Review Article

Geopolymer Synthesis and Alkaline Activation Technique of Fly Ash and Slag Source Material: A Review

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Abstract

The advent of geopolymer and its synthesis from industrial waste rich in silicon and aluminum activated by an alkaline solution has proven a viable alternative to ordinary Portland cement. This review presents background on alkaline activation, geopolymerization technology as well as industrial aluminosilicate-based geopolymeric products produced from a range of low to high calcium fly ash, and metallurgical slags in different combinations. Important synthesis conditions, such as the nature of the source material, the type of alkaline activator, the curing condition, and the mixing procedure were effective determinant factors for desired properties in products. The significance of these parameters on the mechanical performance of products relative to each other is discussed. Advances in synthesis, material processing, and production, such as solid-state mechanism and one-part activation are also presented. Future recommendations on other aluminosilicate sources to be considered are highlighted.

Keywords: Industrial aluminosilicates, Alkaline-activated cements, Geopolymerization, Low-alkaline activators, One-part activation

1 Introduction

Global environmental concerns about the need for a sustainable future have placed the demand for viable material use with less environmental impact. Wastes from industrial activities are produced in millions of tons annually with unequal or unmatched consumption levels. As a result, generated materials from waste pose a disposal challenge. The practiced solution has been the evaluation of the beneficial constituents of these wastes and harnessing them in other applications. In the United Nations 2030 Agenda, steps towards substantially reducing waste generation are iterated as prevention, reduction, recycling, and reuse [1]. However, recycling and reuse options are the most practicable techniques. Thus, these sustainability strategies are driven in every sectors, including the construction industry where the carbon footprint associated with its prime material; cement is sought to be lowered. The production process of cement asides from its high embodied energy is estimated to contribute about 8 percent of global carbon emissions [2]. Hence, the development of complementary and greener alternatives to be used as binders is researched. Geopolymer, an inorganic polymeric material as well as alkaline activated binders, formed from the reaction of aluminosilicate source material and an alkaline activator, have been proposed as an alternative binder to ordinary Portland cement (OPC) [3]. Attempts at clarification between the two terms have been on distinguishing the type and nature of precursors required in each process and the chemical structure of resulting products. Geopolymer is said to be synthesized from low calcium precursors with highly reactive alumina and silica, such as metakaolin, fly ash, and volcanic ash, while alkaline activated binders, such as alkaline activated slag (AAS) effectively use high calcium precursors, such as slag [4]. Another distinctive argument is that geopolymerization process tends to yield a more stable and durable product comprising of a 3-D alkali framework structure of aluminosilicate. Whereas AAS produces a calcium silicate hydrated gel with silicon present in a one-dimensional chain [5]

According to Hassan *et al.* [6], the use of geopolymer binders can reduce carbon dioxide emission to about 80% in comparison with OPC when industrial wastes are used as precursors [6]. Asides from contribution towards the reduction in greenhouse gas effect and energy conservation benefit, the premise on which geopolymer cement and alkaline activated materials (AAM) have been proposed including comparative or higher mechanical properties, less shrinkage, and excellent durability [7]. However, these parameters are dependent on a range of factors including reactivity of precursors, alkaline activator, curing condition as well as mixing procedure or technique. Hence, a tailored solution through correct mixed design for each material selection and mixing technique to optimize the properties or associated cost for a targeted application is required [8]. In well-synthesized formulation, the application of geopolymers extends to structural concrete, soil stabilization [9], encapsulation of hazardous wastes [5], repair and strengthening composite [10] amongst others.

Much research has been devoted to the development and understanding of this class of materials over the past three decades [10]–[15] particularly in developed countries. Each study provided the knowledge of material behavior, microstructural characterization, possible blends, and application of developed AAM or geopolymer products. These geopolymers based on fly ash and slag material are intensively studied. However, there is still a wide gap in the development and field use of this class of material in developing countries, particularly in Africa. Some of the reasons for this slower development pace can be attributed to the entrenched position of OPC in the industry, the expense associated with traditional alkaline, and the lack of technical knowledge of large-scale geopolymer production. Therefore, the objective of this paper is to examine, discuss and critique the recent research efforts within the last decade on alkaline activation of fly ash and slag materials and the successful synthesis of geopolymer binders in the construction industry context. In addition, discussion of the prevailing factors affecting the performance of fly ash and slag based geopolymer is included.

2 Geopolymer Technology

Polymers are macromolecules made from the polymerization of many monomers in a chain or network of repeating units. Therefore, geopolymers are compounds or minerals formed from the combination of smaller molecules known as oligomers into a covalently bonded network, for example, silico-oxide (-Si-O-Si-O-) and silico-aluminate (-Si-O-Al-O-) [7]. Geopolymer synthesis is built on the two possible reaction routes of aluminosilicate source materials. One is an acidic medium synthesis [12] and another one is an alkaline medium - alkaline hydroxide or alkaline silicate [13]–[15], which could result in a three-dimensional inorganic amorphous structure.

Major criteria for developing a stable geopolymer include a highly amorphous source material possessing adequate reactive glassy content, having low water demand, and its ability to release aluminum easily. Rudimentary geopolymerization mechanism steps comprise; the dissolution of solid alumino-silicate oxides in an alkaline solution, diffusion of dissolved Al and Si, gel formation phase resulting from the polymerization of the added solution, and Al and Si, and lastly hardening of the gel phase [16]. The kinetics of each step varies depending on the type of aluminosilicate precursor, the solid-to-liquid ratio, the solution concentration, alkali, water content, and the reaction condition [17]. The schematic representation of the geopolymerization process is presented in Figure 1.

