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Geopolymers in construction - Recent developments

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Abstract

Geopolymers are inorganic materials that result from the alkali activation of aluminosilicates. The aluminosilicates source materials can either occur naturally (e.g. kaolin, metakaolin, rice husk ash, volcanic rock powders) or produced by industrial processes (e.g. fly-ash, blast furnace slag). While the potential application of geopolymers as construction materials (e.g. concrete manufacturing and soil stabilization) has been studied in the past, their widespread use has been limited. This is mainly because the technology is still relatively new and research in this field is still emerging. However, the use of geopolymers in lieu of conventional binders (e.g. cement and lime) has substantial environmental advantages particularly in terms of the energy expended for their production and greenhouse gas emissions. The current trend to enhance sustainability practices in the construction industry has recently driven research in this area. This paper aims to offer a comprehensive overview of past studies on geopolymers synthesised from various precursors, the factors affecting geopolymerisation process, their microstructural characteristics as well as mechanical, chemical, thermal and environmental properties of geopolymers. Further, recent developments associated with the use of geopolymers as construction materials in civil engineering applications have also been discussed. Research findings show that geopolymers can achieve comparable or superior performance to conventional binders and/or concrete in terms of shear strength and durability but with a reduced environmental footprint.

Keywords: geopolymers, construction material, concrete manufacturing, soil stabilization, sustainability

1. Introduction

Over the years, lime and cement have been the preferred binding agents adopted in the civil engineering industry. Indeed, they are widely used for the preparation of concrete mixes as well as stabilization of various types of soils. They facilitate the bonding of aggregate particles through hydration and pozzolanic reactions, thus increasing the strength, shrinkage and enhancing permeability characteristics. However, the processes associated with the production of these materials are very energy intensive and lead to the emission of large quantities of greenhouse gases, especially carbon dioxide (CO₂). [1]. For instance, approximately 0.9 tonne of CO₂ is released in the production of one tonne of cement [2]. Furthermore, the mining of the raw material sources, e.g. quarried rock, used in the production of these binders is not environmentally attractive or sustainable. Therefore, alternative binders based on more sustainable materials are preferred in lieu of conventional cementitious binders, e.g. geopolymers. In addition, as the geopolymer raw materials are often waste by-products from other industrial processes (e.g. fly ash, blast furnace slag); their use promotes more sustainable practices in the construction industry both in terms of cost (reduction up to 30%) and greenhouse emissions (reductions up to 80%) [3]. Past studies report that geopolymers based on metakaolin, fly ash and other materials have contributed to the increase in compressive strength, improvement of hydraulic and thermal properties, acid resistance and sulphate corrosion resistance of concrete as well as soil mixtures. Compressive strengths more than 65 MPa have been reported by alkali activation of class F fly ash using sodium hydroxide (12 M) and sodium silicate solutions by curing at 85°C for 24 hours [4]. This paper aims to showcase the most common uses of geopolymers in the civil engineering industry. First, a review on the mechanism of geopolymerization process is presented and then results of past studies having different geopolymer base materials and examples of civil engineering

applications are described.

2. Geopolymer Synthesis

The geopolymers are synthesized as a result of a chemical reaction between solid aluminosilicate compounds and a highly concentrated alkali hydroxide or silicate solution [5]. The aluminosilicate compounds may occur naturally in the form of kaolin, metakaolin or may be obtained from industrial wastes sources such as fly ash and slag, deriving from coal fired power plants and the steel making industry (e.g. blast furnace slag), respectively.

The dissolution of the aluminosilicate source material by hydrolysis due to alkaline activator produces aluminate and silicate species, and is generally explained as the mechanism responsible for transformation of the aluminosilicate particles during geopolymerization [1]. After dissolution the species are incorporated into the aqueous phase that reacts with silicates in the activator solution. The amorphous aluminosilicates are dissolved rapidly at high pH concentrations resulting in highly saturated aluminosilicate solution. This results in the formation of a gel like structure and due to condensation, large networks are formed by oligomers in the aqueous stage. This process results in the release of water which helps in the formation of a hydrated gel. This gel structure is termed as bi-phasic, with the aluminosilicate binder and water as the two phases. The conversion time between the aqueous supersaturated aluminosilicate solution to gel depends on the source material composition, activator solution concentration and synthesis conditions. After gelation process, the system keeps on rearranging as the linkages of the gel network enhance, resulting in the three-dimensional aluminosilicate network commonly known as geopolymers. A schematic summary of this process is depicted in Fig. 1. Nucleation phase of the aluminosilicate material and formation of polymeric species,

is primarily dependent on thermodynamic and kinetic parameters (e.g. synthesis conditions such as temperature and mixing) and explains the two first steps proposed by Glukhovsky (1959). Growth is the phase during which the nuclei reach a critical size and crystals begin to mature. These processes of development and reorganization of aluminosilicate bonds determine the microstructure characteristics and pore size and distribution of the material, which are crucial in determining many physical and chemical properties of geopolymeric materials [1].

From a chemical reaction standpoint, when an alkali hydroxide such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) is exposed to the aluminosilicate compound, it results in the dissolution and hydrolysis of aluminum and silicon, as follows,



The alkali aluminosilicate reaction is followed by the formation of a gel, which continues to rearrange and reorganize its amorphous 3-D structure. Thus, the system has multiple gel phases. The final stage is hardening in which the whole system is polymerized and becomes a solidified mass.

The physical, chemical, mechanical, hydraulic and thermal properties of the geopolymers greatly depend on the raw material from which they have been derived [6]. There are two main categories that can be used to distinguish geopolymers, i.e. the elementary units of polymeric chains and origin of geopolymers base material. Three main classes of polymeric chains may be defined, as follows:

- PSDS Si-O-Al-O-Si-O-Si-O - poly(sialate-disiloxo),
- PSS Si-O-Al-O-Si-O - poly(sialate-siloxo),
- PS Si-O-Al-O – polysialate.

The main base materials of geopolymers (i.e. pozzolanic aluminosilicate material) for instance are: fly ash, metakaolin, various types of rocks, volcanic agglomerates, silicas, and fossil materials.

3. Nanoparticle precursor source materials

Various materials such as fly ash, silica fume, rice husk ash, red mud, ground granulated blast furnace slag among others have been found effective in the production of geopolymers [7]. Several nanoparticles when added can contribute in enhancing the structural properties of geopolymer concrete and mortars [8]. Jindal et al. (2020) have reviewed the effect of different nanomaterials such as nanosilica (NS), nanotitania (NT), nanoalumina (NA), nano clay and carbon nanotubes. It was reported that their usage can significantly improve mechanical and durability properties of geopolymers [9].

Nanosilica is widely used in preparation of geopolymer concrete. Nano particles of silicon dioxide (SiO_2) result in densification of concrete mix, therefore enhancing the strength and durability of the materials. Phoo-ngernkham et al. (2014) have reported a higher compressive strength of 51.8 MPa with 2% addition of nano- SiO_2 to high calcium fly-ash based geopolymers. Percentages higher than that resulted in a decrease in strength values due to excessive presence of nanoparticles resulting in a less dense structure [10]. Gao et al. (2015) also found the addition of 2% nanosilica to be the optimum amount for fly-ash/slag based geopolymer concrete. It enhanced the pore microstructure and densification of the geopolymer concrete [11]. Wang et al. (2019) have recently verified this trend as well where they replaced the slag with nanosilica (0.5-3%) and found that the maximum compressive strength (54 MPa) was achieved at 2% and decreased beyond it [12].

Alomayri (2019) carried a detailed experimental investigation on the addition of nanoalumina to fly-ash based geopolymer mortars. The maximum compressive strength (30 MPa) was achieved at 2% addition of nanoalumina. The nanoalumina accelerated the geopolymerisation reaction resulting in a denser geopolymeric gel [13]. It was observed that just like nanosilica, nanoalumina also has notable effects on mechanical properties of geopolymer.

Duan et al. (2016) studied the effect of addition of nanotitania (TiO_2) in varying percentages of 1, 3 and 5% on geopolymer concrete specimens prepared by fluidized bed fly-ash. The compressive strengths were proportional to the increase in nanotitania content. However, the increase was rapid up to 28 days as compared to later ages of 56 and 90 days. The increase in strength was witnessed due to enhanced geopolymerisation reactions due to addition of nanotitania thus resulting in densification of the microstructure [14].

Abbasi et al. (2016) have reported that the usage of carbon nanotubes (CNT) improves microstructural characteristics of geopolymer mixes. Multiwall carbon nanotubes were added in metakaolin based geopolymer at 0, 0.5 and 1% concentration. It was found that the compressive strengths and flexural strength of the geopolymer specimens were increased by 32% and 28% respectively. Thus, it was concluded that carbon nanotubes were found helpful in developing homogenous bonding and reducing the development of micro cracks [15].

Rovnanik et al. (2016) also utilised multiwall carbon nanotubes to enhance the fracture resistance properties of fly-ash based geopolymer. The quantity varied from 0.05 to 0.2% by mass of fly-ash. It was found from the fracture tests that the optimum value for improved mechanical characteristics was 0.15% of carbon nanotubes [16].

The research in the usage of nanoparticles in geopolymer preparation is very limited and thus possesses a wide scope for future work. The usage of nanosilica, nanotitania and carbon nanotubes with a variety of other geopolymer precursors can contribute in utilisation of several

waste by-products thus producing environment friendly materials, which can find applications in the construction industry.

4. Microstructure and properties

4.1 Microstructure and composition

The characteristics of geopolymers derived from various sources may have similarities but their physical, chemical and mechanical properties may differ to a large amount depending upon the type of raw material being used. Therefore, it is important to study the precursor materials along with their reaction behaviour with the activator solution at microstructural level. Fig. 2 illustrates the typical microstructure of two geopolymers obtained using the same alkali activation solution (8M sodium hydroxide, NaOH) and two different precursor materials, i.e. metakaolin (Fig. 2a) and class F fly ash (Fig 2b) reported by Duxson et al. (2007). It can be observed that the microstructures developed during geopolymerization process are very different. The metakaolin particles are sharp and have jagged surfaces thus resulting in greater interlocking and more dense gel formation. In contrast, as the fly ash particles are round and the gelation tends to coat the fly ash particle thus causing a more effective pore reduction and compact matrix.

Pore structure characteristics along with the permeability of alkali-activated materials are crucial parameters that affect their durability and usage as a construction material. Water percolation usually results in chloride and sulphate ion attacks especially in marine environments and can cause deterioration of concrete structures. The pore size distribution, pore shape and pore volume are key players influencing the permeability and ion carrying

capacity of a material [17]. Mercury intrusion porosimetry and scanning electron microscopy techniques have been used in literature for the investigation of pore structure of various geopolymer precursors [17, 18].

Ma et al. (2013) studied the pore characteristics of fly ash and found that the alkali activated fly ash specimens that had larger silica content represented a homogeneous matrix gel structure thus resulting in a pore size ranging from 0.1 to 1 μm . The samples with lower silica content showed limited gel formations and the pore sizes ranged from 0.1 to 10 μm . The increased silica content was related with a denser microstructure thus resulting in lower water permeability [17].

In a microstructure evaluation research carried out by Izquierdo et al. (2009), different samples of fly ash from coal-fired power plants across the Europe were mixed with blast furnace slag and used a potassium hydroxide solution for alkali activation. It was found that the microstructure of the samples consisted of a homogenous geopolymer gel matrix, a dense packing of fly ash and slag particles along with some minor interstitial porosity. Silica was reported to be an abundant constituent of geopolymer matrices and the samples with larger silica content showed higher densification and lower porosity levels, and associated reduction in pore size and increase in compressive strength [19].

The use of fibers in developing environment friendly geopolymer composites for construction has also been investigated in recent years. Cellulose fibers have been utilized for reinforcing various polyester and epoxy matrices. The major benefits include cost effectiveness, ease in availability, higher compressive strength and low toxicity [20]. Woven cotton fabrics have been reported in enhancing the properties of geopolymers used in construction. For instance, Alomayri et al. (2014) utilized cotton fabrics (with various fiber percentages) in fly ash geopolymer mortars prepared by activation of fly ash by a mixture of 8M sodium hydroxide and sodium silicate solutions. It was found that the composite material

had improved flexural strength, modulus of flexure and impact strength. The microstructure analysis revealed that there was a good amount of penetration of geopolymer mortar into the cotton fabric weave which resulted in enhanced bonding between the fiber bundle and geopolymer matrix thus leading to higher flexural strengths [21].

