Properties of geopolymers sourced from construction and demolition waste: A review

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Abstract

Geopolymers have been recognised as a viable replacement to ordinary Portland cement (OPC), providing a cleaner solution since it can significantly reduce greenhouse gas emissions as well as accomplishing effective waste recycling. Construction and demolition waste (CDW) has been recently identified as raw materials for geopolymers due to its availability and high contents of silica and alumina. This paper aimed at reviewing the current state-of-the-art on the geopolymer paste, mortar, and concrete production and their properties, with special attention paid to geopolymers incorporating CDWs. The review covers brief assessment of using CDWs in concrete, the mix design of geopolymer mixtures in addition to identification of the main factors influencing the performance of geopolymer containing CDW. The most recent data related to the mechanical and durability properties of CDW-based geopolymers are presented, while the cost and environmental impacts of using recycled materials in producing geopolymer concretes are also discussed. Geopolymer concretes have a vast range of possible applications, however, there are still several barriers facing commercialisation of geopolymers in construction industry. The review indicated that it is possible to produce geopolymer concretes from CDW-based materials with properties comparable to OPC-based ones; however, the selection of proper material composition should be carefully considered, especially under normal curing conditions.

Keywords: Geopolymer concrete; Mechanical properties; Construction and demolition waste (CDW); Mix design; Sodium silicate; Life cycle assessment.

1. Introduction

Concrete is the most used material in the construction sector, reaching approximately 30 billion tonnes of annual global consumption levels [1], depleting large quantities of ordinary Portland cement (OPC), which is the fundamental binder used to produce conventional concrete. However, the production of cement is associated with serious
harmful environmental issues such as intensive consumption of natural resources and greenhouse gas emissions. 1.5 tons of raw materials are approximately needed to produce one ton of cement, which directly generates around 0.55 tons of CO₂, while the combustion of fuels produces almost 0.4 tons of CO₂, releasing a total of 0.8-1.0 tons of CO₂ emissions [2]. According to Madlool et al. [3], the cement industry is also linked to consuming a significant amount of fossil fuels, representing proximately 12-15% of industrial energy. Globally, it is estimated that the manufacture of OPC generates around 1.35 billion tons of greenhouse gases every year, representing 6-9% of the global greenhouse gas emissions [4], which is mainly caused due to the combustion of fuel in the furnace, de-carbonation of limestone, and consumption of electrical energy. Several chemical processes occur during the calcination of calcium carbonate; however, Equation 1, below, describes the main reactions that occur during the calcination of limestone and aluminosilicate materials [5,6].

\[
5\text{CaCO}_3 + 2\text{SiO}_2 \rightarrow (3\text{CaO}, \text{SiO}_2)(2\text{CaO}, \text{SiO}_2) + 5\text{CO}_2 \\
\]

(1)

Over the past three decades, there has been a growing awareness of the environmental concerns associated with the manufacturing of ordinary concrete, which has driven the researchers and cement industry to search for other methods to produce green sustainable materials. More recently, the World Green Building Council (WGBC) (2019) has published the strategies and guidelines for designing sustainable buildings and infrastructures with a plan to reach 40% lower carbon footprints by 2030, while the target is to attain zero CO₂ emissions by 2050. The main suggested actions are associated with using alternative fuels, capturing carbon dioxide and enhancing energy efficiency inside the furnace, replacing cement with nanoparticles and developing low-impact green concrete products and technology. Accordingly, geopolymers, which belong to the last option, have appeared as one of the most
successful alternatives to OPC-based binders/materials. This is not only related to geopolymers’ favourable environmental impact of reducing the energy consumption [7], and using waste materials, but also due to their superior mechanical and durability characteristics accompanied by the high potential of cost reduction [8], along with the excellent resistance against acids and high temperature [9,10]. Using geopolymers as a OPC substitute can also reduce the overall CO₂ footprint compared to traditional concrete. However, the rate of reduced emissions is widely varied as stated in previous assessments, ranging from 9% [11], to 26-45% [12], and reaching up to around 80% [13]. These huge differences are mainly associated with some key factors including transportation emissions, which are mainly linked to the availability and proximity of raw materials, concrete mixture compositions, activator type/quantity needed and production method used, and high-temperature curing.

Geopolymers are referred to the family of alkali-activated materials, and can be produced by polymerising different types of aluminosilicate precursors through activation processes using highly alkaline liquids and soluble silicates [14,15]. The precursors can originate from natural sources (e.g., clay and kaolinite) [16] or from by-products such as fly ash and ground granulated blast-furnace slag (GGFBS), which are no longer classified as waste materials due to their widespread and successful utilisation in the concrete industry as separate pozzolanic materials. These precursors can be singly used or mixed with each other. Hence, increasing attention is being paid to seeking other resources that can be successfully used in geopolymers to mitigate the huge demand for by-products.

On the other hand, there is an urgent need to find novel approaches to reuse the massive quantities of waste materials, resulting from construction and demolition practices. It is reported that more than 800 million tons of CDW are annually generated
in EU countries [17]. Literature studies have explored the feasibility of incorporating CDW in producing sustainable concretes with satisfactory mechanical and durability performance [18-22]. However, the majority of these studies have mainly concentrated on utilising CDWs as a replacement to natural aggregates.

Recycling and re-using CDWs as geopolymer sources can offer a sustainable solution for reducing their ecological impact and decreasing OPC demand. More recent studies [23-26] showed an excellent opportunity for CDWs to be used as aluminosilicate source materials for geopolymer binders. This is especially important considering the massive quantities of fine silt particles that are rich in crystalline aluminosilicates, resulting from demolishing of structures. However, the target of developing a high-sustainability CDW-based geopolymers with sufficient mechanical, fresh, and structural properties has not been completely investigated. Limitedly available research in the literature has only focused on quantifying the materials utilised for producing paste and mortar as well as testing their mechanical and microstructural properties [27,28], whilst no significant work has been found on CDW-based geopolymer concrete. Based on the available findings, it is possible to attain sufficient mechanical properties by using CDW-based constituents solely, while better performance can be achieved by combining CDWs with low quantities of OPC (up to 30%), reaching up to 102 MPa compressive strength at 28 days [29]. However, the most successful findings were achieved under high-temperature curing (higher than 60 °C) [30-32], since it can enhance the precursors' reactivity and facilitate the geopolymerization process [33], limiting their environmental benefits and in-situ applications.

This paper reviews the current studies related to geopolymer pastes, mortars and concretes, with particular emphasis on CDW-based ones. The paper initially presents
a brief assessment of the use of CDW in concrete, with more attention on incorporating CDW materials in geopolymer as fine/coarse aggregate and precursors, followed by the principle of geopolymerization process and the mixture design of geopolymers in addition to identifying the main factors influencing the performance of geopolymer containing CDW. Then, the most recent data related to the fresh, mechanical and durability properties of CDW-based geopolymer are presented along with the life cycle assessment of using waste materials in geopolymers in terms of cost and environmental aspects. Finally, the barriers and challenges to industry adoption are highlighted with a view on the way forward for future research.

2. Technical feasibility of using CDWs in concrete

Despite the extensive researches conducted on the feasibility of employing CDWs in concrete industry, the current use of CDWs is still limited to low-tech applications such as bases/subbases in road construction and masonry products, while the remaining is being landfilled [34]. It is also recommended that the replacement of natural aggregates by crushed concrete aggregates is to be limited to 30% for structural purposes to maintain the absorption capacity of aggregates less than 5% [35-37]. Similarly, other investigations [38-40] suggested the replacement ratio to be limited to 25%, since no clear changes were observed in concrete properties even under severe conditions compared to that made with natural aggregates. On the other hand, the use of 100% recycled concrete aggregate (RCA) could reduce the mechanical properties of concrete by 10 to 30%, while the absorption capacity might be doubled compared to normal concrete [41,42]. In recent years, different techniques have been suggested to improve the quality of CDW-based aggregates such as mechanical grinding [43], pre-soaking in acid solutions [44], polymer emulsion [45] and accelerated carbonation [46]. The principle of all such techniques, in fact, is mainly based on either, removing
the weak layer of adhered mortar or modifying and strengthening the old mortar. Despite the efficiency of these techniques in improving the quality of recycled aggregates, some barriers, especially those related to economic reasons, are still preventing the widespread reuse to be a realistic option. Many countries are still commercialising since adequate taxes accounting for the environmental impact of its extraction are not implemented. Furthermore, some recycling plants are not highly motivated to improve the quality of recycled aggregates [47]. Several national existing specifications and standards (e.g., RILEM, 1994; NEN-5905, 2010; WBTC, 2002; EHE-08 DIN D, 2002) allow the use of recycled aggregates in producing concrete [48-52]. While some countries like Spain and China, only allow limited of recycled aggregates and require concretes to be produced with at least 90% of natural aggregates with attached mortars [49 ,50], other countries such as the Netherlands and Germany include the use of mixed recycled aggregates for producing concretes in their specifications with variable proportions of crushed concrete, bricks, ceramics and asphalt [51,52]. In Spain, Annex 15 of the Code for Structural Concrete (EHE-08) allows the use of recycled aggregates in concrete as long as the water absorption value does not exceed 7%. In fact, the main concrete codes of practice, for example, Eurocode 2 (2008) and ACI-318 (2014) did not include any clause for structural members with recycled aggregate concrete [53,54]. It should also be considered that the environmental and economic benefits of utilising recycled aggregates are greatly affected by the location of demolition sites and the cost of transportation [55].