Dissolution starts at the addition of the alkaline solution to the source material, resulting in the breaking of the existing covalent bonds between Si-Al-O atoms. The degree of dissolution is dependent on the concentration and amount of the alkaline solution used. Preferential dissolution of Al occurs first due to a weaker Al-O bond, then subsequent release of Si and Al at a steady state [17]. Material dissolution plays a key role in the process, as subsequent

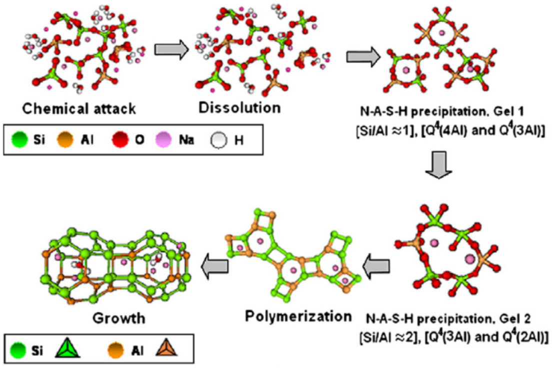

Figure 1: Typical geopolymerization process [16].

polycondensation depends on the amount of Al and Si initially dissolved. Given the rising accumulation of silica and alumina monomers in the system, contact between dissolved products enhances coagulation, which further leads to condensation. The hardening of the geopolymer system is assumed to be a result of the polycondensation of silicate and aluminate species. As such, the physical and mechanical properties of geopolymer binders can be tailored through the adjustment of the synthesis condition to meet the requirement of the application. For example, curing conditions, Si/Al and Na/Al ratios, activator concentration, and type are factors that can be tweaked to achieve this [18].

Most of the modeled mechanisms available in studies used pure materials as metakaolin, therefore for less pure precursors; variation in mechanism should be expected [19]. Waste material precursor, for instance, lower quality fly ash with impurities is a typical example of this. Therefore, the detailing of geopolymerization chemistry from these materials could be challenging due to possible simultaneous reactions of the impurities. Parallel reactions in addition to the part played by impurities in precursors remain unclear [20], [21]. Boonserm *et al.* [22] researched geopolymerization improvement of bottom ash by the addition of fly ash and flue gas desulphurization gypsum (FGDG). High FGDG composition was found to obstruct the geopolymerization process, as well as the development of a thenardite phase, which occurred as a form of impurity within the system. Consequently, all geopolymer mortars of this composition resulted in low strength not exceeding 1.0 MPa. This implies likely reactions occurrence as well as their roles in the geopolymerization stages require more depth. Due to this challenge, more ambiguity is added to the adoption of these materials by the construction industry with strict requirements and expectations on material performance as well as a lesser margin for uncertainty.

Notably, the expansion in the application highlights a difference in the binder regarded as the gel and geopolymeric products resulting from the addition of filler materials, for example geopolymer concrete. However, geopolymeric products do not have stoichiometry configuration and contain a range of amorphous, semi-crystalline, and crystalline structures. Microstructural characteristics are time and temperature-dependent, and this product can be amorphous at room temperature with a crystalline matrix resulting at a temperature above 500 °C. Synthesized products are also expected to change with the nature of source materials and activator. For instance, the product from the alkaline activation of precursors with different calcium content varies. With a waste glass activator, N-A-S-H gel was formed from low calcium precursors while C-A-S-H gel resulted from high calcium precursors [23].

3 Activation Constituent and Influencing Factors

The material list for which geopolymer can be synthesized keeps growing from the initial aluminosilicate source in early research. The main materials required for the synthesis are an aluminosilicate source also known as the precursor and an alkaline activator. Aluminosilicate material from industrial wastes highlights the deep-seated interests in geopolymers and AAM as a waste utilization means amongst its other benefits.

3.1 *Industrial source material*

Industrial activities such as coal combustion, metallurgical process, and other processes yield by-products or wastes with potential depending on the chemical composition. Stemmed interest in these materials is due to their potential as supplementary cementitious material with proven results in the different applications as part replacements for Portland cement. Theoretically, materials containing aluminium, and silicon possess the ability to undergo geopolymerization and form geopolymers under suitable conditions [24]. Much research has reported geopolymer synthesis from industrial by-products [11], [25], [26]. However, the suitability of these waste materials from the industrial process has relations to the trace level of heavy metals and their non-toxic nature. Materials containing a high level of toxic components are not desirable or suitable for use [27].

The reactivity of aluminosilicate sources depends on chemical makeup, mineralogy composition, glassy phase content, morphology, and fineness. Particularly, geopolymerization is governed by the amorphous phase fraction and the accessible Si and Al cations in the source material. Materials possessing large amorphous phase content are easily activated with mid-range alkaline molarity, while those with lower fractions of amorphous phase require a higher concentration of alkaline solution [28]. Iron and silica-rich crystalline phases are reported to remain unchanged in geopolymer products from the starting source material. The role of Fe remains unclear, and their effects may be on a case-by-case basis for the considered precursors. [29] Onisei et. al. suggested that there are chances of the cations being network modifiers or formers, charge suppliers, or that they precipitate as crystalline phases. In slag, high MgO content influenced the reaction kinetics, microstructure strength development through the formation of hydrotalcilite structure [30]. The effect of other oxide compositions as SO3 in geopolymerization is yet to be known and influence is only envisaged as observed with conventional concrete.

Trends in geopolymer binder formulation include the exploration of source material blends. That is the combination of two or more aluminosilicate sources, particularly where the usage is complimentary for the derivation of the desired properties. The alkaline activator combination of hydroxides and silicates are already in use by many authors in geopolymer synthesis [4], [13], [31], [32]. For example, the setting time of a geopolymer system is largely controlled by individual material alumina content, which is found to increase with increasing SiO_2/Al_2O_3 ratio [33]. Blends of two aluminosilicate source materials in suitable ratios may likely adjust the SiO_2/Al_2O_3 in base material for geopolymer synthesis and consequently, an improvement in strength [34]. To accelerate the setting time of fresh geopolymer concrete as well as enable room-temperature curing, a percentage of calcium-rich source material, such as ground granulated blast furnace slag may be added to the blend [35], [36]. The secondary calcium source was found to improve the mechanical properties in addition to the shortened setting time. Bernal *et al.* [37] assessed a binder based on the combination of GGBFS and metakaolin alkaline activation. The metakaolin addition serves to regulate the rapid setting experienced with alkaline activated GGBFS.

