Indian Journal of Engineering & Materials Sciences
Vol. 28, October 2021, pp. 433-445

Review Article

Influence of industrial by-products on the behavior of geopolymer concrete for sustainable development

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Received: 15 January 2021; Accepted: 11 August 2021

Carbon dioxide emission in cement industries is a great concern for environment, which is increasing day by day. Therefore, it is very essential to find a possible material that can be used as a replacement of cement. Geopolymer concrete is a kind of inorganic concrete elucidating the formal usage of industrial and natural waste in either single or combined form. Geopolymers are amorphous covalently bonded by a 3D network of inorganic molecules of aluminosilicate material. The formation of geopolymer concrete is greatly influenced by several factors such as binder chemical reaction, curing temperature/period, molarity of the solution, and rate of polymerization. The curing temperature helps in deciding the properties of geopolymer. Performance variables for geopolymer concrete such as selection of alkaline binder with pozzolana (Fly ash, slag, silica fume etc.) and interrelationship of GPC, reinforcing agent in geopolymer concrete with components responsible for durability are summarized in detail. The durability of concrete is reviewed with structure with shrinkage-resistant, resistant to sulfate attack, and consequences of carbonation. The various consequences of corrosion are also summarized in last of present review paper. Different research findings in this paper proves successfully that geopolymer is better construction material as compare to cement-based concrete.

Keywords: Sustainable material, Alkaline binder, Durability, Shrinkage, Corrosion, Geopolymer concrete

1 Introduction

Cement is the backbone of the construction industry and, there is a high demand for all kinds of cement. The high demand by construction industries led to a drastic increase in the manufacturing/production of cement (i.e. Portland cement)[1]. The volume of cement-manufactured concrete is only second to the available volume of water on the planet[2]. In the case of cement-based normal concrete, Portland cement is used to bind the aggregates, emitting a reasonable amount of CO_2 gas during the manufacturing of concrete[3]. The emission of CO_2 imposes a serious environmental impact on the earth's climate[4]. It is well established that the consumption of cement is a continuous process and will increase in upcoming years[5]. Due to growing demand in residential, commercial, and transportation sectors, the rate of utilization of cement in various fields in India is increasing[6] and will reach up to approximately 550 million tonnes by 2050, as illustrated in Fig. 1[7]. Such a huge demand for cement promotes the excessive emission of CO_2 in the environment.

Figure 2 demonstrates the trend of carbon dioxide emission from the worldwide manufacturing units of cement production. It is clear from Fig. 2 that cement production from the 1990s played an important role in visualizing the overall estimation of greenhouse gases. Additionally, after the 1990s, the rate of emission is an important one in respective global carbon policies[8]. To overcome CO_2 emission problem, some researchers have tried to focus on cement-less concrete, which utilizes the waste materials along with perfect adhesive binder for properly holding the aggregates[9].

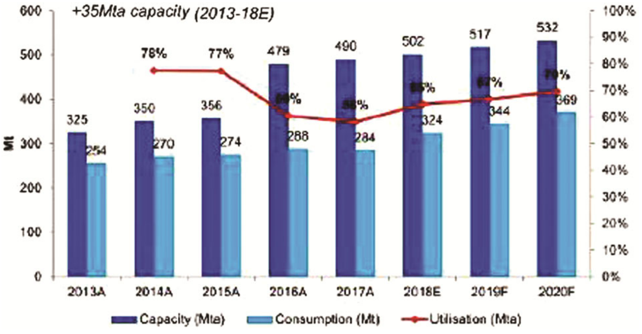

Fig. 1 — India's supply growth and demand for cement[6].

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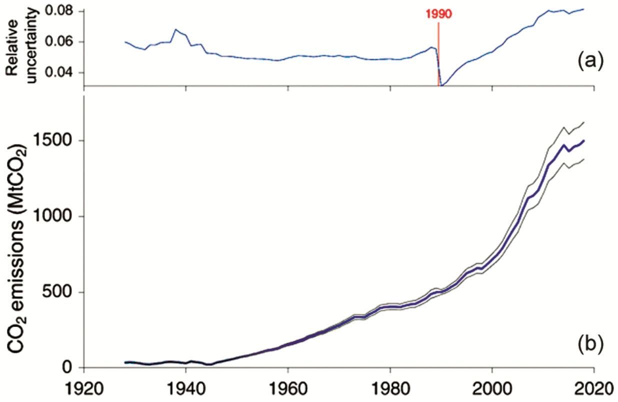

Fig. 2 — Global estimates of CO_2 production from cementing process units having 95% reliance level[8].

The utilized waste materials are in the form of supplementary cementing materials and are commonly known as SCM's[10]. These SCM's are industrial by-products or natural pozzolans. The natural pozzolans are derived from natural sources such as volcanic activities, volcanic tuffs, calcined clay (CC), calcined shale (CS), and metakaolin (MK)[11]. In some cases, by-products such as, silica fume (SF), fly ash (FA), rice husk ash (RHA), and ground granulated blast furnace slag (GGBFS) are used[12] which are derived during and after the operation of manufacturing entities. The solid inorganic product produced in the mining and metallic industry, energy production, chemical industry, or building industry has the ability for recycling and reuse is often referred as an industry by-product[13]. The inclusion of SCM's in concrete enhances the performance of concrete and reduces the dumping problem of these industrial wastes with a reduction of CO_2 emission the environment. Amritphale *et al.*[14] report the study on compressive strength which increases by the usage of biopolymer rice husk and revealed that the lesser nano-particle size of geopolymeric cementitious material helps in the densification of the geopolymer concrete.