On the other hand, some other studies highlighted the improper properties caused by the low quality of fine waste grains, which are mainly correlated to their low bulk density and specific gravity in addition to the higher porosity, abrasion loss and water absorption, subsequently leading to low mechanical and durability properties [56,57].
However, the results obtained from other studies suggested that up to 50% weight replacement of natural sand by CDW-based fine particles might have insignificant effects on the concrete characteristics [58]. On the other hand, the use of CDW constituents without any treatment as a substitution for either fine or coarse aggregates is not advisable, and it can highly negatively affect the properties of concrete due to expected high increments in porosity and water absorption accompanied by a density drop [59,60]. According to Sata and Chindaprasirt [61], CDWs can be utilised as aggregates in geopolymer concrete with possible enhancement in some characteristics such as thermal insulation and low density; however, a slight reduction in durability and mechanical properties would be expected, similar to the case of conventional concrete.

Recently, the effects of CDW-based fine particles used in geopolymer mortars as an alternative to natural sand have been investigated [62]. The findings illustrated that the partial use of such aggregates could lead to even higher flexural and compressive strengths compared to natural sand since a denser geopolymer is formed at paste-aggregate interfaces. However, the full inclusion of CDW-based aggregates as a substitution to natural sand in geopolymer mixtures should be avoided, especially under aggressive conditions due to highly increased absorption capacity of CDW-based mixtures. Therefore, it is recommended not to exceed 25% of recycled fine aggregate in concrete mixtures as a replacement to natural sand to obtain mechanical properties comparable to those with natural aggregates [63]. During the crushing process, a considerable amount of fine powder is generated, accounting for approximately 15 to 20% of total waste concrete [64]. Studies conducted on the use of this powder as a partial replacement to cement are limited in number. Kim and Choi [65] found that adding concrete waste powders to geopolymer mortar had a significant
detrimental impact on the fluidity and compressive strength, and it is preferable not to exceed 15% as a replacement rate. In a recent study, Ma et al. [66] highlighted that using up to 30% CDW powder in conventional concrete instead of OPC can facilitate the hydration process and minimise the permeability and porosity, while the higher ratios could lead to significantly negative effects, especially on properties like frost resistance and chloride ion permeability. Schoon et al. [67] highlighted the viability of partially employing fine powder from recycled concrete as an alternative source for producing Portland cement clinker. The waste hydrated cement obtained from the separation of fine recycled aggregate would be of significant importance in the chain of the cement industry. This is mainly attributed to the presence of inorganic substances forming after the drying process, which have almost similar chemical compositions found in the raw clinker and its use in replacing natural quarried minerals, reducing the consumption of raw materials. However, the quantity of waste hydrated cement used as a raw powder in producing Portland cement clinker is limited by the chemical composition of waste, particularly the CaO/SiO$_2$ ratio [68]. Nevertheless, these approaches have not addressed the problem of CO$_2$ emissions in a fundamental way, and they still represent significant environmental risks due to the low potential rate of use of CDW-based powders in conventional concrete. Such powder is mostly composed of hydrated cement rubble, unhydrated cement particles, fine powder of aggregates/bricks, which can meet the fundamental characteristics of geopolymer source materials considering their aluminosilicate compositions.

3. Geopolymerization process

Geopolymers can be considered as alkali-activated binders or amorphous alkali aluminosilicates [19]. During the geopolymerization process, inorganic compounds are generated after several complex chemical reactions between the aluminosilicate
oxides in highly alkaline environments to form three-dimensional polymeric Si-O-Al-O chains as the main alkaline aluminosilicate gel. Several research investigations have been conducted on the chemical reactions of geopolymers [69-71]. The mechanism of geopolymer is highly dependent on the nature of alkaline activator as well as the chemical composition of precursors. Due to the numerous components in the liquid phase, all reactions take place at the same time and affect each other [72]. Thus, the geopolymerization mechanisms are more complex than OPC hydration. According to Davidovits [69], the mechanism process of geopolymers consists mostly of four phases. The alkali activator firstly breaks Al-O and Si-O bonds in the aluminosilicate materials, releasing Al-O and Si-O tetrahedral monomers (Dissolution), before being diffused in the reaction system (Diffusion). According to the concept of chemical equilibrium, the concentrations of silicon and aluminum drop on the particle surface due to diffusion, while the dissolving process proceeds. In the next stage (polycondensation), Al-O and Si-O tetrahedral are converted into amorphous -Si-O-Al-O-structures or even zeolite crystals during the polymerization process. Finally, the dehydration process takes place, resulting in a hardened geopolymer with great mechanical strength (Hardening). It should be noted that the geopolymerization process for geopolymer materials sourced from varying raw materials are not identical, although they fundamentally follow the aforementioned reaction sequence. The initial stage, termed as the dissolution stage, involves dissolving alumina and silicate in the precursors, forming SiO₄ and AlO₄. Therefore, only precursors with aluminosilicate content can be used to produce geopolymer [70]. In the second stage (agglomeration), the condensation process starts when the dissolved ingredients react with each other as well as with alkali cations (K⁺ or Na⁺). Geopolymerization occurs in the last stage by poly-condensation of such dissolved ingredients, consequently forming a three-
dimensional aluminosilicate (Si–O–Al–O) structure in an amorphous to semi-crystalline form as given in Equations 2 and 3, below [72, 73].

\[
\begin{align*}
(Si_2O_2Al_2O_3)n + H_2O + OH^- & \rightarrow Si(OH)_4 + Al(OH)_4^- \\
Si(OH)_4 + Al(OH)_4^- & \rightarrow (Si-O-Al-O)n + 4H_2O
\end{align*}
\]

Unlike the Davidovits model, the conceptual model presented by Glukhovsky [71] divided geopolymerization processes into deconstruction, gels formation, polycondensation, and crystallization to eventually produce a 3D network structure of geopolymer. The main difference seems with Davidovits mode is the polycondensation process that is separated into two steps, namely gelation, and reconstitution. Gelation requires de-hydration to generate oligomeric gels when aluminosilicates are saturated, whilst reconstitution covers the rearranging of the oligomeric gels. It is worth noting that water plays no role in geopolymerization reactions, and it simply improves the workability of the mixtures, in contrast to the hydration process of OPC concrete [69, 72].

As exhibited in Fig. 1, the formation of the final gel is highly dependent on the nature of aluminosilicates as well as the activator used. Calcium aluminosilicate hydrate (C-A-S-H) gel is the main product formed in the presence of precursors with high-calcium content such as GGBFS and class C fly ash, which is similar to calcium silicate hydrate (C-S-H) gel formed through the hydration of OPC. However, amorphous aluminosilicate gels (N,K-A-S-H) are formed as a result of the geopolymerization of precursors with low CaO/SiO\(_2\) ratios, such as clay and class F fly ash. According to Garcia-Lodeiro et al. [31], the stability of N-A-S-H structure is heavily affected by pH alkalinity. At low alkalinity, sodium is partially replaced by calcium, resulting in the formation of C-(N)-A-S-H gel. When the pH exceeds 12, the presence of CaO
destabilises the N-A-S-H, resulting in the formation of the C-A-S-H type phase. The nature of the alkaline solution can also affect the structure of the final gel, since different atoms of Al and Si can be found in the hydroxide or silicate used [73]. Although potassium hydroxide provides higher alkalinity, sodium hydroxide has shown a higher capacity to dissolve silicate and aluminate species [74].