Table 1 illustrates the possible constituent range found in a few industrial wastes. The given range shows the potential of these materials as excellent source materials in geopolymer synthesis or alkaline activation. Typically, fly ash and granulated blast furnace slag are the two precursors with a high range of CaO composition as presented in the Table 1.

Table 1: Typical range of oxide composition of selected industrial aluminosilicate source materials [13], [26], [32], [38], [39]

Oxides (%)	Materials			
	Fly Ash	GGBFS	Copper Slag	Ferronickel Slag
SiO_2	29.90–50	32–42	23.9–33.5	32–41
Al_2O_3	16–32	6–19	1.0–5.3	8–14
CaO	4–28.20	35–48	1.0–6.06	0.71–3.73
Fe_2O_3	4.9–7.0	0.1–0.49	13.6–59.1	34–39
SO_3	1.72–8.52	1–4	1.0–2.12	-
MgO	0.78–6.74	3–14	0.80–2.8	2.76–5.43
Na_2O	0.67–6.30	0.3–1.2	0.5–0.81	-

3.1.1 Fly ash

The production of fly ash from the burning process of coal at power plants has no chemical specification. Hence, there is a wide variation in the physio-chemical and mineralogical properties of the material. The observed variation depends on several factors, such as the nature of the burnt coal, combustion conditions, collection means, storage as well as methods of handling [40]. In essence, variation may occur in fly ash from different generating plants despite being obtained from the same coal. In areas with available markets for the ash in blended cement, for example the US, and Australia, quality control and the need for high-quality ash can be achieved. However, for most plants in the developing world like Africa, a major focus is placed on electricity generation as against the quality control of ash being a waste material. Therefore, inconsistency may arise in the properties and quality of fly ash available locally. The implication of this to a component attribute sensitive system as geopolymer synthesis is in the developed product and the wide range of mix proportions in different studies [31], [41]–[44]. Variation in the different constituent phases within the ashes could mean geopolymers of similar properties may not result from their utilizations even at similar activation conditions [45]. Though the investigation of this challenge to geopolymer synthesis has been researched in some studies, however lack of harmonization in results to aid the proper identification of solutions to the problem and addressing synthesis expectations.

Zhang [40] investigated the mechanical properties of GPC synthesized from 25 different fly ash sources across the US. Although the strength range was wide among the fly ash types to as low as 2.7 MPa in a class C GPC and 12 MPa from one of the class F. Class F however developed lower strength with an average of 36 MPa compared to the 50 MPa average obtained from class C. The observation here disagreed with the performance generalization of the class C ash [46] as showing poor reactivity with alkaline activators as a result of their high calcium and low glass composition. Zhang [40] researched 8 class F fly ash available in the Australian market on the influence of chemical compositions, particle size, and reactivity in geopolymer synthesis for close-range assessment. The influence of particle size was found to be more significant than the reactive silicate component of bulk material in the strength development of the geopolymer. Within the same class of fly ash, geopolymers from fly ash denoted as E in the study failed to develop measurable strength at 7 days and only achieved 8.7 MPa at 28 days. Dludlu *et al.* [47] synthesized geopolymers using 3 class F fly ash from different plants in South Africa. Though they all were suitable for geopolymer production, the observed difference was in reactivity and the degree of polymerization, which increased for 2 ashes with a higher SiO_2/Al_2O_3 ratio.

In most publications, class F ash as defined by ASTM C 618, is used in geopolymer synthesis under a low calcium system grouping [48], [49]. The low calcium composition requirement of source material for geopolymers is based on the predominant gel formation in the system, which is N-A-S-H gel. Even more important is the fact that class F ash possesses higher amorphous content than class C [21]. Geopolymers synthesized from class C ash possess higher compressive strength in comparison to class F geopolymers due to the significant development of C-S-H phases from the calcium-rich ash during synthesis. However, the latter is more stable against chemical attacks in an acidic medium [50].

Wijaya [41] investigated the factors that influence the strength and setting time of fly ash-based geopolymer pastes. The report identified two primary chemical properties of fly ash that are contributory to compressive strength, namely the CaO content and the Si/Al ratio. The authors observed that an increase in the content of CaO in pastes made from fly ash with a higher content of CaO, increased paste compressive strength. Their study attributed the observation to the role of CaO in aiding the occurrence of both a polymerization and hydration reaction within the system. The simultaneous occurrence of these two reactions is said to create strength gain. Some geopolymerization and alkaline activation of the different types of fly ash and the product strength are presented in Table 2.

Table 2: Fly ash-based geopolymer source material composition and product strength

Ash Composition (%)			**Class**	**Activator**	**Mechanical Compressive (MPa)**	**Strength Flexure (MPa)**	**Ref.**
SiO_2	**Al_2O_3**	**Fe_2O_3**					
53.09	24.80	8.01	F	NaOH	Up to 73	-	[46]
54.77	21.57	7.33	F	NaOH +cleaning solution	Up to 16	≤5.5	[47]
20.7	9.01	32.0	C	NaOH + Na_2SiO_3	Up to 72.5	-	[31]
30.7	16.0	6.8	C	NaOH + Na_2SiO_3	About 78	-	[32]
29.9	16.7	4.9	C	Na_2CO_3	About 8	-	[35]
62.91	27.15	3.23	F	NaOH + Na_2SiO_3	Up to 60	-	[30]
57.06	18.82	5.43	F	NaOH + Na_2SiO_3	Up to 51	-	[48]

Results from the reviewed literature in Table 2 suggested that there is no a specific standard on the kind of fly ash suitable for geopolymer production. Depending on the synthesis condition, the compressive strength values, and performance of products from the table suggests other intrinsic factors, which should be considered along with the selection of the fly ash toward the targeted performance objective. However, this does not imply all fly ash sources are suitable for use. Other quality assessment features, such as low SO3, LOI, and low concentration of heavy metals may be considered in the choice of best materials to curtail poor reactivity. Therefore the characterization of fly ash is essential before use [51].