In the same context, polymer concrete was introduced to reduce the CO_2 emission with rapid early strength, improved lower permeability, better resistance to physical and chemical attacks, and magnificent resistance to fire. In this polymer concrete, geopolymer is used to establish a chain reaction to lock the particles. The term geopolymer was first introduced in 1978 by Prof. Devidovits for the material, identified as a network of inorganic molecules[15]. With the advancement in scientific technology, the emergence/modifications in the present technology have gained popularity. Gupta *et at.*[16] prepared the advanced geopolymeric cementitious material which ensures the relative strength of the conventional concrete higher than 28.5%. Also, Mudgal *et al.*[17] prepared a ready-to-use geopolymer precursor that was formed with the additional chemical reactivity of geopolymeric binder. Besides this, brick based on the pozzolana containing the geopolymer binder is also the new emerging tool in the present scientific community[18].

Polymer concrete made of geopolymer has better durability in controlled environment and appropriate testing and proper quality assurance during casting, placing and curing periods[19]. Chindaprasirt and Chalee[20] reported that the ingress of chloride and coefficient of chloride diffusion decreased as the molarity of sodium hydroxide solution increased while dealing with the fly ash-based geopolymer concrete (FAGPC) during and after three-year exposure. Kupwade-Patil & Allouche[21] validated the results obtained by Chindaprasirt and Chalee[20] as there was a low level of chloride ions injection observed in fly ash-based geopolymer concrete specimens, implying the exhibition of the small number of chloride contents, porosity and very lesser footprints of corrosion in rebars.

Farhan *et al.*[22] performed the investigations of corrosive effects on the bond between fiber-reinforced geopolymer concrete (FRGPC) and reinforced steel bars, by providing the potential differences for accelerated corrosion on three types of steel fibers i.e. deformed macro steel fibers, hybrid steel fibers, and simply straight micro steel fiber embedded in reinforced geopolymer concrete, GPC. They reported that the inclusion of steel fibers greatly helped in increasing the bond strength of FRGPC. On the other hand, the strength of GPC is the key element that governs all featured characterization. Fernandez-Jimenez *et al.*[23] showed that higher compressive strength and the better reinforcing bond can be achieved with lesser shrinkage in FAGPC in considerably lesser time as compared with OPC concrete specimen. D. Bondar *et al.*[24] reported that the concrete made of alkali-activated natural pozzolans (AANP) and cured in a sealed environment with a higher water to binder ratio have a lower ratio of drying shrinkage which resulted in good strength acquisition due to long curing of the geopolymer concrete.

Thus, in the present review paper, an attempt has been made to compile the comprehensive knowledge of eco-friendly geopolymer concrete, various reaction

& application domains with unique properties. Targeted durable properties of the geopolymer concrete are also included in the present study based on and critical analysis using controlled variables and their consequences.

2 Materials and Methods

The details related to the materials used in the present work and the methods applied to compile the work are described in following sections.

2.1 Reaction mechanism in geopolymer concrete

Geopolymer concrete (GPC) is eco-friendly, synthetic concrete[25]. It is polymerized by fusion of inorganic alkaline activators and Si-Al material. Thus, a lower amount of CO_2 emission has lower environmental health issues by construction industry[26]. The alkaline activators (AA) used in making GPC are in the form of hydroxide and silicates of sodium and potassium (Na^+, K^+)[27]. They can be used as a single or combination of both. It is recommended to use both hydroxide and silicate of Na^+/ K^+ binder from either catagory; as a single use of either activator from both the category results in the in-effective holding of aggregates in proper manner and reaction rate will be slower leading to less heat of hydration, hence compromising on early-age strength[28].

Geopolymers are amorphous covalently bonded by a three-dimensional network of inorganic molecules of aluminosilicate material[29]. The reaction mechanism of geopolymer concrete can be expressed by empirical formula as follows in Eq 1.

$$\alpha_n\{-(SiO_2)_x - Al{-}O\}_n \cdot \beta H_2O \qquad \ldots (1)$$

where, α is the positively charged ions of sodium (Na^+) or potassium (K^+), X is 1, 2, 3 or maybe greater than three, *n* is the degree or rate of polymerization, and β is water content required for binding[30].

The alkaline activation of low calcium, alumina rich and silicates materials results in precipitations of predominant reactive products of an amorphous alkali aluminosilicate hydrate gel, commonly known as N-A-S-H gel. Besides, the secondary reactive compound formed are Na-chabazite, zeolite, zeolite P, zeolite Y, hydroxy sodalite and faujasite[31,32]. The presence of high calcium content and high pH causes the formation of C-A-S-H gel, rather than N-A-S-H. Hence, it can be concluded that the presence of calcium ions alters the formation of N-A-S-H gel, wherein a part of sodium is replaced by the calcium ions[33]. However, in the pure state of geopolymer, the silicate (Si^{4+}) and aluminate (Al^{3+}) cations are tetrahedrally coordinated and attached by the oxygen bond and generally, in the case of alkaline activation; sodium or potassium cations were attached to the alumina compounds (AlO_4^-) as shown in Fig. 3[34].

The process of polymerization is exothermic. However, this behavior can be seen by the polycondensation of a similar or different class of monomers. The chain reaction of polymerization can be visualized by chemical reaction given in Fig. 3.

The formation of geopolymer concrete is greatly influenced by several factors such as binder chemical reaction, curing temperature, curing period, the molarity of the solution, calcium content, and rate of polymerization[35]. However, the selection of the appropriate parameter depends upon the application area. Some guidelines have been established for the curing of geopolymer concrete to meet the desired strength and microstructural properties[36].

Generally, heat curing or oven curing is preferred to speed up the rate of polycondensation. Heat curing or oven curing ensures the high reactivity and early age strength of the concrete[38]. In such curing processes, samples are kept in an environment generally at a higher temperature than normal temperature to increase the reactivity and chemical reaction inside the concrete blocks. Thus, the alkaline activation process increases and reduces the ion mobilization, and therefore provides more energy to the reactant particles for reactions[39].

