Geopolymers and Their Uses: Review

D D Burduhos Nergis¹, M M A B Abdullah², P Vizureanu¹* and M F M Tahir²

¹Technical University “Gheorghe Asachi” of Iasi-Romania, Department of Technologies and Equipments for Materials Processing, Blvd. Mangeron, No. 51, 700050, Iasi, Romania
²Center of Excellent Geopolymer and Green Technology, School of Materials Engineering, University Malaysia Perlis, P. O Box 77, D/A Pejabat Pos Besar Kangar, Perlis 01000, Malaysia

E-mail: peviz2002@yahoo.com

Abstract. Outlining the past-present history of the study of alumino-silicate materials, it is well known that geopolymers are inorganic polymers obtained from chemical reaction, also known as geopolymerisation, between an alkaline solution and a solid reach in aluminium and silicone. There is still some controversy surrounding the alkaline activators used to create geopolymer concrete, because homogeneous mixture composed of two (NaOH and Na₂SO₃) or more chemical in varying proportions are usually highly corrosive and hard to handle. In order to overcome Portland cement many wastes have been used in recent studies to create “friendly” cements by geopolymerisation. In this short review we present basic information’s about how to create and use geopolymers, alkaline activators and raw materials that can be used and conclusions. One question that needs to be asked: Can those materials replace on large scale Portland cement?

1. Introduction

The geopolymer concept was introduced by Joseph Davidovits in 1976 for alkali aluminosilicate binders. [1] The transformation of kaolinite into tridimensional tecto-aluminosilicates used for the polycondensation of organic resins at low temperature is very similar with the thermosetting method of these materials. The result of the process is a nanocomposite that looks like an artificial rock. The geosynthesis take place itself in great abundance in nature. The crust of Earth is composed, in 55% of volume, from siloxo-sialates and sialates, yet, just only 12% are pure silica or quartz. The geosynthesis process is based on changes induced in crystallography of silica backbone by the aluminium ion (6-fold or 4-fold coordination) and on the chemical changes produced by the same aluminium ion [2].

These materials possess chemical composition similar to zeolites consisting of a polymeric Si–O–Al framework, different properties and amorphous structure. Their properties are highly depending of: the Al-Si source, the activator, the aggregate source and its grading, the water source, the mix quantities of each material, the hardening/curing time, the temperature, the dimensions of particles, the calcium concentration, the heat treatment, if applied [3-5].

Depending of cost and the final desired properties, there are a wide range of raw materials that can be used to create geopolymers, such as: metakaolin [6], red mud [7], fly ash [8, 9], different wastes [10], etc. During manufacturing, the emission of CO₂ and energy consumption is very low
comparative with Portland cement, this new binder offer a strong reduction of the global warming by releasing just 169 kg CO$_2$/m$^3$ when ordinary Portland cements release 306 kg CO$_2$/m$^3$ for the same mechanical properties, which represents a decrease of emission by 45% [11].

2. Obtaining of geopolymers

Geopolymers are inorganic polymeric materials obtained by mixing of a dry solid (aluminosilicate) with an alkaline solution and other constituents, if necessary. The major constituent is the source material, this one must be rich in silicone (Si) and aluminum (Al), they could be natural minerals such as clays, kaolinite, etc. or red mud, fly ashes, slags, etc. known as “waste” materials. The liquid is usually based on sodium (hydroxide or silicate) or potassium (hydroxide or silicate) with are soluble alkali metals. [12] The time of hardening is very short, in first 4 hours of setting they obtain 70% of the final compressive strength [13].

The structures of geopolymers consist in three dimensional silico-aluminate links (sialate) of SiO$_4$ and AlO$_4$ tetrahedra with share all the oxygen atoms, designed as in Table 1. Geopolymer matrix presents an empirical Formule 1, as following:

$$M^+ v \{ (SiO_2)_x - AlO_2^{-}\} v^* aH_2O$$

Where: M$^+$ - Alkali cation of K+, Na$^+$; v – degree of polymerization; x – Si/Al ratio, a – the amount of water, if necessary (when the alkali activator is solid, a specific amount of water is necessary to create the reaction environment, if the activator is liquid, there is no need of supplementary water). The properties of the geopolymer are highly depending of the value of z (z = 1-15, up to 300), for high value of z (z>3) geopolymers exhibit adhesive and rubbery properties, their structure being a linear 2-D network, when the value of z is low (z ≤ 3) the material presents stiff and brittle properties and a cross-linked 3-D network.

