



Geopolymer as Sustainable Binder of the 21st Century: A Review

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Abstract: Geopolymer is a new sustainable building material, developed to reduce CO₂ foot print of existing cementing material. The material offers mechanical properties comparable to Ordinary Portland cements. Advantages associated with this material include thermal stability, acid resistance, compact structure, low density and ability to encapsulate hazardous wastes. Mainly composed of waste ashes and land fill material, this material shows multiple level of sustainability. Although, most of the research is focused in the field of construction industry, there is other utilization of this material. Catalysis, coating, encapsulation of hazardous waste and separation are some of the other applications. This review discusses a brief introduction geopolymer, its history and utilization in various fields. Goals for future research are also included as part of this review.

Keywords: Geopolymer, Fly ash, Metakaolin, Binder, Coating.

1. Introduction: Ordinary Portland cement (OPC) and OPC based systems contribute for nearly 8% of the world's total carbon dioxide discharge into the environment. Most of this CO₂ is produced either by carbonation of calcium carbonate or in terms of fuel utilized for clinker formation[1]. To encounter the growing needs of the developing world, cement production is going on, leading to

increased CO₂ discharge. Besides the increasing carbon foot print, the high temperature durability and corrosion resistance of the OPC has been questioned. The growing demand for environmentally benign binders and construction materials motivated researchers to focus in this area.

“Geopolymer” was formally introduced by J. Davidovits, as an alternative to OPC [2]. Different terminologies e.g. alkali activated materials (AAM) and inorganic alumino silicate etc. have been used by various researchers for this materials [1]. The basic characteristics of this materials is the tetrahedrally coordinated silicon and aluminium oxides, linked and cross linked through Si-O-T (T= Si/Al) bonds. Geopolymer (GP) is synthesized by the alkali activation of raw aluminosilicate rich material, fabricated at ambient temperature [3]. Key differences between OPC and GP include the starting material, synthesis protocol and nature of alkalies used. Interestingly, GP are synthesized either from waste ashes e.g. coal fly ash (FA), slag ash, granulated blast furnace slag(GBFS), palm oil fuel ash (POFA) and rice husk ash(RA), or from thermally activated kaolin. Coal fly ash and metakaolin (MK) are most frequently cited in the literature as starting materials [4]. Presently, approx. 780 million ton of FA is generated by coal based thermal power plants in the world, with an ascending trend [5]. GP can be considered a sustainable, innovative and valuable sinkhole for this huge amount of FA. MK being produced at 600°C has been found lesser sustainable than FA although the FA has a varying and complex chemical and phase’s composition [5].

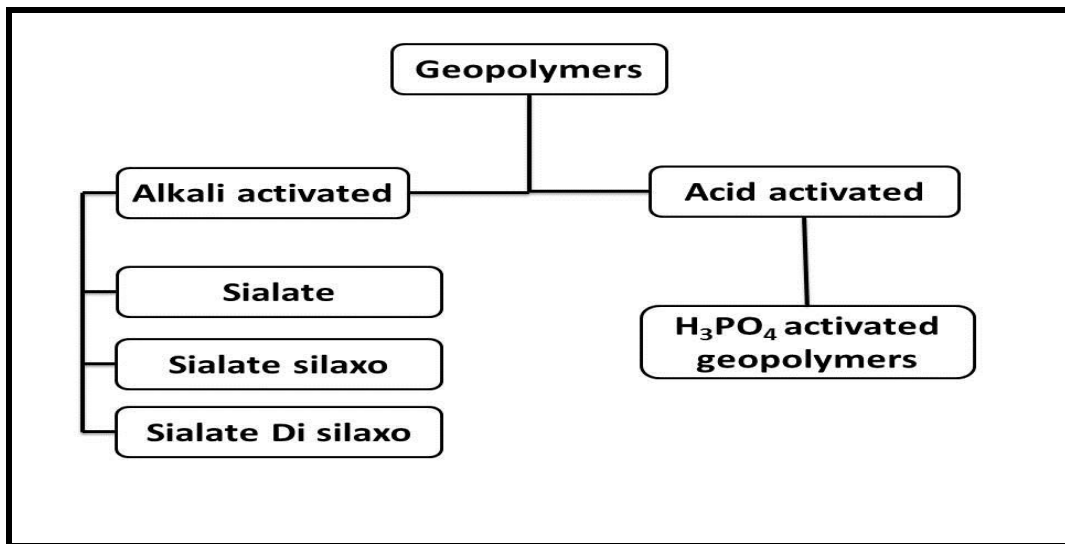
In the last decade, the chemistry and applications of GP has been focused in various fields to address its durability. Thanks to J. Provis et.al for providing an insight of the geopolymer structure, mechanism and kinetics [6]. Extensive work is reported by this group with a focus on geopolymer gel (NASH), comparable to OPC gel (CSH)[1]. Besides an alternative to OPC, GP has also been investigated for numerous other applications. The interchangeable alkali cations were utilized as cation exchange sites for fabrication of novel catalysts and photo catalyst[7,8]. Novel applications of this material included coating (medicine, fertilizer, intumescent and corrosion), separation membranes, adsorbents and immobilization of nuclear waste etc. [3,9].