2.2 Synthesis, design derivatives and dependency of geopolymer concrete

The lesser output of CO_2 during the manufacturing and production phase is desirable from a sustainable environment protection point of view[8]. In this context, eco-friendly concrete can be considered as one of the advantageous ones. However, the preparation of geopolymer concrete involves systematically designed footsteps. These steps involve the acquisition of raw materials from plants in the form of natural or artificial pozzolans, known as supplementary cementing materials (SCM's). SCMs have either less or no cementing properties[40]. The selection of these raw

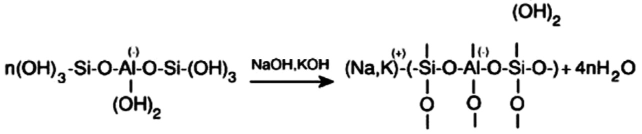

Fig. 3 — The chain reaction of polymerization for geopolymer concrete [37].

materials depends upon several factors. These factors maybe optimum cost, unique demand, accessibility of SCM's and appropriate method available for implementing these pozzolans in concrete preparation. Figure 4 demonstrates the stages related to the formation of geopolymer concrete from raw material to hardened geopolymer concrete. It also shows the various testing methods used to analyze the behavior of concrete under different environmental conditions.

Before mixing raw materials, the selection of an alkaline binder is very important. It is suggested that the use combination of the alkaline binder is most preferable. The dependent variables of better performance of this concrete are the selection of water to solid ratio, water to binder ratio, the molarity of preferred alkali solution, a ratio of SiO_2 to Na_2O by mass, and percentages of the corresponding Na_2O by SCM's[38].

The alkaline cementitious material possesses different proportions of lime, silica, and alumina content. The hybridizations of these constituents result in the formation of different gels[41]. In a study[42], the stages developed contain the formations of C-S-H gel and geopolymeric gel during the initial reaction period of MK and slag-based alkaline activation. However, the evolution of these different stages of formation heavily dependent on the MK/ slag ratio and alkalinity of these activators. The reactive products of this C-S-H gel together with geopolymeric gel originate in slightly low alkalinity.

2.3 Effect of curing conditions

The synchronization of units involves the mixing of all the resources in a planned manner. Temperature influences the performance of geopolymer concrete. Temperature increases inside and outside of the

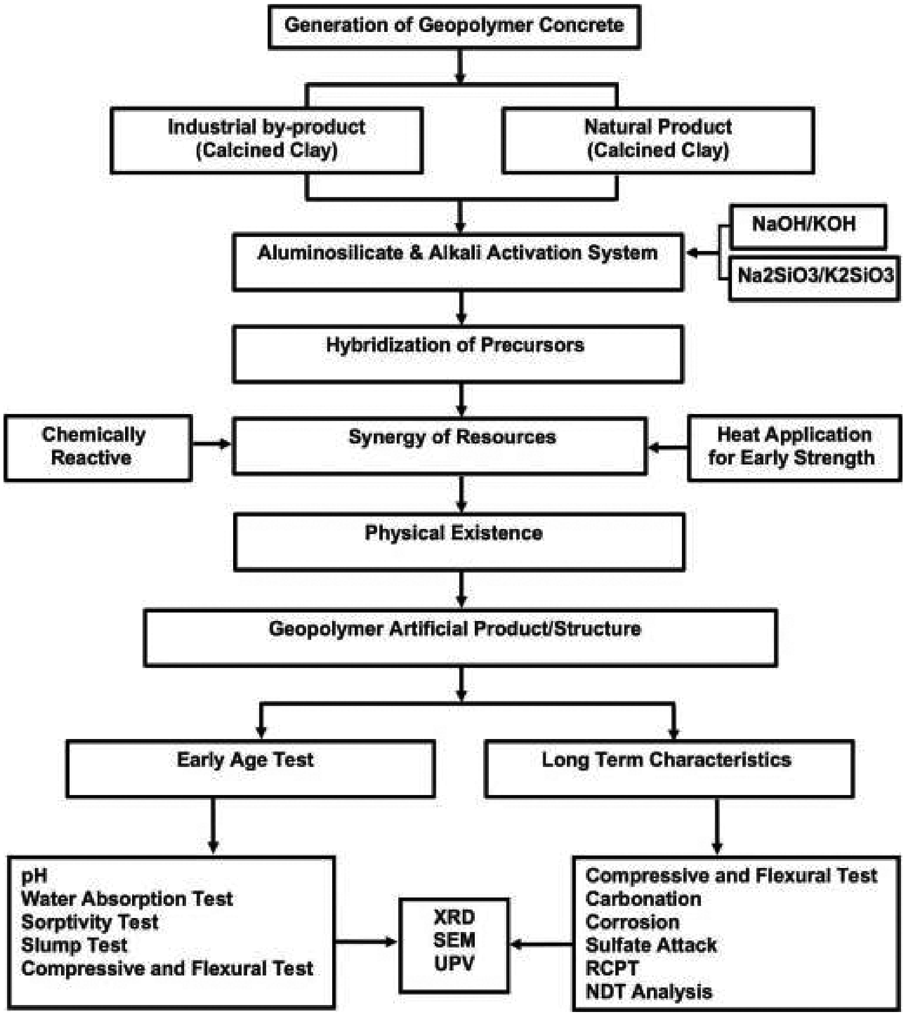

Fig. 4 — Schematic representation of interrelationship of geopolymer concrete from an early stage to later periods covering all the aspects of geopolymer concrete & test methods at desirable stretches.