3.1.2 Metallurgical slags

GGBFS from the extraction of iron is the most referenced slag form in slag-related formulation or usage [3], [26], [27], [52]–[54]. Exhaustively explored in the production of slag cement, there is a growing interest in the investigation of other metallurgical slags particularly their potential for alkaline activation. Typically, the use of GGBFS in alkaline activated material is due to its high calcium oxide content, and for this reason, it is often used as complementary material in fly ash-slag-based geopolymer synthesis. This is to improve the setting time, which is slower in fly ash-based systems, through the release of free calcium ions, which will enhance geopolymer gel formation [55]. Nath and Kumar [56] reported corex slag to achieve similar performance to GGBFS in FA geopolymer synthesis due to similar composition range.

Not all variants of slag can exhibit this behavior in alkaline activation owing to the difference in the chemical composition of individual waste material. For example, non-ferrous metallurgical slags (such as lead slag, copper slag and FeNi slag) are rich in Fe, minor Si and Al deficient [57]. Table 3 shows the compositional variation of three types of slag as well as some similarities and strengths of the activated product . Some of the slags have high silica but very low alumina content, which is indicative of how the material will perform in sole activation. Hence, such types of slag are most suitable for pairing with other aluminosilicate sources.

Aliabdo *et al.* [49] studied the factors affecting the mechanical properties of alkali-activated blast furnace slag concrete, such as sodium hydroxide molarity, sodium hydroxide to silicate mass ratio, alkaline solution to slag content, curing temperature, and time. The results show 90% of its compressive strength was attained by the alkaline activated slag concrete at 7 days, which shows alkali-activated slag concrete has and can gain high early strength.

Table 3: Alkaline activated slag source material composition and product strength

Slag Type	**Slag Composition (%)**			**Activator**	**Compressive Strength (MPa)**	**Ref.**
	SiO_2	**Al_2O_3**	**Fe_2O_3**			
GBFS	33.8	13.7	0.4	Na_2SiO_3 + Na_2CO_3	≤ 63	[53]
CS	33.05	2.79	13.6	NaOH + Na_2SiO_3	≤ 44.8	[13]
GBFS	31.6	14.6	1.1	Na_2CO_3	-	[30]
GBFS	36.74	10.78	0.42	Na_2SiO_3	≤ 78	[49]
GBFS	32.93	14.98	0.79	Na AlO_2 + Na_2SiO_3	≤ 90	[58]
FeNi	32.74	8.32	39.74	Na_2SiO_3	≤15.78	[59]

From the results of studies presented in Table 3, almost all types of slag contain a similar composition of silica (SiO_2) and comparable values for alumina content except for copper slag, which typically has a low alumina range. The difference, however, is the higher calcium oxide composition in GBFS than in the other forms of slag. Also, the lowest strength of about 15.78 MPa is observed with the slag type, which has the highest iron oxide content. The deduction disagrees with a previous observation that iron is not necessarily deleterious to geopolymer formation [20]. Considering the performance of slag as sole precursors in AAS [27], [29], [58], [60] or as binary blends with other precursors [13], [55], [61]–[66] in studies, GBFS resulted in optimal performance.

3.2 *Particle size and shape*

Physical properties such as particle size and shape influence the behavior of precursors in activation. The microstructure of some of these precursors is exemplified by the SEM images (Figure 2), which indicate distinctive morphological features. The fly ash particles are spheroidal with varying sphere sizes. In comparison, slag particles are irregularly shaped with the majority being angular. The importance of these features is seen in the reactivity of materials as well as the morphology of the geopolymer products [67], [68].

Reactivity is improved by the increase in particle surface area and reduction in particle size, which is both achieved through mechanical activation or grinding. This consequently speeds up hydration [69], including enhancing the properties of AAM [56]. The observed influence of particle sizing on alkaline activation and synthesis is explained in terms of reactivity and pore reduction within the structure. Finer particle size distribution in geopolymer matrix results in denser microstructure and better strength characteristics [70]. The fine particles can fill micro-voids within the structure [34], decrease the loss of free water during curing, and consequently reduce the formation of fine cracks. In terms of reactivity, the dissolution rate of Al and Si from precursors can be affected by the size of the particles as a higher degree of geopolymerization is achieved through the increase of specific surface area in the fine particles [34]. The spherical shape of fly ash particles reduces its water demand and aids the workability of the resulting mix whereas, particles as clay and slag with plate-like morphology exhibit a higher water demand in the mix [40], [43], [71].

It is suggested that the change in reactivity could also result from changes in the amorphous phase SiO_2 with particle size [72]. Using particle range 0.125–0.25 mm, the reactive component of sampled fly ash decreased initially and then increased with ash particle size. Similarly, Chindaprasirt *et al.* [73] used particles in the range of 9–25 microns for FA-based geopolymer synthesis. Mixes with finer ash set faster than coarse particles mixes. A higher glassy phase in the finer portions than the coarse portion contributed to the improved reaction rate. The evaluation of both studies indicates the reactivity observation is dependent on ash type and source. In essence, the active phase content of the material can also determine the level of reaction in the mix.

