

Review

Fire Resistance Behaviour of Geopolymer Concrete: An Overview

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Abstract: Even though, an innovative inorganic family of geopolymer concretes are eye-catching potential building materials, it is quite essential to comprehend the fire and thermal resistance of these structural materials at a very high temperature and also when experiencing fire with a view to make certain not only the safety and security of lives and properties but also to establish them as more sustainable edifice materials for future. The experimental and field observations of degree of cracking, spalling and loss of strength within the geopolymer concretes subsequent to exposure at elevated temperature and incidences of occurrences of disastrous fires extend an indication of their resistance against such severely catastrophic conditions. The impact of heat and fire on mechanical attributes viz., mechanical-compressive strength, flexural behavior, elastic modulus; durability—thermal shrinkage; chemical stability; the impact of thermal creep on compressive strength; and microstructure properties—XRD, FTIR, NMR, SEM as well as physico-chemical modifications of geopolymer composites subsequent to their exposures at elevated temperatures is reviewed in depth. The present scientific state-of-the-art review manuscript aimed to assess the fire and thermal resistance of geopolymer concrete along with its thermo-chemistry at a towering temperature in order to introduce this novel, most modern, user and eco-benign construction materials as potentially promising, sustainable, durable, thermal and fire-resistant building materials promoting their optimal and apposite applications for construction and infrastructure industries.



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1. Introduction

Conditio sine qua non, the energy-saving, preservation of environments, mitigation of emissions of Green House Gases (GHG) or relief to earth-heating, conservation of confined natural resources, waste disposal and its recycling, as well as energy-producing through innovative sources, etc. have been increasingly turned out to be the global concerns for the sustainable development of our existing planet—the earth. These are the core reasons why world researchers are attracted by ground-breaking geopolymer technology and working more and more concentrations and interest on geopolymer composites considering them most promising to address above referred dilemmas.

“Geopolymers” are component of the existing and prospect toolkit of “sustainable cementitious binder systems” [1,2], that can be synthesized from an extensive range of precursors rich in alumina and silica, with diverse accessibility, reactivity, and of course, cost-effectiveness across the planet. Quite recently, they have aroused as a most modern binder with ecologically sustainability attributes [2,3]. Their ceramic-like characteristics established them as thermal and fire-resistant materials [4,5]. The production process i.e., geopolymerization interestingly displays low carbon footprints and lower energy ingesting which is roughly 60% lesser than the present OPC-production [5–12], as well as the reaction kinetics requires low-temperature conditions at just atmospheric pressure. Not only have that, nine times less CO₂ emissions helps to relief the great dilemma of global warming as compared to existing OPC producing clinker’s emissions [4,13–18]. The process is based

upon polymer kinetics of reaction from one or several precursors, including low and high calcium fly ash, metakaolin, fly-ash and blast furnace slag and a mix of both, bottom ash incinerated etc. The process is accompanied by a mixture of various materials and activators of alkaline nature resulting ultimately in an earthenware resembling inorganic structure [7–30]. Of which, heat-cured, geopolymer concrete based on Metakaolin and low calcium fly ash is believed to be a model edifice material. Precast geopolymeric concrete structures viz., columns, beams, walls, slabs, etc. can also be manufactured successfully with these materials. In the context of Metakaolin, the thermal dihydroxylation process of kaolin enhances its solubility in alkaline medium proving it as an outstanding precursor for yielding inorganic geopolymers through geopolymerization.

Interestingly, they can be generated by incorporating a variety of profuse wastes otherwise filling land spaces and thus, creating health hazards, pollutions of environments, soils, surface and ground waters. That is why; world researchers are focusing on this new-fangled Geopolymer technique more and more. Consequently, geopolymer composites are novel, well-liked, versatile, one-size-fits-all solution and multitalented to meet future structural materials necessities and hopefully capable enough to establish themselves as a future alternative of OPC-system. What is more to add, these most modern construction materials are significant owing to its environmental benevolence and outstanding mechanical, durability and thermal properties as well as excellent resistance to fire and severely adverse freeze-thaw conditions.

Looking to history, in late 1978, the word “Geopolymer” was firstly coined by a French prof. Joseph Davidovit for three-dimensional amorphous alumina-silicates [4]. Usually, they are produced through the geopolymerization reaction kinetics among aluminate and silicate embodying precursor and suitable alkali activator at low temperature in an alkaline medium. The dissolution of aluminosilicates in the company of an alkaline silicate activator takes place which is regulated by poly-condensation and polymerization reactions whereby the setting time ranges from one to forty-eight hours, thus, they are condensed polymers based upon silicate and aluminate entities. Initially, the resultant structures were categorized by prof. Davidovit [4] as being sialates, sialate-siloxo, and sialate-disiloxo. These materials are mixes that can consolidate even at room temperature. In aftermath of catastrophic fire incidences in different parts of the world, a new concern cropped up in front of concrete technologists to search for more competent fire and thermal resistant construction materials. This is the root cause of their being magnetized towards geopolymers since they do not experience decomposition of the binder phase as found in the case of OPC-system at towering temperature exposure proving their chemical stability. Strength endurance of construction composites at higher temperature exposure is of meticulous significance for structures. Reinforced concrete (RC) structures might be the victims of fire during their service life. It is a universal fact that molecular structures are steady up to firm definite temperatures only. This steadiness may get affected while conditions of temperature fluctuate. The level of temperature is the deep-seated parameter supported by exposure time and heating rates to influence the molecular structure; therefore, it is answerable for the deterioration of concretes. The mechanical characteristics and rigidity of concrete mitigate drastically resulting in a strength loss of concrete at very high temperatures because of modifications of physical and chemical nature [31,32]. These molecular changes accompanied by micro-structural stresses lead to a loss in terms of mechanical properties like compressive strength of the material. Additionally, the spalling of OPC-concrete take place in the incidents of disastrous fires causing a swift layered loss in a context of the cover of concrete, prospectively piloting to the exposure of the core reinforcements inside the concrete to elevated temperature owing to cataclysmic fires [31].

The referred decline in the strength is accompanied through the $\text{Ca}(\text{OH})_2$ -dihydroxylation ranging from 400–500 °C as well as occurs incessant Calcium-Silica-Hydrate (C-S-H)—dehydration at 105 °C in cement concrete matrix of OPC-concrete. The differentiation in the context of thermal expansion or contraction amongst the aggregates and the binder matrix of cement paste of OPC-concrete causes stresses at the interface which is accountable

for momentous crack development that contributes to the diminution in the stiffness and mechanical strengths of concrete. Moreover, the thermal gradient of OPC-concrete contributes to its pitiable performance at very high temperatures. Endeavors have, accordingly, been made to search for alternative building materials with great fire and thermal resistance at elevated temperature both in terms of losses in strength and resistance to the spalling crisis too. Auspiciously, the inorganic framework of geopolymers is inherently fire-resistant having exceptional thermal stability with an only slight degradation of gel structure up to 700–800 °C. [33]. This can be regarded as the most noteworthy benefit of geopolymers over OPC-based composites since the latter one deteriorates because of the dehydration of content of hydrates. Geopolymers had proved themselves largely stable chemically when underwent exposure to elevated temperature [33–37].

Although, numerous investigations have been conducted on the studies of durability and mechanical characteristics of geopolymer especially considering the influence of very high temperatures, they mostly carried upon dissimilar geopolymers synthesized with diverse kinds of precursors and activators. For illustration, the combinations used were of fly ash and Na-activators, or fly ash and sodium plus potassium activators, or fly ash together with slag and Na-activator, or metakaolin and mixed Na plus K containing activators, etc [38–45]. However, the class F type fly ash is giftedly abundant in alumina as well as silica having the inferior quantity of low oxide of calcium permits its superior stability at a lofty temperature in the cases of fire than others amongst all the above-referred precursors. Not merely have that, it is cost-effective with ease of access as compared to other raw materials. It was revealed that geopolymers based on fly ash underwent little damage, on comparing to their metakaolin counterparts, because of containing huge quantities of interconnected pores that permitted moisture to flee on elevated temperature exposure [44]. In the event of geopolymers based on metakaolin, thermal shrinkage, as well as phase stability with high ceiling temperatures are affected in the choice of the alkaline cation either Na, K or a combination of both for geopolymer mixture [33,35]. The referred inorganic nature indicates its utilization in thermal applications like fire-resistant products [46–48]. This fire-resistant potential of geopolymers is the key property of geopolymeric composites particularly of fly ash based is highly significant. The research have been conducted to develop geopolymeric materials as a heat resistant [4,34,37,49–53], cement and concrete, escorting to facilitate their applications as fire-proof panels, refractory materials for lower temperature [54], tooling for the foundries, as thermal insulators [46,55–63], thermal energy storing GPCs, as in airplanes as well as ships [47,64], etc. Commonly, gradual heating levels and prolonged periods at temperature are imposed on the refractory products, whilst fire resistance is intended to experience rapid initial temperature acceleration for a relatively short time. The applications of geopolymer concrete as fire-resistant building material necessitate examining its thermal performances at a micro, i.e., micro-structural or chemical stability, resistance to deformation, as well as strength and spalling resistance of the material when exposed to an elevated temperature. Subsequent to fire broke out, the cooling cycle must essentially be quick on account of vast amounts of water trying to extinguish it or a sluggish reduce if the fire is permitted to put out owing to fuel exhaustion. Since the geopolymers possess enhanced pore volume connectivity in comparison with OPC, they remarkably boost the transportation of water from the binder with accompanied mitigated spalling through higher temperature exposure [42,44]. Generally speaking, the diverse geopolymer concretes synthesized with various source materials and activators are exhibiting exceptional resistance against fire and thermal at elevated temperature, however, they should be reviewed systematically for this excellence in order to make them viable and acceptable for such kind of infrastructures and constructions whereby the risk of fire incidences and towering thermal impacts are likely to crop up.