concrete specimen should be properly ensured. This temperature can be provided by an oven or furnace. When all the precursors are hybridized well and placed properly, the application of heat should be properly ensured to increase the phase of the initial reaction. This reaction ensures the rate of gain of early strength. It is recommended that the ideal rate of temperature for polymerization ranges between 60^0C to 100^0C. However, the gain of strength without losing variables can be seen up to 200^0C. Above 600^0C, the specimen loses its strength more rapidly and beyond 800^0C, the loss of strength is very steep[43]. It is seen that a reduction of 65% in compressive strength beyond 800^0C was experimentally calculated which is much more than the assumed variation which relies on the test materials, the molarity of alkaline solution and fusion of activators with supplementary materials. Okoye *et al.*[44] prepared the geopolymer concrete using fly ash and kaolin admixtures. The samples were heat cured for temperatures of 80^0C, 100^0C and 120^0C. They revealed that the compressive strength increased with increasing the curing time, and curing temperature. Also, the partial substitution of fly ash with kaolin leads to the higher compressive strength in compared with ordinary concrete. In another study, Okoye *et al.*[45] reported that the increasing percentages of silica fume on fly ash-based geopolymer concrete (FAGPC) when cured for heat temperature of 100^0C also enhance the compressive, flexure, and tensile strength whereas workability of the geopolymer concrete gets reduced due to the compactness and denser core matrix of the concrete. Prabhu *et al.*[46] noticed in his study that the curing conditions affects the mechanical strength of the geopolymer concrete. They stated that geopolymer concrete under ambient curing condition having 90% fly ash and 10% GGBS along with steel fibers greatly improve the mechanical properties and provides the better synergy between different source materials. Subramanian & Elavenil[47] validate the findings of Prabhu *et al*. They also show that there is a direct relationship between curing condition and strength of the concrete. They revealed that the addition of slag in FAGPC up to 30%, reduces the workability of the GPC while simultaneously increases the strength of the concrete.

Sarker *et al.*[48] expand the temperature range of FAGPC up to 1000^0C. They showed in his study that geopolymer concrete can sustain the temperature variation up to 1000^0C without visible spalling of the surface showing better resistance to cracking and spalling as shown in Fig. 5, whereas the Portland cement concrete starts spalling from 800^0C. Figure 5 shows the change in colors of geopolymer concrete after heat application at different temperature ranges. The compressive strength of geopolymer concrete was comparable with normal OPC concrete. Nazari *et al.*[49] analyzed the behavior of FAGPC under alternate thermal shock reaction. The specimens were heated for 400^0C to 1000^0C. They showed that the behavior of geopolymer concrete display superior microstructure and mechanical properties during air and water cooling.

2.4 Selection of Alkaline binder with Pozzolans and interrelationship of GPC

Binder and pozzolans are inter-related to each other. Generally, the selection of pozzolans and

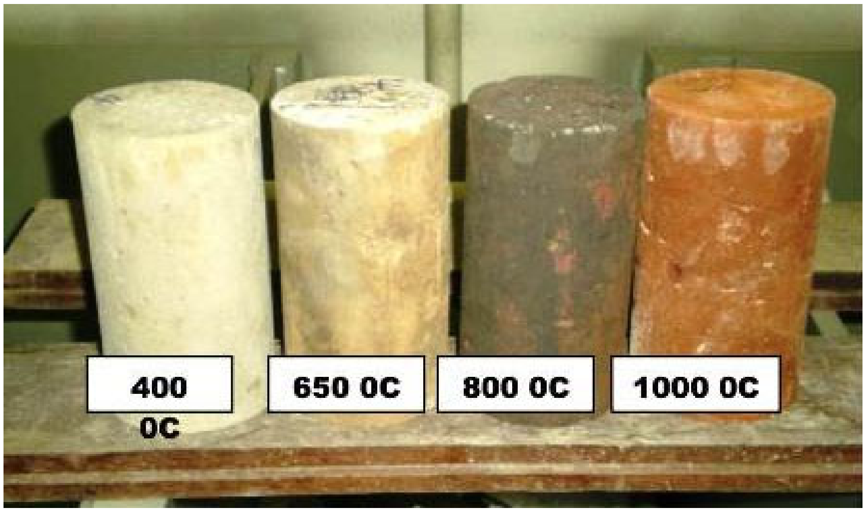

Fig. 5 — Appearance of geopolymer concrete after heat application at different temperature[48].

binder rests on the viscosity of the solution, the kinetics of pozzolana chargeable ions, the diffusivity of ions into the solution and the desirable strength & alkali or acid resistance. It was found that the pozzolans are truly dependent on the alkaline binders in the geopolymer concrete. Notably, metakaolin is the only pozzolana who uses potassium-based binders. The NaOH and Na_2SiO_3 are preferable over the KOH and K_2SiO_3 because the diffusion of sodium ions in the water is easier and its reactivity is higher as compared to the potassium ions[50].

2.5 Reinforcing agent in geopolymer concrete

Studies show that geopolymer concrete possesses significant some level of shrinkage when it is heated and cured above 200°C. This will own reducing a portion of mechanical strength and less water to reacting chemical compounds which causes concrete to behave like a brittle structural member[51]. This brittle nature of geopolymer concrete may be introduced by several factors such as curing conditions, curing regime, nature, and composition of alkaline binder, size and shape of the aggregate and also the thickness of the structural member. Hence, to overcome the brittle action of geopolymer concrete, several researchers are trying to improve the brittle action by transferring this to the ductile one by introducing the various fibers in the geopolymer concrete[52]. These fibers may be randomly or unidirectional oriented in the mixture, holding a certain fraction in the total volume of concrete[53].

Several fibers such as E- glass, basalt fiber, Kevlar fiber, woven fabrics, sisal fibers, mat fibers, cotton fiber, polypropylene steel fiber, high alumina fiber, polyvinyl alcohol (PVA) fiber, ultra-high molecular weight polyethylene fiber (PE fiber) and sometimes waste rubber tire fibers are used in geopolymer concrete. They may be inserted to limit the extent of cracking due to rising temperature and other conditions & to provide protection by developing the toughness of the system by restricting the macro and micro-cracks in the matrix system[54,55]. Several studies have been performed to demonstrate the extent of fiber inclusion by different researchers in controlling the macro and micro-cracks developed inside the geopolymer concrete. The fiber reinforced concrete is cured under different heat amount and test under the severe conditions for industrial and domestic usage.