It is a well-known fact that sulphate ions from natural or wastewater streams contribute to deterioration of Ordinary Portland Cement (OPC) based construction materials. The sulphate ions cause stress, expansion and thus result in strength loss. Geopolymers have been found to be more resistant against sulphate attacks. The mineralogy and microstructure of geopolymer materials is very different from Ordinary Portland Cement and thus contributes towards better strength and durability. Baščarević et al. (2015) studied the sulphate attack behavior of fly ash based geopolymers obtained from two coal-fired power plants in Serbia. The mineralogical composition of Kolubara fly ash revealed higher content of Quartz some of which remain unreacted during geopolymerization and resulted in lower compressive strengths. The specimens prepared were immersed in sodium sulphate (50g/L) solution for 365 days. A small decrease in mechanical strength (up to 10%) of Svilajnac fly ash geopolymer was witnessed after 365 days whereas the strength of Kolubara fly ash geopolymer was decreased at 28 days which however increased till 365 days. This was reported to be due to the higher porosity of Kolubara fly ash geopolymer which resulted in continuing alkaline reaction in the presence of sulphate solution [22].

Schmucker et al. (2005) studied the microstructure of a sodium polysialate siloxo geopolymer. The geopolymer samples were prepared by the alkaline activation of kaolinite with sodium hydroxide and sodium silicate solution. The sample had a silica to alumina ($\text{SiO}_2:\text{Al}_2\text{O}_3$) ratio of 3.3, a sodium oxide to silica ($\text{Na}_2\text{O}:\text{SiO}_2$) ratio of 0.25 and water to sodium oxide ($\text{H}_2\text{O}:\text{Na}_2\text{O}$) ratio of 10. The stiff geopolymer paste was moulded in a cylindrical mould, sealed with a plastic film and air dried at ambient temperature for 60 minutes and then

cured at 65°C for 90 minutes. The plastic seal was removed and the sample was air dried at 65°C for another 60 minutes. The scanning electron microscope (SEM) micrographs revealed some areas of inhomogeneity within the aluminosilicate matrix. There were unreacted relicts of kaolinite, which were identified, in the energy dispersive spectroscopy (EDS) analysis as areas with atomic ratio between silica and alumina to be 1:1. Some other grains contained only silicon, which were termed to be the quartz grains that tend to survive high alkaline environment in geopolymerization [23].

4.2 Curing and Aging effect on microstructure and properties

The dissolution of aluminosilicate material and the formation of geopolymer gels is highly accelerated as the temperature is raised [1]. The strength gain at an early age is sometimes slow due to the lack of calcium content in various precursors and may result in a larger setting time of geopolymers [24]. In these conditions, methods that can accelerate the curing process or modify the chemical reactions, such as heat curing and addition of high calcium additives such as blast furnace slag respectively, are vital to achieve high early age strength [25].

Traditionally, oven curing at temperatures 60-120°C have been reported to enhance the early age strength. Chindapasirt et al. (2007) studied geopolymer mortars prepared using Class-C fly ash, sodium hydroxide (NaOH) activating solution of 10, 15 and 20M concentrations. The sodium silicate to sodium hydroxide ($\text{Na}_2\text{SiO}_3/\text{NaOH}$) ratios used were 0.67, 1.0, 1.5 and 3. The specimens were oven cured at 30, 45, 60, 75 and 90°C for 1, 2, 3 and 4 days. The compressive strength of samples was observed to increase with increase in curing time. At elevated temperatures (i.e. 60°C), curing for longer duration resulted in a decrease in

the unconfined compressive strength (UCS) as shown in the Fig. 3 (a). Furthermore, Fig. 3(b) shows that in this study, the optimum temperature was found to be 75°C, after which the UCS decreased sharply. Similarly, other studies have reported a decrease in the compressive strength at elevated curing temperatures for other precursor materials and alkali activators. For instance, Fig. 4 shows a reduction of UCS for a slag mixed with sugar cane bagasse based geopolymers [26] cured at 65°C. This behaviour is likely associated with the formation of microfissures derived from the drying shrinkage process at high temperatures thus causing strength reduction compared to specimens cured at ambient temperature conditions. Similar observations have also been reported for geopolymers based on meta-kaolin precursor (Mo et al., 2014). Interestingly while the aluminosilicate source material is substantially different, the optimal curing temperature for which a larger compressive strength is achieved is around the same value as in the class F based geopolymers (60-70 °C). It is noteworthy that other studies on fly ash based geopolymers mortars (de Vargas et al. 2011) reported a similar behaviour for smaller Na₂O/SiO₂ (N/S) molar ratios (i.e. 0.2) but a different trend, i.e. increase in compressive strength with temperatures up to 80 °C for specimens prepared at N/S of 0.3 and 0.4.

Shin et al. (2019) studied the effect of curing temperature on the compressive strengths of geopolymer concrete (GPC). Sodium hydroxide (12M) and sodium silicate solutions were used as an alkali activator for fly ash and ground granulated blast furnace slag (GGBFS). The curing temperatures selected were 20, 35, 45, 60, 80 °C, and the curing durations were selected as 3, 9, 15 and 24 hours. Eleven different combinations of minimum and maximum curing temperatures as well as curing durations were investigated. In general, it was found that the compressive strengths of the specimens increased as the maximum curing temperature was increased. The highest compressive strengths were of the samples subjected to maximum curing temperature and for the longest duration. For most of the samples, there was no noticeable increase in the compressive strength after 28 days of curing. It was concluded that

the combined effect of maximum temperature (T_{\max}) and maximum duration (t_{\max}) for majority of the samples was found to have a key effect on early strength of GPC. A similar compressive strength could be achieved at a lower t_{\max} and higher T_{\max} [27].

Different curing conditions especially in the early period of geopolymer formation are one of the key factors affecting the compressive strengths and other mechanical properties of geopolymers. Mo et al. (2014) investigated the relationship between curing conditions and process of geopolymerisation. Metakaolin samples were activated by a mixture of sodium hydroxide and sodium silicate solutions and casted into 20 mm cubical moulds. The samples were then cured at 20, 40, 60, 80 and 100°C. Impedance analysis was used to investigate the geopolymerisation process; studying the electrical conductivity of the samples at different curing temperatures and relating it with the different phases of geopolymerisation. It was found that the electrical conductivity of the slurries increased with the increase in curing temperatures especially when the metakaolin particles were still in the dissolution phase. After a certain peak, decreasing trend was witnessed owing to the fact that the particles were rearranging into a polymerised gel. It was concluded that the curing temperatures had an inverse relation with the initial and final setting time of geopolymer slurries as temperature elevation resulted in accelerated polycondensation of metakaolin. The raise in curing temperatures resulted in increased compressive strengths as the process of gel formation was rapid and the pore sizes were reduced. This is valid up to an optimum temperature (in this case, 60 °C) beyond which the setting is so rapid that it prevents the transformation into dense and compact structure of geopolymer mortars [28].

Kubba et al. (2018) however reported a decrease in geopolymer mortar strengths with elevated temperatures. They blended a mixture of fly ash, ground granulated blast furnace slag and palm oil fuel ash in different proportions. The materials were activated with different alkaline solutions i.e. sodium hydroxide (8M), sodium silicate and a mixture of sodium silicate

and sodium hydroxide solution in a ratio of 3:1. The geopolymer mortars thus formed were cured at 27, 60 and 90 °C curing temperatures. The strength values were determined at 1, 7 and 28 days. It was found that for all the sample mixes, the compressive strengths of the geopolymer mortars were reduced with increasing curing temperatures. The main reason highlighted was the formation of C-S-H linkages with coarser microstructure that led to increased porosity and cracks. The strength values increased till 28 days due to continuing geopolymerisation reactions [29].

A recent study proposed by Dong et al. (2017) suggested the use of a solar curing method which aims to reduce the cost and carbon emissions associated with the manufacturing process of high strength geopolymer concrete, compared to conventional high temperature oven curing [30]. The samples were prepared with a binder that constituted of 50% fly ash and 50% ground granulated blast furnace slag (GGBFS). A 12M sodium hydroxide (NaOH) solution mixed with sodium silicate solution in a ratio of 1:2.5 was used as an alkali activator. The control specimens were cured in ambient conditions and two solar curing methods were developed. In the solar curing grey (SCG) method, the specimen cylinders are painted with a shade of grey corresponding to 40% black on a grey-scale chart. In solar curing black (SCB) method, the specimen cylinders are covered with a layer of bubble wrap with the bottom surface painted black, and the bubble side is placed facing the sun to create the greenhouse effect. The cylinders were cured for 1, 3, 7, 14 and 28 days. The ambient temperature was kept at 21°C while the temperatures for solar curing grey (SCG) and solar curing black (SCB) remained in the 40°C to 60°C and 60°C to 80°C range, respectively. Solar curing had a positive impact on the compressive strength gaining and it should be noted that the temperature range achieved through solar curing is comparable to optimal range of oven curing. Fig. 5 shows a comparison between the three different methods performance with curing time in terms of UCS. It can be observed that within a day, solar curing grey (SCG) and solar curing black (SCB) specimens

showed an increase of 70.2% and 93.3% in compressive strength compared to the control specimens, respectively.

Furthermore, Fig. 5 also illustrates that the geopolymer develops a major portion of its strength gain (more than 70%) in the first seven days showing only a slight increase in UCS with aging there onwards regardless of the method of curing adopted. For instance, the strength gain for the SCB specimens is almost 87 MPa in the first 7 days, whereas a marginal increase of 5% (5MPa) is recorded for specimens aged to 28 days (92MPa). These observations are also consistent with an earlier study on binary binder geopolymer (metakaolin and silica fume) by Yaseri et al. (2017) that also reported rapid increase in UCS at early age and a insignificant increase with curing time [31]. Vargas et al., 2011 also reported a similar behaviour but noted that the long term strength gain (28 to 180 days) is also influenced by the nitrate to bisulphide (N/S) molar ratio, i.e. a greater gain was observed for specimens having a larger N/S molar ratio.

4.3 Mechanical properties in terms of alkali solutions concentration, silicon to aluminium (Si/Al) and silicon dioxide to aluminium oxide ($\text{SiO}_2/\text{Al}_2\text{O}_3$) molar ratios

The evaluation of the mechanical strength of geopolymers is vital in view of its application in the construction industry. The reason for strength gain is primarily attributed to the formation of gel structure and its densification with time as well as the reduction in pore size [1, 32-34]. This in turn is influenced by the concentration of alkali solutions as well as silicon to aluminium (Si/Al) molar ratios.

Geopolymers derived from different aluminosilicate precursors with varying concentrations of activators have been known to produce different compressive strengths. For instance, Top and

Vapur (2018) reported 28 day compressive strengths up to 50 MPa using fly ash as the geopolymer source material as shown in the Fig. 6.

It is evident from data reported in past studies that the concentration of alkaline activator plays a major role in the reactivity, pore structure, aluminosilicate gel formation and thus various mechanical and chemical properties of resulting geopolymers. [35-39]. A concentrated alkaline solution (high pH) is required for the dissolution of aluminosilicate source materials.[38, 40-42].

The effect of concentration of alkaline activator was investigated by Gorhan and Kurklu (2014). A fly ash based geopolymer mortar was prepared by activating it with a solution of sodium hydroxide at different molar concentrations i.e. 3, 6 and 9M along with sodium silicate solution. The mixes were cured at 65°C and 85°C for 24 hours. It was found that the optimum concentration for the activator solution was 6M as the highest compressive strength was achieved from this, both at 65°C (21.3 MPa) and 85°C (22 MPa). It was found that at a lower concentration of activator solution, the dissolution of fly ash is very limited whereas at very high alkali concentrations, in earlier stages of reactions, the dissolved species precipitate rapidly and thus the polycondensation process is hindered [42].