The bulk of related studies have thrown lights on the residual compressive strength of geopolymers following the very high temperatures exposure ranging from 600 to 800 °C. There exist copious of research works were conducted concerning geopolymer composites through employing diverse raw materials viz., metakaolin, rice husk ash, blast furnace slag,

fly ash and amalgamation of diverse source materials at a higher temperature. The alumina silicate polymer has demonstrated the higher intrinsic thermal resistance however the loss in strength on exposure at higher temperatures relies upon the variety of factors. The chief factors influencing the residual strength of geopolymers are the kinds of source material and alkali cation present in activators, diverse content of calcium enclosing raw materials, temperatures for curing and the ratio of activator/binders [42,44,65]. While the interstitial water in geopolymeric frameworks is exposed to high-temperature applications such as 350–400 °C could cause stress thereby cracks propagates and eventually trim down the strength. For that reason, one of the solutions to mitigate cracks and enhance thermal attributes is to prepare the sans pore in geopolymer matrix, which in turn, extend higher mechanical strength [66–68]. The strength impacting mechanisms at high-ceilinged temperatures have been investigated in the context of effects of pore pressure as well as phase-transformations [42,44,65]. In the middle-of-the-road cases, the residual compressive strength of geopolymers was monitored to be greater than the initial compressive strength when examined prior to the exposure of thermal.

Nevertheless, the supplement of aggregates mitigated the compressive strength of geopolymer concrete subsequent to exposure at 800 °C [69]. This is assigned to the fact that the compressive strength performance is affected by thermal incompatibility besides chemical changes and pore pressure. This thermal incompatibility takes place at higher temperatures due to heterogeneous distribution of temperature and the variations in the coefficient of multi-phase materials for thermal expansion of the components. Concerning multi-phase material, whilst the inconsistent thermal distortion obtaining from the non-uniform distortion amongst components of the phase cannot be maintained through the sample, the degradation of strength found to take place because of the commencement and propagation of cracks. By and large, the impact of thermal discordancy on compressive strength is affected by the degree to which samples could be deformed with no development of fracture, that is, the ductility or decreases brittleness of the material.

Also, preceding works have demonstrated that geopolymers exhibit exceptional thermal steadiness at the micro-scale [34,37,70]. The resistance capability of material against change in volume and crack development due to thermal effect as well as to keep hold of its compressive strength even at towering temperatures are the resistance to deformation, as well as strength and spalling resistance, thermal stability, correspondingly. An earlier investigation on the influence of soaring temperature on weight loss, thermal shrinkage, and chemistry of metakaolin based geopolymers was carried out [35]. Furthermore, Bernal et al. [70] have examined the influence of temperature on compressive strength of geopolymers based on metakaolin plus Ground Granulated Blast Furnace Slag (GGBS) but the investigations were made by using merely a single Si/Al molar ratio. The earlier research works pilots to understand that Si/Al ratio influences greatly not merely the microstructure but also the mechanical attributes of the geopolymer manufactured at ambient temperature [71,72]. Therefore, the factor of Si/Al molar ratio is possibly to impact crucially the presentation of mechanical and micro-structure types of geopolymeric materials as well when exposed to greater temperatures. Moreover, the past research to figure out the thermo-chemistry and thermal properties had well-thought-out geopolymers based on fly ash with a target for ratios of amorphous Si/Al of bigger than two [39,56]. The amorphous content present in fly ash, Si/Al ratio commanded the response to the exposure of thermal with elevated ratios providing enhanced response when subjected up to 1000 °C temperature. The application of a lower ratio of Si/Al to manufacture geopolymers for increased resistance against thermal is evaluated. A past study was performed by Kong et al. [65] exploring the impacts of several factors like temperature of calcination of kaolin as well as ratios of activator/metakaolin and Si/Al on compressive strength, i.e., macro-scale; of geopolymers synthesized with metakaolin on subjecting to very high temperatures. Hitherto, the basic mechanisms controlling the compressive strength performance at macro-scale are not comprehended. Rickard et al. [39] had tested five dissimilar fly ashes based geopolymers at targeted ratios of Si/Al for 2.0, 2.5 and 3.0 and revealed that diminishing

the quantity of aluminate or silicate supplemented through the activator solutions provided strength enhancements or retaining subsequent to the exposure of thermal. Geopolymer with lower Si/Al ratio amorphous fly ash exhibited brilliant early compressive strength, which diminished swiftly following thermal exposure. The thermo-explosion or degradation of material over a controlled temperature system by the thermo-analytical technique of Dilatometry for measurement of geopolymerically synthesized materials with this fly ash showed immense expansion events which, due to unreacted residue silicate materials, were assigned to the expansion. The application of filler materials considered thermally stable is commonly found placing in other materials technology for minimizing thermal shrinkage or expansion, e.g., the adding up of inorganic type fillers is well-known to alter the attributes for thermal extension of polymers of organic nature. Several researchers have assessed the influence of the supplement of fillers and aggregates on thermal characteristics of geopolymer. The totalling of granite and quartz aggregates to geopolymer mortars produced with metakaolin whereby the addition of 20 wt.% aggregate to the said mortar had mitigated the shrinkage by almost 50% in the range of 23 to 500 °C [73] have studied. More decline in the context of shrinkage was attained by escalating the quantity of aggregate to 40 wt.%. A supplement of up to 30 wt.% of alumina to metakaolin based geopolymers produced by using potassium silicate as an activator [74]. The measurement of thermal volume shrinkage of samples after subjected to higher temperature have also been taken by them and they monitored momentous mitigations concerning shrinkage figures beyond 20 wt.% additions of alumina. In particular, this was recorded above 800 °C, escorting to conclude that the existence of alumina was valuable for dropping thermal shrinkage and accelerates the crystallisation on set temperature as well as the extent of crystallisation fillers, together with Al plus K containing geopolymer based on metakaolin. The inorganic type fillers were found absent in the micro-structure may be owing to either a geopolymer gel coating or the particles of filler reacting in the geopolymerisation kinetics making them indistinguishable [75]. Metakaolin based geopolymers activated with potassium-containing activators which were filled by alumina or fine quartz to estimate the thermal characteristics of the blends. The best possible shrinkage of the controlled geopolymer was found was 17% at 1000 °C which was declined to 12 and 13% by the adding up of the alumina and quartz respectively [55]. Naturally occurring mineral fibres of wollastonite used to reinforce metakaolin-geopolymer [76]. Its stiffness was found to augment as a volume of fibre accelerated to 5 vol.% of Wollastonite is well-matched with the higher level of pH used in the formation of geopolymer paste [76]. Accordingly, fillers such as wollastonite and alumina, which are thermally stable can be incorporated with the geopolymeric mixture to enhance the resistance against thermal through minimizing shrinkage throughout heating process. The factors influencing the resistance against thermal of geopolymer based on metakaolin as confirmed through the dilatometric technique are the alkaline cation employed and the molar ratio for Si/Al. Duxson et al. [33] have analysed several geopolymer formations through dilatometry contrary to thermal with diverse alkaline cations as well as molar ratios for Si/Al. In this case, four diverse steps are met with like, firstly, the enclosed water in the micro-pores evaporates up to 100 °C sans causing shrinkage. Secondly, free water is removed over 200 °C, in the third step, a degree of restructuring takes places between 300–600 °C while the fourth step involves the appearance of a significant shrinkage owing to the viscous flow monitored beyond 600 °C. Particularly, the ratio of Si/Al molar ratio is answerable for the appearance of viscous flow; especially, superior is the ratio of Si/Al, the more is the enhance in the quantity of the viscous flow. The same phenomenon was also observed by other studies in the thermal resistance analysis carried out on metakaolin based geopolymers synthesized with potassium or sodium-containing activators [37,77,78]. Similarly, also witnessed the similar mechanisms on formations of fly ash-based geopolymers. The accumulation of reinforcements in geopolymer mixes to enhance mechanical characteristics and resistance against thermal at high temperature. Basalt, glass as well as carbon type fibres can be incorporated into the geopolymers to provide fire-resistant materials. The dissimilar