Geopolymer concrete experiences brittle action and a considerable shrinkage and deformation however this shrinkage and deformation can be controlled by preparing a fiber-rich concrete matrix. Liand Xu[56] reported that the inclusion of basalt fiber into the geopolymer concrete matrix enhances the energy-absorbing characteristic (more absorption rate by 8.9% to 13.2% through 0.3% basalt fiber addition) and deformation rates, whereas no increment in compressive strength observed. The temperature and quantity of fibers affect the microstructure and strength of the concrete greatly. Tanyildizi and Yonar[57] reveal that the curing of FA-GPC including PVA at 60°C, has higher compressive and flexural strength. He also concluded that the increment in mechanical strength is dependent on fiber proportions in the geopolymer concrete. Bernal *et al.*[58] also demonstrated that the addition of fibers not only increases the capacity of geopolymer concrete but also increases the toughness properties. They reported that the fibers were capable of filling the pores or void spaces in the solution and making the concrete more rigid to be capable of resisting the ultimate load capacity and in sustaining the durability parameters. Alomayri *et al.*[52] proved from their study that fiber orientation plays a crucial role in the concrete matrix. They show that horizontally orientated fiber was capable of sustaining more ultimate loads and resistance to the deformation's resistance over the vertically placed fibers. From a durability point of view, Borhan[59] revealed that reaction with lime (CaO) with the basalt fiber in the presence of a rich percentage of glass content; can be beneficial in controlling the alkali-silica reaction (ASR).

The cracking pattern of the fiber matrix can be seen in Fig. 6. As shown in Fig. 6 (a and b), the width of crack formation is dissimilar, depending upon the type of fiber's nature and curing conditions. Fig. 6(a) demonstrates the uniform distribution of cracks of GPC cured at ambient temperature, whereas distinguished closed packed and irregular cracks can be visible in PVA-SHGC shown in Fig. 6(b). The population of fiber interface assists in maintaining the higher first crack-strength of PVA-SHGC cured at

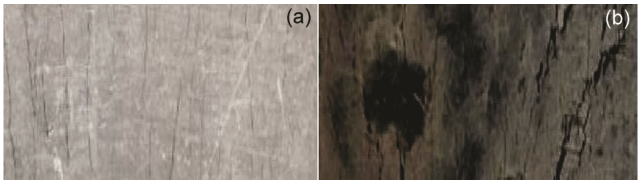

Fig. 6 — Cracks Pattern of (a) ambient temperature cured including Polyethylene- Strain hardening geopolymer composite (PE-SHGC) and (b) heat cured including Poly Vinyl Alcohol-Strain hardening geopolymer composite (PVA-SHGC)[54].

ambient temperature and responsible for the vigorous chemical bond in the polyvinyl alcohol fibers as shown in Fig. 6(b) whereas, the ultimate strength of the PVA fibers is dependent upon slip hardening coefficient and frictional bond strength[60,61].

Yunsheng *et al.*[62] confirms that slag at 50% (by mass) in geopolymer concrete, steam cured has superior mechanical performance and shows effective immobilization of copper and lead-heavy metal ions. The size and shape of fibers also play an important role in understanding the behavior of concrete[63]. Short fibers can increase the percentages of durable properties, whereas long narrow fibers may retard the same. Short fibers of PVA on FAGPC as on increasing percentages fractions, improves the failure mode from brittle action to the ductile one & superior stiffness with closely packed molecules. Such concretes are excellent to oppose acid attack[64]. Mucsi *et al.*[53] check the possibilities of incorporation of rubber along with steel fibers in FAGPC with the size of rubber tires < 4 mm to >8mm, having 12 M NaOH & Na-K glass water. Although, it is evident that the addition of fiber improves the strength but incorporation of tire waste into GPC results in lower strength. The waste tire rubber was not only fiber which was used to study the brittle and durable behavior under extreme conditions. The use of high tenacity carbon, PVCA, E-glass, and PVC were also incorporated in MK-GPC to analyze the nature of catastrophic failure[65]. Moreover, the use of carbon fiber, and PVC had excellent energy adsorption capacity and the addition of micro steel was as efficient in making the bond between GPC & steel fibers, and in reducing shrinkage & increasing mechanical strength.

Hence, the incorporation of various fibers is widely utilized in controlling the properties. These properties are ultimately attributed to the service life of the structures. The durability of such structures made from fiber reinforced concrete is perfectly comparable with ordinary Portland concrete in many ways.

3 Results and Discussion

3.1 Durability of geopolymer concrete

Historic monuments are capable of surviving from thousands of years due to unique material characterization. Ancient concrete which is cementing material, gain greater resistance by chemical and mechanical strikes at a millennial lifespan of the structures[66]. Such a classic technique was firstly utilized by Greek and later on by Romans. These techniques were widely applied to hydraulic systems, walls, floor, and pipes or cisterns using a single or multi-layer of lime mortar; thickness ranging from 1 cm to 3 cm and sometimes up to 6 cm. The high density, high compressive strength, excellent a impermeability and durability were the characteristic of the mortar made from lime and pozzolana, marble powder for fillers, natural fine aggregates and volcanic ashes[67]. Romans were capable of producing the extreme durable concrete characteristic in which the pozzolanic reactions takes place in between hydrated lime and volcanic glass which producing the C-A-S-H gel responsible for binding the aggregate particle in a respective manner however improved resilience through the formation of Al-tobermorite gel and creation of new products in micro-cracks creating more packed and stable bonding between the mortar matrix[68].

For durability and sustainability point of view, Roman systems for concrete modal can substantially be used for bringing down the emission of GHG's gases into the atmosphere[66]. However, the practice of roman techniques is obsolete now days. In past decades, the use of cement-based structures was popular due to easiness in handling and quick application of cement-based structure. The disadvantages of this traditional operation are the environmental pollution through continuous production of cement and its concrete structures. The structures made from cement concrete are not efficient after longer period. Several defects such as reduced mechanical strength, visible efflorescence, cracks, lesser resistant to corrosion and not able to withstand at higher temperatures. Hence, there is a current need to introducing a new innovative system that produces the structures which are more serviceable and benefit to the society. Some of features that required by geopolymer concrete is discussed in following sub-sections.