Table 1. Types of poly(sialates) [14].

| Poly(sialate)               | Poly(sialate-siloxo)              | Poly(sialate-disiloxo)             | Poly(sialate-disiloxo)             | Sialate link |
|-----------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-------------|
| -Si-O-Al-O-                  | -Si-O-Al-O-Si-O-                   | -Si-O-Al-O-Si-O-                   | -Si-O-Al-O-Si-O-                   | Si:Al = 1   |
| Si:Al = 2                    | Si:Al = 3                         | Si:Al = 3                         | Si:Al > 3                         | Si:Al = 3   |

The geopolymer result after the exothermic process carried out through oligomers, process known as geopolimerization, is a polymer with very long reticular network, where the specific tetragonal network of aluminates (AlO$_4$) and groups of silicates (SiO$_4$) are, also, present. The bond between these tetrahedrons is equilibrated by alkali ions of: K$^+$, Na$^+$ or Li$^+$. In general, geopolimerization can be divided into three stages, see Figure 1. First of them is dissolution, when the solid alumino-silicates material is dissolved because of the water and alkali activator presence. After eliminating a small amount of water, the reorientation starts, now the group atoms take their place in the structure. During the solidification (at 20 Celsius degree or higher approximate 1000 °C) the water is almost totally eliminated and the material shows his final form. [15-17].
2.1. Materials for geopolymers
Because of the fact that any material rich in aluminium and silicone see Figure 2, can be used as raw materials, there are many materials that can be used to create geopolymers. Kaolinite was the first material widely used in geopolymer synthesis [20] after successfully uses of this new material, the scientists start developing new raw materials, such as calcinated clays [21] or industrial waste (e.g. slag [22], ashes [23], waste glass [24], aluminium mine tailings [25], etc.) and natural silico-aluminates (e.g. pure Al2O3–2SiO2 powder) [26], zeolites [27], etc.).

2.2. Geopolymers obtained using metakaolin
The first use of geopolymers was as building products [29], this products include fire-resistant chipboard panels, made from a wooden core faced with two coatings and ceramic tiles water-resistant at temperatures lower than 450°C, without firing. At 150°C kaolinite that is one of the clay components reacted with caustic soda. The industrial applications of this kaolinite reaction with alkali began in the ceramic industry with Olsen in 1934.

The alumino-silicate kaolinite reacts with NaOH at 100°C - 150°C and polycondenses into hydrated sodalite (a tectoaluminosilicate), or hydrosodalite, Formule 2.

\[
\text{Si}_2\text{O}_5\text{Al}_2\text{(OH)}_4 + \text{NaOH} \rightarrow \text{Na}(-\text{Si-O-Al-O})_n
\]
Kaolin, after being calcinated at temperatures between 650°C and 750°C, is the main source of metakaolinite. Kaolin is a phyllosilicate, consisting of alternate layers of silica and alumina in tetrahedral and octahedral coordination, respectively. This electrically neutral crystalline layer structure, which is a common characteristic of clay minerals, leads to a fine particle size and plate like morphology and allows the particles to move readily over one another, giving rise to physical properties such as softness, soapy feel and easy cleavage. Kaolinite is the mineralogical term for hydrated aluminium disilicate, Al$_2$SiO$_4$(OH)$_4$, the primary constituent of kaolin (40–70%). Other minerals comprising kaolin include quartz, muscovite-like micas and rutile. When kaolin heated to temperature of 650–900 °C, it loses 14% of its mass in bound hydroxylions. This heat treatment, or calcination, breaks down the structure of kaolin such that the alumina and silica layers become puckered and lose their long-range order. Resulting from this dehydroxylation and disorder is metakaolinite, a highly reactive transition phase, amorphous material with pozzolanic and latent hydraulic reactivity, suitable for use in cementing applications [30].

Metakaolin-based geopolymers can be manufactured consistently with a high level of predictability in hardened characteristics, see Figure 3, displays compressive strengths and porosities for both metakaolin geopolymers and metakaolin/fly ash mixtures.