specimens upheld 50% of the value of flexural strength subsequent to a thermal exposure period 600 °C for 1 h and 1000 °C for the glass, carbon and basalt fibres. A good-quality adhesion has been reported among a matrix of the geopolymer as well as the pre- and post-the thermal exposure of fibres at 600 °C temperature. The viscous flow appearance alters the behaviour of geopolymer and the observance among the matrix as well as fibres rely upon the different dilatometric coefficients, while the temperature attains 1000 °C. Accordingly, the mechanical characteristics and resistance against geopolymers elevated heat can be enhanced through the adding up of reinforcements in the matrix. The basalt and Carbon fibres had the best outcome. For the most part, the shrinkage of geopolymer is estimated during the action of the heat at 1000 °C [33]. Merely little illustrations for the research on the shrinkage performance of the geopolymers at a lower temperature is found. The drying shrinkage property of geopolymer concrete found with declining when slag content augments and sodium silicate to sodium hydroxide ratio trims down. What is more, the hydration sphere, total cation, and stability of aluminium species are stated to be key factors affecting the sensitivity of geopolymers with a metakaolin dependent ambient temperature drying shrinkage. The supplement of a minute quantity up to 1.6% ammonium molybdate slims down of shrinkage at higher temperature [79]. Geopolymers manufactured by sand do not found pursue the predictable tendency concerning shrinkage as well as a supplement of an around 10% sand do not allow the disintegration of specimens upon when subjected to thermal action at 110 °C [80]. Sprinkling, pouring as well as extrusion are the key techniques for the shaping of ceramic materials that involve employing slurries which diverge as to the viscosity of slurry necessitated to perform the shaping course of action. In the context of the spraying method, the viscosity of the mixture has to be lower; accordingly, allowing the alteration in the little drops, as well as a spray gun is required for the deposition process. Whereas in the case of the extrusion method, the screw forces to the slurry with the help of die, and the material ought to be viscous sufficient to safeguard its shape. These techniques engrossed dissimilar values of viscosity that are scarcely appropriate for geopolymer manufacturing. The technique of pouring could be employed even for higher viscosity. Nevertheless, the eloquence of the mix must be higher adequate to fill up the voids of the moulds. Geopolymers exhibit modifications in the context of viscosity by the setting kinetics. Therefore, shaping by the technique of pouring is most likely the most apposite process for geopolymers. On the other hand, Duan et al. [81] have delved into durability and microstructural attributes of metakaolin and fly ash-based geopolymer and summed up that the said materials displayed superior durability and denser microstructure in comparison with OPC-counterparts on subjecting them to soaring temperatures. A drop concerning mechanical attributes of diverse formations following thermal process at 200 °C, irrespective of the kinds of fibres employed as strengthening materials like carbon, basalt as well as glass monitored [82]. Geopolymers, when freshly manufactured are in form of liquid with poles apart viscosity values; for this reason, it is necessary to employ shaping techniques alike ceramic solutions and suspensions. Ranjbaret et al. [40] have concentrated on the study of the impacts and adaptability of POFA as a substitution material in geopolymer mortar prepared with fly ash. Their findings piloted them to achieve early high compressive strength in the context of geopolymer prepared with fly ash in comparison with POFA incorporated geopolymer. Sarker et al. [83] have experimented on towering temperature effect of exposure of fly ash-based GPC and its OPC-counterpart up to 1000 °C and their findings concluded that GPC samples were observed to undergo lesser damage than the counterpart samples of OPC-concrete subsequent to elevated temperature exposure. Passive fire protection (PFP) is a measure to safeguard structures and industrial paraphernalia against fortuitous incidences of fire. The materials which are competent enough for fireproofing stay away from sudden heating of the structures and mitigate the deterioration of the mechanical attributes of the structural parts [84]. Nowadays, a trend to apply cementitious aggregates mixed with light inorganic elements possessing appropriate thermal characteristics, viz., vermiculite, are usually employed for the thermal insulation of fixed installations [85].

Quite recently, on the basis of a small number of considerations, PFP-systems had emerged out as possible utilizations of geopolymers for elevated thermal resistance due to their intrinsic structure having inorganic nature [86], absence of ignition or discharge of smoke even subsequent to extended heat flux exposure, and high-quality fortification during rigorous fire resistance examinations. What is more, the diversity of parameters entailed in the geopolymerization such as precursors, activator solutions, and conditions for curing permits for the couture of the attributes of the mixture to fireproofing uses. Novel components viz., Perlite or hydrogen peroxide can be supplemented to trim down material's thermal conductivity ahead. The impacts of time of exposure and cooling rates on the residual compressive strength of the concrete after exposure [87,88]. The time for exposure of one to two hours was found sufficient for the temperature to break through the cubic specimens and grounds for the majority of the loss with regard to compressive strength. The influence of elevated temperature mitigated the time necessitated to cause strength losses, which is linked to the augment of thermal conductivity at lofty temperatures. Subsequent to the exposure for one hour, 80, 70, 60 and 30% for 200, 400, 600 and 800 °C the residual strength was found respectively. Cooling rates and rates for heating have displayed no impact on the concrete's residual compressive strength when subjected to 600 °C and ahead of, excluding little influences at inferior temperatures, probably on account of the building up of pore-pressure. Moreover, the impacts of diverse cooling rates on concrete were experimented by Khoury [89]. The shrinkage or cooling strain depended on the interaction among aggregate and cement developing cracks and not associated with the age of concrete, the early presence of moisture or rate of heating. Moreover, the influence of elevated temperature strain rate and heat on the residual compressive strength of blended concrete enclosing silica fumes plus fly ash [90]. The noteworthy loss concerning strength was recorded after 400 °C temperature. In addition, Kong and Sanjayan [91] have accounted a 25% drop in the context of compressive strength of the cubic specimen of metakaolin incorporating geopolymer paste following the exposure at 800 °C for 10 min. A standard and elevated strength concrete with pozzolans. Metakaolin based concrete had been found with enhanced strength till 200 °C temperature exposure, and upheld superior strengths till 400 °C than concrete with fly ash, silica fume incorporating concrete and usual conventional OPC-concrete. Following 400 °C, the higher strength concretes swiftly get deteriorated. The concrete-based on metakaolin had demonstrated the minimum ultimate residual strength in spite of exhibiting improved initial strength gain, signalling that it is, in particular, vulnerable to a definite higher range of temperature. The disparities in the concrete performance containing pozzolanic materials at elevated temperature exposure are widespread. The good stability and higher initial strength gains among 200–400 °C followed by express deterioration and lower ultimate compressive strength than reference concrete is generally accounted [92,93]. Ductility is notably influenced the residual compressive resistance of geopolymer mortars following the exposure at 800 °C [94]. Following the middle-of-the-road literature published till date, the said materials achieve their crucial point at around 600–800 °C. The dimensional stability of the materials is seriously influenced gravely and bending strength is also significantly get affected in this temperature range, whereas the compressive strength was found enhanced. The referred impact is assigned to the partial sintering which occurred at those range of heating or somewhat at elevated temperatures. In accordance with the proposal of Khoury [95], the disassociation of $\text{Ca}(\text{OH})_2$ at a temperature of 300–400 °C, as well as gigantic and abrupt creep, are more often than not the root cause of failure at 600 °C, at 700 °C dissociation of CaCO_3 , ceramic binding as well as absolute water losses at 800 °C along with melting point at 1200–1350 °C. Wang et al. [96] have monitored the temperature of 900 °C as an imperative transition temperature concerning metakaolin incorporating geopolymers, whereby the geopolymer partly melts and coagulates in the vicinity. Still, significant interspaces were found present at 900 °C temperature which distinct the melted structures. Several researchers have tested the thermal attributes of fly ash-based geopolymers subjected to uniform heating regimes through a furnace. The striking thermal characteristics of geopolymers have put forward

their appropriateness to employ them in fireproofing applications whereby the prerequisite for the material would be to withstand against fluctuating temperature heating with superior heat rates. The past studies have thrown lights on the geopolymer manufactured with diverse source materials viz., metakaolin, rice husk ash, blast furnace slag, fly ash, etc. at lofty temperature range [97]. Despite the fact that inorganic alumino-silicate geopolymers integrally exhibit the higher resistance against thermal, the strength loss is found to occur at towering temperatures relying on a variety of factors like nature of precursor, alkali activator solution as well as interstitial water present in the structures of geopolymers and its evaporation when subjected to higher temperatures of 350–400 °C, that could create stress thereby resulting in the initiation of cracks eventually escorting to the strength loss. Consequently, one of the solutions to minimise the development of cracks and enhance the thermal attributes is to manufacture the sans pore geopolymer mixture, through which will extend improved mechanical strength. The fly ash-based geopolymers have demonstrated better fire resistance in comparison with fly ash mixed with supplementary materials. Zhang et al. [98] have accounted that during thermal exposure of geopolymer based on fly ash as well as metakaolin at towering temperature, the degradation concerning bending as well as tensile strength was found advanced, but it was observed inferior concerning bonding and compressive strength in comparison with OPC-system. This kind of analyses, published outcomes and demonstrating excellent resistance against thermal, sustainable mechanical performance, etc. are the core reasons why the geopolymer with fly ash has drawn further attention amid researchers [69,99]. Fan et al. [100] have studied the thermo-mechanical attributes and micro-structure modifications previous to and following the heating process as well as the cooling process of geopolymers based on fly ash at 500 and 800 °C under dissimilar reaction kinetics situations. On the other hand, Duan et al. [81] have examined the microstructure and durability of metakaolin as well as geopolymer with fly ash and determined that geopolymer represents superior durability attributes and having denser microstructure to OPC system, while subjected to not only very high temperatures but also under the chemical environment of the aggressive type. Demirel et al. [101] have revealed the influence of lofty temperature on mechanical characteristics of concrete manufactured with silica fume and finely ground pumice. The outcomes have displayed that the addition of the mineral materials to concrete had diminished both, i.e., compressive strength as well as unit weight. Not merely have that, escalating the temperature beyond 600 °C has influenced the compressive strength on account of losses in concrete samples weight was more boosted for concrete mixes having both silica fume and fly ash. Duan et al. [81] have investigated the impact of silica fume (0–30%) substitution on thermal resistance examinations of geopolymer paste with fly ash and monitored that the compressive performance is escalating with the addition of silica fume. Sarker et al. [83] have experimented at an elevated temperature at 1000 °C in the case of both, geopolymer based on fly ash and counterpart OPC-concrete. They monitored that the former have suffered lesser damage than the specimens of OPC system.