More recently, a growing trend is noticed towards mix formulation for geopolymer synthesis consisted upon the FA/MK and secondary aluminosilicate e.g. slag ash, POFA and rice husk ash etc. [4]. The convincing mechanical properties and durability offered by GP, is motivating community for commercial applications of this material. In this review, recent advances in the field of geopolymerization are explored with a focus on construction and building sector. Detailed description of classification of GP and an overview of various raw materials and activating solutions is provided. At the end, some conclusions have been derived, while certain recommendations have been suggested for future researches.

2. Review of the recent literature

2.1. Classification of geopolymers: Geopolymers are broadly classified as acid activated and alkali activated geopolymers as shown in Fig.1. Acid activated geopolymers were recently introduced, having properties comparable to alkali activated materials e.g. Parera et.al reported that phosphoric acid activated metakaolin produced 30% higher cold crushing strength than their alkali activated counterparts [10]. The higher porosity of this group of polymers suggested their possible application in waste water treatment and as an adsorbent [11]. Acid activated geopolymers have not been explored and further research in this field is required. Alkali activated GP are materials of special interest in the past four decades due to their superior properties compared to OPC. Based on the alumino silicate matrix they are classified as sialate, sialate silaxo and sialate di silaxo.

Figure 1 Classification of geopolymers



Each class offers certain specific properties making them suitable for specific applications e.g. sialate di silaxo showed enhance fire and corrosion resistance due to more siloxane bonding compared to sialate. Formation of geopolymers is controlled by the $\text{SiO}_2/\text{Al}_2\text{O}_3$ and water/solid ratios [3,9]. The chemistry of geopolymers is largely varied with the variation in composition and treatment of raw materials.

2.2. Raw materials: Reaction of starting material with alkali activator in the presence of water is termed as geopolymerization. Starting materials are checked for pozzolanic content i.e. $\text{SiO}_2 + \text{Al}_2\text{O}_3$, according to ASTM C-618 [12]. Now, with the advanced mixing technologies, mix designs comprised of pozzolanic and semi pozzolanic waste materials have been reported. Table 1 shows a review of the very recent literature of different types of starting materials used. Initially, most of the GP related studies were focused on use of FA and MK as starting material. To address the environmental issues, caused by volcanic, palm oil, rice husk and municipal incinerator ashes etc., these materials have been successfully utilized as supplementary raw materials, along with FA and MK as major component [4,7,13-16]. Utilization of Nano silica and nano alumina (1-10%) resulted into shortening in setting

time, accompanied with performance enhancements. It has been found that there is no direct alternative to FA and MK and usually mixed formulations are used [17].