In a study carried out by Nath and Kumar (2019), class F fly ash was activated using sodium hydroxide solutions with 6, 8 and 10M concentrations. It was found that as the concentration of alkaline solution increased, the activation energy of the geopolymerization reaction also increased because of higher extent of dissolution as well more reactant available to complete the process of geopolymerisation [43].

The effect of concentration of alkali activators on compressive strength characteristics of ground granulated blast furnace slag and natural pozzolan based geopolymers were studied by Nadoushan and Ramezani pour (2016). The precursors were activated by 6, 8 and 10 M concentrations of sodium hydroxide as well as potassium hydroxide solutions. After blending

for a couple of minutes, sodium silicate solution was mixed in order to form a geopolymer paste. The samples were sealed in plastic bags and cured at ambient conditions. The samples were tested for compressive strength evaluation at 7, 14, 21, 28 and 91 days. It was noted that the optimum concentration of the alkaline solution was 8M while 6M and 10M solutions gave lower strength values. At lower concentration of alkaline solution, the dissolution process was found to be very limited. Further, 10M activator solution resulted in precipitation of dissolved species and thus inhibited complete geopolymerisation [44].

Williamson and Juenger (2016) studied the role of activating solution concentration on the behaviour of fly ash based geopolymer concrete. Alkali activated fly ash mortar cubes (50mmx50mmx50mm) were prepared using 4, 6, 7, 8, 9, 10 and 11M concentration sodium hydroxide solutions. The samples were cured at 60°C for one day and then kept at 38°C till the time of testing at 7 and 28 days. It was observed that the specimens prepared using 8M concentration solution showed the highest compressive strengths for both 7 days (32 MPa) and 28 days (38 MPa). The trend was found to be consistent with the literature [36, 45]. It was concluded that the increase in compressive strengths with increasing concentration of alkaline solutions was a result of enhanced dissolution of aluminosilicate glassy phases at higher pH values [1, 45-47]. However, the decrease in compressive strengths beyond optimum concentration of alkaline solution was due to the increased viscosity of activator solution and unreacted silica and alumina in the geopolymer mix [46, 48, 49].

Lahoti et al. (2018) studied different mixes of metakaolin and silica fume as a geopolymer source material at varying silicon to aluminium (Si/Al) ratios ranging from 1.03 to 2 and compressive strengths up to 62 MPa were attained for curing at ambient conditions.

In a study carried out by Lizcano et al. (2012), metakaolin (53% SiO₂, 43.8%Al₂O₃ and 3% impurities) was used as a source material for production of geopolymers. The alkaline activator solutions were prepared by dissolution of sodium and potassium hydroxide in

deionised water and then mixing silicon dioxide (SiO_2) in them with a 24 hours stirring. The Si/Al ratios of the solutions were kept at 1.25, 1.5, 2.0 and 2.5. The solutions were mixed with metakaolin and samples were cured at 80°C for 24 and 48 hours. The samples were kept at ambient conditions for one day prior to testing. It was found that the Young's modulus of the mixes increased up to a Si/Al ratio of 2.0 beyond which it had started decreasing. This could be due to the increase in the density of the samples with increasing Si/Al ratio. The compressive strengths increased ranging from 32 to 37 MPa for the samples having Si/Al ratio of 1.5 after which a decrease was witnessed. Increase in the Si/Al ratio with higher concentrations of silicates resulted in the increased viscosity of solutions thus contributing to inhomogeneous mixing, more percentage of unreacted metakaolin as well as higher porous microstructures thus resulting in lower mechanical strength. [50].

He et al. (2016) studied the geopolymerisation behaviour of metakaolin samples activated by potassium silicate solutions along with fused silica powder. The Si/Al ratios were kept at 2.0, 2.5, 3.0, 3.5 and 4.0. The geopolymer samples prepared after mixing were cured at 70°C for 48 hrs and then further cured for 24 hrs after demoulding. It was seen that the Young's modulus for the samples increased from 36 to 92 MPa as the Si/Al ratios increased from 2.0 to 4.0. This was reported to be a result of more developed Si-O-Si bonds as well as increase in the densification of microstructure [51].

In a study carried out by Asif et al. (2015), the effect of Si/Al ratios was investigated for fly ash based geopolymers to be used for coating applications. Sodium hydroxide (12M) and sodium silicate solutions were used as alkaline activators for fly ash. The samples were prepared with 1.85, 2.0, 2.5 and 3.0 Si/Al ratios. The compressive strengths of all the samples were investigated after ambient curing for 28 days. It was observed that the strength of samples increased till Si/Al ratio 2.0 after which a drop was noted for the sample with ratios 2.5 and 3.0. It was seen that the samples with 1.85 Si/Al ratio had a dense but porous microstructure

therefore resulting in lower strengths. Mixes with Si/Al ratio 2.0 exhibited highest strength as the pores and cracks were minimised. In Si/Al ratios higher than 2.0, the higher quantity of unreacted silica was witnessed along with non-uniformity of mixes due to higher viscosity of activating solution [52].

Timakul et al. (2015) have also investigated the effect of Si/Al ratios on class C fly ash based geopolymers. Sodium hydroxide (5M) mixed with sodium silicate solutions were used for activation. The Si/Al ratios were kept to be 2.6, 2.65, 2.8 and 3.0. The samples prepared were cured at 75°C for a duration ranging from 24 to 96 hours. The samples were then further cured for 28 days at room temperature. The compressive strengths for all the samples ranged from 22 MPa to 40MPa with the samples having the Si/Al ratios 2.65 exhibiting the highest strength for all the curing durations. It was evident from the SEM images that these mixes had higher densification and less porosity. As the Si/Al ratio was increased further, the unreacted silica, higher porosity and early crack formation resulted in lower strengths of the geopolymer mixes [53].

In a research carried out by He et al. (2013) on red mud (RM) and rice-husk ash (RHA) based geopolymers, it was reported that the effect of Si/Al ratios was significant on the strength characterisation of the industrial waste material. The RHA/RM ratios were varied ranging from 0.3, 0.4, 0.5 and 0.6 in order to achieve different Si/Al ratios. The corresponding Si/Al ratios were 1.68, 2.24, 2.80 and 3.35. The activating solution used was sodium hydroxide with varying alkalinity (2, 4 and 6M) while the ambient curing duration ranged from 14 to 49 days. It was observed that the compressive strength and ductility of the mixes increased as the Si/Al ratios increased from 1.68 to 2.80. This was reported to be a result of improved Si-O-Si bonding as well as enhanced ductility with the increase of RHA. These characteristics decreased however for the mix with Si/Al ratio 3.35 for the reason that other synthesis parameters

influenced the mechanical properties such as large particle size of RHA and more percentage of unreacted RHA in the mixture [54].

The effect of Si/Al ratios on the compressive strength of water treatment residue and rice husk ash based geopolymers has been studied by Waijarean et al. (2014). Finely ground water treatment residue (45 μ m retaining) was mixed with rice husk ash (45 μ m retaining) in different proportions so as to give Si/Al ratios 2.0, 3.0, 4.0 and 5.0. The mixtures were then activated by sodium hydroxide solution in order to achieve geopolymerisation. The samples were cured at ambient conditions, stored in plastic bags until testing at 3, 7, 28 and 60 days. It was seen that the geopolymer with Si/Al ratio 2.0 showed the highest compressive strength (almost 19 MPa) whereas the values decreased as the ratios were increased. It was reported that the geopolymer mixes with higher Si/Al ratios exhibited unreacted aluminosilicate materials along with the formation of glass-like phase resulting in weaker gel bonds [55].

Thokchom et al. (2012) studied the strength and microstructural characteristics of low calcium fly ash based geopolymer pastes formed by the activation of sodium hydroxide solutions. Different mixes were prepared with Si/Al ratios 1.7, 1.9 and 2.2. The pastes were then moulded and cured at a temperature of 85°C for 24 hours. After 7 days, the specimens were subjected to elevated temperatures of 300, 600 and 900°C for 2 hrs and then tested for compressive strength evaluation. Three unexposed specimens were tested for initial strength reference purposes. It was observed that the specimens having Si/Al ratio 2.2 retained 63% of the compressive strength even after being exposed at 900°C. The lowest residual strength (about 50%) was possessed by the sample with least Si/Al ratio i.e. 1.7. It was reported that the loss of strength at lower Si/Al ratios at elevated temperatures was due to weaker Si-O-Si bonds as well as shrinkage and microstructure disruption of the specimens [56].

Zhang et al. (2011) worked on the geopolymerization of mine tailings and their usage as a construction material. Class F fly ash was used to adjust the Si/Al ratio of highly reactive

copper mine tailings. The Si/Al ratios in the formed mixes ranged from 1.89 to 7.78. Sodium hydroxide solutions (5, 10 and 15M) were used as the alkaline activating solution. It was found that the unconfined compressive strengths were the highest (up to 22MPa) for Si/Al ratios 1.89 for all the concentrations of sodium hydroxide. Higher ratios led to unreacted aluminosilicate source thus resulting in weaker geopolymeric bonds [57].

In general, it was found that the Si/Al ratio ranges between 1 to 3 for enhanced geopolymerisation depending upon the source material [58-63]. Hence it is essential to determine the optimum Si/Al ratio for any particular source material in order to achieve desired characteristics.

A recent study reported the effect of different binder to solution ratio (B/S) and different Si/Al molar ratio in the synthesis of binary binder (metakaolin and silica fume) based geopolymer paste on their workability, setting and compressive strength [31]. It was reported a decrease in setting time as the B/S ratio and Si/Al ratio increase. Furthermore, an increase in Si/Al ratio at constant B/S ratio resulted in better workability and reduction of flow time. An increase of B/S ratio improves compressive strength, however when the B/S is high (e.g. >1.6), larger Si/Al molar ratios may not necessarily contribute to an increase in strength, as there is an increased unreacted silicate oligomers in the system. The results of this study indicate that for maximum compressive strength an optimal combination of B/S and Si/Al molar ratios needs to be investigated.

4.4 *Chemical properties*

The geopolymers possess various characteristics such as enhanced chemical resistance against sulphate and chloride attacks [32, 64, 65] and thus gain their importance over ordinary

Portland cement (OPC) concrete in many cases.

In highly aggressive aqueous environments, the physical and chemical degradation of ordinary Portland cement (OPC) concrete structures may hinder their applications [66]. In such conditions, where external sulphate attack due to exposure to sea water or waste water and acid attacks (occurring naturally or as a result of anthropogenic activities) are likely to happen, geopolymers can prove to be an important alternative (Kwasny et al., 2018). In fact, previous studies reported that low calcium geopolymers show high acid resistance [67, 68]. There are different parameters in the mix-design of geopolymers that can influence their acid resistance characteristics. The pore size distribution of the binder matrix is influenced by the alkali ion of the activator solution [67]. The particle size distribution of the dry binder is affected by the addition of micro or nano-silica as it enhances the packing density of the solid particles thus improving the microstructure in the hardening phase and it alters the chemical composition by increasing the silicon dioxide (SiO_2) content [69]. The dissolved silicate content in the activator solution influences the crystallisation of the reactants and may impact the chemical properties as well. The calcium oxide (CaO) percentage of the binder seems to be the most important parameter as during a sulphate attack, gypsum is formed due to precipitation of calcium [68]. The gypsum apparently blocks the pores thus preventing the material from further corrosion [70].

Kwasny et al. (2018) compared the sulphate and acid resistance properties of ordinary Portland cement (OPC) and lithomarge based geopolymer mortars. It was reported that the calcined lithomarge geopolymer binder's exhibit compressive strengths exceeding 50MPa. In this study, two geopolymer mortars (GPM) and two Portland cement mortars (PCM) mixes were prepared. The samples were cured for 21 days at approximately constant temperature of 21°C. The samples were immersed in 0.352 mol/L solutions of sodium sulphate and magnesium sulphate for 52 weeks to investigate the sulphate attack resistance as well as kept

in different 0.52mol/L sulphuric acid and hydrochloric acid solutions for 8 weeks to investigate acid attack resistance. It was found that the GPM samples showed no evidence of cracking, expansion or discolouration as a result of sulphate solution attack. On the other side, PCM samples had micro-cracking along with lateral and longitudinal expansion. The GPM samples showed better resistance in sulphuric and hydrochloric acid environments as exhibited by lower surface deterioration and lower mass loss. This is shown in the Fig. 7. The main mechanism behind GPM deterioration was dealumination of the geopolymer microstructure [71]. As compared to the hydrochloric acid solutions, the sulphuric acid solutions caused higher surface deterioration, mass loss and microstructural deformation.