2. Methodology

Across-the-board literature research was carried out to recognize access as well as assess allied accessible information on record, which are the pedagogic theories and cited cases of the fusion work. Quite recently, a key sub-discipline of geopolymeric inorganic composites, polymers with inorganic origin or innovative geopolymer technology is one of the swiftly progressing research fields in the past couple of years. With a view to comprehend in-depth the most up-to-date and the emerging drift of geopolymer as edifice material, the key-words of “geopolymer”, “thermal behaviour”, “elevated temperature”, “temperature” and “fire resistance”, have been methodically recovered, by means of bibliographic databases of “Springer”, “Elsevier”, “Taylor and Francis”, “Wiley” and “Hindawi” too in the interest to congregate an absolute gathering of data for the present study. Moreover, the meticulous data analyses and categorization is executed on the basis of a thoughtful comprehension of titles, graphical abstract, highlights, abstracts, keywords, full texts,

conclusions, and perceptions. A few synthesis techniques portrayals were represented through figures, diagrams and tables which were utilized as references in the present paper. The referred data from literature stand for an extensive synopsis of the advancement, depiction and utilization of the fire resistance by geopolymer composites. The micro-structural methods viz., XRD, SEM, FTIR, NMR are accounted in the present review manuscript. The said methods are handy for healthier comprehension of the intrinsic associations of structure, micro-and pore-structures of the geopolymer construction composites.

3. Impact of Fire on Concrete

3.1. Physico-Chemical Modifications

Prior to the evaluation of the concrete performance in context to durability, it is significant to study the impact of fire on concrete along with its multi-scale and multi-phase components. There is inherent fire resistance in geopolymeric materials. They have an inorganic structure and do not burn like polymers that are organic. They are non-toxic and smoking, and, relative to conventional ceramic composites, have a low processing temperature. Table 1 illustrates physical and chemical modifications on geopolymer composites when exposed to fire.

Table 1. Previous literatures on Impact of fire on Geopolymer.

Reference	Observations
Zhang et al. [98]	The geopolymer mortar manifests higher bending and tensile strength temperature degradation than OPC mortar, but inferior degradation in compressive and bond strength.
Hosan et al. [102]	The compressive strength is significantly improved with the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio 3, where the residual compressive resistance is raised up to 600 °C.
Duan et al. [103]	The compressive resistance of geopolymers diminished during thermal cycles. The losses in mass and compressive strength amplified with rise in temperature.
Zhang et al. [104]	The geopolymer samples prepared with metakaolin and fly ash display analogous bending and compressive performance, both at ambient temperatures and after exposure to high temperatures as for OPC specimens. In practical building applications, geopolymers based on metakaolin and fly ash therefore deliver a viable alternate to traditional OPC.
Lahoti et al. [105]	The geopolymer with potassium was substantially amended (30–40%) as well as the geopolymer made with sodium was declined (10%) and after exposure to elevated temperatures, the strength of a mixed sodium and of a potassium geopolymer remained unaffected.
Kong and Sanjayan [43]	The research designates the two major features for geopolymer activity at a high temperature (800 °C) i.e., specimen and aggregate sizes. The size of aggregates greater than 10 mm lead to in healthier strength at low and high temperatures. The thermal instability between the geopolymer matrix and aggregates is the outcome of a heavy loss of geopolymer concrete at elevated temperatures.
Samal [106]	The geopolymers had a significant effect on thermal shrinkage decline as Si/Al ratios amplified due to trim down in porosity during the process of dehydroxylation as well as sintering.
Sarker et al. [83]	Following the fire exposures, less harm was observed to the geopolymer concrete samples as regards cracking than to the OPC concrete specimens. There was considerable spalling in the concrete cylinders of the OPC for exposures between 800 and 1000 °C though geopolymer concrete samples were not spalled. In particular, the samples of geopolymer concrete maintained higher strength than the specimens of OPC.

Table 1. Cont.

Reference	Observations
Pan et al. [107]	The strength of geopolymer was up by 192% at 550 °C in contrast to the original strength value, while the strength of OPC paste changed slightly. The percentage residual strength of both geopolymer and OPC concrete after exposure to 550 °C was nevertheless close.
Lahoti et al. [108]	Upon high-temperature exposure to 900 °C, all the geopolymer specimens experienced reduced compressive strength. While the geopolymer mixes disclosed strong chemical stability on a microscale, their volumes at mesoscale were poorly stable and thermal shrinking was extremely high.
Mathew and Joseph [109]	At ambient temperature, the deformation attributes of geopolymer concrete beams are identical to those of reinforced cement beams. The strain compatibility method, therefore, underestimates the deformation behaviour of strengthened geopolymer concrete beams when exposed to high temperatures.
Kljajević et al. [110]	Cross-linking of polymer changes in geopolymer samples at 600 °C reduces the number of bonding of Si-O-Na. Thermal action at 900 °C declines oxygen and articulated sodium significantly, following major morphological changes, i.e., the creation of a complex pore structure.
Sivasakthi et al. [111]	The geopolymer paste and mortar's linear dimensional stability remnants unchanged until 800 °C. 10% of the addition of micro silica has more filling effect, thus growing compressive strength by damaging the integrity of the bulk specimen of geopolymer composites.
Luhar et al. [5]	The rubberized geopolymer concrete, loss of strength at elevated temperatures is only somewhat more than the control geopolymer concrete, due to the possible inconsistencies of the integral materials coefficients of thermal expansion.

3.2. Spalling of Concrete

Fire exposure results in elevation of the temperatures, which might cause spalling in the concrete impacting damagingly the concrete integrity, ultimately leading to compromise its mechanical characteristics specially the compressive strength. The said spalling of concrete might even turn out to be the cause of the collapse of crucial structural units [112,113]. The accumulation of vapour pressure in pores and the uneven distribution of thermal stresses are two root causes for explosive spalling. The vaporization of entrapped water results due to the exposure at a towering temperature [114]. The water from the internal part of concrete has a propensity to travel towards the external portion. The formulated layer additional resist the vapour movement as of the internal part of concrete which sequentially augments the pore pressure. If the rate of heating is higher and the concrete pore structure is amply denser, the escape of the vapour layer is not quick enough causing huge pore pressure development and causes the spalling and afterwards the disintegration of structural elements if the concrete tensile performance is not sufficient. Figure 1 displays a pore pressure enlargement could ground for the concrete spall due to thermal process [115]. The progress of a thermal gradient in concrete at lofty temperatures is another factor [116]. While the surface temperature of the concrete escalates, a few compressive stresses grow parallel to the surface heated at lofty temperature, whereby, some tensile stresses took place at perpendicularly. If these differential stresses surpass the concrete's tensile strength, they spall out as depicted in Figure 2. In addition to these two factors, the concrete matrix cracking may occur due to the acceleration of the temperature on account of the hydrate's chemical decomposition, a differential decline of the concrete paste's shrinkage, thermal instability and coarse aggregate expansion. The elastic and thermal incompatibility of aggregates, as well as the cementitious mixture at higher temperatures can also result in cracking in the ITZ (interfacial transition zone) among phases, accordingly, deterioration of concrete and helping the abovementioned ruinous procedures [112].

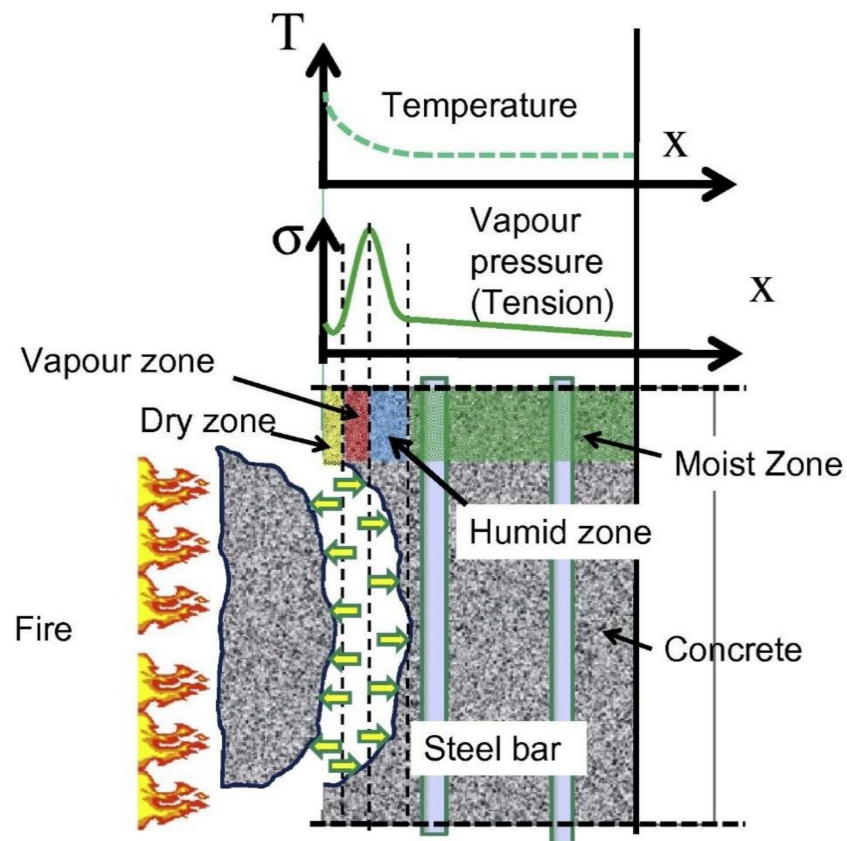


Figure 1. Mechanism of spalling of concrete due to vapour pressure [117].

