

A REVIEW ON GEOPOLYMERISATION PROCESS AND AFFECTING FACTORS OF ALKALI ACTIVATED MATERIALS

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Abstract:

Geopolymer concrete (GPC) is made from silica and alumina-rich materials that can be used as a substitute for ordinary Portland cement (OPC). GPC has a reduced carbon footprint and uses less energy than OPC. It also reuses waste materials and can be more cost-effective for long-life infrastructure construction. Geopolymerisation is the process to develop inorganic polymers by mixing alumino-silicate powders with alkaline activators for preparing an alternative of most widely used construction material portland cement concrete (PC concrete). CO₂ emission released in environment during portland cement production can be reduced up to some extent by using geopolymer concrete (GPC) instead of PC concrete. This state-of-the-art review presents the advancements in geopolymerisation with respect to its affecting factors like properties of binders, methods of binder activation and curing condition. This paper attempts to elucidate chemistry and reaction mechanisms for identifying the gaps in the existing body of knowledge and summarizes with proposals of suitable approaches to improve the potential of geopolymerisation. The viewpoint of this review is to have more understanding about geopolymerisation technology and contributing to the sustainable development of the construction sector.

Keywords – Alkaline activators, Mechanical activation, Precursors, Oxide ratios.

1. INTRODUCTION

Geopolymers, also called alkali activated materials are compounds of aluminium and silicium; Si-O-Al-O bond is the building element of chemical chains and chemically defined as (K-Ca)(Si-O-Al-O-Si-O-) poly (sialate-siloxo) [20]. For the synthesis of geopolymers, three sources namely raw materials, inactive filler and geopolymer liquor are needed. Raw materials could be natural (alumino-silicate) minerals or industrial wastes such as fly ash, slag, and waste glass. Inactive filler, mainly kaolinite or metakaolinite is used for the supply of Al³⁺ ions. Geopolymer liquor is an alkali hydroxide solution required for the dissolution of raw materials while sodium (or potassium) silicate solution acts as binder, alkali activator and dispersant or plasticiser [33]. Geopolymerization can be considered a viable technology to transform industrial wastes into utilisable materials because of using certain industrial wastes, such as fly ash, blast furnace slag and mine tailings contain sufficient amounts of reactive alumina and silica as raw materials [24].

2. FACTORS AFFECTING THE GEOPOLYMERISATION

In this paper, the factors are reviewed which affect the properties of geopolymerisation process in alkali-activated material and concluded by suggesting techniques to enhance the properties of it. Here are the factors affecting the properties of alkali-activated materials:

- Chemical composition and concentration of activator
- Nature of the precursor
- Methods for activation of precursor
- Conditions of hydrothermal process

2.1 Chemical composition and concentration of activator

Alkaline activators are the essential component in alkaline cement design and development. Physical properties of geopolymer concrete are depending on nature, oxide ratios, cation and concentration of alkaline activators used.

2.1.1 Nature of activators

Activators used in alkali activated materials are normally alkaline salts or caustic solutions like sodium hydroxide (NaOH), potassium hydroxide (KOH), potassium silicate (K_2SiO_3) and sodium silicate (Na_2SiO_3) are capable of liberating the aluminate and silicate monomers in the aluminosilicate material, which further dissolves and form an aluminosilicate gel [2]. The amount of dissolution increases with increasing the level of alkalinity. However, in case of sodium hydroxide and potassium hydroxide, it has been shown that sodium hydroxide can liberate more silicate and aluminate monomers than potassium hydroxide [30]. Bakharev et al. [32] carried out that activating slag with sodium silicate gave the best compressive strength compared to sodium carbonate and sodium hydroxide.