3.3 *Alkaline activators*

Alkaline activators play a key role in geopolymer synthesis by accelerating the breaking up of structure and bond in the precursors for the release of Al and Si ions. They are derived from soluble alkali metals, which are usually sodium or potassium based activators [76]. Generally, the activators commonly used in aluminosilicates are alkaline hydroxides, alkaline silicates, or blends of the two in certain conditions to increase the alkalinity of the resulting solution as higher alkalinity is known to promote dissolution and reaction rate [11]. Sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) are the most utilized activator combination due to their high pH, though some potassium compounds, such as potassium hydroxide (KOH) and (K_2SiO_3) have been previously used. NaOH and Na_2SiO_3 solutions yield impressive, activated material but other activators are required to solve the cost, handling problem, and efflorescence typically associated with NaOH [43].

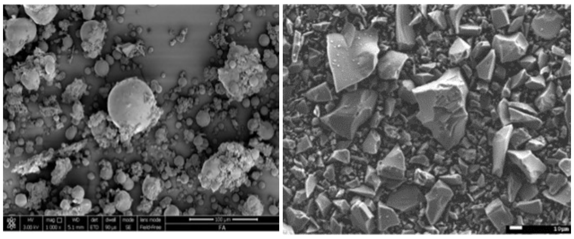
(a) (b)

Figure 2: SEM image of (a) fly ash [74] and (b) Granulated blast furnace slag [75].

The solution can be the use of a moderate pH solution or near-neutral salt, which are comparatively cheaper and easy to handle. Sodium carbonate (Na_2CO_3), lime (CaO), and hydrated lime ($Ca(OH)_2$) are promising alternatives to the typically used alkaline solution [77]. Although, sodium carbonate activation results in lower early age strength compared to those activated with silicate and hydroxide. The resulting lower early strength is associated with the initial formation of sodium-calcium carbonate, which slows the activation reaction. An advantage to consider is that sodium carbonate results in lower drying shrinkage of AAM compared to those activated with sodium silicate [78].

The nature of the alkaline solution and its concentration determines the reactivity and ensuing mechanical products. Changes in activator concentration are usually used to control the setting, the hardening time, and the compressive strength of the product. Typically, higher molarity of NaOH and sodium silicate will give higher strength [79]. Though, results from Park *et al.* [39] indicate excess alkali in the system will adversely affect strength. The authors reported faster strength development with 5% Na_2CO_3 but increasing the dosage of the activator adversely reduced the rate of strength development. Hence, there is an optimum level of concentration or composition required for mechanical strength increase.

Despite extensive literature available on activator dosage, no consensus is reached on the optimal concentration for different activator types. Though things to consider are efflorescence and economic factors resulting from high concentration [14]. Increasing the activator molarity enhances source material dissolution and the formation of a dense microstructure, however, geopolymerization can be hindered by the presence of excessive alkali concentration that causes the affinity for precipitation before condensation in the reaction mechanism [70].

Also, in the two alkali species, the rate at which dissolution takes place is higher in NaOH than in KOH solutions, particularly when using the most reactive materials [11]. Similarly, the pore size, shape, and distribution differ depending on the type of alkali for sodium and potassium-based activators. K_2SiO_3 produces samples having higher specific surface area, while Na_2SiO_3 activation results in a large distribution of small pores [45]. Water glass (sodium silicate) contributes to rapid hardening and high compressive strength. Though, short set times and consequently shrinkage can occur [26]. To control the shortfalls of each sodium hydroxide/silicate solution, the use of both in combination is common.Mohsen and Mostafa [79] found the mixture of NaOH and Na_2SiO_3 to achieve higher strength than sole NaOH activation in their study on geopolymer bricks.

Development in activators has also seen the exploration of sodium borate solution in the activation of precursors [45], [61], sodium aluminate [58], and a cleaning solution from the aluminum casting industry [80]. Boron was substituted for aluminum in the inorganic polymer structure to produce a new class of material [45]. The pastes made in the study had a compressive strength of up to 56 MPa. In similar developments, the role of boron inclusion in the silicate framework was explained on the improvement in mechanical strength and structural morphology of fly ash-slag based geopolymer [61]. Substituting water-glass solution with anhydrous borax yields a higher pH of the medium, which consequently results in faster dissolution of Al species than the Si. Initially, gel formation is prolonged by the lesser availability of reactive silica. The Ca/Si ratio in the matrix reduced due to the electrostatic attraction between the $[SiO_4]$ and $[BO_4]$ ion. Therefore, availability of $[SiO_4]$ ion reduces to allow the formation of a more homogeneous (C, N)-A- (S, B)-H gel structure exhibiting better compressive strength. Also, borax matrix shows a dense structure with no surface cracks since activator consumes smaller amount of water and less pore water within the matrix. The application of a cleaning solution as an alkali activator for the activation of fly ash and glass powder was also investigated [80]. The cleaning solution activator resulted in comparative strength with 8 M NaOH solution in fly ash activation and performed better than the latter with the glass powder.

Results from these studies explain the importance of utilizing not only the required amount but also the most suitable type of alkali activator for each precursor for the best activation results. Since these results vary with the precursors used, the testing of the activator with the material is advised to be conducted before use in mortars or concrete applications. Aluminosilicate materials grouping and suitable activators are illustrated in Figure 3. For slag activation, the use of activators with concentrations of Na_2O higher than 5% of slag weight fails to yield a significant increase in strength. Despite a consensus on activator concentration, [14] suggested a 2–4 M concentration order is required for slag-based cement preparation. Investigation of the mechanisms that worked with each activator choice and comparison with the composition range of precursors can enhance the activation process in future research.

Another salient point is the cost of activators and supply availability, which in the global development and widespread use of geopolymer and AAM material would be expensive to use in construction by developing countries in Africa. Locally available and cheaper alternative activator sources, such as lime, soda ash, red mud, paper sludge [81] and others, which have been reported with great potential in geopolymer synthesis and alkaline activation should be explored more in this region.