3.2 Structure with shrinkage resistant

Geopolymers are capable of sustaining the high temperature which is substantially utilized in manufacturing the ceramics like structures. The increase in temperature may raise the problems to the microstructure cracks and can affect the setting times. Deventer *et al.*[40] reported that a low content of calcium preferably lime promotes the higher setting time and consecutively later strength development[69]. Aslani and Asif revealed that the fly ash-based geopolymer concrete can undergo strength development cured up to 600^{o}C, in which samples may show micro-cracks on the surface, but they exhibit compressive strength in a good manner. Moreover, Rao *et al.*[43] reported a considerable rise in compressive strength can be observed up to 200^{o}C and as the temperature increases, the drop in strength, as well as loss of weights, also took place; as increasing the temperature leads to the evaporation of pore water.

In determining the performance of the geopolymer concrete (GPC), the temperature is not only the key function that controls the other parameters but the size of aggregates and incompatibility of the temperature gradient between the core matrix and surface profile also affects the behavior of GPC. Kong and Sanjayan[70] proved that the lesser size of aggregate (<10 mm) are more responsible for cracking and spalling of the GPC, while larger particle (>10 mm) are relevant to the high temperature, beyond 600^{o}C or more. The discoloration of GPC can be seen due to the transfer of iron ion[49]. The performance of the geopolymer concrete with supplementary cementitious materials like fly ash, slag, metakaolin, and calcined clays have a good impact in controlling the shrinkage properties. However, the fly ash-based geopolymer concrete has superior resistance to creep and shrinkage actions[71].

3.3 Resistant to sulfate attack

Sulfate attack is the most common phenomenon in sulfate-rich environments from the soil, transport fluid, seawater, groundwater, sewage wastewater and chemical industries[72]. In general, sulfate attack is the interaction between the composites of concrete and the sulfate ions which form an expensive new product[73]. The rise of this new product resulting in loss of strength due to low alkalinity with greater permeability, cracks in the pore structure i.e., micro-cracks, expansions and loss of integrity of the structure. Several attempts have been recognized for overcoming to the sulfate attack, in which it can be possible to negotiate the sulfate attack by applying some particular SCM's like slag and the use of slag-based cement. Ozcan and Karakoç revealed that ferrochrome slag (EFS) is more capable of resisting the deterioration of concrete and improve the overall strength of geopolymer concrete over the slag (BFS) based geopolymer concrete. On the other hand, the addition of nano-silica improves the mechanical strength and increases the life span of the fly ash-based geopolymer concrete under severe sulfate environment by reducing the porosity and permeability of the specimen[74]. Guo *et al.*[75] use the mixture of fibers (mineral and organic fibers) to prevent the cracks due to sulfates. They observed that the combination of fibers was much capable of reducing the crack formation and yield the highest strength as obtained from the normal preparation. They were also concluded that the crack formation of the specimen was dependent on the intensity or severity of the sulfate ions with relative environment exposures. Rajamane *et al.*[76] enumerate in their study that geopolymer concrete is more prone to acid resistance than the Portland cement concrete. According to them, the resistance of GPC was extremely higher from both kind of cement i.e., Ordinary Portland cement and Portland Pozzolana Cement when the sample taken into consideration for 90 days curing.

Figure 7 shows the SEM-EDX images for alkali-aggregate slag mortar specimen cured at temperatures of 23^{0}C, 35^{0}C, and 80^{0}C for initial 24 hours and thereafter, for one year in the relative environment[77]. The analysis reveals that there is a formation of cracks due to the shrinkage and also has the partial hydration of the particles for all the groups i.e. a, b and c in Fig. 7[78]. The presence of hydration elements viz Ca, Si, Al, Mg, and Na were also observed in the EDX analysis. These elements were a major contributor to the formation of hydrotalcite (HT) and C-A-S-H gel formation[79]. Overall, the alkali-activated slag matrix system is much capable of resisting the sulfate attack depending upon the attraction forces of ions[80].

3.4 Consequences of carbonation

In the modern era, carbonation is a major threat to the health of concrete framework due to the deterioration of reinforced steel bars to a great extent, resulting in compromising the structure strength and loss of lives and money[81]. Carbonation is the reaction of the atmospheric carbon dioxide with the calcium hydroxide in the presence of moisture in the concrete specimen. The diffusion of CO_2 with the calcium hydroxide generates the calcium carbonate. Hence conversion of this process imparts fewer carbonate molecules of calcium which ultimately diminish the pH concentration of concrete thereby resulting in more voids in the sample, increasing the concrete porosity[82]. This creation of pores in the concrete specimen is a result of a low pH below 9 or low alkalinity of the pore system[83]. The lowering of alkalinity or pH in the pore system leads to the