![Diagram showing the chemical compositions of the precursors](image)

**Fig. 1.** Final gels formed based on the chemical compositions of the precursors [75].

4. **Mixture design of geopolymers**

To date, there is no standard method for the mix design of geopolymers; however, several mix designs have been experimented by the researchers during the last decade [76-78]. In contrast to OPC-based concrete, development of mix proportions for geopolymer concretes is more complex due to higher number of ingredients involved in the matrix [79]. The approaches documented in the literature so far have been categorised into three groups based on design principles, namely target strength approach, performance-based approach, and statistically factorial model approach. The majority of these mix designs are mainly based on the trial and error approach due to the large number of parameters involved in the geopolymer concrete.
production. In the mix design methodology for geopolymer concrete proposed by Rangan et al. [80], the density of geopolymer concrete was considered to be 2400 kg/m$^3$, which cannot always be reliable because of the many possible types and amounts of components used, while the total content of aggregates was set to 80%. This approach does not account for the specific gravity of the materials used. Anuradha et al. [78] proposed a design approach for several grades of geopolymer concretes based on Indian standards. The activator solution content used was found to be excessive for the predicted strength. In this method, precursors’ content and activator solution to precursors ratio were chosen based on the desired strength, while the fine aggregates were kept constant. Later, Ferdous et al. [76] modified the mix design of geopolymer concrete to cover densities, air contents, specific gravities of components, workability and compressive strength. However, the main challenge that emerged with this process was the determination of the alkaline activator to binder ratio. Pavithra et al. [81] suggested a relationship between water-binder ratio (W/B) and compressive strength by fixing the activator content, allowing the design of mixtures to be more flexible in terms of activator content and desired strength, while the aggregate content was calculated by using the grading curve of combined aggregates. Moreover, Li et al. [82] suggested guidelines for selecting the proportions of geopolymer mixtures with a strength of 40-80 MPa. In their technique, the principles of compact packing of aggregates and Taguchi method were adopted. In concrete design, the main targets are mostly workability and compressive strength; hence, these targets are used to determine the contents of precursors, activators, aggregates and water. In conventional concrete, the workability and strength can be modified by water content (water-binder ratio [W/B]) and binder content (paste-aggregate ratio) [83]. Similarly, the binder in the geopolymer system is formed as a result of alkaline
activation reactions [84], and thus, the type, quantity, and concentration of alkaline solution used need to be considered. In geopolymer concrete, alkaline solution is a costly component, and from the economic point of view, the amount of alkaline solution should be minimised, while maintaining the desired workability and strength [81]. The flow chart in Fig. 2 summarises the overall mixture design process for geopolymer concrete (GPC) as suggested by Li et al. [84]. The alkaline activator-to-binder ratio (AL/B) can initially be selected, using the relationship between W/B and the desired compressive strength described in ACI 211.1 [85] for conventional concrete. Similar to the W/B ratio in concrete, AL/B represents the total mass of alkaline solutions to the mass of precursors; however, the compressive strength of geopolymer is often higher than that of conventional concrete at the same AL/B ratio. Then, the amount of binder can be calculated according to one of three methods, namely fixed water content, fixed binder content, and fixed paste content. The constant water content is governed by the aggregate size and required workability based on ACI 211.1 standard [85] for cement-based concrete. According to Reddy et al. [86], 200 kg/m$^3$ alkaline solution can be sufficient to provide satisfactory workability for geopolymer mixtures. Moreover, the constant binder content is typically selected based on available research and does not consider aggregate characteristics. For example, Junaid et al. [87] indicated that 360–420 kg/m$^3$ of fly ash (FA) content can be used to produce geopolymer with good strength (25–60 MPa), whilst Ferdous et al. [76] suggested some relationships to select FA content according to AL/B and compressive strength. However, using different sources of precursors materials can affect the findings, especially CDW-based materials, which require modification of binder content. The quantity of aggregates can be determined based on the absolute volume method. Sing et al. [88] suggested a relationship between the packing density of aggregates, binder content and
compressive strength in geopolymer mortars, which might be applied for geopolymer concrete. The packing fraction technique uses volumetric proportioning of fine and coarse aggregates based on optimising the best particle gradation curve obtained. The principle of this approach is to choose a particle size distribution that can fill the gaps between small and big particles with the paste, which, in turn, can improve the workability and compressive strength at early ages [84-89]. Statistical modelling approaches such as the Taguchi technique might also be applied for designing geopolymer concretes, considering the main parameters in geopolymers. The Taguchi technique employs a factorial design approach that needs the use of orthogonal arrays of experimental designs with many variables. Orthogonal arrays are mainly used to minimise the uncontrollable factors during design; thus such technique might be used to assess a single property by maximising the interaction of various factors [90,91]. However, this approach is restricted to certain levels and cannot always be applied, and hence a large database is required in order to develop this method.

It can be concluded that although some methods are suggested, further developments on these methods are still needed, considering the variations of the materials used (e.g., CDW) and other influencing parameters. It should be noted that testing at the age of 28 days is not always ideal for determining the final properties of geopolymers due to the variations of the materials used. For instance, the activated mixtures based on slag and metakaolin can reach their ultimate strength sooner than 28 days, whilst the fly ash based mixtures continue developing strength even after the 28-day testing period [92].
5. Mechanical properties of CDW-based geopolymers

5.1. Main parameters affecting CDW-based geopolymers

In this section, the main parameters affecting the synthesis of geopolymers are identified and discussed, especially their influence on compressive strength. In fact, the mechanical and microstructural properties of geopolymers can be influenced by...
different parameters, which could be directly linked to three main factors; the source of precursors, the activator used and curing conditions [93]. The nature of precursors has a significant impact on the geopolymerization reactions, including the chemical composition, the possible pozzolanic activity of precursors and the distribution of their particles, which can vary greatly, resulting in considerable changes in the characteristics obtained. Meanwhile, geopolymer structure can also be affected by the different aspects of alkaline activators, namely hydroxide concentration, silicate-to-sodium ratio, and the ratio between the precursors and activators. Furthermore, the method and period applied for curing also strongly affect the structure of geopolymers. Therefore, the effect of various parameters on the performance of geopolymer mixtures will be discussed in the following section.

5.1.1. Effect of precursor

5.1.1.1. Source of aluminosilicates

Significant progress has been made in the field of geopolymer research, particularly in the presence of common materials used (i.e., supplementary cementitious materials [SCM]) as precursors [84]. According to Van Jaarsveld et al, [95], any aluminosilicate material with possible pozzolanic capability might be utilised as a source material (precursor) for geopolymers. Therefore, in the last few years, investigations have been carried out on the inclusion of CDWs as aluminosilicate sources in alkali-activated mixes [95,96]. The results obtained from the relatively limited studies in this area indicated the high possibility of benefiting from such waste materials (e.g., brick, ceramic tile, concrete and glass) since they have high contents of main components required for the geopolymerization process, such as silica, calcium and aluminium. However, there are still significant challenges for synthesising geopolymers from such materials. Moreover, the properties obtained from such geopolymers can greatly vary
based on the composition of the materials used. While some studies focused on using a single source of CDW [96,97], others investigated the performance of mixed CDW-based components with different levels of replacement or even without any component separation to simulate the realistic cases [27, 98]. Geopolymers produced from waste bricks and ceramic powder exhibited much higher mechanical characteristics in comparison to that containing only waste concrete, reaching compressive strength of 58 MPa after 7 days of heat curing [31], however, recycled glass showed relatively low enhancement in strength [98]. The variations in the performance of CDW-based geopolymers can be ascribed to the varying levels of chemical compositions of precursors, particularly alumina, silica, calcium, iron and magnesium. The ranges of the chemical composition of aluminosilicate precursors (including CDW-based ones) collected from different investigations [7,24,25,31,96,99-107] are presented in Table 1. It can be noted that the high quantity of SiO₂ can be found in both bricks and tiles (50-70%) with less amount of Al₂O₃ (10-20%), compared to concrete waste with SiO₂ range of only 23-42% of and Al₂O₃ of 4-10% available in concrete waste. Therefore, the high contents of Al and Si ions can be easily stabilised during the activation process and subsequently participate in forming Si-O-Al bonds [31]. On the other hand, only waste concrete contains a sufficient quantity of CaO, while other CDWs (e.g., bricks and tiles) have only low ratios of calcium. The presence of the high content of CaO in waste concrete is mostly linked to the drop of concrete strength as it consumes a large part of NaOH solution [94,108]. Thus, balancing the main elements (i.e. SiO₂, Na₂O, Al₂O₃ and CaO) is crucial for the geopolymerization process to attain an ideal geopolymer synthesis.