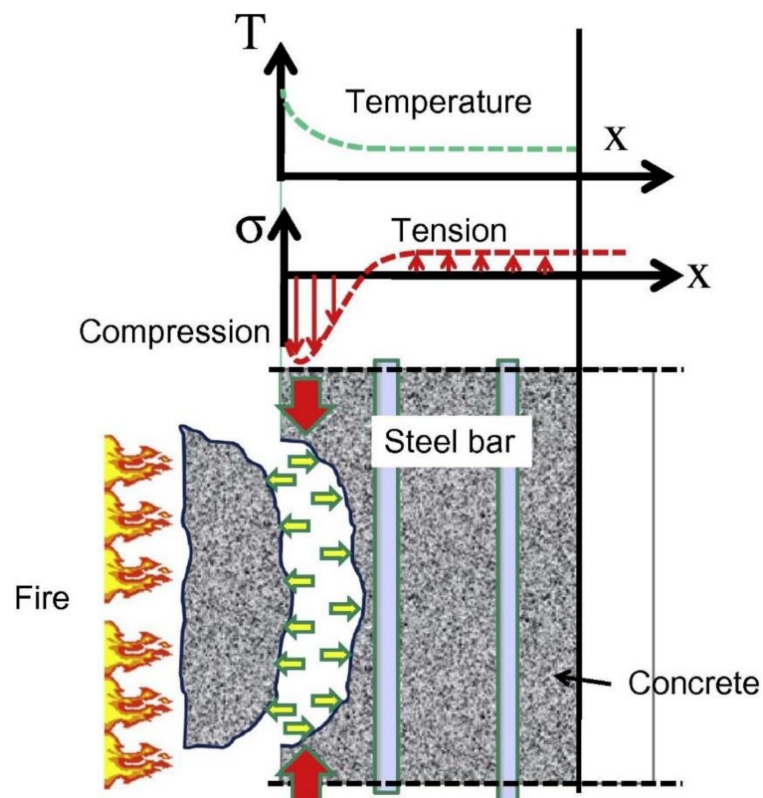


Figure 2. Mechanism of spalling of concrete due to thermal dilation [117].

4. Post-Fire Properties

4.1. Residue Compressive Strength

Hosan et al. [102] represent the impacts of potassium and sodium activator on mechanical compressive strength attributes and appearance alterations of geopolymer made by class F fly ash subjected to very high temperatures. The geopolymer pastes manufactured with sodium activator had demonstrated high compressive resistance at ambient temperature as well as advanced compressive strength at high temperature up to 400 °C than the potassium-containing counterpart. The compressive strength of geopolymer produced with potassium activator at 600 °C is somewhat greater than its sodium-containing counterpart. The geopolymer paste having been prepared with potassium activator had displayed superior compressive strengths at each elevated temperatures in comparison with ambient atmospheric temperature to counterpart produced with sodium counterpart. The geopolymer paste synthesized utilizing potassium activator with a ratio of K_2SiO_3/KOH as 3 had demonstrated the highest residual compressive strength at all towering temperature in comparison at the ambient temperature than its counterpart whereby the use of sodium activators is made. Duan et al. [103] have revealed the influences of silica fume on performance characteristics of geopolymer based on fly ash under thermal cycles. The compressive strength of geopolymer escalates with boosting silica fume content. The adding up of silica fume is apposite for achieving rapid strength growth in geopolymer. The compressive strength of geopolymer falls substantially under thermal cycles, specifically subsequent to 56 no. thermal cycles. The compressive strength losses augment at the temperature escalates from 200–800 °C. The structure of pore of geopolymer degrades subsequent to thermal cycles. However, the percentage decline is constant still a strength following exposure of thermal was found good enough. The outcomes of the research on metakaolin plus fly ash blended geopolymer binders as a precursor especially formulated for their utilization as fire resistance materials have exhibited excellent results, for instance, geopolymer binders manufactured with 50% metakaolin as well as 50% fly ash contributed optimal compressive strength as well as best possible bending both at ambient atmospheric temperature and subsequent to exposure to a higher temperature. Zhang et al. [104]. The compressive resistance and bending of geopolymer composites found enhanced to some extent following the exposure at 100 °C and then decline in the range of 100–800 °C. The discordancy among shrinkage of geopolymer binders and expansion of aggregates, outcomes in strength loss besides cracking of geopolymer concrete subsequent to exposure at elevated temperatures. The geopolymer composites synthesized with Metakaolin plus fly ash displayed analogous compressive strength and bending as compared to that of mixes of OPC-system for ambient temperature as well as following the exposure at higher temperatures. Lahoti et al. [105] had accounted the impact of alkalis i.e., potassium, sodium, or a combination of both, etc. on the strength performance of geopolymers whereby fly ash is used as a precursor and have been subjected to higher temperature aspiring to structural type applications. The upshots have demonstrated alkali cation has a robust impact on the compressive resistance of geopolymers based on fly ash following the high-temperature exposure. Generally, geopolymer formed with potassium cations has exhibited strength improvement while in contrast, geopolymer with sodium has demonstrated mitigated strength. However, the strength of geopolymers with sodium and potassium-based remained constant even after the towering temperature. Moreover, Kong and Sanjayan [43], had monitored the findings of investigations on the influence of higher temperature on geopolymer composites prepared with fly ash whereby a variety of experimental parameters have been tested viz., size of the specimen, aggregate size and kind as well as the type of superplasticizer. Of which, the research work identifies the size of specimen and aggregate as the two key factors controlling the behaviour of geopolymer at very high temperatures like 800 °C. The sizes of aggregate greater to 10 mm have shown good strength resistance at ambient as well as towering temperatures conditions. The strength losses of geopolymer concrete on very high temperature is assigned to a thermal disparity among the aggregates and the geopolymer mix. Consequently,

the aggregate size is an imperative feature for confirming the behaviour of geopolymer concrete at elevated temperatures. Aggregates having a smaller size such as less than 10 mm encourage widespread cracking and spalling in the geopolymer concrete whereas those having larger aggregates, say, greater than 10 mm are more stable at towering temperatures. In opposition, the concrete performance at a very higher temperature using superplasticizer is also found deprived. An application of superplasticisers is not advantageous in the context of geopolymer concrete for performance at soaring temperature. The thermal incompatibility among aggregates and the geopolymer matrix is the most probable reason for the loss in strength concerning geopolymer concrete samples at very high temperatures. This had been established through comparing the geopolymer concretes manufactured with two dissimilar aggregates sizes through markedly dissimilar thermal attributes, whereby the specimen with larger discordancy piloted to higher strength loss. Sarker et al. [83] have reported that following the exposure at 400 °C, the compressive strength of geopolymer concretes are found ranging between 93–107%, and that of OPC-concrete was recorded as 90%. It was found ranging among 59–82% for GPC and 52% for OPC-concrete after 650 °C. Consequently, the geopolymer concrete kept hold of greater strength that compares to the OPC-concrete samples up to 650 °C. The residual strengths of the concrete had shown a range in between 21–29% at exposures at a temperature of 800 °C and 11–16% subsequent to 1000 °C. On the other hand, Lahoti et al. [108] the impact of disparity in context to the ratio of Si/Al molar on volume stability, that is, mesoscale and strength endurance, i.e., macro-scale attributes of metakaolin geopolymers have been discovered. It has been monitored that all the geopolymer specimens suffered diminution concerning compressive strength following an exposure at 300 °C. Geopolymer specimen with a ratio of Si/Al-1.75 having maximum compressive resistance of 6 MPa subsequent to exposure at 900 °C. It was monitored that owing to the higher extent of smash up due to cracking and lower residual compressive resistance; it is necessary to enhance the macro-scale stabilization of geopolymers with metakaolin for utilizations as fire proof materials of structural kind. Mathewa and Joseph [109], Despite the compressive strength of cube specimens of geopolymer concrete, has not trimmed down in between 600–800 °C owing to polymerization process of primarily non-reacted materials, the load-bearing capability of beams of geopolymer concrete has got mitigated swiftly ahead of 600 °C. The key aspect responsible for this phenomenon is the strength capacity decline of reinforcing steel which brought about a loss in load-carrying ability of beams of geopolymer concrete when subjected to temperatures beyond 600 °C. Pan and Sanjayan [118] have recognized two divergent behaviour patterns before reaching glass transition performance. The strength of the geopolymer has demonstrated an augment in between 200–290 °C, while also suffering noteworthy contraction due to further geopolymerisation. During temperature range of 380–520 °C, a further escalation in context to strength was monitored, but in case of geopolymer got superior at this stage. Constant pre-load prior to thermal process seems to have no influence on the compressive resistance of geopolymer samples in a thermal condition. Nevertheless, the rising applied stress escorts to elevated contraction at towering temperature. The supplementary strength loss in the course of the cooling puts forward that geopolymer samples are vulnerable to smash up ensuing from thermal shock. Vickers et al. [119], had summed up that the application of lower ratios of Si: Al in geopolymers based on fly ash have resulted in enhanced strength subsequent to 1000 °C temperature. The utilization of acicular Wollastonite provided improved flexural and compressive strengths retention following firing. Moreover, the adding up of alumina enhanced the compressive strength subsequent to firing, but the grade employed exhibited a higher level of water absorption in the course of mixing. The absorption of water had influenced the process of geopolymerization pessimistically as demonstrated by the lower strengths. Alumina having lesser surface area might be more fitting to permit higher adding up levels of aggregate or filler which would make easy the manufacturing of concrete and mortar [111]. The effect of adding up of micro silica quantity of 0, 5, as well as 10% in the geopolymer composites based on fly ash were investigated for their strength

properties at both room temperature as well as at 800 °C. The investigational findings from their research proposed that the compressive resistance of geopolymers is found to augment through the adding up micro silica of 5% then trimmed down by supplement of micro silica of 10%. The recorded compressive strength of geopolymer composites (paste, mortar as well as concrete) incorporating 5% micro silica was found to be as 34, 35 and 29 MPa correspondingly with a constant ratio of Si/Al as 1.9. The micro-silica had contributed for the development of denser and more compact microstructure, which had improved the compressive strength.