Table 1 An overview of various raw materials used for geopolymer synthesis

Sr. no.	Raw material used	Composition	Application	Ref.
1.	FA	100%	Coating	[18]
2.	MK	100%	Building material	[19]
3.	(POFA+GBFS):FA	P+G:FA=1.8	Building material	[13]
4.	GBFS+FA	GBFS= 30-55%	Building material	[15]
5.	Steel Slag	100%	Photo catalysis	[14]
6.	Volcanic Ash	100%	Construction	[20]
7.	Rice husk Ash	1-10%	Construction	[16]
8.	Nano SiO ₂ & Al ₂ O ₃		Construction	[17]

2.3. **Activating solutions:** As discussed in section 2, two different activating systems are used for geopolymerization i.e. phosphoric acid and alkalis. In this section alkali activation system will be discussed in detail. In the first era of geopolymers technology, sodium hydroxide and sodium silicate were employed as activating solutions. These solutions were combined before mixing with raw materials, in an exothermic reaction. With the development and progress in this technology, novel activating solutions and methodologies have been investigated. Table 02 shows different types of alkali activating solutions used for geopolymerization.

Table 2 Alkaline activators used in geopolymerization

Sr. no.	Activating solutions used	Examples	Applications	Ref.
1.	Alkali metal hydroxide (AMH)	NaOH, KOH, LiOH	Coating	[18]
2.	Alkali metal silicate (AMS)	Na ₂ SiO ₃ , K ₂ SiO ₃	Coating	[9]
3.	AMHS	Na ₂ SiO ₃ +NaOH	Coating	[9]
4.	AMHS+ nano silica	Na ₂ SiO ₃ +NaOH+SiO ₂	Effect of nano	[17]
5.	Metal aluminate	NaAlO ₂	One part GP	[21]
6.	Metal carbonate	Na ₂ CO ₃	One part GP	[22]
7.	Red mud	Red mud+ NaOH	Novel GP	[23]

8.	Rice husk ash	RHA+ NaOH	Building	[24]
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New trends in alkali activation includes addition of nano materials, sodium aluminate and alkali activators synthesized from biomass ashes [24]. Compressive strength attained by rice husk ash derived geopolymers is comparable to the standard alkali activated system. Being economical, ecological and less corrosive, it is suggested that future work may be focused on biomass ash derived alkali activators. Compressive strength is the mostly varied with variation in activators as described in next section.

2.4. Mechanical properties of geopolymers: Compressive strength (CS) is an indication of the compactness and strength of a building material. Most of the geopolymer work reported is consisted upon an extensive discussion of CS and its relation with time, temperature, chemical composition, starting material and activating solutions. Besides CS, flexural strength was also reported in the recent papers. It was observed that AMHS based GPs produced higher CS compared to other activating systems e.g. Susan et.al reported a 7th day CS of 75 MPa with AMHS, whereas, approximately 50 MPa was produced by RHA and fumed silica based activators [24]. Most of the GPs attained maximum CS within 7 days and only partial increase has been recorded in certain cases. Few papers also reported the descending trend in CS with increasing time. This trend was explained on the formation of crystalline zeolites at extended curing time. More recently compressive strength was linked with the degree of GP formation using Averami kinetics model.

3. Conclusions and Future recommendations: Following conclusions were drawn;

- a) Geopolymers are superior to OPC in terms of economy, ecology and durability at high temperature.
- b) New raw materials e.g. RHA, POFA, GBFS, steel slag and volcanic ash serves better when in combination with FA or MK.
- c) Novel alkali activator systems derived from biomass ash offer enhanced sustainability.
- d) The mechanical properties of RHA derived activator systems are comparable with conventional AHMS systems.

Following future recommendations are suggested.

- a) Investigation to synthesize ambient temperature, one part geopolymer system is highly recommended for possible replacement of OPC.
- b) Incorporation of biomass ashes in geopolymer systems is recommended.
- c) Preparation and utilization of biomass derived alkali activators needs further investigations with a focus on silica rich ashes e.g. RHA and POFA.

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6. References.

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