Table 1. Chemical composition ranges for different aluminosilicate materials [7,24,25,31,96,99-107].
5.1.1.2. Addition of supplementary cementitious materials

Considering the chemical compositions of CDWs, additional sources of precursors such as OPC [102, 109], GGBFS [24], metakaolin and fly ash [110] can be incorporated to aid in producing denser and stronger geopolymers. For instance, if bricks are used as a precursor, GGBFS can be recommended to be added to cover the CaO shortage, while in the case of use of concrete waste, metakaolin or fly ash inclusion can nourish the results as they contain high quantities of SiO. The activation process of CDW is exceedingly slow, resulting in decreased/no strength growth at early ages most probably due to lower calcium concentration and crystalline form. Some relevant studies [111] reported that the use of waste bricks as precursors did not exhibit any strength development at early ages, while the compressive strength was clearly improved when waste bricks were combined with GGBFS as also reported by Rakihmova et al. [106] who suggested that bricks waste can be used in mixture with GGBFS up to 60%. This can be justified since GGBFS acts as a source of calcium, providing substantial quantities of Ca$^{2+}$, Si$^{4+}$ and Al$^{3+}$ to be leached out during the activation process, resulting in a rapid enhancement in strength. In a recent study, Mahmoodi et al. [25] investigated the influence of the most common types of SCMs (i.e., FA-C, FA-F, GGBFS and metakaolin [MK]) on the compressive strength of
geopolymer binders made from waste concrete and bricks under ambient conditions. CDW powder in the mixtures was partially replaced by abovementioned SCMs (15%, 30% and 45%) and confirmed that the inclusion of varying percentages of SCMs leads to a significant enhancement in the compressive strengths of all mixtures tested, compared to mixtures with no SCM substitution (Fig. 3). However, the use of GGBFS (45%) showed an outstanding enhancement rate (almost 208%) at 28 days, whilst using the same replacement level with MK, FA-C and FA-F led to 80%, 45% and 33% improvements in strength, respectively. This can be due to that the balanced levels of Si/Al and Na/Si with sufficient OH⁻ and Na⁺ contents may have provided an improved breakage of the bonds as Si-O-Si, Al-O-Si, Al-O-Al, and Ca-O, which were available in waste concrete/bricks and GGBFS [112]. Therefore, further amorphous C-A-S-H, C-S-H and N-A-S-H would be formed.

![Graph showing the effect of inclusion of SCMs on the compressive strength of CDW-based geopolymers](image)

**Fig. 3.** Effect of inclusion of SCMs on the compressive strength of CDW-based geopolymers [25].

It is also stated that during the geopolymerization process, lower concentrations of alkaline activators are needed for calcium-rich precursors. For instance, Krivenko and Kavalerova [113] found that activator concentration between 5–20% is needed to
activate the binder made with fly ash and metakaolin, while only 2-8% could be sufficient to activate GGBFS-based geopolymers that are rich in calcium. Calcium found in GGBFS can adjust sodium aluminosilicate gel (N-A-S-H) by partially substituting sodium ions with calcium, in turn, contributing to the formation of (C, (N-)-A-S-H) gels. The latter can improve the stiffness of the geopolymer mixture, especially at room temperature [114]. The presence of free calcium ions in during geopolymerization may also accelerate the dissolution of aluminosilicates, increasing the heat of hydration and subsequently, enhancing the strength development of geopolymers [115]. Adding calcium oxide in the form of calcium hydroxide into mixtures as an additive can also effectively enhance the durability and strength of geopolymers as it can improve the low reactivity of aluminosilicates available in waste materials as well as accelerate the setting process [116]. However, there is a general agreement that a material containing more than 20% CaO is not favourable for synthesising geopolymers owing to its rapid setting.

It is important to note that the predominant products of geopolymers prepared from clay-originated CDWs such as red clay bricks, hollow bricks and roof tiles are N-A-S-H gels with zeolite-like structures, whereas sodium silicate gels mainly forms in glass-based geopolymers [98]. Similarly, the main product from high-calcium precursors (e.g., GGBFS) is the C-A-S-H gels, which are similar to that formed during the hydration of OPC (C-S-H). However, using low-calcium precursors such as calcined clays and FA-F mainly results in the formation of amorphous N-A-S-H gels in 3D structures [25,75].

5.1.1.3. Fineness of particles

Besides the nature of precursors, the fineness of its particles plays a crucial role in determining the characteristics of geopolymers. Finer particles of precursors could
offer higher reactivity and stronger geopolymerization, which, in turn, helps in producing stronger paste with a denser microstructure. This is mainly associated with the higher specific surface area achieved in finer source materials, accelerating the reaction rate since the process of dissolution occurs faster, leading to a shorter setting time and earlier development of strength. However, the improvements in mechanical and durability performances can only be obtained by the balance between higher water requirement and fineness of source materials. As stated by Komnitsas [31], the compressive strength of geopolymers can be substantially improved when the sizes of CDW-based particles are lower than 150 μm and D_{50} is less than 15 μm. As exhibited in Fig. 4, the compressive strength of tile-based geopolymers activated by 10M-NaOH is increased by more than 50% when the particle size decreased from 477 μm to 140 μm [31]. Similar observations were reported on samples prepared with bricks, when the particle size reduced to from 350 μm to 140 μm, the compressive strength reached around 35 MPa. The strength of geopolymers made from waste concrete was doubled when the finer particles (190 μm) were used instead of coarser ones (400 μm). According to Hue et al. [107], only particles that are smaller than 125 μm can be alkali activated due to their higher reactivity, whilst others [24,117,118] highly recommended that the particle size of CDW-based ingredients should be finer than 75 μm to be used as precursors.
Fig. 4. Effect of particle size of precursors on the compressive strength of geopolymers [31].

5.1.2. Effect of alkaline activator

Alkaline activator plays a crucial role in the geopolymerization process, especially at the initial stages. Performance of geopolymers is significantly affected by many parameters linked to the activator, such as the reactivity of the activator (which is related to the type/composition), the concentration used for activating the binder, and the ratio between the activators and binder, as discussed below.

5.1.2.1. Type of activator

Alkaline activators are primarily used as a solution prepared by the soluble alkali elements in the form of hydroxide or silicate or a combination of both. Sodium hydroxide (NaOH) dissolved in water is commonly used for dissolving the agents in the precursors either alone or mixed with sodium silicate (Na$_2$SiO$_3$) to form the alkaline solution [119,120]. Na$_2$SiO$_3$ can further help in enhancing the compressive strength and accelerating the geopolymerization process [121]. This mainly occurs as the polycondensation process proceeds much faster when soluble sodium silicate is coupled with alkaline hydroxides rather than using alkaline hydroxides alone [31,122].
Precursors can also be activated by sodium carbonate, potassium silicate and potassium hydroxide [123], however, the relatively higher cost of such activators could be one of the main reasons behind the limitation of their use, compared to those prepared by sodium hydroxide and sodium silicate. In comparison to sodium hydroxide, potassium hydroxide can provide more alkalinity to the mixtures; however, sodium hydroxide is more commonly preferred in practice as it has better ability to release aluminate and silicate monomers [124]. The use of alkaline activator solutions is considered one of the main practical limitations of geopolymers due to their high cost and carbon footprint associated with their production process, especially in the case of sodium silicate [125]. Notably, the production of sodium silicate requires significant energy for melting sodium carbonate with silica sand in the furnace at temperatures ranging from 1400 to 1500°C [126]. To enhance the commercial viability of geopolymers, it is critical to minimise the costs associated with the production of activators while retaining their environmental friendliness and performance. More recently, alternative activator solutions have been synthesised from silica-rich waste materials including bottom ash [127], rice husk ash [126], glass waste [128] and precipitated silica [129]. The silica extracted from such sources and dissolved in alkaline solutions showed the possibility of reducing footprint emissions by up to about 50% compared to those generated from the commercial ones [130,131]. However, the performance of such activators can vary widely based on some key factors, including the amorphous silica content, extraction method and particle size. To aid in understanding the chemical composition of diverse silica-rich wastes, Alnahhal et al. [132] developed a ternary diagram to illustrate the main oxides of various silica-rich wastes utilised in the literature, as presented in Fig. 5.
It can be inferred that the combination of sodium silicate and sodium hydroxide seems the most effective way that can be used to activate geopolymer mixtures derived from CDWs; however, adopting alternative activators produced from waste materials can be highly beneficial in terms of saving cost and energy.

