastructural development [85]. Hence, it is vital to study carefully and evaluate the mechanical and chemical characteristics and financial benefits of various kinds of GP-cement produced utilizing agricultural and IW to determine the research gaps. The literature review is projected to recommend guidelines for contractors, engineers, project managers, and industrial sectors, besides assisting in the development of new sustainable construction materials created through the GP technique [86].

4.1. Parameters for the Mixture of GP

Alkaline-activated material is a huge classification of materials that combines different kinds of binder products obtained from chemical reactions involving alkaline metal sources, whether in the solid or solution state and A–S powder. The alkaline sources, namely carbonate, sulfates, alkali–hydroxides, Al\(_2\)O\(_3\), SiO\(_2\), and cations, are able to increase the pH and act as a catalyst or speed up the solid solution of the source material. Alkali silicates and hydroxides are generally used as AAs, in which the characteristics of the activators play a vital role in the activation process [87,88].

4.2. Effects of Potential Hydrogen (PH)

The main role of the alkaline activator is to facilitate the dissolution of the A–Ss and catalyze the reaction, normally at a higher pH level. Silicates and alkali-hydroxides produce the highest pH values, followed by carbonates and sulfates, which create the moderate alkaline condition. Normally, a pH higher than 11 is a prerequisite for activating sols. It is noted that the maximum pH level for GGBFS or the FA is approximately 13 to 13.6 [89]. Furthermore, the effect of pH on the activation of pozzolanic materials depends significantly on the kind of activator because the solubility of calcium decreases at higher pH levels, but the solubility of SiO\(_2\) and aluminum increases. Nevertheless, the sodium hydroxide (NaOH) solution activation occurs at a higher pH level than Na\(_2\)SiO\(_3\) sols with similar alkali concentrations. Hence, the quantity of reacting pozzolanic substances compared
to the presence of various types of activators will help in developing better performance in the mechanical strength of silicates than those activated with NaOH. This is caused by calcium–silicate–hydrate (C-S-H) gel that is created when the additional silica reacts with the calcium ions derived from the dissolved ash materials [90,91]. Normally, the activators utilized for A–Ss activations with low content of calcium are those with a pH similar to 8 M of NaOH solution. A decrease in the alkaline level will have a negative influence on the mechanical strength of the cement because the generated ionic bonding in the activator’s binding system is not high enough to sufficiently hydrolyze the aluminum and SiO$_2$ in the resource material [92]. Studies have indicated that mixture design range and methodology parameters affect the mechanical strength and rheological properties of GP concrete incorporating FA. Ling et al. [25] studied the importance of four design factors, liquid/FA ratio, SiO$_2$/Na$_2$O ratio, temp. of concrete curing, and the concentration of AA in the time setting and strength of GP concrete mixed with FA with high content of calcium oxide. The findings revealed that the SiO$_2$/Na$_2$O ratio was noted to accelerate the setting time of the blended FA-GP concrete and decrease the strength response as the ratio increased. It was observed that an increase in the concentration of the AA led to a prolonged setting time for the combination containing SiO$_2$/Na$_2$O with a ratio of 1:1.5, but when the SiO$_2$/Na$_2$O ratio was raised to 2.0, the setting time was shorter. However, the compressive strength of these GP mixes has improved. Moreover, laboratory findings noted that higher temp. applied for hydration of the concrete resulted in an increase in the compressive strength of the blended concrete [93]. Zhang and Feng [26] noted that water, temp., and molar concentration of AA (NaOH) significantly affect the development of the mechanical features of FA GPs, which are rich in calcium oxides. Furthermore, Abdullah et al. [23] noted that mixed design parameters, for instance, the Na$_2$SiO$_3$/NaOH ratio, the alkaline activator/fly ratio, and temp. of concrete hydration affect the compressive strength of FA GP concrete. The experiments carried out in the laboratory revealed that for 12 M of NaOH solution, the masses of 2.5 and 2 for the Na$_2$SiO$_3$/NaOH and FA/alkaline activator ratios, respectively, created maximum compressive strength results. The findings from relevant literature studies [94,95] noted that an FA/alkaline activator ratio in the range of 3.3–4 is required to produce GP concrete with improved and better compressive strength performance. Moreover, Sathonsaowaphak et al. [30] noted that FA-GP's concrete in the range of 1.4 to 2.3 FA/alkaline activators ratio produced compressive strengths in the range of 42 to 52 N/mm$^2$. Nevertheless, the findings also noted that the optimum Na$_2$SiO$_3$/NaOH ratio is 1.5.