4.2. Post-Heating Visual Observation of Samples

Hosan et al. [102] had investigated the impacts of very high temperature on physical performance of both Sodium and Potassium based activator employed for synthesis of fly ash-based geopolymers. It was monitored that there was no formation of cracks in both types of geopolymers up to 400 °C. Nevertheless, the geopolymer synthesized with sodium-activators has displayed indications of cracks at 600 °C which turned to be worst at the temperature of 800 °C, whereby so many deep cracks were developed on the surface. Nevertheless, the geopolymer manufactured with Potassium activator survived from the formation of surface cracking at 600 °C temperature, but there were fine cracks propagate at 800 °C temperature. The losses in mass and volumetric shrinkage of geopolymer paste synthesized with Potassium activator is inferior to its Sodium counterpart. When the Potassium based activator employed for the synthesis of geopolymer pastes, it demonstrated lesser surface cracks than that of geopolymer paste prepared with Sodium based activator. Lahoti et al. [105] demonstrate the visible alterations in the look of the three specimens when subjected to dissimilar regimes of temperature. The geopolymer specimens become reddish-brown colour, particularly after 900 °C. This alteration of colour may be assigned to the iron oxidation present in fly ash [102,120].

Cracking behaviour and smash up to the geopolymer mixture could also be monitored on account of contraction of pores, evaporation of free water from the pores resulting in cracks propagation that caused shrinkage of the specimens. Nevertheless, the Potassium-activator based geopolymer has demonstrated less significant damage subsequent to exposure at 500 and 900 °C in comparison with the Na plus K and only Na based geopolymer. This monitoring links through the dilatometry scrutinises linked to the high stability to volume (Figure 3) of the mixtures Potassium based geopolymer. Samal [106], have revealed physical attributes of the fibre, matrix, and fibre reinforced geopolymer composites at room temperature. As a function of temperature at 101 and 248 °C, the DSC curve of the geopolymer composite at room temperature shows two peaks, of which, the first peak, i.e., at 101 °C helps to water vapour evaporation, dehydration, as well as the contribution of the second peak is the losses in a mass of geopolymer matrix at 248 °C temperature [121]. Sarker et al. [83]. Normally, heat passed through at a swifter in geopolymer concrete specimens than that of OPC-concrete specimens when subjected to fire exposure. The momentous alterations in context to colour have taken place in geopolymer specimens beyond 650 °C temperature exposure, varying from brown colour to red colour. A noteworthy spalling occurs in the samples of OPC-concrete on heating through fire at temperature exposure of 800 and 1000 °C. On the opposite side, spalling was not taken place in geopolymer samples subjected to identical temperature exposures. All-embracing cracking on the surface became visible in the OPC concrete specimens following at 400, 650, 800 as well as 1000 °C temperature exposure. Nevertheless, merely inconsequential cracking on the surface was monitored in the geopolymer samples exposed at 800 and 1000 °C temperature. This exhibit enhanced resistance to cracking and spalling of geopolymer concrete as compared to OPC-concrete samples in a fire. Lahoti et al. [108] have revealed the damage pattern, the visual appearance and alteration of color of geopolymer specimens following the exposure at the elevated temperature regimes. On account of exposure of geopolymer specimens at 300 °C, evaporation of free water from the pores takes place on specimens developing the cracking. Numerous extensive and finer cracks were recorded. Subsequent to exposure at 900 °C, geopolymer

specimens put on show more perceptible smash up through cracks than it was observed at 300 °C. Mathewa and Joseph [109], have made known that the load conforming to the formation of an initial crack in geopolymer beams slims down with enhance in temperature of exposure which relies upon the depth of concrete cover to the reinforcement. At the exposure of 800 °C temperature, the beam having 20 mm concrete cover cracked by 66% of the cracking load at ambient atmospheric temperature, whereas the beam having 40 mm cover of concrete cracked merely at 75% of the referred load. Rickard and Riessen [57], have noted that every single one of the tested panels demonstrated surface cracks following the fire testing on both the cold and hot sides. The cracking was not monitored to formulate on the cold phase of the specimens until subsequent to the period of early dehydration of one hour ended suggestive of the absence of wide-ranging damage through evaporation of water. Probably, the core reason of the crack formation on the cold phase of the specimens was owing to discrepancy shrinkage of the hot phase to the cold phase of the specimen that is an adequately hot phase to sinter, i.e., among 600 and 900 °C, would have contracted much more than the cooler regions, ensuing the crack development.

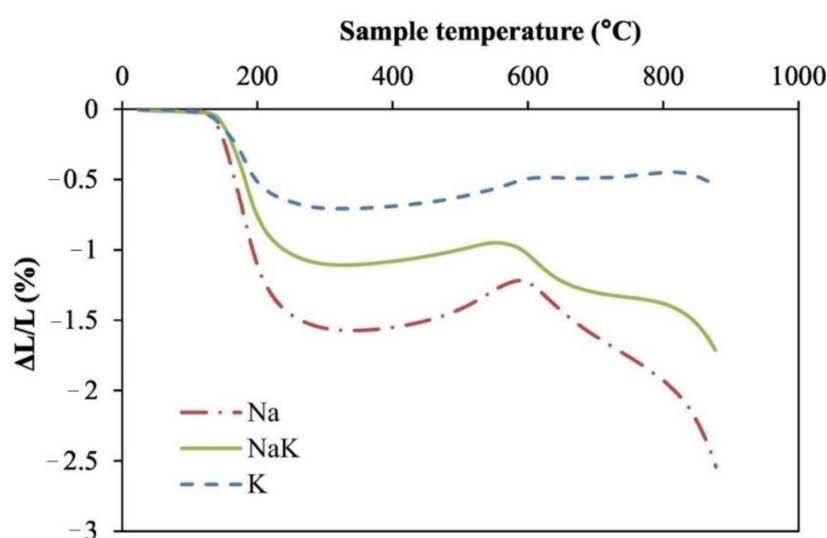


Figure 3. Thermal distortion of the geopolymers by dilatometry process [105].

4.3. Pore Structure

Duan et al. [103] have furnished quantitative upshots on the pore structure of the geopolymer incorporating fly ash as well as sans silica fume was achieved. It has been observed obviously that the geopolymer pores are refined through the adding up of silica fume. In comparison with the reference concrete, the silica fume-based concrete has comparatively lesser porosity. The decreasing tendency of the accumulative pore volume can be monitored while silica fume addition of 10, 20 and 30% were made, correspondingly. The drop off in context to porosity has occurred on account of the filling up of the pore spaces step by step within the geopolymer by the silica fume. Duan et al. [103] also concluded that the pozzolanic impact and filling of silica fume encourages the geopolymer synthesis that ultimately escorts to a denser structure. Lahoti et al. [105], have studied the distribution of pore size in the geopolymer specimens and observations have been made in this regard (Figure 4). In accordance, different Sodium and Potassium activators when used for manufacturing geopolymer at room temperature, these materials also found with dissimilar distributions of pore size. For instance, Potassium based geopolymer found with pore distribution over an extensive pore size range in comparison with Sodium based geopolymer having most of the pores with an average size of 40 nm. The referred modification might be linked to the smaller degree of chemical recorded for potassium-based geopolymers, i.e., less significant Al, Si and added Al–O–Al as well as Si–O–Si

bonding, in comparison with Sodium-geopolymers. The advanced structural ailment for Potassium based geopolymer may be responsible for the extensive sizes of pore detected.