![Ternary diagram for the major oxides found in silica-rich waste source materials](image)

**Fig. 5.** Ternary diagram for the major oxides found in silica-rich waste source materials [132].

### 4.1.2.2. Concentration of hydroxide solution

Sodium hydroxide and potassium hydroxide are mainly used to dissolve the atoms of Al and Si, and their concentration, which is mostly expressed in terms of molarity, is another factor to be considered. Generally, a highly alkaline medium is required for hydrolysing the aluminosilicate particles. The mechanical properties of geopolymers improve with increasing hydroxide concentrations, yet, this improvement is not consistent, which implies for the presence of an optimal alkali concentration range and is likely associated with the higher degree of leaching of silica and alumina [133]. The poor performance at low concentrations of NaOH is mainly related to the insufficient
alkalinity of the system, causing a decrease in the dissolution rate of silica and alumina in the CDW-based precursors, which in turn negatively affects the geopolymerization reaction degree. As the concentration of sodium hydroxide solution rises, more OH− ions come into contact with CDW-based particles, increasing the dissolving rate of Si and Al, in addition to enhancing the concentration of Al4+ and Si3+ in the activator used. These dissolved atoms interreact with each other to generate aluminosilicate oligomers, which are then dehydrated and condensed to produce aluminosilicate gels, leading to higher stiffness and strength [31]. However, the exceptionally high molarity in the solution may lead to the dissolving of the aluminosilicate oligomers, which can, then, be transformed into aluminate and silicate molecules, reducing the content of oligomers in the liquid phase and impeding the polycondensation process [107]. Furthermore, the high alkalinity of the activator could enhance the possibility of adsorbing Na+ on the precursors’ surface, interacting with Al-OH and Si-OH, reducing the adhesion between the solid insoluble particles and aluminosilicate gel in the system, and eventually diminishing the final strength of the geopolymer matrix [134]. Using high molarity-NaOH could also increase the possibility of shrinkage, especially for mixtures with the low W/B ratio. The possible reason for the reduction in strength might be linked to the high viscosity of the activator solution, hindering the leaching of Al and Si atoms. Thus, the ratio of alkaline activators in the mixture needs to be carefully considered during the mixture design of geopolymers. Fig. 6 shows the effect of varying concentrations of sodium hydroxide on the compressive strength of CDW-based geopolymers. It can be noted that the increase of NaOH molarity can significantly promote the strength of geopolymer mixtures, however, the excess sodium hydroxide may adversely affect the mechanical strengths of geopolymers. It may be deduced that although the molarity of sodium hydroxide can be defined for
each type of CDW material based on the reactivity of its particles, the best performance mostly can be achieved with molarity ranging from 8-12M.

![Graph showing the relationship between NaOH concentration and compressive strength of geopolymers.](image)

**Fig. 6.** Relationship between NaOH concentration and compressive strength of geopolymers.

5.1.2.3. Ratio of silicate to hydroxide

The use of mixture of sodium silicate and sodium hydroxide in geopolymers led to better mechanical and durability characteristics, compared to those containing sodium hydroxide alone, since the structure of geopolymers activated by sodium hydroxide is quite different from those activated by the combination of both [135]. The use of hydroxides solely can only be helpful in disassembling the Al and Si ions in the precursors, whilst the inclusion of sodium silicate promotes the condensation process [106,136]. As explained by Duxson et al. [13], the existence of sodium silicate causes an increment in the soluble silica (Si–O–) content, providing the ideal conditions for the formation of CDW-based geopolymer structure. Besides, sodium silicate can ensure a better interface between the gel matrix and unreacted particles, improving
the mechanical performances of the aluminosilicate binders [71]. On the other hand, the excess quantity of silicates in geopolymer mixtures can hinder the geopolymerization process. Thus, it should be pointed out that the optimal amount of soluble silicate can vary based on the components of the mixture. Different optimum ratios of sodium silicate to sodium hydroxide were reported; however, the majority of the available studies conducted on compressive strength of CDW-based geopolymer [107,122,137] indicated that the optimum ratio of Na₂SiO₃/NaOH ratio would be in the range of 1.5-2.5 as illustrated in Fig. 7.

![Fig. 7](image_url) Influence of sodium silicate-to-sodium hydroxide ratio on the compressive strength of CDW-based geopolymers.

5.1.3. Effect of curing conditions

Curing condition and duration are among the most important parameters during the whole geopolymerization process due to their role in optimising the quality of geopolymers [107]. Different curing conditions have been studied to determine the ideal conditions to produce geopolymers with mechanical and durability performances comparable to OPC. To maximise the potential of polymerizing CDW-based precursors, curing conditions as steam curing, saline water, room temperature, and autoclave have been reported in the literature [25,103,138]. Providing an effective
geopolymerization with CDWs under ambient conditions without SCM/OPC substitution is still an issue under investigation. However, the most intriguing findings on waste-based geopolymers were obtained under high-temperature curing (60-110 °C) [30,139-142], limiting their applications to the production of precast structural elements. Thermal treatment offers faster dissolution of silica and alumina species in addition to accelerating the degree and rate of poly-condensation, leading to production of stronger gels at early ages, and thus making the mixtures stronger and denser. Though increased curing temperatures can efficiently enhance the mechanical characteristics of geopolymers within a specific range, exposure to very high temperatures or extending the period of curing can adversely influence the characteristics of geopolymers. This mainly occurs due to the loss of humidity needed for the polymerization, since part of the water required for polymerization process could be readily evaporated, preventing the formation of the final gels [143,144] and leading to the formation of cracks and drying shrinkage [145]. This can be supported by the results obtained from the model suggested by Palomo et al. [114], who reported that the strength of geopolymers almost doubled when the temperature increased from 45 °C to 65 °C, whereas only 15% strength gain was achieved by increasing the temperature from 65 °C to 85 °C. Within this context, previous studies indicated that geopolymers based on low-calcium fly ash could give excellent mechanical performances under elevated temperature curing, while under ambient conditions strength development remained relatively lower [146,147].

5.1.4. Chemical compositions of precursors and alkaline activators

In the geopolymerization process, the molar ratio of oxides (SiO₂, Al₂O₃, Na₂O, CaO) or their atomic ratio can be used as a controlling factor for determining the content of precursor and alkaline activator. Generally, the high content of Si has a strong
influence on the formation of large amounts of alkaline aluminosilicate gels [148], whereas the amount of Al in the precursor determines the network formation and chemical structure [149]. Since the roles of Si and Al in synthesising geopolymers are interrelated, the ratio of Si/Al is utilised to express the relationship between the activators and precursors. The ideal Si/Al ratio refers to the molar quantities of SiO$_2$ and Al$_2$O$_3$ in the system, which can greatly vary, depending on the reactive characteristics and compositions present in the activators and precursors. According to Vásquez et al. [102], the optimal ratios of SiO$_2$/Al$_2$O$_3$ for CDW-based geopolymer system cured at room temperature is 10.0, whilst it was reported 10.5 and 8 for the binary systems containing 30% OPC and 10% MK, respectively. The Si content in the matrix determines whether the condensation occurs at Al-Si or Si-Si in geopolymerization caused by poly-condensation of hydrolysed Al and Si atoms. Condensation occurs primarily between Al-Si species at low Si/Al ratios, resulting in poly (sialate) polymer structure; however, as the Si/Al ratio rises, more Si species are produced due to hydrolysis of SiO$_2$, resulting in oligomeric silicates. Increasing these ratios provide the production of denser geopolymer gels, which binds the unreacted particles and directly enhances the strength performance.

6. Fresh properties of CDW-based geopolymers

6.1. Workability and flowability

Fresh properties of geopolymers (i.e., workability, stability and flowability) are generally worse than that of normal concrete owing to the highly viscous silicate mixture components. The workability of CDW-based geopolymers is dependent on the source of aluminosilicate, while the influence of alkaline liquid concentration and the ratio of silicate-to-hydroxide seems more influential [26]. Wong et al. [101] found that
the flowability of geopolymer matrix decreased with higher quantities of brick powder at all concentrations of sodium hydroxide tested due to the presence of unreacted particles of waste bricks with porous surface, resulting in rapid absorbing of water from the mixture and reducing the free water in the fresh mix [105]. The irregular shape of CDW-based particles may also cause a reduction in workability [24]. It is reported that higher flowability can be achieved by increasing the quantities of waste concrete powder rather than bricks waste [26]. This might be attributed to the variation in the physical and chemical characteristics of the two materials as concrete waste has a smaller surface area compared to waste bricks, and thus extra water is needed for the unreacted particles of waste bricks, causing a change in the fresh properties of the mixes. However, as shown in Fig. 8, Wong et al. [101] indicated that the flowability of CDW-based geopolymers is mostly affected by the change in Na₂O/SiO₂ and SiO₂/Al₂O₃ ratios rather than the content of the precursors used. This enhancement is probably due to the high content of soluble silica, causing faster dissolution, and resulting in more plastic and workable mixtures [150]. The high contents of Na₂O with increasing Na₂O/SiO₂ ratios in CDW-based geopolymers may contribute to the production of larger quantities of OH/hydroxyl groups, which in turn cause breaking of siloxo (SAO-Si) and sialate (Si-O-Al) bonds in CDW-based precursors [140], leading to greater dissolution and flow rate [150]. Increasing the silicate-to-hydroxide ratio can also lead to decrease in the slump of the matrix, especially at the ratio of 2.5 [151].
Fig. 8. Effect of SiO$_2$/Al$_2$O$_3$ and Na$_2$O/SiO$_2$ ratios on the flowability of CDW-based geopolymers [101].