2.1.2 Oxide ratios of activators

The chemical composition of the original raw material and its mineralogical characteristics (primarily its amorphous or vitreous phase content and the presence of minority crystalline phases) are determinants in the formation of the main reaction products comprising alkaline cements: C-A-S-H gels (alkaline activation of high silica, high-calcium materials such as slag) and N-A-S-H gels (alkaline activation of high-silica, high-alumina materials such as fly ash and metakaolin) [25]. Z. Pan et al. [27] has concluded that the hydration products of alkali–slag–red mud cement (ASRC) are mostly C-S-H gel with very low Ca/Si ratio of 0.8–1.2, very small particle size of hundreds of nanometers and very irregular shape in morphology. The CaO content of the source material appears to strengthen the geopolymer by forming amorphously structured Ca–Al–Si gel and that's why the CaO can be introduced in the form of an aqueous suspension to improve the physical and mechanical properties of geopolymers [31].

In aluminosilicate (fly ash and metakaolin) alkaline activation, the silica and alumina content of the raw material unquestionably plays an essential role in the degree of reaction as well as in the composition and structure of the products [25]. The setting time of the geopolymer systems is mainly controlled by the alumina content and increases with increasing SiO_2/Al_2O_3 ratios in the initial mixture [31]. Due to increase in Na_2O/Al_2O_3 ratio, alkali-activated binders that contain sodium-based activators have been reported to be more vulnerable to efflorescence. When Na_2O exists in an unreacted state increases, it can accelerate relatively easy movement of sodium ions in the aluminosilicate structure which is a product of the alkali-activated binder [26]. Tero Luukkonen et al. [8] tested the effect of silica-modulus (molar ratio of SiO_2/Na_2O) on alkali activator solution and concluded that physical properties of geopolymers vary with silica-modulus.

2.1.3 Cation

The process of geopolymerisation involves leaching, diffusion, condensation and hardening steps. When the powdery solid comes into contact with the alkaline solution, hydroxide (OH^-) of the alkaline solution breaks the bonds of the silicon and aluminum species of the powdery precursor and in the course of the subsequent polycondensation reaction, the dissolved species form the geopolymer network [34]. The presence of OH^- ions not only catalyses the hydrolytic reactions involved in the various stages of alkaline activation, but also raises the pH to the values required for initial precursor dissolution and the subsequent condensation reactions [25]. Higher amounts of hydroxyl ions promote polymerization by facilitating the dissociation of different silicate and aluminate species. The most significant factor that controls the compressive strength of fly ash-based geopolymers is the pH of the initial alkali metal silicate precursor [31].

The cation of the activator alkaline solution provides the positive charge that maintains the solution electroneutrality [11]. Chao Li et al. [16] confirmed that the depolymerized calcium aluminosilicate glass network, largely controls reactivity, forming cations are Si^{4+} and Al^{3+} , and the divalent Ca^{2+} and Mg^{2+} act as network modifiers along with any alkalis present and a formula is described for the degree of depolymerization (DP) as follows:

$$DP = \frac{n(CaO) - 2n(MgO) - n(Al_2O_3) - n(SO_3)}{n(SiO_2) - 2n(MgO) - 0.5n(Al_2O_3)} \quad (1)$$

The serious drawbacks of geopolymers with sodium based activators are leachability and efflorescence. Halina Szklorzova et al. [6] concluded that the efflorescence increases strongly with increasing content of sodium ions containing activator and can be minimized by the influence of potassium ion in activator.

Bo Yuan et al. [23] reported that increasing the proportions of red mud in the mixes increased the pH values of the pore solution at all ages but the alkalinity of the pore solution in all mixes increased rapidly during the first day after mixing and declined afterward. Prinya Chindapasirt et al. [12] reported that calcium ions from Portland Cement and Calcium Hydroxide can be incorporated into the high calcium fly ash geopolymer to produce reasonably fast setting mixtures with significant strength improvement complying with the strength requirement for repair material.