In a study carried out by Bakharev (2005), fly ash obtained from Gladstone in Australia was used as a source material to synthesize geopolymers. The activating solutions used were sodium silicate, sodium hydroxide and a mixture of sodium hydroxide and potassium hydroxide. The concentration of sodium in each solution was kept constant at 8% whereas the solution to binder ratio was kept at 0.3. The samples prepared were cured for 24 hours at room temperature, then heat cured at 95°C for 24 hours and then again cooled at room temperature for 48 hours prior to testing. For testing the resistance of geopolymers against sulphate attack, the solutions used were 5% sodium sulphate, 5 % magnesium sulphate and a mixture of 5% sodium sulphate and 5% magnesium sulphate. The compressive strength of the samples was tested at 0, 30, 60, 90, 120 and 150 days of immersion into the sulphate solutions. For comparison purposes, samples of Ordinary Portland Cement and Ordinary Portland cement partially replaced by 20% fly ash were also prepared. It was observed that the geopolymer samples had no visual changes even after months of immersion in the sulphate solutions. The surface was as smooth as it was when prepared and no deposition was reported. The weight gains in the geopolymer samples (0.4-2.1%) were very less as compared to OPC samples (9.1%). The Ordinary Portland Cement as well as Ordinary Portland Cement plus fly ash

samples showed some appearance changes in the magnesium sulphate solution where they were covered by a 1 mm thick white layer. Cracking around the corners was observed in the samples immersed in sodium sulphate while marked deterioration was witnessed in the sodium plus magnesium sulphate solution. The compressive strength for the geopolymer samples fluctuated with time and some decreases as well as increases were observed for different activated fly ash samples in all sulphate solutions. However, Ordinary Portland Cement as well as Ordinary Portland Cement plus fly ash samples showed a drastic decrease in compressive strength of 35 and 19% respectively. The reason reported was the nature and characteristics of the aluminosilicate polymeric gel which prevented the geopolymer samples from deterioration even at higher concentrations of sulphate solutions. Further, it was concluded that the fluctuation in the compressive strengths of geopolymer samples depended on the activator used in sample preparation as well as type and concentration of cation in the sulphate media [72].

Concrete structures when exposed to marine environments can deteriorate due to aggressive wave action, chemical attack in the form of chlorides and sulphates in seawater and various other climatic agents. Reddy et al. (2013) have investigated the behaviour of low calcium fly ash based geopolymer concrete in corrosive marine environment. ASTM Type I Portland cement was used to prepare concrete samples as a control mix whereas the geopolymer concrete specimens were prepared by completely replacing the cement with ASTM Class-F fly ash. The alkaline solutions used were a mixture of sodium hydroxide and sodium silicate solutions. 8M and 14M sodium hydroxide solutions were used in the preparation of the alkaline activator. The cylinders and reinforced beams using rebars were kept in the moulds for 4 and 5 days respectively. Then oven cured at 60°C for 24 hours and then cured at ambient temperature up to 28 days. The corrosion technique used was an accelerated laboratory electrochemical method. The samples were immersed in a saline solution and the chemical action was simulated by inducing different intensities of corrosion

into the reinforcement using direct potential. The 28 days compressive strengths achieved for the oven cured samples were 39.9 MPa (8M) and 60.2 MPa (14M) whereas the ambient cured samples showed 33 MPa. Further, the geopolymer samples did not exhibit total destruction upon failure, thus representing toughness of the geopolymer paste. The corrosion current for the geopolymer samples decreased for approximately 80 hours and then remained constant whereas for the cement samples it decreased in the first 15 hours and then increased until 300 hours of the test. Further, in the mass loss measurement analysis, it was observed that after accelerated corrosion, the mass of the reinforcement in OPC samples decreased by 51-72%. However, the bars in the geopolymer concrete mixes showed 0% mass losses. Hence, it was suggested that geopolymer concrete mixes show a more stable behaviour in corrosive environments and could be more suitable for use in marine conditions [73].

Sturm et al. (2018) studied the acid resistance behaviour of alkali activated materials. In this study, three different type of silica starting materials, a micro silica, a silica produced by thermal treatment of chlorosilane production residues and flue gas neutralisation, and rice husk ash were used to prepare mortars. The sodium aluminate (NaAlO_2) was used as a solid activator. Ground granulated blast furnace slag (GGBFS) was used in some specimens to enhance the calcium content of the mixture.

The microstructure analysis of the specimens showed that the water immersed specimens possessed a glass-like microstructure indicating the geopolymer gel. However, the acid immersed specimens exhibited debris-like structure which are thought to be precipitated silica gel [65]. The microstructures of geopolymers became more porous upon acid attacks however, in this case the precipitated silica gel supported the corroded layer to some extent thus preventing the inner regions from acid attack to some degree, as it can be observed from the Fig.8.

4.5 *Thermal properties*

Geopolymers also possess enhanced thermal resistance property. In a fire scenario, a good geopolymer building material needs to possess strong chemical stability, resistance to deformation as well as strength endurance [32]. Geopolymers such as metakaolin and fly ash tend to have good fire resistances even at temperatures up to 1000°C [74-76]. When geopolymers are exposed to elevated temperatures, shrinkage occurs as a result of evaporation of water from the structure [77].

Thermal resistance properties for Ordinary Portland cement binders are low especially at temperatures beyond 600°C [78]. A research carried out on hard coal fly ash geopolymer revealed high compressive strength and low shrinkage at temperatures up to 1000°C. 8M sodium hydroxide solution was used as an activator whereas the fly ash was partially replaced in fractions (0-20%) with pure calcium hydroxide powder. The samples casted were kept at 40°C for 3 days and then stored over water for another 21 days at room temperature. The samples were heat treated at 600, 800 and 1000°C at a rate of 5°C per minute and kept there for 60 minutes after which compressive strength tests were carried out. The temperature resistance was determined through dilation tests up to a temperature of 1,100 °C using the Linseis-dilatometer L75. A constant stress of 0.05 MPa was kept on the sample to determine creep under compression. It was found through the quantitative phase analysis by Rietveld refinement that the samples having 8% calcium hydroxide possessed maximum amount of nepheline at 800°C and feldspar at 1000°C which contributed to its high 28 day compressive strength (39 MPa) and low shrinkage (1.7%). The aluminosilicate bonds and calcium silicate hydrate linkages contributed to the overall strength and stability of the fly ash based geopolymer binder even at such high temperatures [78].

In a study carried out by Samal et al. (2017), metakaolin was used as the source material for geopolymer preparation. The samples were treated at various temperatures beginning from room temperature, 200°C, 400°C, 600°C, 800°C and then 1000°C.

It was observed through scanning electron microscope (SEM) images that micro-cracks appeared on the surface at 200°C. At 400°C, the metakaolin geopolymer began to swell along with the enhancement of cracks thus dividing the surface into pockets. Significant thermal expansion led to the development of more vivid swell pockets at 600°C. The expansion was more prominent at 800°C while the matrix began to melt at 1000°C as shown in the Fig. 9. Hence, it was concluded that the micro-crack development, expansion and swelling behaviour may lead to spalling of the geopolymer. During thermal expansion, the increased porosity resulted in a cage-like structure which caused loss of mass and spalling [74].

Rickard et al. (2011) conducted a research on the thermal properties of fly ash based geopolymers where the source material was obtained from three power plants; Collie power station (Western Australia), Eraring power station (New South Wales) and Tarong power station (Queensland) in Australia. The fly ash had different chemical compositions owing to the fact that their characteristics would vary depending on the coal source and burning conditions. X-ray fluorescence tests revealed the percentages of silica (SiO_2) and alumina (Al_2O_3) for all the fly ashes i.e. Collie (SiO_2 51.4%, Al_2O_3 26.9%), Eraring (SiO_2 65.5%, Al_2O_3 23%) and Tarong (SiO_2 73.7%, Al_2O_3 22.4%). Different geopolymer samples were synthesized where the main compositional variable, Silicon to Aluminium ratio (Si/Al), was varied between 2 and 3. The mechanical strength of the geopolymers was tested at room temperature as well as after exposure to 1000°C. It was seen that the Collie fly ash geopolymer exhibited highest 28 days compressive strength (128 MPa) at room temperature as compared to Eraring (31 MPa) and Tarong (26 MPa). This was due to different geopolymerisation levels of the different mixes. Better conversion of amorphous aluminosilicates into geopolymer gel led to stronger

bonds thus contributing to higher strength. Further, the low Si/Al ratio samples showed higher compressive strengths as compared to the other ones. However, in case of post fire-exposure strengths, it was observed that higher Si/Al ratios led to better compressive strengths as for Eraring and Tarong fly ash based geopolymers. Sintering of aluminosilicates of geopolymers and unreacted fly ash is reported to be a reason for the inter-particle connectivity thus resulting in higher strengths. It was suggested that fly ash based geopolymers become brittle after firing [79].

In another detailed study conducted by Lahoti et al. (2018), metakaolin, one of the most common model precursor was employed for the study of thermal behaviour of geopolymers owing to good mechanical and fire resistance properties. The study illustrated that the fire resistance should be investigated at micro, meso and macro scales. The micro-scale thermal resistance indicates micro-structural chemical stability of the material when subjected to high temperatures. The meso-scale thermal resistance refers to the ability of the material to resist cracking and volumetric changes. The macro-scale thermal stability is the strength endurance or the ability of the material to maintain its compressive strength at elevated temperatures. The samples prepared in different mix designs were cured for 7 days under ambient conditions and then were subjected to 300°C and 900°C. The compressive strength reduced after exposure to high temperature as shown in the Fig. 10, however the samples maintained structural integrity. It was concluded that all metakaolin geopolymer samples experienced reduction in compressive strengths after exposure to 300°C. The geopolymer mixes exhibited good chemical stability at micro-scale but revealed poor volume stability at meso-scale and low residual strength at macro-scale against 900°C exposure [32].

4.6 Durability properties

Past studies have adopted various performance parameters such as abrasion resistance, frost resistance, shrinkage resistance, carbonation resistance and reported that geopolymer concrete compares favourably to Ordinary Portland Cement (OPC) concrete in terms of durability properties [80, 81].

As the geopolymer concrete can be used as a patching material, the evaluation of abrasion resistance properties is critical [82]. For instance, Ganesan et al. (2015) studied the abrasion resistance of OPC and fly-ash based geopolymer concretes as well as steel fibre reinforced concrete. The study revealed that weight loss values for geopolymer concrete were less (0.24%) compared to conventional OPC concrete and steel fibre reinforced concrete (0.33%) [83].

Nuaklong et al. (2016) have reported that the geopolymer concrete with natural aggregates exhibit lower values of abrasion weight loss by nearly 20% as compared to recycled aggregates [84]. In a study carried out by Wongsa et al. (2016), it was found that geopolymer concrete with natural aggregates shows less than 50% abrasion weight loss values in comparison with geopolymer concrete using bottom ash as aggregate [85]. Moreover, the addition of various fibres can also improve the abrasion resistance properties of geopolymer concretes. Ganesan et al. (2015) reported that the abrasion weight loss for geopolymer concrete specimens reinforced using steel fibre was much less (0.12%) than that of geopolymer concrete (0.24%) [83]. The research carried by Celik et al. (2018) shows that addition of polyvinyl alcohol (PVA) fibres and basalt fibre can improve the mechanical and abrasion resistance properties of geopolymer composites [86]. Hence it was found in the past researches that geopolymer concrete has performed better in terms of abrasion resistance as compared to OPC concrete.