6.1.1. Effect of superplasticizers

The type of superplasticizers employed has also a variable impact on the fresh properties of geopolymers. Alerfaei et al. [152] assessed the influence of different types of commercial superplasticizers (SP) (i.e., melamine (MS), polycarboxylate (PS) and naphthalene (NS)) on the fresh behaviour of geopolymers using a constant ratio (1.0%, by weight) with all mixtures. As presented in Fig. 9, the findings revealed the effectiveness of all superplasticizers used in improving the workability, reaching up to almost 250% enhancement in slump rate without a notable decrease in compressive strength, although PS exhibited the most plasticizing effect compared to others. Nevertheless, different results were reported in another study [153] for the same types of SP, concluding that only PS was beneficial, attaining almost 46% enhancement in slump, whereas the other ones tested (i.e., MS and NS) achieved only 8% and 3% higher slump rate, respectively, with a slight reduction in strength in comparison to control mixtures. The superior performance of PS is likely due to its steric hindrance and electrostatic repulsion [154]. It is also stated that adding 1.5-3.0% naphthalene-
based SP to geopolymers could be the optimum amount to enhance the workability [155], whilst other types of SP, namely polyacrylate copolymer, and vinyl-copolymer, did not provide any workability or strength improvement [156].

![Fig. 9](image_url) Effect of different SP types on the workability of geopolymers [152].

### 6.2. Setting time

The setting time is a crucial factor for in-situ applications, since it determines the time available for transport, placement, and compacting of geopolymers. Using higher concentrations of sodium hydroxide can clearly reduce both the initial and final setting time of CDW-based geopolymer mixtures, which is directly related to increase in the heat of hydration as well as acceleration of the process of dissolution and polymerisation, leading to a shorter setting time [150]. This may also be attributed to increased Na content in the mixture, since the ratios of Si and Na would be changed with the changes in the NaOH molarity [157]. Accordingly, it is highly recommended to prepare NaOH solution with the required molarity one day prior to mixing with aluminosilicate precursors by dissolving NaOH flakes in water to ensure the completion of chemical reactions [158-160]. The setting time of mixes produced from CDW is found to be delayed with higher contents of sodium silicate, giving longer time for Al and Si to be dissolved to enhance geopolymerization process [70,103].
Incorporating GGBFS, MK and OPC into CDW-based geopolymers can significantly accelerate the initial and final setting of the geopolymerization process. This is mostly owing to the presence of higher quantities of Ca\(^{2+}\) ions in the matrix, leading them to be reacted with aluminosilicates and Na\(^{+}\) ions more at higher alkaline concentrations, forming N-A-S-H gels, which in turn converts into C-A-S-H gels [161], resulting in accelerated process of coagulation and condensation, and hence reduced setting time [162]. Faster setting of geopolymers incorporated with GGBFS and MK is also related to the virtual characteristics such as the size and shape of the particles. In fact, the grains of MK and GGBFS mostly have finer particles and more angular shapes compared to those extracted from CDWs. Therefore, it is recommended to use these calcium-rich products in producing CDW-based geopolymers to accelerate the delayed setting, especially under ambient temperatures. However, the use of high contents of GGBFS in the mixture can significantly reduce the setting time, especially over 50%, causing difficulties in the handling of the mixtures [163]. The dissolution of CDW-based geopolymers is greatly influenced by the variations in alkaline molarity. Huo et al. [107] found that the precipitation of Si\(^{4+}\) in geopolymers produced from concrete waste accelerated with the higher concentrations of NaOH. As it can be seen from Fig.10, the average participation level of Si\(^{4+}\) ions for the molarities of 10, 14 and 18M was higher than 130 mg/l, which, in fact, was considerably higher than that reported for 6 M. The low concentration of NaOH solution (6M) was unsufficient for dissolving the silicate and aluminate species in CDWs, hindering the rate of geopolymerization reactions. By increasing the concentration of alkaline solution, more OH\(^{-}\) ions come into contact with the surface of CDW-based particles, increasing the rate of dissolution of the Si-Al phase and the concentration of Al\(4^{+}\) and Si\(^{3+}\) in the liquid phase, which in turn collide with each other to produce aluminosilicate gels.
However, the highest concentration (18M) did not lead to better results, which is attributed to the delay in the mobility of ions, caused due thickening of alkaline activator, preventing further ions from leaching out [164]. Thus, it can be said that using either low concentration (6 M) or high concentration (18M) of alkaline solution is not favourable for hydrolyzing and precipitating Si4+ ions from the solid aluminosilicate precursors. The findings also indicated that the precipitation of Si4+ in CDW-based geopolymers reached the maximum after approximately 10 minutes for all NaOH concentrations used, while it tended to be stable after around 20 minutes for all NaOH concentrations.

In terms of rheology, the aluminosilicate precursor has also a significant influence on the temporal development of yield stress and plastic viscosity. Rovnaník and Rakhimov [116] found that the geopolymers made with brick powder exhibited the lowest rheological performances in terms of both yield stress and plastic viscosity, while the use of MK caused a gradual increase in the yield stress. This can be attributed to the higher reactivity of MK since it is mainly composed of amorphous deformed aluminium structure; hence, allowing it to be quickly dissolved and instantaneous gelation of aluminosilicate oligomers. According to Kashani et al. [165], alkali hydroxides produce a substantial rise in the yield stress of an alkali-activated paste, whilst sodium silicate causes a reduction in the yield stress because of the deflocculating and plasticizing effects of silicate ions. The temporal development of yield stress and plastic viscosity are significantly affected by the type of precursors used. Using large quantities of CDW-based powders in geopolymer mixtures caused almost negligible changes in the viscosity, leading to more delay in the yield stress due to reduced presence of reactive amorphous phases [166].
7. Durability Properties of CDW-based geopolymers

7.1. Exposure to high temperature

Geopolymers generally exhibit better resistance to high temperatures than OPC-based mixtures [161]. It is stated that geopolymers can easily withstand elevated temperatures between 800-1000 °C without any deterioration [167]. Limited information is available on the mechanical characteristic of CDW-based geopolymers after exposure to high temperature conditions (i.e., thermal stability). Fig. 11 presents the stability of geopolymer pastes sourced from CDW-based ingredients under various levels of elevated temperature ranging between 400 and 800 °C as reported in previous studies [31,168]. As can be noted, there is a gradual decrease in the compressive strength of all tested samples with the increase in temperature. The reduction due to increased levels of temperature is mainly attributed to increased porosity and shrinkage of the mixture accompanied by the weight loss, causing the reorganisation of Si–Al bonds, and consequently leading to the development of microcracks [169]. Thermal instability in geopolymers is influenced by the source of CDW-based materials [170]. As can be also observed from Fig.11, the geopolymers
made by bricks showed high resistance to decomposition compared to those made by concrete and tiles, which is likely associated with the formation of extra crystalline phases under heating due to greater amount of Al$_2$O$_3$ content in the bricks.

![Graph showing resistance of CDW-based geopolymers to high temperature exposure.](image)

**Fig. 11.** Resistance of CDW-based geopolymers to high temperature exposure.

### 7.2. Acid resistance

Detrimental effects of acids on geopolymers mainly occur as a result of the interactions between the acid solutions and calcium compounds, which cause tensile stress cracking of the matrix. Vafaei and Allahverdi [171] investigated the performance of geopolymer mortars prepared by the use of waste bricks and GGBS, compared to two types of cement mortars, namely OPC and high alumina cement under acid attack (sulphuric and hydrochloric acids) for six months. The results showed that OPC mortar exhibited significant degradation under both acidic solutions due to high calcium concentration. This was mainly because H$^+$ ions found in the acid solutions led to the breakdown of calcium aluminate hydrate, which was the fundamental binder in the mortar. Compared to CDW-based geopolymer mortars, more severe damage was observed on the mixtures prepared by high alumina cement exposed to both acidic
liquids. Geopolymer specimens exhibited a better resistance against hydrochloric acid attack, yet, only minor damages were observed for mixtures exposed to sulfuric acid (Fig. 12).