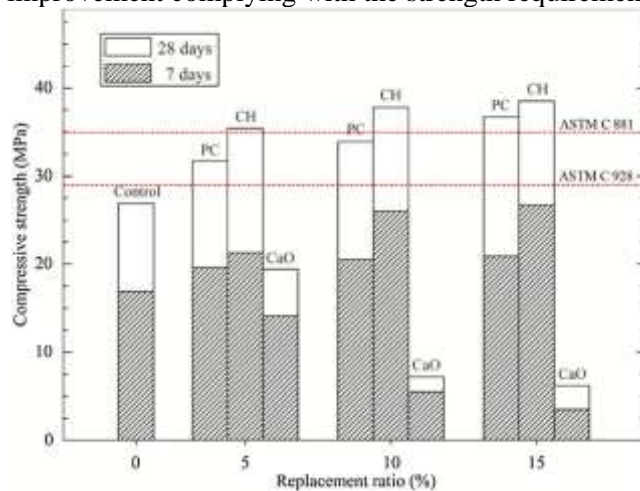


Fig.1 Compressive strength of alkali-activated high calcium FA pastes with different calcium-rich compounds [12]

2.1.4 Concentration of alkaline activators

An increase in the concentration of activators can reduce the flow of alkaline solution due to quick formation of reaction products, especially when there is high amount of alkali available in the system [2]. Guohao Fang et al. [22] reported that increasing the sodium hydroxide molarity would affect the silica modulus (molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$) of the alkaline liquid and increase the hydroxide ion concentration in mixtures, which would decrease workability, accelerate dissolution of raw materials, reduce setting time and increase compressive strength of alkali activated materials. Sujitra Onutai et al. [10] indicated that the bending strength increased with an increase of NaOH concentration.

As we know, chemical reaction takes place while using chemical activators in geopolymer concrete and it shows adverse effects while adding more or less chemicals than the requirement. So, it is essential to find optimum content of activator for better results. A better understanding the effects of alkaline activators such as NaOH and Na_2SiO_3 solutions on the hydration mechanism of alkali activated slag could show to optimize the alkaline activators [13]. Ali A. Aliabdo et al. [15] concluded that lower additional water content and higher NaOH molarity upto 16M give good mechanical properties with the reduction in workability of fly ash based Geopolymer concrete.

2.2 Nature of the precursor

The usability of a precursor in alkali activation depends significantly on the reactivity of particles (which is defined by mineralogy and specific surface area), type of alkaline activator, and curing temperature [9]. Aluminosilicate precursors differ from region to region making it very versatile and locally adaptable. They differ in terms of availability, reactivity, cost and value [14]. As the solid precursor for production of alkali-activated materials or geopolymers, most common aluminosilicate supplementary cementitious materials are suitable for use, with blast furnace slag, coal fly ash, calcined clays and natural pozzolans having been demonstrated to give good results. Other materials which are less commonly used in general Portland cement blends, but which have pozzolanic or hydraulic

character such as Fe-rich clays, various slags from ferrous and non-ferrous metallurgy if air- or water-cooled to a reactive state and then finely ground, clay-rich sludges resulting from water treatment or kaolin purification, red mud, ground coal bottom ash, agricultural waste ashes and fly ashes which do not meet the criteria specified in standards for use in Portland cement are also of value in alkali-activation, although in the case of non-ferrous and steelmaking slags the leachability of toxic components must be considered with care [7]. Pavel Rovnaník et al. [1] concluded that alkali-activated fly ash (precursor) reached higher flexural and compressive strengths as a result of larger specific surface, higher pozzolanic activity and more compact microstructure. Kim Hyeok-Jung et al. [26] concluded that the efflorescence area increases with increasing replacement ratio of red mud and still appeared after first cleaning of surface; however it gradually decreases with the repetition of the test.