3.4 *Liquid-to-solid ratio (L/S)*

An important phenomenon in the activation or synthesis process is the water demand for source material. This effect is on the setting, drying, as well as hardening of the product. High water demand could cause shrinkage or loss of strength due to increase in porosity [82]. In examining the effect liquid to solid on alkaline activated binder behavior, the ratios between 0.18 to 0.29 in geopolymer mixes were varied [3], [83]. The workability of the fresh pastes increased with an increase in liquid to solid ratio, however, the compressive strength of hardened paste declined by more than 50%. Below the L/S ratio of 0.2, the mix was stiff due to

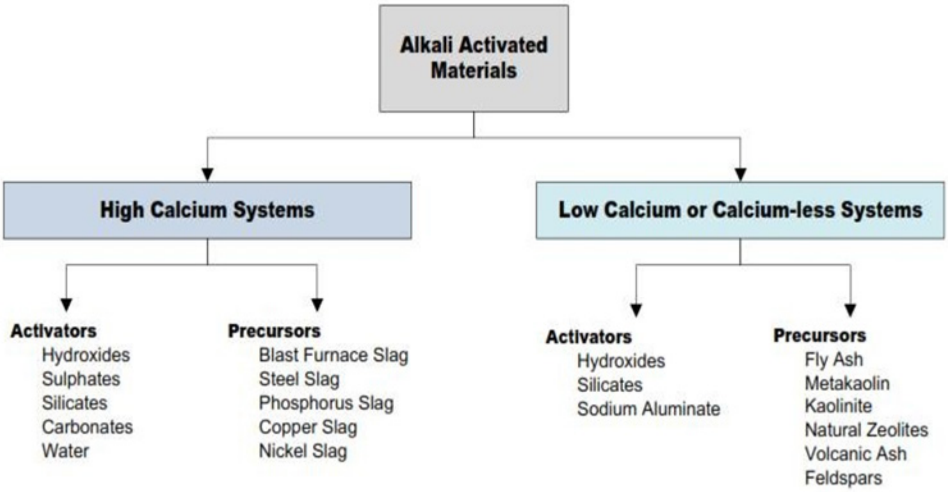

Figure 3: Precursors and suitable activator choice for alkaline activated material binders [4].

insufficient wetting of the particles. It was suggested that achieving the workability required with minimum water-to-binder ratio. From the results , pastes of high workability were obtained at 0.5 L/S ratio due to the reduction in friction between particles as a result of free water molecules within the mix [84]. Though workability is also attributed to the morphology of source material. L/S ratio of 0.5 also exhibited the highest setting time of a range between 0.4–0.5. Free water molecules that earlier resulted in higher workability delayed the hydration products formation, hence the slower rate of setting.

Also, a high L/S ratio reduced the activator molarity. The effect of this is on the surface hydroxylation of fly ash particles resulting in low Si and Al species available in the aqueous phase. Thereby giving poor strength to developed pastes [3]. An L/S ratio of 0.4 gave the best result for mechanical strength observation of the specified range. Geopolymer mix with higher fly ash composition was reported that it required a lower L/S ratio of 0.33 in comparison with calcined clay synthesized geopolymer requiring an L/S ratio of 0.4 [71]. From the reviewed studies, the better activation result is achieved between an L/S ratio of 0.3–0.4, while considering a balance between the fresh state and mechanical performance of the synthesized product.

3.5 *Si to Al ratio*

Precursor chemical property dominantly affecting the strength of geopolymer is the reactive Si and Al available. Source material silica and alumina content play a vital role in the extent of reaction and the composition as well as the structure of activated binder products. Of more importance is the availability of aluminum and its release during the reaction since silicon deficiency in the source material can be corrected by the addition of soluble silicates from activators. However, the bulk silica and alumina composition of the source material are not all participating in the gel formation [50]. For example, the crystalline phases in some materials, such as quartz and mullite remain unchanged during activation [14]. In essence, though the phase may amount to the increase in Si/Al ratio within the system, however, it does not contribute to the soluble Si required for the gel formation. The starting Si/Al ratio of 2 to 4 in the source material was suggested for an excellent performance of the activated or synthesized product [73], [85].

Geopolymer Si/Al ratio has shown convergence towards a range for better results, irrespective of source material type. The increased performance of geopolymer product relative to the Si/Al ratio for two different precursors can be compared based on the studies of fly ash [41] and metakaolin [86] source materials, respectively. Wijaya [41] synthesized fly ash-based geopolymer pastes with high strength when the ratio of Si to Al lies around 2, which was illustrated by the cluster of points within the region when compressive strength was plotted against the Si/Al ratio. Above the range of 2 for Si/Al ratio, a decrease in the compressive strength was observed. A comparable plot profile was obtained with a metakaolin based geopolymer [86]. The optimum compressive strength achieved around the Si/Al ratio of 2 agrees with earlier studies [48] on similar findings in alkaline activated fly ash cement and the results of [50]. Therefore, the deduction of this relationship irrespective of source material type was demonstrated. Poor strength values were obtained in the study for Si/Al of 1 and 5. The phenomenon is explained by the initial preferential dissolution of Al from aluminosilicate source, which increases with the Si/Al ratio and stabilizes at a ratio of 2. The polymerization and condensation of aluminate monomers reach a balance at this ratio. At higher Si/Al ratios, however, excess soluble silicate weakens the strength of geopolymer through the formation of silicate derivates instead, since mechanical strength is rather dependent on the formation of N-A-S-H gel [86].

Though there are some divergent views on this observation as the study [87]. Geopolymer with a Si/Al ratio of 4 had better mechanical strength than those within the range of 2–2.5 due to increasing Si-O-Si bonds in the matrix, which are known to be stronger than Si-O-Al bonds. However, the samples had poor stability and showed efflorescence on the surface than the geopolymers with a Si/Al ratio of 2–2.5. Though a crucial factor, compressive strength trend as a function of this ratio varies across materials and has an intrinsic relationship with other factors of synthesis.