An important parameter in the evaluation of durability characteristics of concrete is the frost resistance especially for underwater structures applications or in locations where the temperatures are very low. The frost resistance is assessed by the weight loss percentage and change in the dynamic modulus of elasticity after freezing-thawing cycles. While the study of frost resistance is relatively well established for OPC concrete, results for geopolymer concrete are limited. Wang et al. (2010) reported that the weight loss for OPC concrete and geopolymer concrete remain the same up to 100 freezing-thawing cycles. However, from 100 to 200 cycles it increases drastically for OPC concrete whereas no change is observed for geopolymer concrete, thus exhibiting better durability characteristics [82]. Yuan et al. (2020) have reported enhanced frost resistance characteristics of Class F fly-ash and slag based geopolymers reinforced by polypropylene (PP) fibre, polyvinyl alcohol (PVA) fibre and steel (S) fibre under a coupled effect of 20 MPa compressive stress and 125 freezing cycles. The propagation of micro-cracks was suppressed and water penetration depth was reduced for the fibre reinforced geopolymer concrete specimens [87]. Pilehvar et al. (2019) studied the frost resistance behaviour of OPC concrete and fly-ash/slag based geopolymer concrete specimens containing micro-encapsulated phase change materials (MPCM). It was found that compressive strength for OPC specimens was greatly reduced (44 MPa) as compared to geopolymer concrete (74 MPa) samples after being exposed to 28 freeze-thaw cycles [88].

Another major factor in the assessment of durability properties of construction materials is the drying shrinkage, which is the difference between autogenous and total shrinkage. The loss of moisture during the hydration process as well temperature changes during hardening of concrete contribute to drying shrinkage. Olivia and Nikraz (2012) results revealed that drying shrinkage properties of fly-ash based geopolymer concrete compares favourably with OPC concrete specimens [89]. Albitar et al. (2015) investigated the strength characteristics of granulated lead smelter slag (GLSS) and fly-ash based geopolymer concrete specimens. It was

found that specimens containing larger proportions of GLSS contributed to a reduction of drying shrinkage in the fly-ash based geopolymer concrete [90]. Gunasekera et al. (2019) studied drying shrinkage properties for fly-ash based geopolymer concrete from various sources and similarly lower drying shrinkage was observed for geopolymer concrete [91]. Muttashar et al. (2018) studied geopolymer concrete specimens having spent garnet as sand replacement. The drying shrinkage of the geopolymer specimens having garnet was smaller than those prepared with sand [92]. Humad et al. (2019) reported that higher fly-ash contents in geopolymer concrete reduced drying shrinkage and substantially lowered autogenous shrinkage whereas the usage of alkali activators having lower alkali moduli could increase the autogenous shrinkage [93].

Carbonation resistance is an important performance parameter for concrete applications. For geopolymer concretes, accelerated carbonation method is adopted to assess its durability. Huang et al. (2018) assessed the carbonization rate from ion migration perspective and reported that fly-ash based geopolymer concrete showed higher carbonation resistance as compared to geopolymer concrete [94]. Li and Li (2018) presented a modified rate of carbonation model for fly-ash and blast furnace slag based geopolymer concrete. It was found that higher blast furnace slag content enhanced the carbonation resistance. Further, as the curing temperatures reached from 20 °C to 60 °C the carbonation depth was reduced by almost one third, thus proving that heat curing resulted in improved carbonation resistance [95]. Apart from binder types and curing temperatures, alkaline activators and type of aggregates can also affect the carbonation resistance properties of concrete. Pasupathy et al. (2016) investigated the carbonation depth and pH values of fly-ash and slag based geopolymer concrete slabs. The slabs had been exposed to outdoor environment for eight years. The introduction of sodium silicate as alkaline activator component exhibited negative effects on the carbonation resistance [96]. Muttashar et al. (2018) found that garnet as a replacement for sand in slag based geopolymer concretes reduced

carbonation depth. The carbonation depth decreased from 12.8mm to 6.4mm as the garnet percentage in concrete specimens was increased from 0% to 100% [92].

Finally, based on the results of numerous past studies on the durability characteristics it is clear that geopolymer concrete performance is much superior compared to OPC concrete.

4.7 Environmental impact evaluation

Ordinary Portland cement and concrete are used globally in the construction industry but have major negative environmental impacts [97, 98]. In a report documented by Andrew (2018) of Centre for International Climate Research Oslo (CICERO) Norway, approximately 4 billion tonnes of cement were produced in 2016 globally [99]. Nearly 50 billion tonnes of concrete are produced annually all over the world. The cement industry contributes to about 10% of the total greenhouse gas emissions globally and utilises 1.5 billion Gigajoules (GJ) of energy annually. One tonne of cement produces about 900 kg of CO_{2-e} and consumes about 5 GJ of energy thus making it highly energy intensive [2]. It was found from previous researches that greener cements prepared by geopolymerization reduce the greenhouse gas (GHG) emissions by almost one half [100].

Nguyen et al. (2018) used the life cycle assessment (LCA) technique for evaluating the environmental impact from feedstock extraction to the manufacturing of the cementitious binders [101]. The production costs such as transportation, energy, material and capital costs were also analysed. Five different type of materials were incorporated into study, namely Ordinary Portland Cement (OPC), fly ash cement, slag cement, metakaolin based geopolymer and high limestone alkali activated slag cement (HLAASC). The cost of production of all the cements was taken as the sum of feedstock, transportation, process and capital costs. The

feedstock cost of fly ash was estimated between \$40-80/tonne. Slag costs about \$60-100/tonne. The transportation costs and greenhouse gas emissions of various modes was determined as shown in the Table 1.

The most drastic differences are seen in comparing the GHG emissions and primary energy at the processing stage of all the binders as shown in the Fig 11 and 12. Thus, the LCA models that calculated the energy requirements and GHG emissions along with the cost analysis concluded that the slag cement, fly ash cement, HLAASC and metakaolin geopolymer reduce the life cycle GHG production as compared to OPC. The prices are highly competitive to OPC where these source materials are easily available.

Mc Lellan et al. (2011) have reported similar results in a comparative study focussing on the feedstock extraction as well as production impacts of various fly ash based geopolymer mixes as compared to Ordinary Portland Concrete. In typical geopolymer mixes, greenhouse gas emissions have found to be significantly reduced (271-425 kg CO₂ eq. per tonne) as compared to OPC products (760 kg CO₂ eq. per tonne). This study validated the previous findings as there was up to 94% decrease in emissions as well as 72% decrease in production costs. One of the major contributors towards the emissions for geopolymer mixes was caustic soda. Optimizing the amount of the alkali activator could help in reducing the carbon impacts of geopolymers. Hence, it was concluded that there was a huge potential in the emission and cost reductions depending upon the particular formulation of geopolymer mixes and extraction sources [102].

Habert et al. (2011) conducted an environmental evaluation of geopolymer based concrete production using Life Cycle Assessment (LCA) methodology. They confirmed the negative trend towards the global warming impact but found the geopolymers to be responsible for increase in other environmental impact parameters. For instance, the human toxicity was reported to be 105.4 kg 1,4-DB eq. (dichlorobenzene equivalent) in comparison to 18.9 kg 1,4-

DB eq. for OPC concrete. Freshwater eco-toxicity in case of OPC concrete was 2.52 kg 1,4-DB eq. whereas rose up to 27.01 kg 1,4-DB eq. for geopolymer concrete. The reason for the higher human toxicity impacts was mainly sodium silicate solution required for the geopolymerisation of alumino-silicate source materials. It was concluded that fly ash and granulated blast furnace slag based geopolymer concretes have lesser environmental impacts as they are activated using low quantities of sodium silicate solution. The mix design for geopolymer concrete should be taken into account so as to optimise the Si/Al ratio in order to minimise the usage of sodium silicate solution [103].

Robayo-Salazar et al. (2017) also found similar observations while investigating the eco-efficiency of alkali activated cements based on red clay brick wastes. The global warming potential of these hybrid cement pastes was studied which led to the conclusion that OPC content along with the amount of alkaline activator is responsible for increase in carbon emissions. Sodium silicate though a major contributor towards strength releases 0.926 kg CO₂ eq. per kg and its use should be minimised in order to reduce greenhouse emissions. [104].

In another study by Petrillo et al. (2016), an environmental evaluation has been made between geopolymeric and OPC masonry blocks. The Life Cycle Assessment (LCA) approach has been utilised to assess the environmental impacts. The life cycle stages considered were material acquisition, processing and transport. The materials used to make geopolymeric blocks were recycled clay and blast furnace slag as precursors while 5M NaOH and sodium silicate solution was used as an alkali activator. The OPC blocks were prepared using Type II cement along with fine and coarse aggregates. A comparison of the characterization phases of both the block units is given in the Table 2. The geopolymeric study reveals negative values mostly that indicates savings. The positive values on the other hand show a burden on the environment [105]. It can be seen that the acidification or eutrophication impacts of the geopolymer blocks are far less as compared to the OPC ones. This means that the nutrients (especially phosphorus

and nitrogen) in the geopolymer blocks will not be leached out in the water bodies in high concentrations. Therefore, they will not promote excessive growth of plants and algae, which could cause oxygen depletion of the water body. Similarly, the quantification of the burden of mortality from carcinogenic contents (in terms of disability-adjusted life years) in geopolymer paving blocks is nearly halved as compared to OPC blocks. Another major difference can be witnessed in terms of the disease burden attributable to human health owing to the climate change. The impact of geopolymer blocks on water and vector borne diseases as well as the risk of natural disasters due to global climate change is negative as compared to OPC pavers. Further, the geopolymer blocks do not result in the release of harmful compounds (such as chlorofluorocarbons) which could result in the depletion of ozone layer and contribute to climate change and health hazards associated with it. Also, the human and marine toxicity levels indicate a negative trend thus, not contributing to eco-life damages.

Hence it can be easily said that the geopolymers have a positive impact on the environment as compared to the conventional ordinary Portland cement (OPC). Their usage can definitely contribute towards a cleaner and sustainable construction practice.

Fahim Huseien et al. (2017) studied the usage of geopolymer mortars as an efficient and sustainable repair materials. Various mixes of fly ash, metakaolin and blast furnace slag were used for the geopolymer concrete production. The temperature requirements for calcination of geopolymers was found to be half of that needed for the decarbonation of lime. This could easily lead to 50-60% reduction in the carbon dioxide emissions as compared to OPC concrete [106].

Apart from the carbon footprint investigations, another important aspect that needs a thorough study is the leaching behaviour of geopolymers. Tigue et al. (2018) studied the leaching characteristics of geopolymer prepared by alkali activation of a mixture of coal fly ash (23%) and soil (67%) with sodium hydroxide (5%) and sodium silicate (5%) solution. High

leachability was witnessed for aluminium (Al), sodium (Na), calcium (Ca), silicon (Si) and iron (Fe). Initial higher contents of Al (120 ppm), Na (18721 ppm) and Si (18 ppm) are due to their higher initial content in the raw material as well as the alkaline activator. After 5 cycles it was found that the Na had leached about 19% owing to the excessive alkali content in the mixture. However, the lower solubility of Fe and traces of heavy metals such as arsenic (As) and chromium (Cr) showed their incorporation in the geopolymeric gel [107].

In a research carried out by Bai et al. (2019), a metakaolin based geopolymer was prepared using several industrial wastes such as fly ash, steel furnace slag and brake pad waste. All the wastes were grounded in a Los Angeles abrasion tester and the fines lesser than 75 μ m in size were mixed with metakaolin for the preparation of geopolymers in various compositions. The metakaolin was partially replaced (10, 20 and 30%) with the waste powder and activated by sodium silicate and sodium hydroxide solution. The heavy metal content in the waste materials was of grave concern and was therefore tested for leaching characteristics. It was found that the amount of heavy metals (Sr, Cr and Ba) leached into the solution from geopolymer was way less than the solid waste [108]. This was in agreement with the findings of previous researchers that geopolymerization of heavy metals resulted in a decreased mobility of heavy metal ions [62, 109-114].

5. *Applications in Civil Engineering*

The properties of geopolymers such as high compressive strength, better acid and thermal resistance, low carbon emissions, low energy requirements for processing etc. have justified their usage in civil engineering in comparison with conventional cementitious materials like cement and lime.