2.3 Methods for activation of precursor

2.3.1 Chemical activation of precursor

Conventional (two-part) geopolymers are formed by a reaction between a concentrated aqueous solution of alkali hydroxide, silicate, carbonate, or sulfate, for instance, and solid aluminosilicate precursor, that is, two parts in addition to water. In one-part alkali-activation, precursors are mixed with solid alkali activator and water is added to initiate the reaction with dry materials [3]. However, the impracticalities related to handling large amounts of viscous, corrosive, and hazardous alkali activator solutions has put pressure on the development of one-part or “just add water” geopolymers that could be used similarly to OPC. In one-part mixtures, only a dry mixture is needed in addition to water. The dry mixture is prepared by mixing a solid alkali-activator with a solid aluminosilicate precursor with or without a calcination step [18].

2.3.2 Mechanical activation of precursor

“Physically active” materials only do not form hydration products, but they do affect the physical structure and the properties of blended binders. Nailia R. Rakhimova et al. [21] proposed “Physically and chemically active (Mechanochemically activated)” materials to consider “inert” mineral admixtures as “physically active”, and “reactive” as “chemically active” since the latter form hydration products with binding properties. Elijah Adesanya et al. [9] used mechanochemically activated binders as an alkali activated materials in their research and concluded that mechanical activation of phyllite can increase its reactivity under alkaline conditions through structural changes of the particle’s crystal structure and decreased particle size. Mechanical activation was done by milling the as-received material which had a median particle size of 13.90 μm and was then milled for 9 min and 15 min using a vibratory disc mill (RS 200, Retsch GmbH, Haan, Germany) [9]. Matalakah et al. [17] used a mechanochemical activation method in which fly ash was ball-milled with dry-blended activators (CaO, MgO and NaOH) and observed that Na, Ca, and Mg were incorporated in the fly ash structure due to disruption of the aluminosilicate bonds, which resulted in improved properties (higher strength, greater moisture resistance, and finer microstructure) compared to raw materials that were separately milled and then blended.

J. Temuujin et al. [30] concluded that mechanical activation of the fly ash can increase the reactivity of it causing faster dissolution resulted in an 80% increase in compressive strength compared to the raw fly ash based geopolymer. The mechanical activation of the fly ash can destroy some of the spherical morphology of the fly ash and reduced the range of sphere sizes, both of which will reduce the “ball bearing effect” and consequently reducing the workability [30]. Faris Matalakah et al. [19] compared properties of mechanochemically alkali activated cement paste with Portland cement paste and it is indicated that the yield stress and plastic viscosity of the alkali activated cement paste is about 30% and 100% higher than that of the Portland cement paste respectively. It is showed with Fig.2 and Fig.3 that the alkali activated cement concrete provided significantly more resistance to plastic shrinkage cracking and lowers bleeding when compared with Portland cement concrete.

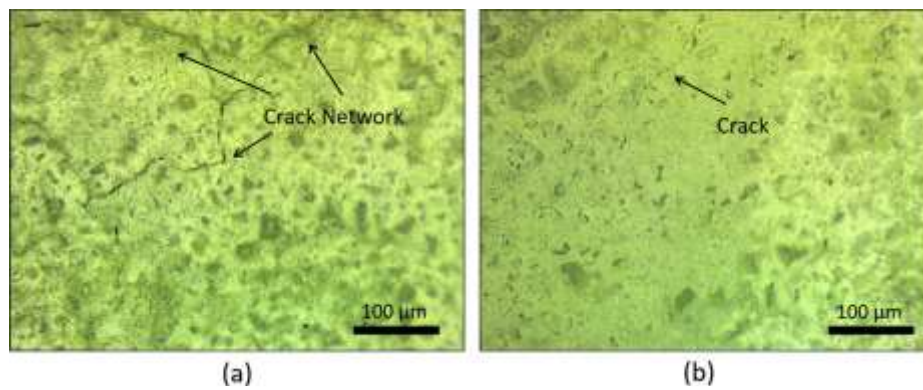


Fig.2 Optic microscope images for the concrete specimens' surfaces exposed to drying conditions; (a) Portland cement concrete and (b) alkali activated cement concrete [19].