3.6 *Curing techniques*

In addition to other factors, curing conditions also have a major effect on the microstructural and mechanical strength development in most cementitious systems. Like OPC, geopolymer synthesis and alkaline activation perform better under certain controlled environments. The kinetics and degree of the reaction that produce geopolymer with a stronger Al-Si-O network are enhanced by higher curing temperature; achieving proper mechanics at ambient temperature is a challenge for successful geopolymer concrete synthesis [88]. Curing techniques explored in geopolymer and alkaline activation-related studies are curing temperature, relative humidity, curing environment, and curing duration. Ambient and elevated temperature curing is generally applied and compared in most syntheses [4]. The temperature in the range of 50–80 °C is commonly used for successful geopolymerization [88]. Elevated temperature is achieved either by dry curing in an oven, or heat steam curing of samples [66], though curing of samples under direct sunlight has also been reviewed [35], [89].

Palomo and Fernández-Jiménez [12] and Khan *et al.* [90] observed that mechanical strength increases rapidly with temperature. Their reports also provided detail of a threshold at which the mechanical strength may increase or decrease with temperature and time. There was a finding [18] elucidates the points raised by the previous study. The study explored the temperature range between 60 and 120 °C at the same curing regime. The optimal curing temperature for both mixes made with 10M and 15M NaOH solution is about 90 °C after which a decline in compressive strength is observed. The results for the lower concentration mixes were similar for 60 and 120 °C, therefore an increase in temperature had no significant effect on the compressive strength values obtained at the earlier temperature. Though an increase in reaction time and temperature has been reported to positively affect geopolymerization.

However, comparable studies show that these factors only enhance early age mechanics as an increase in temperature and rate of reaction had a negative effect on samples at a later age, as presented in the decreased final sample strengths. The reaction product becomes less over time and an increase in temperature merely degrades the aluminosilicate gels previously formed within the matrix thereby weakening the material structure [88]. Phased curing conditions are also being tested for improving the initial reaction rate [91]. Criado [92] examined the effect of curing conditions on fly ash activation using a NaOH solution. Pastes samples were cured at 85 °C for the initial few hours and then prolonged timing under a relative humidity of >90% and 40–50%. Pastes cured at higher relative humidity showed higher strength.

Vinodhini [93] investigated the effect of curing temperature on a fly ash-slag-based GPC. Their results indicate GPC cured under ambient conditions had excellent compressive strength up to 41.7 MPa, which is an indication that geopolymers binders and concrete can be achieved under a suitable ambient condition in the absence of elevated temperature.

4 Developments in Geopolymer Synthesis and Alkaline Activated Material

This section examines the newer contributions to the technology, material processing and production process, such as solid-state mechanism and one-part activation in the synthesis of geopolymer and alkaline activated materials.

4.1 *One-part activation*

The feasibility of handling liquid corrosive activators in a conventional two-part activation process for the commercialisation of geopolymer technology applications has aided the development of a one-part activation technique [94], [95]. The formulation of a simple and effective method is important to the development of the geopolymer industry [95]. Hence, one-part alkaline activated material is prepared from the dry mixture of solid activator and precursor material, which may be calcinated prior to the addition of water to the mixture. The synthesis potentials of this method include heat liberation at initial mixing with water, which could be beneficial for curing purposes [96]. The strength development trend of mixes with one-part activation was found to be similar and comparable with OPC mixes at 3 and 7 days of age [97]. As some studies [58], [98], show successful synthesis and activation have been achieved with this technique with significant strength value, especially with slag activation.

Suwan and Fan [96] studied the effect of manufacturing process on the mechanism and mechanical properties of fly ash-based geopolymer. The mixing method was highlighted as a salient factor affecting geopolymer properties in this study. The one-part system required higher water content for adequate dissolution and moisture loss makeup. Although the initial rapid setting was observed with this method, the strength of samples was slightly lower compared to the traditional mixing method. Alluding to this are incomplete dissolution and pore formation through rapid moisture loss within the system.

Ren [98] compared the properties of AAS binders from the two different activation approaches. Though similar early mechanical strength resulted for samples from both part activation, one-part activation however gave slightly lower 28-day strength. Also clearly spotted with one-part activation result is fewer formation of C-A-S-H gels, a large formation of macropores and more susceptibility to efflorescence. In the fresh state, longer setting time due to the delayed dissolution of silica and alumina species and consequently the delay in the gelation and condensation steps resulted. Some development in the chemistry of alkaline activated precursors for one-part binders includes the exploration of high temperature techniques which compromises the sustainable advantage of this method [99]. Whereas the ease of commercialization and practicality in the large-scale application remains the driving force for improvement in the one-part activation technique of geopolymer and AAS.

4.2 *Advanced geopolymerization technology via solid-state mechanism*

The manufacture of geopolymers by solid-state mechanism is an innovative approach in geopolymerization technology. This process is achieved by the mechanochemical activation of aluminosilicates and alkali materials through prolonged milling [97]. The milling process at high energy incorporates alkali earth/alkali metal cations into the structure of the aluminosilicates through the disruption of the aluminosilicate bonds. This approach highlights the compounding and activation of fly ash and materials containing alkali earth or alkali metal cations through the introduction of mechanical energy [96]. The added alkali cations destabilize the aluminosilicate content of fly ash by creating a disorder and compounded to yield reactive material with hydraulic properties. The steps involved in the initial reaction for solid state mechanism of advanced geopolymerization differ from the traditional geopolymerization. First, the dissociation of bonds in the glassy Si/Al phase leads to the formation of active unstable silanone species Si=O from siloxane -Si-O-Si-. Next is the reaction of silanone species with water molecules to form silanol. With water, the silanol forms -Si-O-Al- linkages and subsequently geopolymeric gels are formed [97]. The geopolymeric precursors produced through this technique are ready to use onsite requiring only water, thus suitable for fabrication of pre-engineered geopolymeric products.