5. Properties of Agro-Industrial Waste (AIW) Ashes

AIW ashes are utilized as source materials in the AA binder concrete, as they contain an adequate amount of silica and alumina that basically influence its binding ability. The outcomes of GP binders or the blending products depend on the condition of curing, type of metallic alkali, and source materials [96–98]. These elements influence the performance of green concrete. Thus, it is very crucial to note the mineralogical elements of the precursors during the alkali activation GP process. The source materials are usually classified into low-calcium and high-calcium source materials with high contents of A–S. The elemental components of varying AIW ashes include GGBFS, FA, rice-husk ash (RH–SiO$_2$), POA, SBA, and sawdust ash (SA), as noted by several researchers and presented in Figure 7. From the plotted graph, it can be observed that RH–SiO$_2$ possesses a maximum SiO$_2$ content of 80% to 85%, followed by SBA, SA, and FA, while GGBFS possesses a minimum content of 40% to 45% [99,100].
which caused an increase in the source material waste ash samples’ specific gravity response. This is improved by focusing on the incineration or processing methods to obtain an adequate level of relative density and suitable fineness [106–108].

Figure 7. Composition of mineralogical oxides in residual ashes.

FA was noted to contain a maximum content of Al2O3 of approximately 26–32%, but GGBFS only contained 12–16%. Meanwhile, agro-waste ashes contained the least alumina, ranging from 3% to 10%. When the source materials were combined with the metallic alkaline solution, the product obtained was sodium A–S hydrate gel. However, when combined with lime (CaO), the product obtained was calcium A–S hydrate gel [101]. However, GGBFS was observed to contain maximum lime content of approximately 35 to 39%, while FA produced approximately 15 to 23% lime, and the agro-waste ashes produced minimum lime content with RH–SiO2 of approximately 2 to 5%. Furthermore, FA was noted
to contain a maximum amount of ferrite (Fe₂O₃) of approximately 4–10%, but agro-waste ashes and GGBFS contain similar quantities [102,103]. However, FA and GGBFS produced the minimum content of total alkalis at approximately 1% to 4%, while the agro-waste ashes contain higher total alkalis, with POA producing the maximum at approximately 6% to 9%. This is attributed to the higher content of potassium oxide in the agro-waste ashes, whereas ions, for instance, metallic sodium, can help to balance the negative charges in the form of SiO₄ and AlO₄ [104]. Furthermore, the agro-waste ashes were noted to yield a higher LOI, and SBA has a maximum content of approximately 4% when compared to IW ashes, which have a minimum GGBFS of 1.5–2.5%. LOI revealed that the waste ashes contain unburnt carbon that can cause unpleasant performance in the AA binder (AAB) concrete. A large amount of unburnt biomass particles can trigger a larger LOI, which in turn causes uncontrolled burning [105].

Specific gravity is an important factor that influenced the mixing, proportioning, and workability of the ingredients used in the concrete and also affected the performance of the waste ash-based AA binder. Mixing source materials with a minimum specific gravity adds a greater amount of powder to AAB at higher levels of replacement. GGBFS produced the highest specific gravity outcome at approximately 2.8 to 2.95, followed by FA at 2.2 to 2.5, whereas the agro-waste ashes generated minimum results of at least 1.9 to 2.1 with SBA, as illustrated in Figure 8. It can be observed from the graph that the reduction in the values of the LOI is possible because of the removal of fibrous biomass elements, which caused an increase in the source material waste ash samples’ specific gravity response. This is improved by focusing on the incineration or processing methods to obtain an adequate level of relative density and suitable fineness [106–108].