![Graph showing acid resistance of geopolymer mortar in comparison with cement mortars](image)

**Fig. 12.** Acid resistance of geopolymer mortar in comparison with cement mortars [171].

8. Life cycle assessment

McLellan et al. [12] performed a life cycle study on the traditional geopolymer constituents based on costs in Australian market, considering three main issues; the
impact of energy used, greenhouse footprints and cost. The study estimated that geopolymers could minimise the unfavourable emissions between 44–64% compared to OPC-based concrete, but this is highly affected by the transportation distance required for the geopolymer production, resulting in few cases, which cause even higher polluting emissions by up to 14%. In another study, the environmental impact of different types of alkaline solutions (i.e., sodium carbonate, sodium sulfate, sodium hydroxide, and a combination of sodium hydroxide and sodium silicate) used in activating waste hybrid bricks with small quantities of OPC [96]. The environmental impact was identified by the global warming potential values (GWP) (expressed in kg.CO$_2$.eq/MPa) and calculated based on the life cycle analysis of mixtures, considering two influencing factors; the content of OPC and the quantity of activator used. The results indicated that the inclusion of small amounts of OPC by up to 30% would produce eco-efficient geopolymer with compressive strength up to 102 MPa and potentially reduce the global warming by up to 73%. In terms of activators used, the results demonstrated that, although sodium hydroxide exhibited the highest volume of CO$_2$ footprint (1.6010 kg.CO$_2$.eq for each kg used), sodium silicate with a lower rate per kilogram (0.9260 kg.CO$_2$.eq per kg) contributed to the highest pollution rate, since more quantities are used to produce geopolymers with similar properties. On the other hand, the exposure to sodium carbonate and sodium sulphate led to only 0.0098 and 0.2212 kg.CO$_2$.eq per each kg utilised, respectively. The results also illustrated that the use of waste bricks could help in reducing GWP values by up to 77%. In another comprehensive study [172], the environmental and functional aspects of bricks-based geopolymer activated by a mixture of sodium hydroxide and sodium silicate were assessed. The environmental impact was examined by analysing carbon dioxide emissions and energy consumption associated with the geopolymer production. The
combined environmental and functional aspects were expressed in terms of the energy consumption efficiency and carbon dioxide emission efficiency index per one MPa. As depicted in Fig. 13, the findings indicated that the inclusion of 70% of waste bricks in geopolymer provided compatible strength to OPC paste, while 45% on energy and 72% on greenhouse gas emissions can be saved. This is mainly owing to using low quantities of sodium hydroxide and sodium silicate as their detrimental impacts on the environment were more significant, as shown in Table 2. Higher energy consumptions and CO₂ footprints, 63% and 81%, respectively, could be saved, but lower mechanical performances were obtained.

![Energy consumption and GHG emissions](chart.png)

**Fig. 13.** Comparison of consumed energy and CO₂ emissions [172].

**Table 2.** Energy consumption and CO₂ emissions for the CDW-based components [172].

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Energy consumption (MJ/t)</th>
<th>CO₂ emissions (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland cement</td>
<td>2986</td>
<td>829</td>
</tr>
<tr>
<td>Sodium silicate - pure</td>
<td>5462</td>
<td>1514</td>
</tr>
<tr>
<td>Sodium hydroxide - pure</td>
<td>6965</td>
<td>1930</td>
</tr>
<tr>
<td>Waste brick powder</td>
<td>135</td>
<td>28</td>
</tr>
<tr>
<td>Mixing</td>
<td>21</td>
<td>12</td>
</tr>
</tbody>
</table>
Lloyd and Rangan [173] stated that even after accounting for the cost of the alkaline solution required to produce the geopolymer binder, geopolymer concrete is predicted to be 10-30% cheaper than similar concrete prepared from OPC. Accordingly, geopolymers would be expected to be more affordable when CDW-based materials are used as precursors. In a recent study [174], a comprehensive cost analysis on the manufacturing of geopolymer bricks was calculated by using various formulations of bricks (GWB1-5) made by waste bricks and GGBFS, and compared with the geopolymers made by clay (GC) and fired bricks (FB) to determine the economic viability of producing geopolymers at the industrial scale. The cost of producing a metric tonne of bricks and all manufacturing stages of geopolymer bricks were calculated using the brickworks model from the French market. The findings shown in Fig. 14 indicate that geopolymer bricks manufactured from waste bricks could achieve double compressive strength with the same manufacturing cost used for the traditional bricks. They also confirmed that the sodium silicate used in producing a metric tonne of geopolymer is the most dominant factor in terms of cost of ingredients.

![Cost vs Compressive Strength](image_url)

**Fig. 14.** The cost of producing one metric tonne of brick and relative compressive strength of geopolymer [174].
9. Current challenges for industrial applications

Geopolymer technology is gaining popularity as a practical approach to create more environmentally friendly building materials and to address waste management concerns. Commercially, geopolymer technology has been recently developed and applied in some practical engineering projects. However, below are few challenges facing the wide-spread applications of geopolymer concretes (with special emphasis on the CDW-based ones) in the construction sector:

- The variations of CDW properties, as depicted in Table 3, result in variant geopolymer characteristics. Therefore, different trial mixes with various concentrations of alkaline activators are needed to achieve the target performance for each source. However, developing a more efficient waste management system focusing on upscaling of CDW rather than the current practice of downcycling may help in eliminating the effect of this variability.

- The majority of the available investigations used either high dosages of chemical activators, thermal curing treatment or both to produce CDW-based geopolymers having comparable properties to those with OPC. Such requirements increase the production cost or make on-site casting impractical.

- High energy required to produce the commonly used activators such as sodium hydroxide and sodium silicate is another obstacle facing the widespread use of geopolymers. According to [11], almost 60% of carbon dioxide emissions resulting from geopolymer concrete are associated with the production of alkaline activators.

- While the utilisation of high concentrations of activators might enhance the mechanical properties of geopolymers, increased alkalinity can cause some difficulties for the mixtures at fresh state during handling, which necessitates higher contents of superplasticizers.
- Another aspect to be considered in terms of the development of geopolymer concretes is the possibility of efflorescence formation, which can be identified as the formation of salt on the surface of concrete. This phenomenon may occur in geopolymers due to the high content and concentration of alkaline activators. However, the incidence of efflorescence can be minimised by increasing the content of silica and alumina in the mixtures.

10. Conclusions

The current paper reviewed the fundamental factors that have major influences on the properties of geopolymers produced with CDW-based materials. Moreover, the main barriers and challenges faced in implementing geopolymers and the steps required to overcome these issues are also discussed. Following conclusions were drawn:

- Although a few methods for the mix design of geopolymers have been suggested, the trial and error approach is still the most common one due to large number of parameters involved in geopolymer mix design.
- The use of CDW-based materials rich in silica and alumina, such as bricks and ceramics, resulted in better mechanical performances than waste concrete; however, superior performance can be achieved by using different sources of CDW-based materials if the proportions of the activators and heat curing are .
- Higher compressive strengths can be obtained with finer fractions of CDWs, especially if the particle sizes are smaller than 75 μm, while applying thermal curing in temperature range of 60-90 °C can significantly accelerate geopolymerization, improving the mechanical performance and durability.
• Geopolymers with only CDW-based fractions as the binder phase exhibited poor mechanical performance under ambient temperature curing, whilst the inclusion of SCMs such as GGBFS and MK in CDW-based geopolymers can improve the mechanical performance with consideration of the influence of other factors such as the decrease in workability. Hence, it seems an essential factor to use either heat treatment or adding SCM materials for proper synthesis CDW-based geopolymers with acceptable properties.

• The higher concentration of sodium hydroxide can help improve the mechanical properties of geopolymers; however, the best possible performances seem to be obtained with molarity range of 8-12M.

• The use of alkaline activators composed of sodium silicate and sodium hydroxide has been reported as the most effective activators for enhancing the mechanical properties of CDW-based geopolymer matrices, with a recommended sodium silicate-to-sodium hydroxide ratio between 1.5 and 2.5.

• The inclusion of higher ratios of sodium silicate decreases the workability of fresh mixtures owing to the high viscosity of Na$_2$SiO$_3$, whilst increasing the concentration of NaOH can prolong the setting time of geopolymers. The concentration of sodium hydroxide and the amount of CDW-based materials used also influence the workability and the initial and final setting time of geopolymer mixtures.

• Naphthalene-based superplasticizers are the most advisable high-range water-reducing admixtures for geopolymer systems activated solely by NaOH, whilst polycarboxylate-based plasticizers showed the best plasticizing effect amongst other commercial superplasticizers available for geopolymer systems activated by both sodium silicate and sodium hydroxide.
In order to address the challenges identified in this review paper, the following strategies and future research needs are proposed:

- There is a lack of studies on the production of CDW-based geopolymer concretes since the previous works mainly focused on the paste and mortar mixtures.
- Further investigations should be made on producing more cost-effective, environmentally friendly activators, preferably manufactured from waste materials (e.g., waste sodic and waste glass).
- While the inclusion of CDW-based materials in producing geopolymer mixtures can greatly reduce the negative environmental footprint based on some influencing factors such as transportation and mix design, the nature and amount of the alkaline activator used are the most dominant factors that need to be considered in terms of cost.
- Issues related to the cost and environmental impact of current activators used in producing geopolymers are still the main challenges that need to be addressed for making real-time and large-scale applications widespread.
- There is an urgent need to standardize methods, specifications, and guidelines for the mix design of geopolymers based on the divergent characteristics of aluminosilicate precursors and activators used.
- More research is required on synthesising high performance geopolymers with minimal dosages of chemical activators as well as under ambient curing conditions, without any heat treatment. These steps can significantly contribute to producing sustainable products with highly reduced costs.
- Further research is needed on the application of advanced analytical models that can help understand the geopolymerization kinetics, formation of
geopolymeric gels based on the source materials used and identifying the key parameters of designing the mixture to be fabricated.