Table 4 gives a summary of some recent geopolymer and alkaline activated material formulations and processing, with a focus on the test variables, such as source material type, blend ratio, activator type or

Table 4: Geopolymer /AAM formulation and processing from industrial source material

Product	Industrial Aluminosilicate Source	Activator	Mixing Technique	Procedure	Tested Variables	Findings	Ref.
Alkalineactivated FA/GP/SG cement	Fly ash + Lime glass powder + GGBFS blend	NaOH	Two-part activation	Glass powderwas used as part replacementfor fly ash, while SG was kept constant at 50%. Cured at ambient and elevated temperature	Blend ratioactivator concentration alkaline to solid ratio curing temperature	- Curing temperature had the most significant effect. - Flow and setting time improved with GP addition. - Short-term heat curing resulted in early strength gain.	[84]
Fly ash geopolymer	Fly ash	Na_2SiO_3 + $(CH_3)_3CONa$	Two-part activation	Sodium tert-butoxide, sodium silicate and a mix of the activators were used in fly ash activation. Paste cubes were cured at ambient temp.	Activator typeactivator content	- Denser matrix and increased compressive strength with sodium tert-butoxide addition. - Optimum strength obtained at 5 and 10% sodium silicate and tert-butoxide respectively.	[100]
Alkaline activated slag	GBFS	Na_2SiO_3	One-part activation			- Slower hardening rate - Fewer C-A-S-H - More efflorescence compared to two-part activation.	[98]
FA-based geopolymer mortar	Fly ash	NaOH + Na_2SiO_3	Two-part activation	FA was mixed with varying molarity of NaOH, and fine aggregate was added.	Activator combination ratio (SS/SH)NaOH concentration-Liquid-to-solid ratio (L/S)	- Optimum strength value obtained at 12 M NaOH, L/S of 0.5, and SS/SH of 1.5.	[101]
Slag based geopolymer	GBF slag	NaOH + Na_2SiO_3	One-part activation	Dry milling of BFS and activators together prior to water addition.	Milling parameter,BFS/Activator mass ratio, Na_2SiO_3/NaOH mass ratio	Higher compressive strength at 2.5 activator mass ratio milled for 5 min at 200 rpm.	[102]
FA- GGBS based geopolymer	Fly ash, GGB slag	Na_2SiO_3 $B_4Na_2O_7$ NaOH	Two-part activation	80% Fly ash and 20% GGBS blend was activated using borax modified water glass.		- Boron is incorporated in the aluminosilicate framework structure - Compressive strength increases with the introduction of anhydrous borax. Resulting in a dense structure	[61]
Fly ash-slag mortar	Fly ash GGBFS	Na_2CO_3 Na_2SiO_3	One-part activation	Dry mixing of both the alkaline powder with the fine aggregate and water added in parts.	Steam curingactivator concentration. Activator type	- Rapid strength development when heat cured. - An increase in Na_2SiO_3 resulted in a compressive strength jump and a decrease in flexural strength. - Optimum at activator combination	[66]
Flyash-based geopolymer bricks and tiles	Fly ash	NaOH + Na_2SiO_3	Two-part activation	Mixing of the two alkaline activators before addition to fly ash. Fly ash was also used as a fine aggregate substitute.	Curing temperatureaging period NaOH concentration water to fly ash ratio	- Compressive strength increases from 10 M up to 14 M NaOH concentration - No significant change in values between 14 M and 16 M, 60 and 80 °C curings, 7- and 28-days duration - Bricks and tiles performed to standard specification	[103]

concentration, module, and curing conditions. Crucial conclusions from these studies are presented with the considered variables. The main influencing factors with consistent patterns in geopolymer synthesis or alkaline activation highlighted by most authors were source material, blend ratio, activator type, activator concentration, and curing conditions. However, where curing temperature had been studied, peak temperature with no significant effect on the strength development was unidentified. Synthesis of other variations of slag asides GGBFS is not well explored in research with blends.

5 Conclusions

Waste beneficiation in the use of aluminosilicate-rich industrial by-product as fly ash and slag makes geopolymer and alkaline activated material technology valuable. However, intricate knowledge of material reactivity, chemistry, and proportion is required. From this review, the following conclusion was deduced. Source material and activator properties, such as reactive phase, particle size, chemical composition, activator type, and concentration are important factors that influence the strength, microstructure, the behavior of fly ash and slag material during synthesis. In blend activation, the most significant however are blend ratio and activator concentration. For low calcium systems, such as fly ash, a heat curing temperature of about 80 degrees Celsius is sufficient for strength gain, while a liquid-to-solid ratio of about 0.3 is effective. In addition, slag inclusion in fly ash-slag-based geopolymer enhances strength as well as an ambient temperature curing for blended source material synthesis. Corex slag could yield similar results in geopolymer synthesis as the vastly used GBFS under the same activation condition. Hence there is the potential use of other forms of slag. In the synthesis approach, the manufacturing process as one-part activation and solid-state mechanism are practical alternatives to traditional synthesis and activation methods, which could enhance commercialization and extensive use of geopolymer in the construction field. Although, care needs to be taken in developing a well-tailored mix design to reduce the drawbacks of this procedure.

Due to the effective utilization of good quality fly ash and BFS slag in already established applications beyond alkaline activation and geopolymer synthesis, materials with less use and quality such as copper slag, bottom ash, and ash from coal with poor calorific value should be explored. Known for its high iron content, the reactivity of copper slag in a mildly alkaline activator medium, and the microstructural development of the resulting product should be studied to give valuable details on similarities or disparities with known microstructural characteristics of activated GBFS material. Similarly, further research is also required into activator development or bracket expansion of potential activators with economic and sustainability goals as a target.

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I.E.: conceptualization, investigation, reviewing and editing; methodology, writing an original draft; G.M.: conceptualization, reviewing and editing, funding acquisition; O.P.: reviewing and editing. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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