![Figure 8. Specific gravity of residual ashes.](image)

5.1. Industrial-Agro-Waste Ashes-Based AAB Microstructural Properties

The microstructural properties of industrial-agro-waste ash-based AAB (alkali-activated binders) depend largely on the type of waste material used. Different types of industrial-agro-waste ashes have various amounts of alkali-soluble silica, alumina, and calcium that can be used to create the AAB. In addition, the microstructural features of the AAB, such as the particle size, porosity, and chemical composition, will also be affected by the type of industrial-agro-waste ashes used [107]. The physical characteristics and behaviors of AIW ashes appeared to be the same. Nevertheless, they possessed different morphological and microstructural features. Fresh or hardened properties of AA binder concrete were notably influenced by the morphology, surface area, and reactive nature of the waste by-products [109]. Microstructural assessment has been conducted in several recent studies by utilizing various microscopic tools, such as the scanning electron microscope (SEM), optical microscope, and scanning probe microscope (SPM), which are the most commonly used methods for morphological investigations. Figure 9 depicts the findings from relevant
literature studies; the effects of various AIW on GP revealed solid and hollow spherically-shaped particles of various sizes, including cenospheres and plerospheres for FA [110,111]. FA particles of various round shapes significantly improved the workability of FA-based AA binder concrete, allowing it to achieve an acceptable mechanical strength. The findings illustrated in the micrograph plot revealed that SBA contained varying carbon and silica-rich particles in the shapes of fibrous, dumbbell, spherical, irregular, and prismatic. These microstructural particulars notably decreased the practicality and increased the demand for the water/binder ratio. The dumbbell-shaped particles in the SBA samples are noted as phytoliths scattered among the granular fibrous particles. Cordeiro et al. [93] have studied the impact of color, temp., and reactivity on LOI. Beyond 800 °C, recrystallization of amorphous silica to tridymite and cristobalite occurred, and more prism-shaped particles were observed in the micrograph of calcined SBA samples. In addition, the microstructural properties of RH–SiO₂, as displayed in Figure 9, revealed that the particles contained porous, angular, cellular, and irregular shapes and textures [112,113]. The reactive amorphous silica can have a cellular structure; the samples that were cellular and porous contained greater surface area, thereby having greater water-absorption features. Furthermore, the POA morphological features indicated irregularly porous cellular particles with pedospheres that are similar to FA. On the other hand, the SA micrograph revealed irregular particles with fibrous and rough surfaces. Moreover, the GGBFS micrograph revealed particles that are irregular, quadrilateral, and angular [114–116].

![Residual ashes’ SEM micrographs](image-url)

Figure 9. Residual ashes’ SEM micrographs. (a) FA [113], (b) GGBFS [113], (c) SBA [93], (d) RH–SiO₂, (e) POA [97] and (f) SA [116].
5.2. Industrial-Agro-Waste Ashes-Based AAB Mechanical Strength Properties