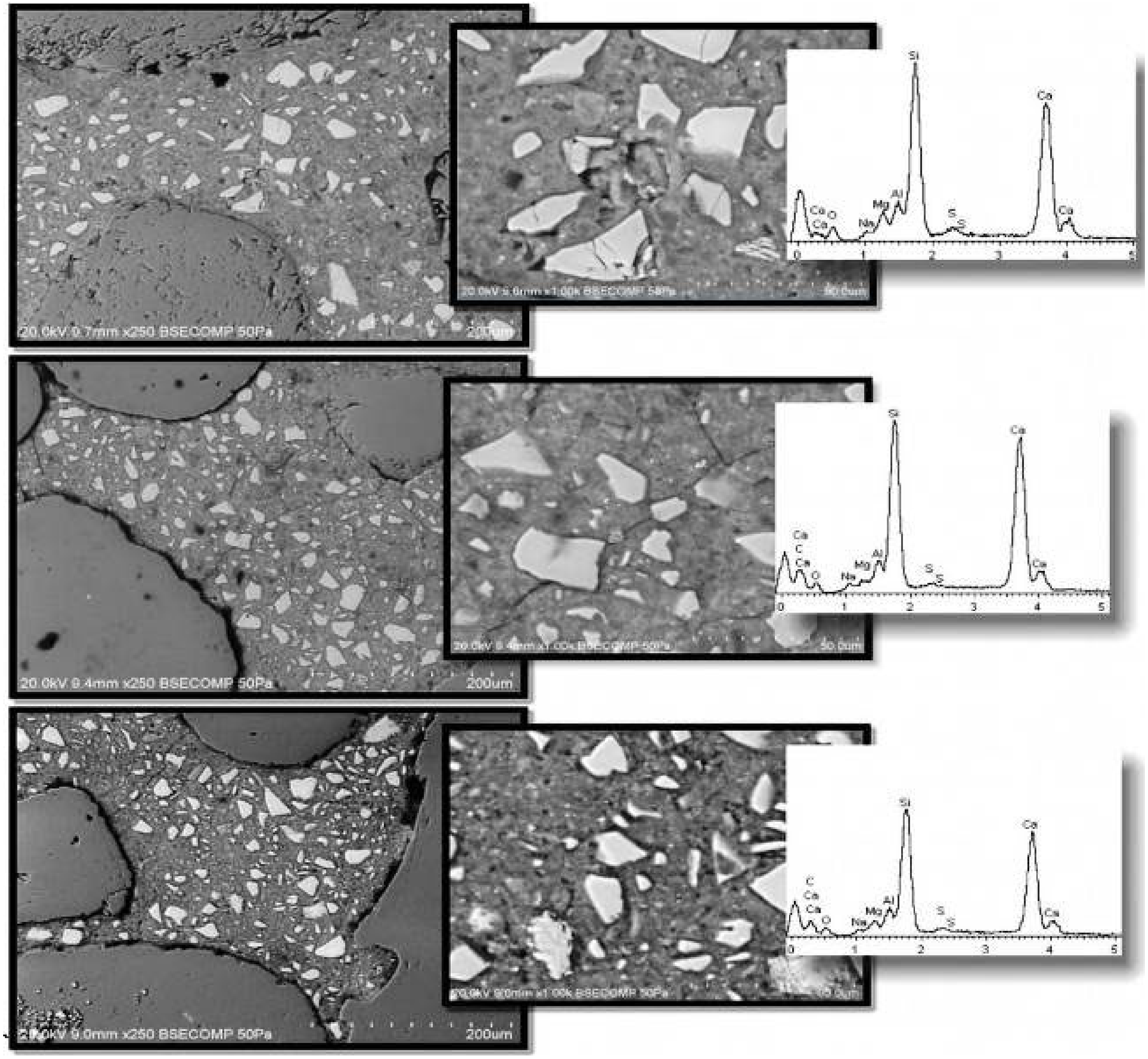

Fig. 7 — SEM-EDX images for alkali aggregate slag (AAS) mortar bars exposed to 5% of sulfate concentration after 1 year of exposition. Curing temperature during the initial 24 hours: (a) 23 ^{0}C; (b) 35^{0}C; (c) 80^{0}C[77].

deterioration of activating passive surface layer of gamma iron hydroxide of reinforcing bars resulting in the corrosion of reinforcing bars[84]. The diffusive reaction can be seen in Eq. 1 and 2.

$$CO_2\,(g) + H_2O(l) \rightarrow H_2CO_3 \qquad \ldots (2)$$

$$H_2CO_3 + Ca(OH)_2(s) \rightarrow CaCO_3(s) + 2H_2O(l) \qquad \ldots (3)$$

Generally, the phenolphthalein indicator is used for examining the extent of carbonation depth. This indicator when sprayed over the concrete specimen, if turns into purple color showing non-carbonated specimen while colorless surfaces indicating a carbonated portion of concrete specimen. Figure 8 indicates the level of carbonation in geopolymer and OPC concrete; in which geopolymer concrete experience the three modes in carbonation depths as a partially carbonated, fully carbonated and non-

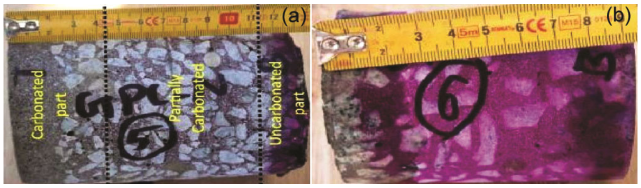

Fig. 8 — Measurement of carbonation of concrete specimen using phenolphthalein indicator (a) Geopolymer Concrete (GPC) & (b) Ordinary Portland Cement (OPC) Concrete[99].

carbonated portion of the concrete. Carbonation can be access by preparing an experimental set up for a natural and controlled accelerated carbonation chamber. Khan *et al.*[84] reported that 1% accelerated carbonation of 6 weeks geopolymer concrete (GPC) was the duplication and or indication of natural carbonation of 18 weeks GPC. They also reveal that the early pH of non-carbonated class F fly ash was lower than the non-carbonated concrete made up of Portland cement (OPC). Lange *et al.*[85] maintained the relative humidity (RH) of 50% for natural and accelerated carbonation with the use of commercial waste having heavy metals in Portland concrete; concluded that the addition of metals to the concrete was beneficial for structural properties as the inclusion of metals solidified the system. C-S-H product was changing as a result of ion mobilization capacity of gel & also portlandite was resulting in filling the pores through the chemical reaction with carbon dioxide.

The degree of carbonation is greatly influenced by the humid environment, alternate wetting or drying cycles, temperature of climate and the exposure conditions. They play an important role in determining the depth of carbonation[86]. However, it becomes easier to access the carbonation depth by mathematical modeling given by Eq. 3.

$$D = D_0 + \lambda(T)^{0.5} \quad \ldots (4)$$

where, D is the carbonation depth (mm), D_0 is the initial carbonation depth (mm), λ is the carbonation rate (mm/year$^{0.5}$) and T is the period (year)[87].