![Figure 3](image)

**Figure 3.** Mechanical Strength and Porosity of Metakaolin Geopolymers [31].

2.3. Geopolymers obtained using ashes

The need of new construction materials with high properties is in a continuous growth and so is the need of reducing of using the natural minerals for this purpose. In this condition the use of ashes in cements or concretes [32] is a great “green” idea. Beside the high chemical, physical and mechanical properties, the positive effect on environment and low emission of CO$_2$, the economical aspect is also important, playing an important role when this material is chosen.

Fly ashes are spherical glassy particles obtained by solidification of coal by-product volatile material. Due to the fusion-in-suspension these fly ash particles are mostly minute solid spheres and hollow ecospheres with some particles even being plerospheres, which are spheres containing smaller spheres.

Fly ash can be divided into two classes based on its source of origin and composition. Class F is a fly ash is obtained from burning of bituminous or anthracite coal and meets this chemical composition SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ ≥ 70%. Class C is normally produced from burning of sub-bituminous or lignite coal and has the following chemical composition SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ ≥ 50% [33].
2.4. Geopolymers obtained using red mud

There are multiple uses of this highly alkaline (pH of the order of 11 or higher) waste generated by aluminium production plants (for 1 tone of aluminium, 2 tones of red mud are deposited) however the reuse rate is very small and this material become a huge problem for the environment [34].

Red mud is a mixing of minerals with complex chemical composition, see Figure 4, where iron has the highest concentration followed by aluminium, silica, calcium, sodium and low concentration of rare earth chemical elements, like: Dy, Er, Yd, Nd, Sm, Eu, Gd, Sc, La, Ce, Y, Pr. Bayer Process consist in dissolving of bauxite with (NaOH) at 175°C resulting aluminium hydroxide Al(OH)3 and 50% -70% red mud. Red mud is usually used to create geopolymer cements with low CO₂ emission, small price and excellent quality [35].

![Typical red mud chemical composition.](image)

2.5. Geopolymers obtained using slags

Blast furnace slag is a foundry residue result from production of cast iron. In this process, the iron is melted and mixed with different additions in order to eliminate the impurities from metal bath, when the slag is expelled on the bath surface it is fast removed and cooled down in water. The result material, slag, has amorphous structure and chemical composition reached in calcium aluminates and silicates. [36] The slags can be used in manufacture of different type of materials [37] and by geopolymerization is used to create binders [38], mortar [39] and different types of concretes with good mechanical properties, see Figure 5 [40].

![Compressive strength value for different types of slags (GBFS)-metakaolin (MK) based geopolymers.](image)
2.6. Alkaline Activators

Activation of the selected pozzolanic material is the most significant factor in producing a mechanically-sound cementitious material via the geopolymerization process. The activators prompt the precipitation and crystallization of the siliceous and aluminous species present in the solution. OH- acts as a catalyst for reactivity, and the metal cation serves to form a structural element and balance the negative framework carried by the tetrahedral aluminum. The initial mechanism of reaction is driven by the ability of the alkaline solution to dissolve the pozzolanic material and release reactive silicon and aluminum into solution. There are multiple activating agents that can be used for geopolymerisation (M-alkali ion): Alkalis, MOH; Strong Salt Acids, M2SO4, Aluminosilicates, M2O * nAl2SO3 * (2-6)SiO2; Aluminates, M2O * nAlO3; Silicates, M2O * nSiO3; Weak acid salts, M3PO4, M2SO3, M2CO3, MF [42].

Figure 6. Compressive strength values depending of NaOH concentration.

Sodium Hydroxide (NaOH) is a geopolymer activator commonly used as alkaline solution. The sodium cations promote better geopolymerisation, compared with potassium cations, due to the fact that they can migrated easy thru the network in the gelatin stage being smaller. The strength value of geopolymers increase with the increasing of NaOH concentration, see Figure 6 at early stages. Yet, the aged material will be compromised due to excessive OH that modifies morphology in a non-uniform one. These types of activated geopolymers are more stable in sulfates and acids environments by having greater crystallinity. Potassium hydroxide (KOH) activator improves the compressive strength of the geopolymers cements and their porosity. K+ will offer a denser final structure compared with other activators because of its high reactivity with the alumino-silicate material [44].