5.1 *Geopolymers in soil stabilization applications*

The use of geopolymers in soil stabilization has become a feasible practice especially on project sites where the engineers are encountered with soft or weak soil strata [115]. These soils lack the strength to support structural loads during construction or throughout the service life. Cristelo et al. (2011) have found various calcium based geopolymers such as fly ash slurry to be very effective in stabilization of deep soil strata through grouting process. In a study carried out by Zhang et al. (2013), alkali activated metakaolin was used to treat lean clay in order to investigate the feasibility of the geopolymers for the purpose of soil stabilization. The results of unconfined compressive strength (UCS) tests showed that 28 days strength of metakaolin (15%) stabilized soil was 4 MPa as compared to 3.5 MPa of the cement (5%) stabilized soil and 0.5 MPa of unstabilised soil as shown in Fig. 13.

The soils stabilized with metakaolin showed more ductile behavior [3]. The metakaolin stabilized soils exhibited low shrinkage behavior (0.5%) especially at 11% metakaolin concentration.

In a similar research carried out by Cristelo et al. (2011), Class F fly ash (low in Ca content) was used along with an alkali activator solution of sodium silicate plus sodium hydroxide [116]. The sodium hydroxide (NaOH) solution was prepared in 10, 12.5 and 15 molar concentrations. The short term strength of 15 molar solution was higher although the 12.5 molar samples showed higher 90 and 365 days' strength. The 15 molar solutions were sometimes too viscous to handle and crystallised at lower temperatures. Further, owing to the economic reasons, the 12.5 molar solutions seemed to be the best option [116].

It was concluded that the use of alkali activated geopolymers in jet grouting is favourable for soil stabilization and comparable to traditional cementitious grouts but the strength gaining aspects need to be explored further.

Zhen Liu et al. (2016) investigated the usage of fly ash in stabilizing loess soil strata. Loess is a type of loose soil which consists mainly of wind transported silt and clay particles [117]. It is found in many parts of the world especially, Central America, Brazil, Central Asia, Europe etc. The soil is primarily made of quartz particles. It was found that alkali activated fly ash binder could bond the soil particles through the formation of alumino silicate gel matrix. The scanning electron microscope (SEM) images and X-ray diffraction (XRD) analyses showed that the microstructure got compacted as the fly ash/loess ratio increased thus confirming the stabilization process as shown in Fig. 14.

Murmu et al. (2020) investigated the potential of fly-ash based geopolymer in stabilisation of black cotton soils for subgrade applications. The fly-ash content varied from 5 to 20% whereas the molarity of sodium hydroxide solution was kept at 5M. The 28 day unconfined compressive strengths increased from 1.2 MPa to 2.7 MPa as the fly-ash content was increased from 5 to 20%. The resilient modulus (M_R) ranged from 132 to 160 MPa for 5 to 20% fly-ash specimens as compared to the untreated black cotton soils which exhibited the value of 30 MPa. The results indicated that the geopolymer mix developed can be effectively employed for stabilising weak subgrade soils for transport infrastructure applications. [118]

Hanegbi et al. (2020) studied the use of metakaolin geopolymer for the stabilisation and dust control of a semi-arid loess soil. The soil specimens were replaced with metakaolin up to 30%. And then activated by sodium silicate and sodium hydroxide solution. The soil mixtures prepared were tested in wind tunnels for dust emission at 6.5 and 9.5 m/s velocities. The PM10 (particulate matter 10 μ m or less) values for geopolymerised mix remained around 0.02 mg/m³ and thus the application resulted in no dust emission. These results demonstrate that the

geopolymerisation technique can be adopted successfully to improve stabilisation of loess soils. [119]

5.2 *Geopolymer concrete applications*

The utilization of geopolymer concrete in construction is increasingly adopted by the construction industry owing to the drawbacks of conventional concrete and the numerous inherent benefits of geopolymers [64, 120]. They come in various forms such as high volume fly ash concrete, ultra-high performance concrete (containing admixtures), lightweight concrete etc. The geopolymer concrete offers various benefits over traditional cement based concrete such as high strength, increased durability, improved workability, reduced permeability and reduction of plastic shrinkage cracking etc. [120]

In a study carried out by Laskar and Talukdar (2017), 21 different samples of ultra-fine ground granulated blast furnace slag (UGGBS) concrete were prepared in various proportions. The fly ash content varied from 0 to 50 percent of the binding agent. Sodium hydroxide (NaOH) was used as an alkali activator ranging from 8M to 14M solutions. It was found that the geopolymer concrete is good at developing initial strength at a very high rate. Its 1 day strength was equal to almost 60% of its 28 days strength [121]. The addition of fly ash on the other hand contributed to betterment in workability of concrete mix but higher percentages (more than 40% of binding agent) reduced the compressive strength.

In a similar research carried by Deb et al. (2014), Class F fly ash was used as a main binding agent along with partial replacement of fly ash in this study. The alkaline activator used was a mixture of sodium hydroxide (14M) and sodium silicate solution. The sodium silicate to sodium hydroxide ratio (R) was varied from 1.5 to 2.5. The slag content (S) ranged from 0 to 20%. After compaction, the samples were cured in ambient conditions around 20°C

and 75% relative humidity. The compressive strength of the concrete samples was increased with increasing percentage of slag. However it was decreased when the sodium silicate to sodium hydroxide ratio was increased [122]. This can be seen from the following Fig. 15.

Top and Vapur (2018) have also reported using fly ash as the main material for geopolymer concrete production and have achieved 28 days compressive strength up to 50 MPa as shown in the Fig. 16.

Lee et al. (2019) conducted a study on fly ash and ground granulated blast furnace slag geopolymer concrete. Geopolymer mortars were prepared with 30% slag and 70% fly ash. The geopolymer mixes were activated by sodium silicate and sodium hydroxide solution. For the preparation of geopolymer concrete, the ground granulated blast furnace slag and fly ash were mixed in a 1:1 ratio. After thorough blending, activator sodium hydroxide solutions with concentrations 2, 3, 4, 5 and 6M were mixed whereas the geopolymer:sand:gravel ratios were kept at 1:2.5:2.4. The cylindrical samples were cured both indoors (sealed in plastic and cured at room temperatures) and outdoors on a roof top. The compressive strength tests were performed at 14, 28, 56, 90, 180 and 270 days. It was found that the outdoor curing resulted in a decrease in the compressive strength for various samples owing to drying and shrinkage as compared to the ones sealed in plastic bags and stored indoors. Further it was observed that the strength of the geopolymer concrete was enhanced as the curing days were increased [123]. The conclusions drawn were in agreement to the findings in literature [124-128].

In a project report published by Wagners Australia, Glasby et al. (2015) have documented a large-scale commercial application of geopolymer concrete at the Brisbane West Wellcamp airport (BWWA), Australia where approximately 40,000 cubic meters of fly ash based geopolymer concrete was supplied by Wagners for the construction of 435 mm thick heavy duty pavements in the northern end of runway, aircraft turning areas, taxiway on the

western side as well as hangars on the eastern side of the runway. The airport is fully functional with commercial flights being operated by Qantas Link since November, 2014.

5.3 Coastal or Marine applications

Geopolymer concrete can be considered as a suitable option for marine construction primarily because of low permeability and its superior durability characteristics. The dense microstructure of geopolymer concrete results in a low permeability that inhibit the penetration of sea water [129]. Ismail et al. (2013) have reported that the aluminosilicate geopolymeric gels are chemically stable in sea water and can provide a sustainable alternative solution for marine structures. [130].

Mahmood et al. (2020) investigated the use of fly-ash and steel furnace slag aggregate based high density geopolymer for coastal protection structures. Compressive strengths up to 37 MPa were achieved and a size reduction (30 to 40%) for breakwater structures was proposed without compromising the structural performance of the material. This resulted in a reduction in material requirements as well as overall carbon footprint [131]. Fan et al. (2018) have also reported enhanced properties of fly-ash based geopolymer mortars when exposed to different aggressive environments such as seawater and acidic environments. [132].

5.4 Self-cleaning concrete applications for inhibiting microbial attack

Self-cleaning concrete can be employed for cleaner and greener construction. The self-cleaning characteristics of geopolymer concrete can contribute to enhanced building aesthetics

[8]. Zailan et al. (2016) reviewed the properties of self-cleaning geopolymer concrete and explained that the photocatalytic materials such as titania (TiO_2) and zinc oxide (ZnO) are effective. Self-cleaning geopolymer concrete having photocatalysts can decompose organic matter in the presence of ultraviolet (UV) radiations. The addition of above materials contribute to the formation of stronger geopolymer links and thus increases its compressive strength [133]. Strini et al. (2016) also found that geopolymers containing titania (TiO_2) can assist in the process associated with the degradation of nitric oxide (NO) [134].

In addition, the higher alkalinity values (pH 10-12) of geopolymer concrete inhibits microbial activity on the surface. However, as the geopolymer concrete ages, the pH decreases and it drops to levels below 9, the surface degradation due to microbial attack begins. Adak et al. (2015) found that the microbial colonies cause biodeterioration that lead to surface damage. Silver nano particles have been found to possess anti-bacterial properties and silver silica modified geopolymer mortar proves to be more efficient than OPC mortars in applications in CO_2 rich environments [135].

5.5 *Mortars applications*

Geopolymer mortars have properties similar to natural rocks such as granite and marble. They can find applications in building conservation practices where cultural heritage is restored for future generations. Due to their enhanced durability characteristics especially in harsh environments, geopolymers can be employed as an alternative to conventional cement mortars in building restoration. Allali et al. (2016) reported that a metakaolin based geopolymer having calcium carbonate (CaCO_3) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) can be used as mortar for restoration of historical buildings [136].

Zeobond (2012) reports the use of a commercial geopolymer concrete ready-mix with steel reinforcement for slabs and footpaths in Melbourne (Australia). Zeobond (2012) and Rocla (2011) have produced and tested according to relevant Australian standards various precast pipes, railway sleepers, pavers and have installed them in several construction projects across the state.

5.6 *Fire resistance applications*

Jiang et al. (2020) carried a comparative experimental study on the fire resistant properties of geopolymer concrete and OPC concrete specimens. Class C fly-ash was activated using sodium hydroxide and sodium silicate solutions and the specimens prepared were exposed to temperatures up to 1200 °C. The OPC specimens showed severe cracking for temperatures exceeding 800 °C. In contrast, the geopolymer concrete specimens exhibited very few visible cracks and no spalling even at these high temperatures. In addition, the residual compressive strength of geopolymer concrete was higher (54 MPa) than OPC concrete specimens (49 MPa). Based on these findings, geopolymer concrete is better suited for applications where fire resistance and structural performance is critical, e.g. buildings [137].

5.7 *Insulation of buildings*

Zou et al. (2020) carried an experimental investigation on sawdust and metakaolin based geopolymer and found it to be an effective insulation material for buildings. The samples with water to biomass ratio up to 2 were found to exhibit low heat conductivity (0.118-0.125

W/m.K) and potentially were suitable to have a practical application in building insulations [138].

5.8 *Manufacturing of ceramic products*

Azevedo et al. (2020) explored the use ceramic waste as a geopolymer precursor material for producing ceramic roof tiles. Unused clay brick waste known as grog was employed along with sand, potassium hydroxide and sodium silicate powder. The pozzolanic activity index was above 6 MPa which showed it to be compatible with other ceramic materials obtained by conventional firing process. Thus, the ceramic waste could be used as a sustainable material for the production of roof tiles [139].

6. Conclusions

The geopolymers, both in their natural and inorganic form have suitable characteristic to enhance their application in construction practices. The most common applications are typically in soil stabilization and in the concrete industry. While numerous studies have been conducted to establish the use of geopolymer technology more widely (e.g. in coastal infrastructures), there are a number of aspects that need further research in order to exploit the precursor materials to their full potential. Future research in this field will enhance the commercial and industrial success of these materials as an environmentally friendly solution to various issues caused at present due to conventional materials such as cement and lime. For

instance some issues are proposed below for future work.