Cyr *et al.*[88] reported that the meta-kaolin based geopolymer concrete has no issues with the carbonation irrespective of higher temperature and CO_2 rate, since the pH profile of the solution was above the range of steel corrosion after 365 days. He also stated that the change of carbonates (natron) to bicarbonates during the accelerating phase leading to the improper reaction other than the representative of natural carbonation. While, Bernal *et al.*[89] showed that the alterations in natron or trona were resulting in the development of bicarbonates, causing a significant reduction in pH followed by carbonation and corrosion. Figure 8 (a & b) demonstrate the different carbonation zones of cor sample from parent GPC sample identified by the phenolphthalein indicator.

Hence, carbonation creates the problem for reinforcing concrete. To overcome this phenomenon, various strategies are widely applied to the concrete matrix which covers the avoidance of micro-cracks by filling or repairing by the epoxy or grouting, maintaining the lower water to binder ratio, providing additional concrete surface cover, additional surface polishing, lowering the permeation of salt/ ions and increasing the pH or alkalinity of the concrete solution.

3.5 Consequences of corrosion

Corrosion is generally considered a notable problem for the durability of the reinforcing structures[91]. When a structure is subjected to the corrosion issue, it will be dangerous to the health of the reinforcing concrete structures, resulting in huge cost investment for the restoration of such structures. Moreover, corrosion is the consequence of carbonation, low pH, and or low alkalinity of the pore solutions[84] According to the World Corrosion Organization (WCO), the improper design and selection of metals, and underestimates of weather or environmental conditions; could lead to health and safety problems for the bridges, buildings or steel structures resulting in an undesirable investment of approx. US 2.5 trillion dollars annually[92]. Corrosion is the natural process of gradual degradation of the metals chemically reacting with the surrounding environment, converting it into hydroxides, oxides, or sulfides forms through an electrochemical process. Environmental condition for the existing structure plays a crucial role in determining the rate of corrosion. Reddy *et al.*[93] reported that the structures are more susceptible to the corrosion which is built near the seashores, which comes in direct contact with chemical reactions (through the atmosphere and humid climate) causing ionic attacks, salts crystallization, and precipitation of insoluble complex. Karthik *et al.*[94] also show the impact of existing surrounding conditions on the behavior of the concrete.

Corrosion can be visualized by the ingress of CO_2 or through the active participation of chloride ions[95]. Both kinds assure the loss of steel area, loosing of the structural interfacial bond between steel and concrete, drop-in concrete cover and deprivation of strength of the structure[96]. Otieno *et al.*[97] predict that the corrosion rate relies on the concrete quality, concrete cover, and crack width however this corrosion rate can be effectively reduced by adopting SCM's (50% slag and 30% FA) in the concrete. Patil and Allouche[21] reported that the fly ash (Class F) based geopolymer concrete (FAGPC) exhibit better resistance to the chloride diffusion and possible corrosion. Moreover, a more realistic approach should be studied accordingly to validate the surface characterization properties.

Guzman and Gazman[96] revealed in his finite element modeling of the structures which are exposed under natural conditions, experience 30-50% less cracked pressure in the center of rebar and more in corner bars. However, there are great chances of high carbonation, higher chloride penetration, and higher admittance of sulfate ions in the saline environment which contaminate the reinforcing structure by generating steel corrosion and scaling (ingress of sulfates) of the geopolymer concrete[98]. There are many methods available for predicting the rate and nature of corrosion viz. polarization resistance, corrosion current density, corrosion potential, tafel constants, etc. however the results of these tests maybe better certify by the gravimetric mass loss measurement[99]. An analytical approach can be utilized to find out the diffusion coefficient (m^2/s) as given in the Eq. 4

$$C(x,t) = Cs - (Cs - Ci).\,\text{erf}\,(\frac{x}{\sqrt{4.Di.t}}) \qquad \dots (5)$$

where, C_i = initial chloride-ion concentration of the cementitious mixture before submersion in the exposure solution (in mass %); C(x, t) = chloride concentration, measured at depth x and the interface between the exposure liquid and the test specimen, determined by regression analysis (in mass %); x = depth below the exposed surface (in meter); erf = error function and t = time of exposure (in seconds)[21].

4 Conclusion

This review paper covers the widespread behavior of geopolymer concrete in terms of some properties and durability. It is investigated that proper adaptation of geopolymer concrete greatly depends upon the number of factors such as curing temperature, alkaline binder, and the respective water to binder ratio, etc. However, this material's performance will be attributed to the service life of the structure. Geopolymer concrete can be used freely in arid areas and the summer season. Some of the findings from the above review are mentioned as follows:

- As compared to cement concrete, geopolymer concrete reduces CO_2 emission which is a main contributor for global warming.
- The varieties of admixture such as naphthalene sulfonate, citric acid, bio-based superplasticizer, etc. assist in enhancing the mechanical as well as microstructural properties. The optimum dosage of alkaline activator, mineral, and liquid admixture, can be fruitful in reducing the impact of undesirable practical problems.
- Geopolymer concrete can sustain temperature up to 1000^0C without showing major cracks as compared with OPC concrete. Moreover, the optimum temperature range for obtaining satisfactory strength lies between 60^0C to 200^0C. Beyond this, GPC starts losing its strength gradually.
- An improvement over deflection, cracks, lower permeability, and brittle action of geopolymer concrete can be achieved by reinforcing the matrix with available fiber ingredients of appropriate size and shape by transforming the brittle action to the ductile one.
- Finite modeling of reinforcing structures with various natural conditions in preventing sulfate attacks, and growth of corrosion in geopolymer concrete could be a beneficial tool before investing a huge amount in building structures exposed to marine, and sea shores.
- This review paper shows that geopolymer concrete as compared to cement concrete owns better engineering properties. Therefore, it may be used as a structural concrete as a replacement of traditional concrete.

Acknowledgement

The authors are thankful to the management of GLA University, Mathura, INDIA, for their support.

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