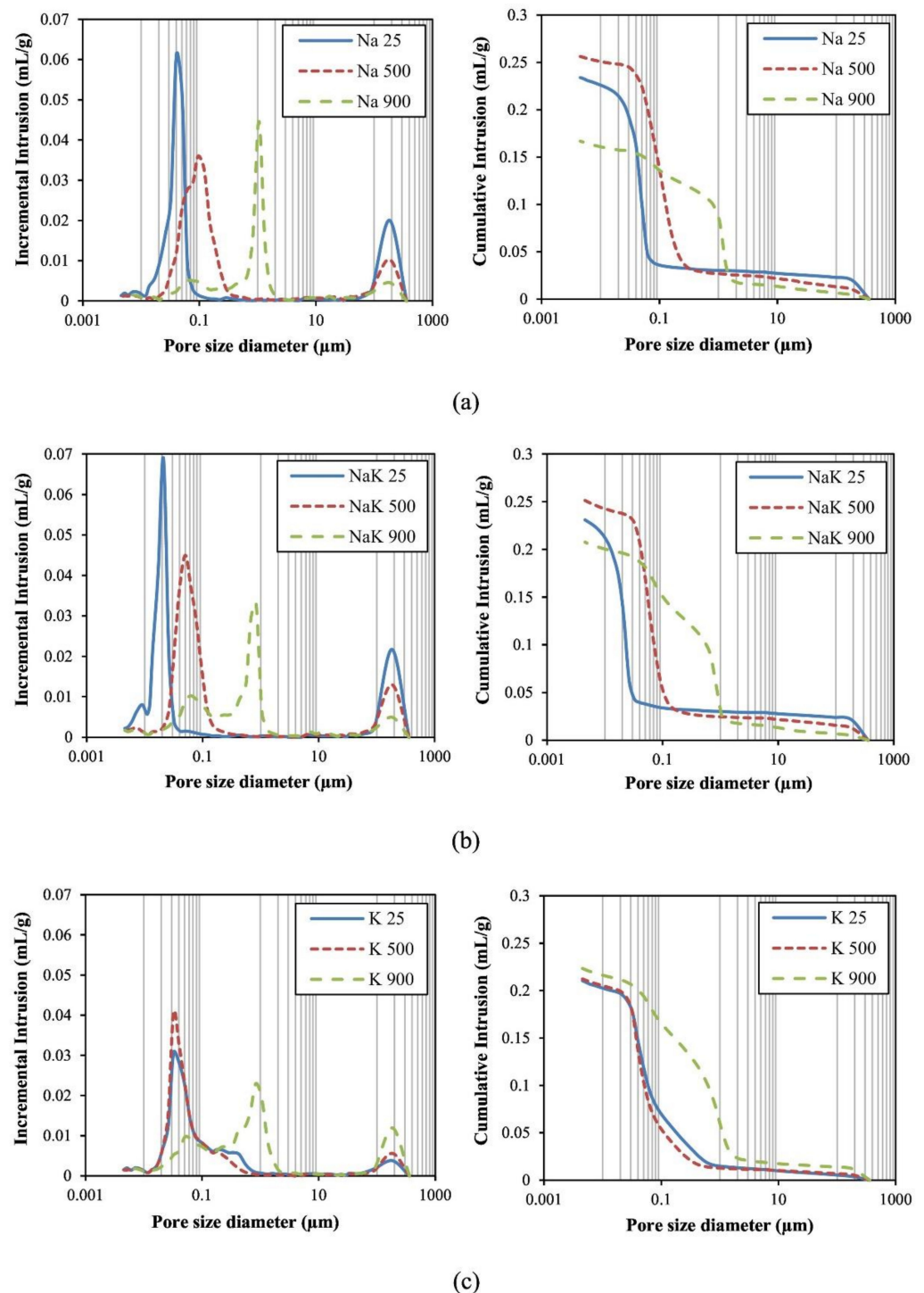


Figure 4. Pore size distribution in geopolymers before and after elevated temperature exposure (a) Na-, (b) NaK-, and (c) K- [105].

4.4. Flexural Behaviour

According to Mathewa and Joseph [109], the relationship of curvature of beams of GPC at ambient atmospheric temperature is analogous to the reinforced concrete beams made through OPC, which could be forecasted employing strain compatibility approach. The stress com-

patibility method underestimates the load curvature at first crack formation when the beam of GPC is subordinate to higher temperatures. As the acceleration in temperature is made, the ductility of the geopolymeric beams trims down speedily. With the escalation of exposure temperature, the beam made through geopolymerization suffers an advanced value of peak curvature with a mitigated final curvature. Their research observed that the beam made with geopolymer concrete had vanished its ductility—64% subsequent to at 800 °C temperature exposure. On the other hand, Vickers et al. [119], an enhancement was noted down in the context of flexural strength of both WOL mixtures that preserved across the absolute range of temperature. The ALOX mixtures were akin to the control which was assigned to the acicular nature of the Wollastonite in comparison with the particulate nature of the alumina whereby the form is made up of minute separate particles.

4.5. Chemical Stability

Lahoti et al. [105], have unearthed the core mechanisms through investigating their chemical stability previous and subsequent to the exposure at towering temperature through a variety of micro-structure analyses as well as methods of characterization. In this study, the binders are found chemically stable with no damage along with the development of new-fangled crystal phases following the exposure at elevated temperature.

4.6. Volume Stability, Mass Loss and Shrinkage

Lahoti et al. [105], have uncovered that the stability of volume fluctuates with the utilized kind of alkali activators. An attribute of geopolymers in the context of thermal deformation is of meticulous importance while calculating the potential for elevated temperature utilizations. The stresses developed due to thermal deformation which ultimately weakens the building material. Looking to the overall thermal shrinkage investigation results, it had been found that merely potassium cation containing geopolymer has exhibited the least thermal deformation which has followed by mix Sodium plus Potassium cations and then by only pure Sodium cations based geopolymers, correspondingly. The development of cracks and gel densification on account of shrinkage, as well as healing of micro-cracks plus pore size alteration because of sintering, were characterised as answerable mechanisms at diverse ranges of temperature. While the formation of crack and magnification of pore mitigated the strength, matrix densification and micro-cracks healing promoted the gain concerning strength. On the whole, it establishes that tailoring of geopolymers could be done as ensuring that stable, as well as improved strengths under exposure of thermal kind, are apprehended, for their utilization in a structural way. Sarker et al. [83], have recorded that the mean losses in a mass of GPC were 4.8% following at 1000 °C temperature exposure. This was chiefly attributed to the moisture losses at lofty temperature. The microstructure of geopolymer had maintained consistently stable and compact subsequent to exposure at elevated temperature through fire. Nevertheless, the loss of strength was primarily due to the strain formulated by the differential growths among the aggregates and matrix of geopolymer. Vickers et al. [119] have evaluated the thermal growth findings which pointed towards striking enhancements concerning the shrinkage through the adding up the filler materials. The early shrinkage occurrence in the temperature range of 60–300 °C could be assigned to the bounding losses, i.e., free water. The totting up of filler materials had inferior down the complete quantity of water which had reflected through lesser values of shrinkage in this zone for the filler enclosing samples. The growth continually happened up to 550–600 °C prior to the beginning of more shrinkage till 800 °C temperature. This is suggestive of enhanced resistance to thermal. Sabbatini et al. [122] have revealed that the shrinkage noticed for every specimen in the range of temperature at 100–200 °C, is on account of dewatering from the specimens and also varies in accordance with an early water quantity as well as the kind of alkali cation existing when the geopolymers were synthesized. The specimens containing K, having the values of shrinkage varying from −0.75 to −2.33%, whereas the specimens were enclosing Na were found with a range among −3.37 to −5.66% at 200 °C. Supplementary shrinkage takes place in between the range

of temperature from 200–500 °C, and it fluctuates by diverse formations. The shrinkage of the geopolymer in the referred range of temperature is owing to the disintegration of a few pores through adsorbed water evaporation. Consequently, the structure of gel resets on the micro-structural echelon. What is more, Vickers et al. [119] has found values of thermal shrinkage –45% for the geopolymer specimens and geopolymer incorporated with 10 vol.% of alumina filler having shrinkage 30%, at 1000 °C. Here, the research work was performed mainly on a metakaolin based geopolymer whereby potassium silicate was employed as an activator.

4.7. Sustainability and Stability of Geopolymer Composite

According to Samal [106], the construction composite with fabrics viz., carbon, basalt and E-glass from E-wastes was subjected to a range of temperatures like 200, 400, 600, 800, 1000 °C and room temperature [RT], within a precise time period in the oven and determined the behaviour of geopolymer sans fibres specimens and geopolymer specimens with fibres at RT. Around 200 °C, due to dehydration of water, as well as evaporation of gasses from the material, there can be smaller pores and voids developed. Analogously, carbon geopolymer composite displays utmost flexural resistance till the 2% strain [123].

Nevertheless, the E-glass geopolymer composite, the slipping process is tracked until 3% strain. Basalt and carbon composite geopolymer have peak point of failure after flexural resistance [39,42,124]. The findings of Vickers et al. [119] give an idea about a noteworthy enhancement in the thermal stability in comparison with past research work [39] whereby geopolymers manufactured with the identical source of fly ash has demonstrated huge extensive actions as the ratio of Si:Al, geopolymer augmented from 2–3. During that research investigations, the compressive strength of samples fired at a temperature of 1000 °C was found inferior to 20 MPa, i.e., further down the strength of 120 MPa in unfired condition. The research effort whereby Si:Al ratio was less than two, the drift in context to compressive capacity is overturned by 132% boost about compressive resistance subsequent to thermal for the control mixture [119].

4.8. Impact of Thermal Creep on Compressive Strength

Pan et al. [107] have revealed that the Transient Creep Data (TCD) of geopolymer had altered slightly in Transitional Thermal Creep (TTC) among 250–550 °C whereas OPC-based paste had considerably established TTC during the referred temperature. Geopolymer had demonstrated a vast scale of a transient creep than OPC based paste at temperatures inferior to 250 °C. During 250–550 °C. Temperature range, the geopolymer has not exhibited any noteworthy augment in transient creep whereas, in the case of OPC-paste, the development of considerable transient creep was monitored.

4.9. Elastic Modulus

Pan et al. [107], have revealed the findings of the elastic modulus of geopolymeric and OPC based pastes. The modulus showed no loss of the OPC based paste up to 550 °C. Contrasting to OPC based paste, the geopolymeric paste's elastic modulus exhibited a momentous boost ahead of 300 °C. The augment in strength-related by the formulation of further geopolymeric gel at a comparatively invariable density, resultant in a homogenous microstructure. In addition, this would enhance a definite surface of a material which can swell over the compressive stress, push it to lower pressure and greater elastic modulus.

4.10. Stress-Strain Behaviour

Pan and Sanjayan [118] have uncovered that the geopolymer shows evidence of glass change behaviour at 560 °C. The strain at acme stress has not considerably altered until 520 °C. Further than glass evolution temperature, the strains quickly augmented attaining around 0.64 value at 680 °C, signifying momentous alteration of a material changes their behaviour from the state of solid to visco-elastic state. The samples of geopolymer have demonstrated an almost vertical downward manner of stress-strain curves following the highest stress at any

temperature provided for examination. These points towards that the geopolymer samples retained a fragile kind of collapse at all the temperatures exposures.

4.11. Progression of Adhesion Bonding

Samal [106] have experimented at 200 °C and found that carbon fibre exhibits partial disintegration in fibre with the highlighted core. Nevertheless, the basalt, as well as E-glass, were found integral in position and with superior adhesion inside the mixture. The mixture of geopolymer demonstrates a homogenous manner with lesser pores. The geopolymeric matrix displays concentration towards the accumulation of the elements in a mixture. When the temperature was escalated at 600 °C, an E-glass fibre performs in width growth and crack development has initiated inside the fibre of basalt type fibre. Nevertheless, carbon type fibre demonstrates the shrinkage or found with mitigated in context to a diameter of the fibre accompanied by slight damage in the periphery. The surface bifurcates into receptacles having a line of smaller thickness cracks monitored on a surface. The smaller sized, as well as micro-pores, are found inside the periphery of basalt fibre at 800 °C.