- More studies on the life cycle assessment of the potential geopolymer mixtures should be conducted to reflect the real economic and environmental benefits obtained from geopolymers compared to conventional concrete.
- More research is still needed in terms of the durability of geopolymers, particularly in the topics related to shrinkage, freeze-thaw resistance and chloride-induced corrosion along with the long-term durability properties of CDW-based geopolymers.
- Investigations on the structural performance of CDW-based geopolymers are very limited. In fact, only two research papers are currently available in the literature, investigating the flexural and shear behaviour of geopolymer concrete beams under ambient conditions using the four-point-bending test [99,192].

**Acknowledgements**

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<table>
<thead>
<tr>
<th>Reference</th>
<th>Mix Type</th>
<th>Aluminosilicates</th>
<th>Activators</th>
<th>curing conditions</th>
<th>C.S (MPa)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>[107]</td>
<td>paste</td>
<td>concrete</td>
<td>NaOH, SS</td>
<td>6, 10, 12, 14, 18</td>
<td>0.5, 1, 1.5, 2, 2.5</td>
<td>20-90 °C for 4, 12, 24, 48 and 72 h</td>
</tr>
<tr>
<td>[141]</td>
<td>mortar</td>
<td>brick, porcelain</td>
<td>NaOH</td>
<td>6, 8, 10</td>
<td>2.0</td>
<td>65 °C/95% RH</td>
</tr>
<tr>
<td>[180]</td>
<td>paste</td>
<td>Bricks, ceramic,</td>
<td>GGBFS, SS, Na2CO3</td>
<td>6, 8, 10, 12, 14</td>
<td>0.75, 1.5</td>
<td>16 h of steam curing, then room temperature with 95% RH</td>
</tr>
<tr>
<td>[30]</td>
<td>paste</td>
<td>concrete, brick,</td>
<td>SS, KOH</td>
<td>8, 10, 12</td>
<td>1.5</td>
<td>room temperature for 24h then 60, 80 and 90 °C</td>
</tr>
<tr>
<td>[175]</td>
<td>paste/mortar</td>
<td>CDW-Mix</td>
<td>NaOH and Na2SO4</td>
<td>6, 10, 11.65</td>
<td>-</td>
<td>room temperature for 24 h</td>
</tr>
<tr>
<td>[176]</td>
<td>paste</td>
<td>concrete</td>
<td>NaOH, SS</td>
<td>5, 10</td>
<td>1, 2</td>
<td>80 °C</td>
</tr>
<tr>
<td>[177]</td>
<td>paste</td>
<td>bricks</td>
<td>MK</td>
<td>NaOH, SS</td>
<td>1.4</td>
<td>4 h room temperature, then 20 h at 40 °C</td>
</tr>
<tr>
<td>[179]</td>
<td>paste</td>
<td>concrete</td>
<td>MK</td>
<td>Ca(OH)2, NOH, SS</td>
<td>1.0</td>
<td>(a) Soaked in water, (b) 40 °C, (c) 80 °C for 24 h</td>
</tr>
<tr>
<td>[161]</td>
<td>paste</td>
<td>ceramic</td>
<td>NaOH, SS, KOH</td>
<td>14</td>
<td>2.5</td>
<td>60 °C/95% RH for 24h</td>
</tr>
<tr>
<td>[140]</td>
<td>mortar</td>
<td>brick</td>
<td>NaOH, SS</td>
<td>10, 12</td>
<td>1.5, 2</td>
<td>65 °C/100% RH for 7 days</td>
</tr>
<tr>
<td>[180]</td>
<td>paste</td>
<td>Bricks, ceramic,</td>
<td>GGBFS, SS, Na2CO3</td>
<td>6, 8, 10, 12, 14</td>
<td>0.75, 1.5</td>
<td>16 h of steam curing, then room temperature with 95% RH</td>
</tr>
</tbody>
</table>
Tile and brick showed better mechanical properties (50-57 MPa) compared to waste concrete owing to high contents of Si and Al. The best performance achieved at 8 and 10 M and at curing temperature of 80-90 °C.

Ambient conditions were insufficient for completing geopolymerization process, reaching 10 MPa as the maximum strength. The addition of GGBFS to brick-based geopolymer clearly improved the main characteristics of geopolymers.

The mixture of 50% FA and 50% waste brick showed the best performance. The use of 20% OPC led to acquisition of paste with double strength compared to that produced without OPC, and the use of hybrid sodium silicate and sodium hydroxide contributed to the achievement of strengths more than 7 times of that using sodium hydroxide alone.

The flowability of mixtures rose with increasing Na₂O concentrations. More pronounced crystal peaks were observed with increasing bricks in the mixes.
<table>
<thead>
<tr>
<th>Ref</th>
<th>Type</th>
<th>Mixtures</th>
<th>Alkali</th>
<th>pH</th>
<th>Temperature</th>
<th>Test Ages</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>mortar</td>
<td>Bricks, ceramic</td>
<td>NaOH, SS</td>
<td>12</td>
<td>1.0</td>
<td>room temp</td>
<td>The high contents of calcium oxide in GGBS significantly densified the CDW-based geopolymer matrix.</td>
</tr>
<tr>
<td>28</td>
<td>mortar</td>
<td>concrete, bricks, ceramic, glass</td>
<td>NaOH, SS</td>
<td>14</td>
<td>1.5</td>
<td>room temp</td>
<td>In comparison to OPC-based paste, geopolymers may save energy up to 45%, and could minimise the greenhouse gas emissions up to 72%.</td>
</tr>
<tr>
<td>25</td>
<td>paste</td>
<td>concrete, bricks, FA-C</td>
<td>NaOH, SS</td>
<td>10</td>
<td>75, 100 °C</td>
<td></td>
<td>The flowability rose with increasing the ratios of Na₂O/SiO₂ and SiO₂/Al₂O₃, whilst setting time shortened with increasing Na₂O/SiO₂ and prolonged with higher SiO₂/Al₂O₃.</td>
</tr>
<tr>
<td>99</td>
<td>paste</td>
<td>Clay bricks, roof tile, hollow bricks</td>
<td>NaOH</td>
<td>10, 15, 19</td>
<td>95, 105, 115, 125 °C for 1, 2, 3 days</td>
<td></td>
<td>Hollow bricks showed the best findings. The main products were N-A-S-H gels.</td>
</tr>
<tr>
<td>75</td>
<td>mortar, concrete</td>
<td>Mixed CDWs</td>
<td>OPC</td>
<td>-</td>
<td>room temp</td>
<td>up to 43.9</td>
<td>The inclusion of 10% OPC in CDW-based geopolymer led to achieving concrete with 33.9 MPa.</td>
</tr>
<tr>
<td>122</td>
<td>mortar</td>
<td>bricks</td>
<td>NaOH, SS</td>
<td>6, 10, 10</td>
<td>1.5, 2, 2.5</td>
<td>room temp</td>
<td>The addition of brick powder significantly reduced the flowability of geopolymer mixes.</td>
</tr>
<tr>
<td>185</td>
<td>mortar</td>
<td>ceramic</td>
<td>NaOH, SS</td>
<td>10</td>
<td>60, 75, 90, 105 °C</td>
<td></td>
<td>The optimal mortar was achieved with solution-to-binder ratio of 0.6 and under 90 °C heat curing.</td>
</tr>
<tr>
<td>105</td>
<td>paste</td>
<td>concrete</td>
<td>FA</td>
<td>10, 14, 18</td>
<td>50 °C for 24 h</td>
<td></td>
<td>Using FA up to 75% as a replacement to bricks in geopolymer can profoundly improve the mechanical properties and the microstructure of the matrix.</td>
</tr>
<tr>
<td>138</td>
<td>paste</td>
<td>Mixed CDWs</td>
<td>NaOH, SS</td>
<td>2, 6, 10, 12</td>
<td>1.1, 1.6, 1.9</td>
<td>room temp</td>
<td>GGBS remarkably enhanced the strength of CDW-based geopolymer at low alkali concentrations (less than 10M), while no improvement was reported at higher molarity (12M or more) in the mixes containing GGBFS more than 25%.</td>
</tr>
<tr>
<td>175</td>
<td>paste/mortar</td>
<td>Mixed CDWs</td>
<td>NaOH, Na₂SO₄</td>
<td>2, 6, 10, 11.65</td>
<td>room temp</td>
<td>Better findings obtained with sodium sulfate in comparison to NaOH at all testing ages.</td>
<td></td>
</tr>
</tbody>
</table>
Table 4. Description of the main factors affecting CDW-based geopolymers.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Mixture</th>
<th>Aluminosilicate Source</th>
<th>Activator</th>
<th>Curing</th>
<th>Tests Applied</th>
<th>Microstructure</th>
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</thead>
<tbody>
<tr>
<td>[186]</td>
<td></td>
<td>CDWs</td>
<td></td>
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<td>[178]</td>
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References