(1) Inherently, to control the production and to improve the performances of geopolymer, the reaction mechanisms in terms of thermodynamics, kinetics, intermediate states structures, and the degrees to which the –Si-O-Al are oligomerized and polymerized. This is vital to enhance the geopolymer performance to support the decision to include additional elements or additives.

(2) Most of geopolymer pastes, mortars and concretes are brittle and prone to cracking. Such behavior not only imposes constraints in applications, but also affects the long-term durability. Investigation of potential additives and adjustment of alkali molar ratios is required to establish a geopolymer that displays strain-hardening behaviour.

(3) There are also emerging applications for geopolymers materials in the removal of toxic metals adsorption and immobilization and carbon dioxide (CO₂) sequestration. However, recent studies show that the performance is still unsatisfactory and research on the recipes component is required. In addition, new applications of fly ash-based geopolymer with biomass can be developed as a class of novel lightweight fireproof materials.

Finally, the geopolymers would definitely prove to be economical and sustainable materials in civil engineering industry.

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Abbreviations and nomenclature

OPC	Ordinary Portland Cement
GPM	Geopolymer mortars
PCM	Portland cement mortars
SEM	Scanning electron microscope
EDS	Energy dispersive spectroscopy
XRD	X-ray diffraction
GGBFS	Ground granulated blast furnace slag
UCS	Unconfined compressive strength
SCG	Solar curing grey
SCB	Solar curing black
NaOH	Sodium hydroxide
Na ₂ SiO ₃	Sodium silicate
CSH	Calcium silicate hydrate
HLAASC	High limestone alkali activated slag cement
GHG	Greenhouse gas
LCA	Life cycle assessment
PVA	Polyvinyl alcohol
N/S	Nitrate to bisulphide
RM	Red mud
DB eq.	Dichlorobenzene equivalent

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List of Tables

Table 1. GHG emissions and cost comparison of various transportation modes

Table 2. Comparison of characterization phases of geopolymetric and OPC blocks

Table 1. GHG emissions and cost comparison of various transportation modes

Mode	GHG Emissions	Primary Energy	Transportation Cost
	(kg.CO ₂ equivalent/tonne-km)	(MJ/tonne-km)	(USD/tonne-km)
Barge	0.016	0.21	0.0028
Train	0.028	0.39	0.018
Truck	0.052	0.73	0.17

Table 2. Comparison of characterization phases of geopolymetric and OPC blocks

Impact Category	Units	OPC Blocks	Geopolymer Blocks
Acidification	PDFm ² yr	0.302	-17.034
Carcinogens	DALY	2.50E-07	1.24E-07
Climate change	DALY	1.43E-06	-5.95E-05
Human toxicity	kg 1,4-DB eq	2.335	-5.679
Marine toxicity	kg 1,4-DB eq	863.434	-830.01
Fossil fuels	MJ surplus	12.931	-565.528
Ozone layer depletion	kg CFC-11 eq	1.054E-06	-3.665E-05

Notes: PDF is Potentially disappeared fraction, DALY is Disability-adjusted life year, DB is Dichlorobenzene, MJ is Mega joules, CFC is Chlorofluorocarbon

List of Figures

Fig. 1. Flowchart for geopolymerization mechanism

Fig. 2. Scanning electron microscope (SEM) images of (a) Metakaolin and (b) class F Fly ash activated by 8M NaOH [1] reproduced with permission.

Fig. 3. Variation in strength gaining with (a) time of heat curing at 60°C and (b) curing temperature (data from [140]).

Fig. 4. Effect of heat curing on unconfined compressive strength (data from [26]).

Fig. 5. Unconfined compressive strength variation with respect to different curing techniques (data from [30]).

Fig. 6. Variation in unconfined compressive strength of fly ash geopolymer with varying activator concentration (data from [64]).

Fig. 7. Visual images showing acid resistance behavior of GPM and PCM Samples (after [71] reproduced with permission)

Fig. 8. Scanning electron microscope (SEM) images showing microstructures of water and acid immersed geopolymer samples (after [65] reproduced with permission)

Fig. 9. Scanning electron microscope (SEM) images of geopolymer matrices at different elevated temperatures (after [74] reproduced with permission)

Fig. 10. Unconfined compressive strength of samples with varying Si/Al ratios when exposed to different temperatures (data from [32]).

Fig 11. Primary energy profile at processing stage of various cementitious binders (data from [101]).

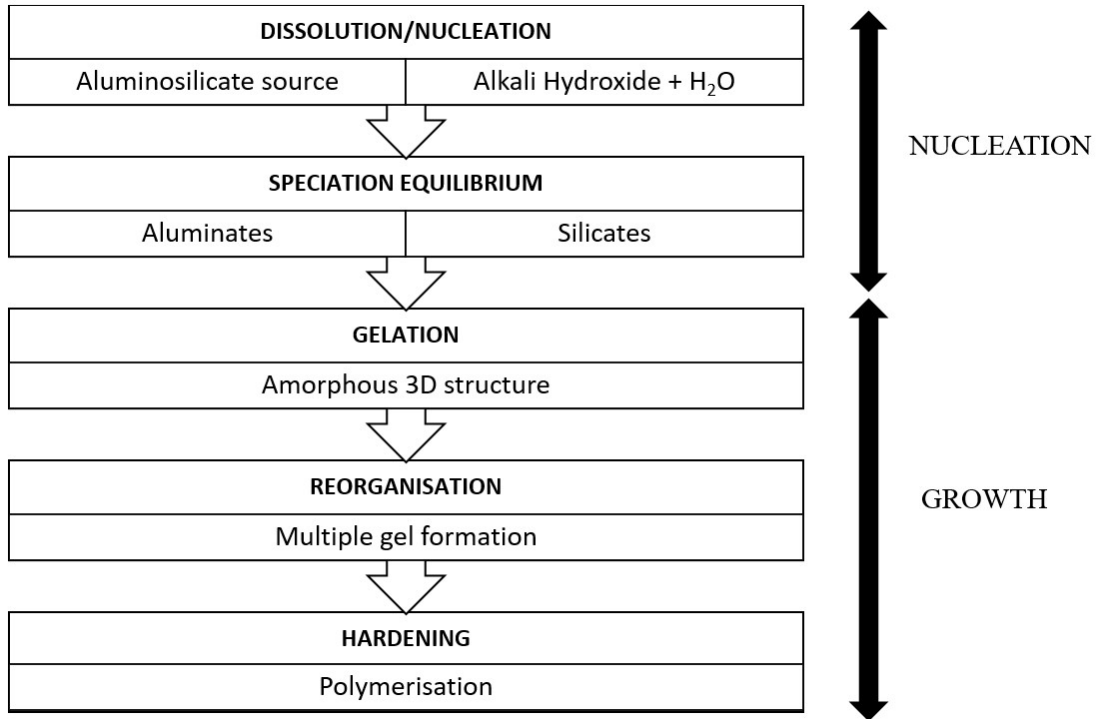
Fig. 12. Greenhouse gas (GHG) emission profile at processing stage of various cementitious binders (data from [101])

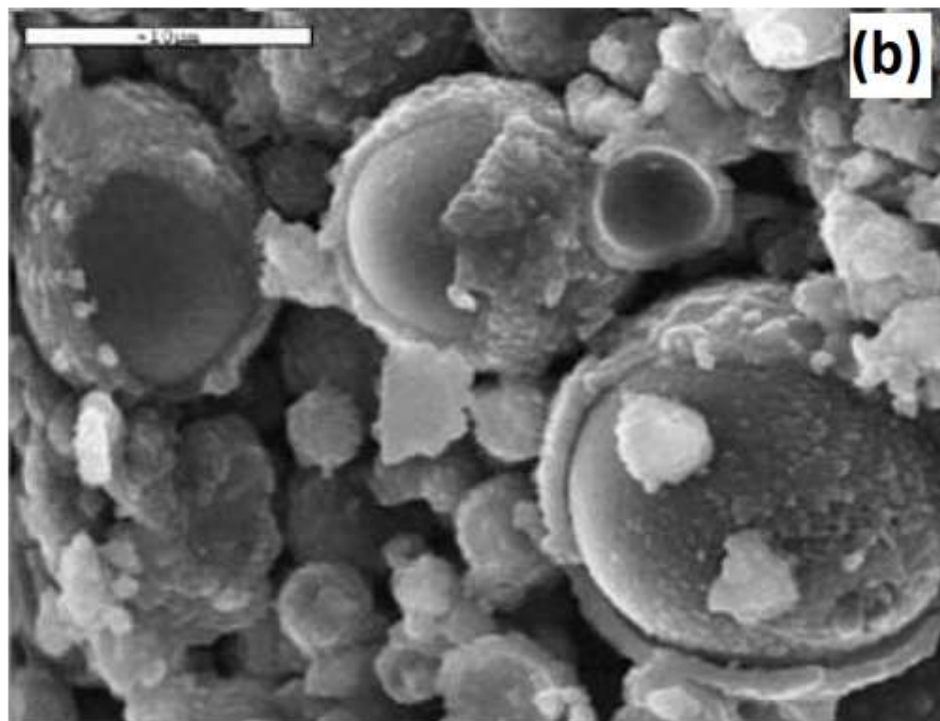
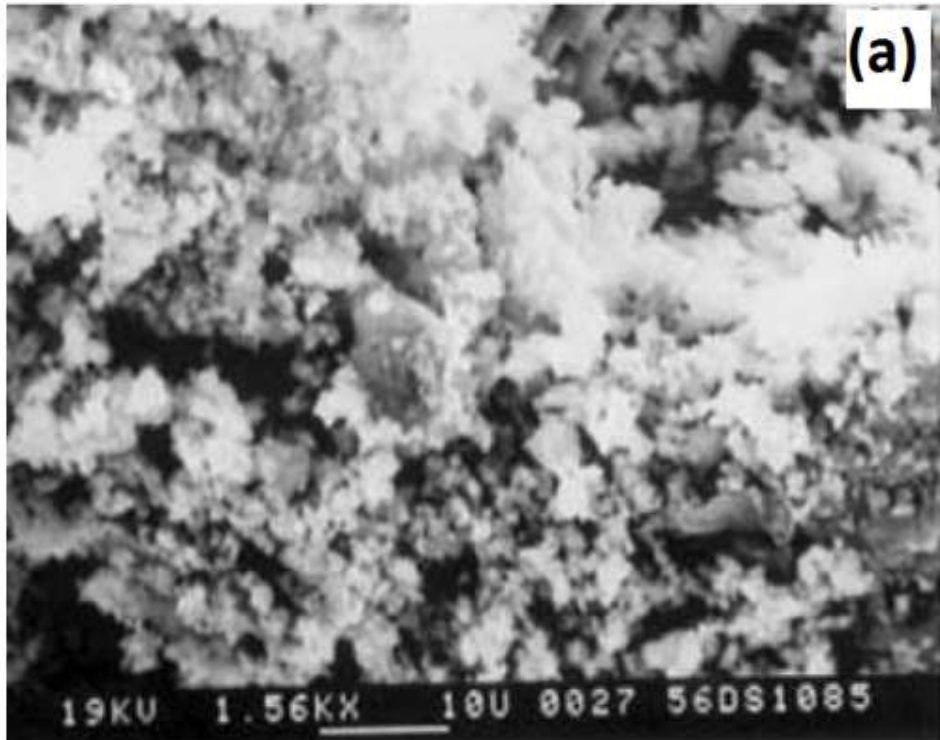
Fig. 13. Graph showing 28 day compressive strength of metakaolin and cement samples (data from [3]).