The influence of activators in the processes of activating alkali and industrial agro-waste ashes is very important in the geo-polymerization reaction to obtain green concrete. Different metallic alkalis at varying concentrations are utilized, such as sodium carbonate (Na$_2$CO$_3$), sodium-hydroxide (NH), sodium silicate (SS), sodium sulfate (Na$_2$SO$_4$), sodium silicate and sodium-hydroxide combination (NH+SS), and potassium hydroxide (KOH) [117]. The literature review revealed that the metallic alkalis NH, SS, and NH+SS were noted as the most commonly used activators for AA binder concrete. Their influence on the compressive strength responses after curing for 28 days was studied using the AIW ash source materials. The GGBFS source material activated with SS (2 M) generated the highest strength result of approximately 80 MPa, as illustrated in Figure 10, which is attributed to the homogenous structure of the blended mix paste morphology in the early phases compared to the NH activator [118,119]. The strength of the outcome generated was greater than the response when NH (4 M) was utilized, and this is equated to the influence of CO$_3$-2 anions. POA mixed with SS AA binder produced concrete with higher compressive strength. FA specimens have a lower compressive strength characteristic than GGBFS-based AA combinations, but with the addition of NH+SS, the highest strength was obtained by the FA combination [120,121]. In addition, when FA and 25% of GGBFS were replaced by SBA and SA combinations, respectively, similar results were obtained. Hence, in terms of AIWs-based AA concrete combinations, NH+SS was noted to be the best metallic alkaline activator to produce increased mechanical strength characteristics. Furthermore, when KOH alkalis are added to SBA source material, a higher initial strength is produced because of the existence of potassium ions in SBA [122,123]. The greater the quantity of alkali metal cations present in the solution, the larger the quantity of Al-O-Si bonds available in the A–S gels and sols. Furthermore, an increase in the quantity of the cations affects the Si and reaction product redistribution, leading to the formation of greater amounts of silicate reactants. The presence of potassium in the solution mix can help the silicates dissolve since it is a larger cation than sodium in the metal electrochemical series. Thus, it helps in geo polymerization that enables an earlier gain in strength than the NaOH-based AA binder samples [124,125].

![Figure 10. Impacts of AA on compressive strength of AAB in 28 days.](image-url)
6. Conclusions

This review assessed the potential of AIW ashes that can be utilized as source materials in AA binder GP concretes to obtain eco-friendly, green, and cost-effective construction materials. The following are the main conclusions that were obtained:

- RH–SiO\(_2\) was noted to contain the maximum silica content, whereas other agro-waste ashes that were studied had silica contents greater than 55%. SA was noted to contain the highest alumina content of approximately 10% for agro-waste ashes. Industrial ashes (GGBFS and FA) contain more alumina and less silica when compared to agro-waste ashes;
- The agro-waste ashes were noted to contain greater reactions in terms of LOI due to fibers present in the ash specimens. Hence, proper procedures for refining and sieving were utilized in helping to reduce LOI. Among the AIW ashes, specific gravity variation features were noted to be important to SBA and hence create a minimum reaction, while POA and FA have similar results ranging from 2.2 to 2.5;
- The AIW ashes contain different microstructural features varying from fibrous, spherical, irregular, and prismatic particles, as detected in the micrographs of GGBFS, SA, and SBA. RH–SiO\(_2\) and POA had cellularly irregular porous structures, whereas FA had solid and hollow spherical-shaped particles of varying sizes;
- The influence of metallic alkaline activators was evaluated, with NH\(_4\)SS being the most effective once mixed with AIW ash source materials. Additionally, the compressive strength rises significantly with the increase in molar concentration from 8 to 10 M for GGBFS, FA, SA, and SBA. Nevertheless, a decrease in strength was noticeable with an increase in molar concentration at approximately 10 M for the POA source material;
- However, the review also identified some challenges associated with the production of agro-industrial waste-based geopolymer concrete, including the variability in the chemical composition of the waste material and the potential environmental and health hazards associated with the acid activation process. Further research is needed to optimize the production process and improve the long-term durability and sustainability of agro-industrial waste-based geopolymer concrete;
- The expensive barrier of the activators was also a major limitation in the apps of AA binder concrete, paving the way for the development of cost-effective materials. Moreover, identifying locally sourced AIW for GP concrete and the definition of mixture proportion standardization for certain materials are the main issues in assessing the feasibility at industrial scales. Additionally, more research is needed to fully understand the long-term durability and sustainability of geopolymer concrete, standardization, and industrial-scale production;
- Furthermore, the use of agro-industrial waste-based geopolymer concrete has emerged as a promising and sustainable solution to traditional cement-based concrete. The review study examined the literature on the use of AIW materials in geopolymer concrete production;
- Further research is required to optimize the AIW ashes incorporation into AA binder GP concretes and to investigate the long-term performance of the materials.


Funding: The Article Processing Charges (APC) of this project are funded by the TRC research project BFP/RGP/EI/21/041 University of Nizwa, OMAN.

Data Availability Statement: Data supporting reported results is in the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.


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