Sodium silicates (Na2SO3) are rare single used activator for geopolymers being usually mixed with NaOH to achieve enough activation potential. It is used mostly for its increasing strength and alkalinity properties. The most used geopolymerisation activator is a combination between Na2SO3 and KOH with different value ratio [45].

2.7. The processing parameters effect

Because of the fact that, the final properties of the geopolymer material are highly depending of the processing parameters, the effect of different processing factors was studied by many scientists [46-49] studied the influencing of four of the main factors: curing temperature and molar ratios of SiO2/Al2O3, Na2O/SiO2 and H2O/Na2O as can be observed in the Figure 6. They conclude that, by increasing this all of these major factors, the mean value of compressive strength decreases. Also, they observed that, the curing temperature have no significant effect on this properties for short period of time. After passing of a limit value of SiO2/ Al2O3 (2.9 %) and Na2O/SiO2 (0.2 %) molar ratio, the system will be saturated with Na+ ions and the formation of oligomers is prevented [50]. The molar ratio of H2O/ Na2O presents the highest negative effect by prevention from dissolving of alumino silicate and by high porosity introduced by water withdrawal, presenting high decrees of properties between concentration of 13.75% and 21.75 % [51].
3. Geopolymers application

Thanks to this low-temperature transformation from kaolinite into hydrosodalite, since 1979 (J. Davidovits) this “mineral” showed great interest for manufacturing of: thermal insulation, [52] fire resistant materials as can be seen in Figure 7, [53] low-tech building materials, [54] foundry industry, [55] decorative stone artifacts, [56] thermal shock refractories, [57] bio-technologies (medicinal applications), [58] infrastructures repair and strengthening composites [59] low energy ceramic tiles, [60] aircraft interior and automobile composites, [61] refractory items, [62] cements and concretes [63] radioactive and toxic waste containment [64].

![Figure 7](image)

Figure 7. Time to flashover (minutes) for various organic resins compared to geopolymer resin [65].

Related to properties, they possess very good volume stability, 4/5 lower shrinkage than Portland cement, as high strength gain in short time, in first 4 hours of setting they obtain 70% of the final compressive strength. Geopolymers, also, present excellent durability, their properties are almost the same after decades, low thermal conductivity and high fire resistance (fig. 6), geopolymer keep their functions at 1000 °C - 1200 °C. The heat conductivity of geopolymer varies from 0.24 w/m·k to 0.3 w/m·k, compared well with lightweight refractory bricks (0.3 w/m·k to 0.438 w/m·k) [66-68].

Depending on the Si/Al ratio and structural chemical network, geopolymers used for low CO2 cements and concretes and radioactive and toxic waste encapsulation are thus with Si/Al ratio 2:1 and 3D network, for bricks and ceramics are thus with Si/Al ratio 1:1 and 3D network, for fire resistant and heat resistant fiber composites are used thus with Si/Al ratio 3:1 and a 2D structure, for sealants used in industry in the range of 200°C and 600 °C are thus with Si/Al ratio 2:1 and 2D structure, for fire protection, fiber glass composites, foundry equipments, heat resisters composites in the range of 200°C - 1000°C and tooling for aeronautics titanium proc. applications are thus with Si/Al ratio 1:1 and 2D structure.

4. Conclusions

The sources of raw materials are very wide, any source of silicates, pozzolanic compound or aluminosilicates that can be dissolved in alkaline solution can be used as a source of production of geopolymers.

Geopolymers can be considered green materials, because to create this new material can be used different industry wastes and they have low emission of CO2 during manufacturing related to the emission of CO2 to manufacture the Portland cement. Geopolymers do not require large energy consumption, for the same quantity of geopolymer cement and Portland cement, the ratio of energy used is 3/5.
Some of them are easy to prepare cooperated with the conventional material, they can be obtained by mixing alumino-silicates materials with strongly alkaline solutions, then curing at room temperature. A reasonable value of strength is gained is short time.

The properties of the final material are highly depending of different factors, like: Si/Al ratio, particle dimension, alkaline activator concentration, calcium quantity, time of hardening/drying and synthesis temperature.

Because of possibility to use local wastes without multiple previous operations to create geopolymers, they present a strong economic advantage.

Geopolymers can be considered as difficult to create, because manufacturing process include corrosive chemical substance that can harm humans, such as sodium hydroxide.

5. References

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