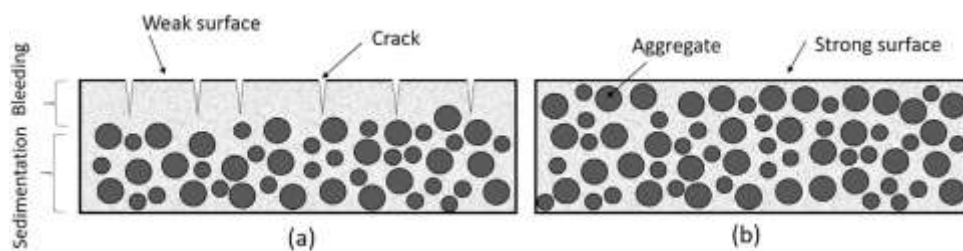


Fig.3 Schematics of the surface composition and cracking in Portland cement concrete (a) and alkali activated cement concrete (b) [19].

2.4 Conditions of hydrothermal process

2.4.1 Heat curing

The geopolymerisation process is normally dependent on mode of curing. Under proper temperature conditions, between 20 °C and 90 °C, and a certain curing time, a gel by ionic interaction solidifies into a solid tridimensional structure, which is the base of geopolymer [11]. Muhd Fadhil Nurrudin et al. [4] reported that the geopolymerisation is faster at higher temperatures and an accelerated strength formation was observed on rock based geopolymer cured at 40 to 80°C. Emeso Beckley Ojo et al. [5] have found that in the saturated condition, sufficient binding for the production of water stable units was achieved only at elevated initial curing temperatures of 105 °C for 5 h revealing the temperature dependence of the process.

2.4.2 Steam Curing

There is a limited experimental work on steam curing of geopolymer concrete and among the few research studies, Yewale et al. [35] have found that strength of geopolymer concrete improves at higher temperature and the optimum strength was found to be 80°C temperature for steam curing, while for water curing, the strength obtained after 28 days was less than the characteristic strength due to the low development of strength at lower temperature.

2.4.3 Ambient Curing

One of the important steps of geopolymer synthesis is curing at elevated temperature for 4–48 h in dry or steam condition but being able to cure at ambient temperature is very important in terms of practical application [30]. So, it is to be checked that mixture of geopolymer concrete fulfills the required properties in ambient or hot curing conditions before implementing on it. It is possible to prepare geopolymer concrete that cure readily at ambient conditions by selecting the solid aluminosilicate, alkali, and supplementary silicate and/or aluminum sources carefully. Tero Luukkonen et al. [18] has concluded that mechanochemical activation (e.g., ball-milling) of the aluminosilicate precursor with the solid

activator seems to be a promising method for overcoming the need to use high temperature during geopolymer cement preparation.

CONCLUSION

1. It is reviewed by the contents collected in this paper that geopolymerisation process is affected by nature and chemical composition of precursors, activators and other ingredients.
2. The binding property of geopolymer concrete is enhanced by increasing molarity, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio, hydroxyl ions, calcium ions and NaOH concentration upto some extent. On the other hand, these lead to low workability and high efflorescence.
3. The methods for activation of precursor can also affect the properties of geopolymer concrete. The mechanical activation (e.g. ball-milling) of precursor before mixing is concluded as promising method for achieving better performance with or without heat curing. Even form of activators, like solid activators (one-part alkali activated materials) and liquid activators (two-part alkali activated materials) can also affect the behavior of geopolymer concrete.
4. The end properties of geopolymer concrete are also depending on method and duration of curing. The curing at elevated temperature from 20 °C to 90 °C for 4 - 48 hours is good for geopolymerisation process. But the precast construction only can be possible in such condition. Lots of researches have been done on geopolymer concrete cured at ambient temperature and it is concluded by few of them that restriction of curing condition can be overcome by changing nature of precursor-activator (e.g. using of solid alkaline activators), method of activation (e.g. mechanical activation of precursor) and replacing ingredients (e.g. replacing fly ash with Portland cement, slag, etc).

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