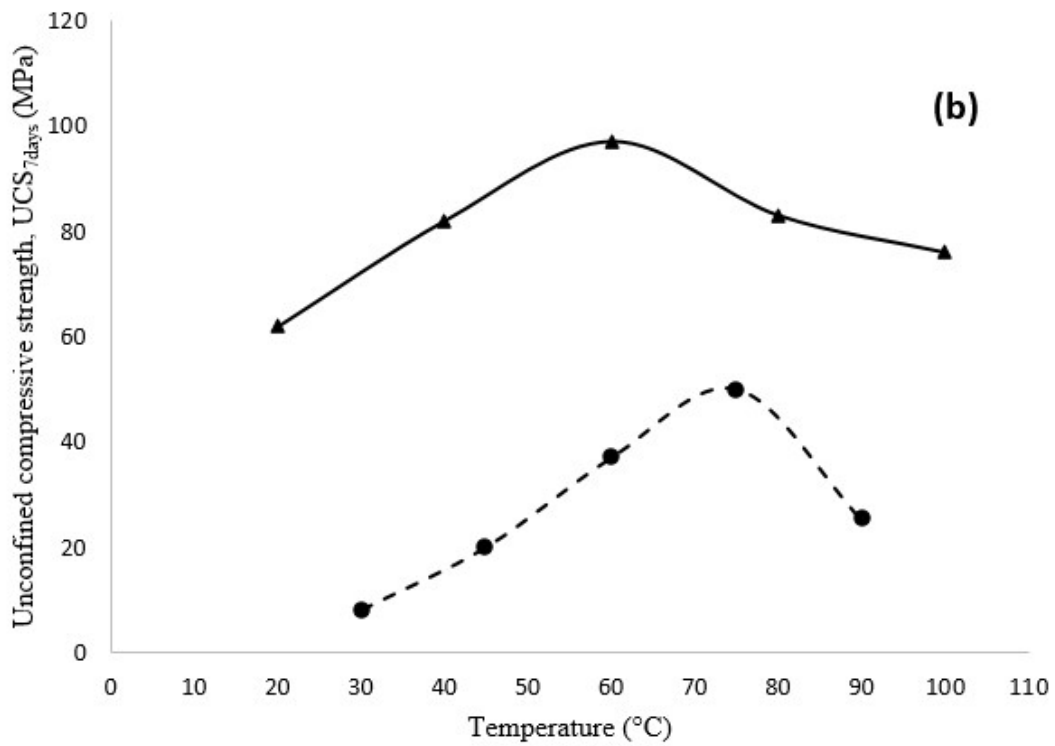
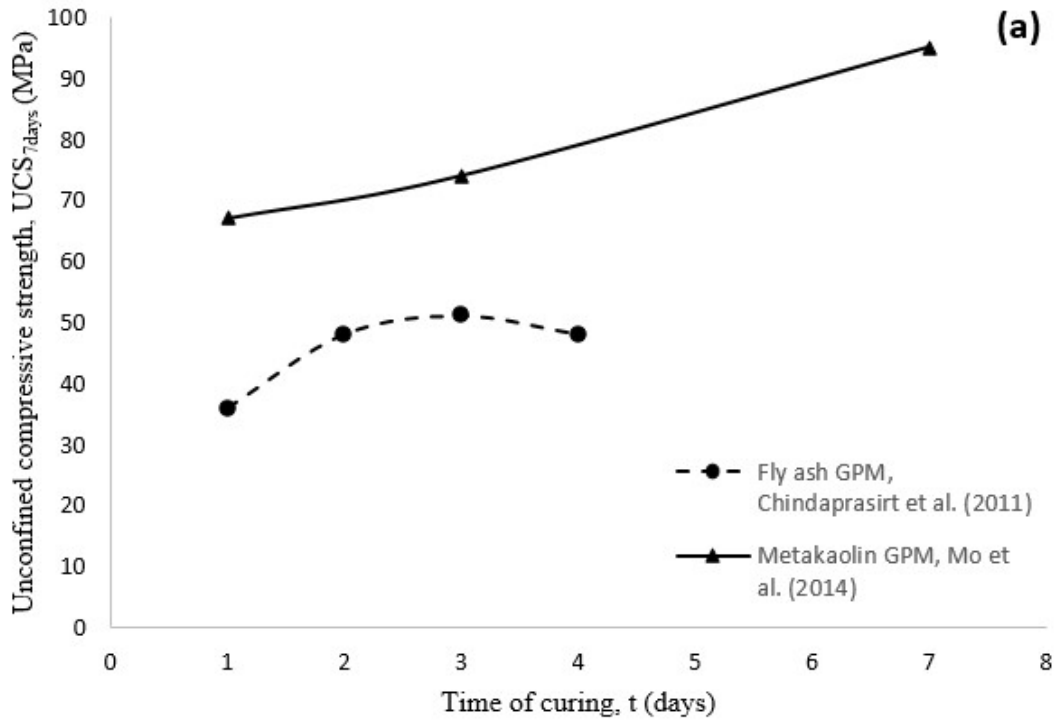
Fig. 14. Scanning electron microscope (SEM) images of geopolymer stabilized loess(after [117] reproduced with permission)

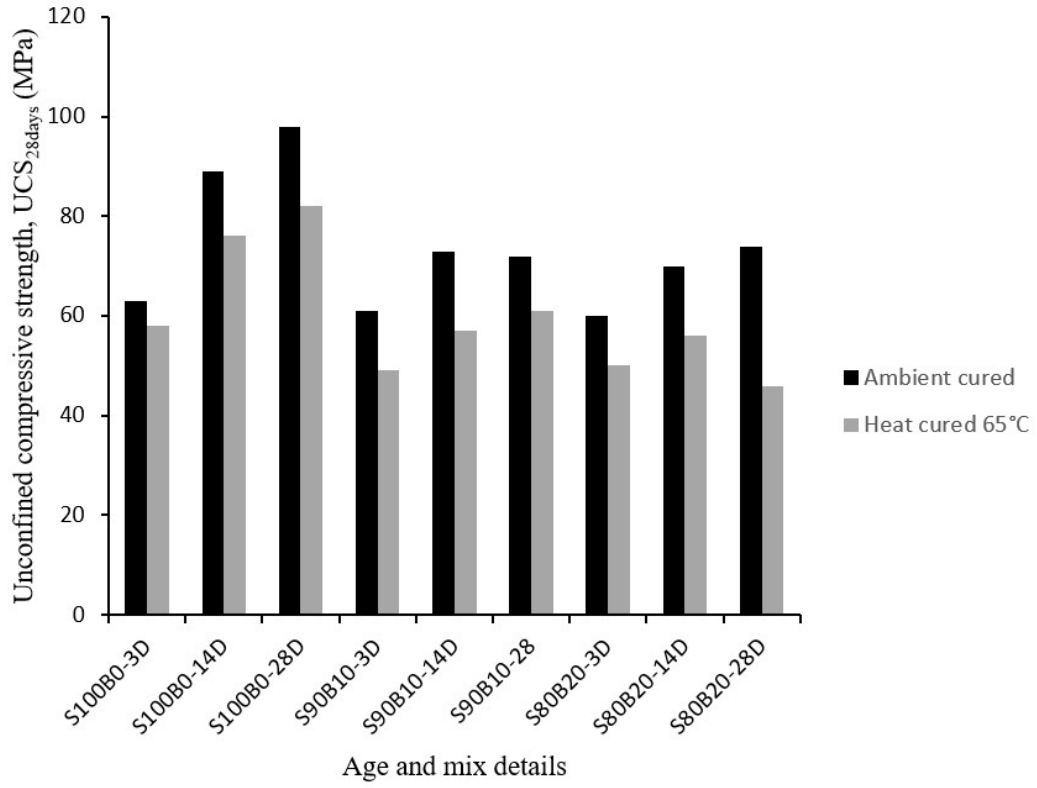
Fig. 15. Variation in unconfined compressive strength of geopolymer concrete w.r.t. slag content and solution ratios (data from [122]).

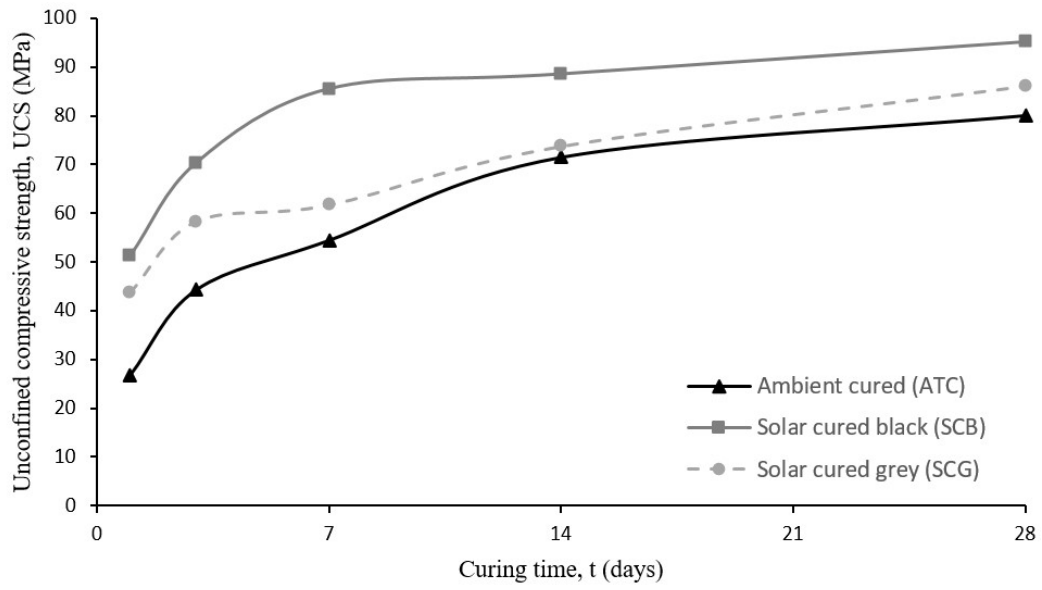
Fig. 16. Unconfined compressive strength variation of geopolymer concrete at different activator concentrations (data from [64]).

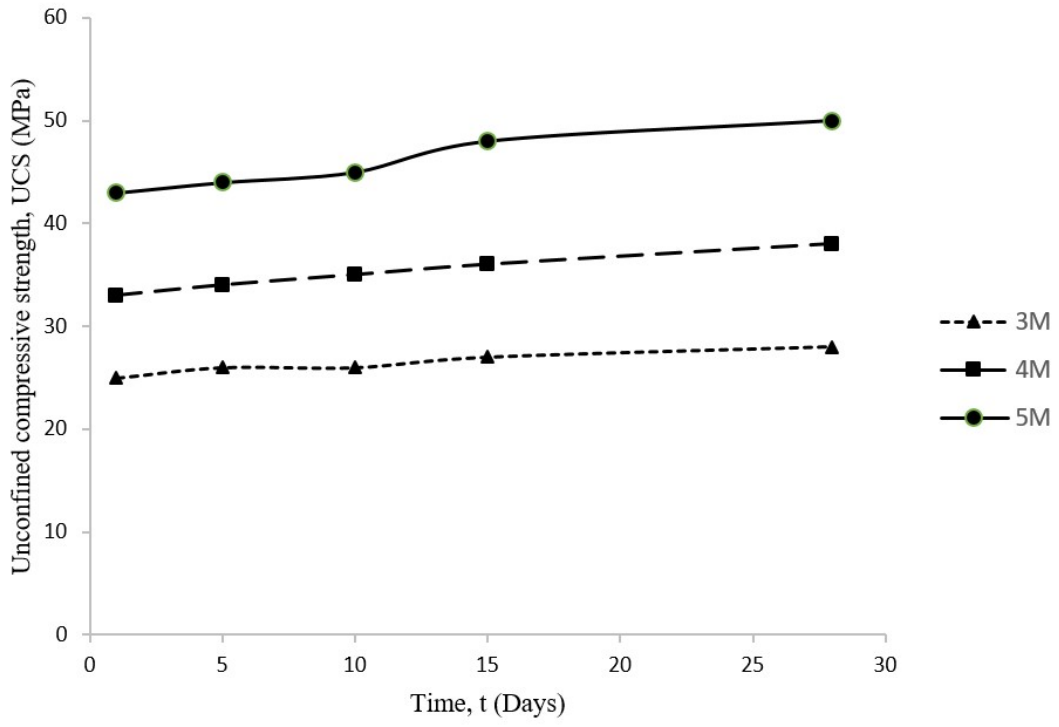
































		GPM-37.5	GPM-60	PCM-37.5	PCM-60
H ₂ SO ₄ concentration [mol/L]	0.10				
	0.31				
	0.52				
HCl concentration [mol/L]	0.10				
	0.31				
	0.52	