5. Life Cycle Assessment

The study of Pozzo et al. [125], evaluated the environment footstep of a novel suggested geopolymeric material for fireproofing. The comparing of the findings is done with a reference lightweight cement-coating for commercial having identical Passive Fire Protection (PFP) performance. They explained the environmental impact of the life cycle visualized production systems for novel geopolymer yields, with meticulous concentration to a new-fangled PFP material. The study of the preceding LCA investigations on geopolymeric materials permitted for the corroboration of the approach and the information resources employed in the analyses. The PFP material of geopolymeric type has low carbon footmarks in comparison with a reference lightweight concrete with analogous applications for fireproofing. Nevertheless, higher environmental loads were calculated for the other influence classes. The allocation of some impacts from the coal life cycle to the fly ash is proved as crucial since it penalizes the geopolymeric substitute. Nevertheless, in the present market scenario, where there found a little advantageous utilization of the fly ash, roundabout zero allocation situation is regarded as practical. The mitigated CO₂-emissions made sure by the geopolymer PFP are linked to the nonattendance of the clinker production course, which is the key factor accountable for the Green House Gas (GHG) emissions in the manufacturing of the cement-PFP mixes. While the elevated impacts concerning depletion of resources, eutrophication, acidification, photochemical smog and toxicity chiefly owe to the energy-intensive production of the alkali-activators, mostly silicate of sodium. The focal suggestions for the enhancement of the kinetics of synthesis to use sodium silicate produced through the hydro-thermal course from an environmental viewpoint and to estimate the partial replacement of sodium silicate with alkali activators derived from the wastes.

6. Micro-Structural Behaviour

Hosan et al. [102] have described the investigations that XRD analysis peaks of mullite and quartz are monitored in geopolymers subsequent to at 400 as well as 800 °C analogous to those found in ambient temperature state (See Figure 5). Fly ash-geopolymer whereby Sodium activators were used for synthesis has displayed higher loss in weight in context to TGA as well as high DTA analysis peak at roughly 100 °C than its counterpart synthesized with Potassium activator subsequent to exposure at 400 °C. The said higher loss in weight in TGA and DTA peak is linked to the losses of combined as well as absorbed water in geopolymeric gels. This indicates that developed geopolymeric gels are retained in the geopolymer manufactured with sodium activators following the exposure at 400 °C than Potassium activator employed system, which is in harmony with the recorded upshots of compressive strength. Subsequent to exposure at 800 °C., a reversed tendency is monitored. Duan et al. [103] made a study to expand the utilization of silica fume and fly

ash to prepared geopolymer mixture under thermal. The residual strength, microstructure, and loss in mass of geopolymer based on fly ash amalgamated with silica fume following the exposure to 7, 28 and 56 thermal cycles on diverse 200, 400 and 800 °C temperature was recorded. The microstructure analysis had made known that the structure of pore of geopolymer humiliates subsequent to thermal cycles. The geopolymeric pores are improved through the supplement of silica fume. The blending of silica fume enhances the thermal resistance as well as optimises the micro-structure of the geopolymer mixture. Geopolymer specimens incorporated with 30% silica fume represent homogenous and dense microstructure with lesser crack development. Samal [106] has revealed that the geopolymer composite reinforced with fibre when exposed to higher temperature it reveals evaporation of gases and hydroxide persuading further crystallized phase of geopolymer. The crystallization phase of dense Na Al-silicate phases viz. nepheline is formulated at a temperature of 800 °C of geopolymer with metakaolin. This is probably assigned owing to the alteration of crystallisation into anorthoclase ($\text{NaAlSi}_3\text{O}_8$) and nepheline (NaAlSiO_4). The mineral phases, namely, hematite, magnetite, and quartz, were possibly mitigated in intensity that indicates the decline in the amount. Following Sarker et al. [83], the geopolymer micro-structures turned to be denser through the enhance of temperature at 1000 °C produced through fire (See Figure 6). The said modification has taken place in the micro-structure on account of sintering as well as additional geopolymerisation process of fly ash through the boost in context of temperature. As a consequence, the geopolymer micro-structure stayed constant subsequent to exposure at towering temperature due to fires. The examinations of Kong et al. [44] have escorted them to report that the geopolymer micro-structure kept constant following exposure to towering temperature through fires whereby a 6% enhance in context to the strength of paste of fly ash geopolymer met with subsequent to exposure to a heating temperature of 800 °C. A strength of geopolymeric paste enhanced through the escalating solidity of the micro-structure at this stage of temperature. Nevertheless, the losses in strength by the samples of concrete following exposure to higher temperature is largely due to the thermal shock as well as incompatibility among thermal extensions of the geopolymeric mixture and aggregates. Another research of Kong and Sanjayan [41] believed that thermal extensions of aggregates and geopolymeric paste are dissimilar at a higher temperature. The referred disparity concerning thermal expansions starts the smash up in concrete that ultimately results in the diminution in compressive strength. Pan et al. [107] have accounted for thermo-gravimetric and differential thermal analyses upshots. The geopolymer suffered a loss in mass with the augment in temperature. The middling mass decline of 10.1% following temperature exposure for the geopolymer was noted. A comparatively higher rate of loss in weight was monitored among room temperature to roughly about 250 °C. The loss in weight that took place in this range of temperature was almost 80% of losses in weight. The referred loss in weight is might be accompanied by the losses of combined as well as adsorbed water in N–A–S–H type gel [126]. Beyond the temperature exposure of 250 °C, there was an incessant weight loss up to 550 °C., however, the weight loss rate slows down noticeably. This weight loss can be attributed by condensation or polymerization to water discharge [33]. Pan et al. [107], had put on show the images of SEM of the geopolymer pastes prior and subsequent to exposure of thermal. In a microstructural study of SEM analysis at a micro level, there was an absence of noticeable crack on the sample following the soaring temperatures. SEM analysis images demonstrate heterogeneous type microstructures which enclose non-reacted elements of ash. The content of non-reacted source materials might be related to the degree of geopolymerisation reaction. Lahoti et al. [108] have monitored using the SEM analysis images that following elevated temperature exposure period, geopolymers prepared by keeping the ratio of Si/Al molar is greater than 1.50 possess and more compact gel structure and smaller porosity in comparison with those having ratio of Si/Al molar less than or equal to 1.50. What is more, they studied the patterns of XRD for the geopolymer and original metakaolin matrix previous and subsequent to revelation to towering temperature for geopolymer

mixtures. The observations for geopolymers have led to the amorphous phase hump in the alkali activator precursor as metakaolin at 2θ angle in consequence of the process of geopolymerisation. Following an exposure at $300\text{ }^{\circ}\text{C}$, every one of the specimens of geopolymer has displayed good quality of thermal stability and nominal phase modifications. While an exposure at $900\text{ }^{\circ}\text{C}$, there can be the development of nepheline for every geopolymer mixtures [127]. Lahoti et al. [108] have studied the FTIR analysis spectra of the pure metakaolin as well as geopolymeric matrix previous and subsequent to at elevated temperature for geopolymer specimens. The key asymmetric extending band for T–O–T bond—whereby T is equal to “Silica” or “Alumina”, in early metakaolin can be noted at 1054 cm^{-1} (Figure 7). The referred band was found to turn into contracted and transfer to more lengthy wavelengths of 957, 961, and 970 cm^{-1} for geopolymer mixtures on account of the process of geopolymerization. Analogous shifts have been monitored formerly by Fernández Jiménez et al. [126]. Kljajević et al. [110], During the ultimate phase of geopolymerization, the stayed behind quartz is validated through XPS, FTIR and XRD analyses. Geopolymer composed of roughly equal quantities of sialate as well as sialate-siloxo units. Geopolymer at $600\text{ }^{\circ}\text{C}$ shows losses in the strength of Si–O–Na bonds indicating the chains of cross-linking of a polymer as well as the whole an enhancement of attributes. As the chemistry of geopolymers was not changed at this exposure of temperature, Na is delimited most likely in the form of NaAlSiO_4 . The thermal action of the specimens of geopolymer at a temperature of $900\text{ }^{\circ}\text{C}$ persuades noticeable alterations with context to its morphology as well as the chemistry of the specimens, manifested as the loss of O_2 and Na. That means, the sialate and siloxo units turned out to be deficient concerning O_2 . What is more, was a formation nepheline crystal phase. Vickers et al. [119] have attained SEM images of cracking the surface of specimens previous as well as subsequent to thermal exposure. The microstructure analysis of the unfired mixture encloses manifold phases together with geopolymer gel with non-reacted fly ash particles with a variety of sizes. Following the firing, the micro-structure is found more homogeneous with a smaller quantity of disintegration. There found an obvious augment quantity of coarse pores in comparison with the unfired mixture micro-structure. According to [111], the MAS-NMR (^{29}Si and ^{27}Al) spectra of the sample demonstrated the existence of supplementary reaction yield gel N–A–S–H rich both in Al and Si in the mixtures. The formulation of the referred yields has enhanced the strength attributes in composites (paste as well as mortar) at room temperature as well as at $800\text{ }^{\circ}\text{C}$. The amorphous nature of the fly ash with micro-silica lends a hand to develop more reacted creation like Hydroxysodalite also outlining further dehydrated phases of Nepheline (AlNaSiO_4) and Albite ($\text{NaAlSi}_3\text{O}_8$) at $800\text{ }^{\circ}\text{C}$, was monitored by means XRD (Figure 8). The structural stability of material at $800\text{ }^{\circ}\text{C}$ was also inveterate by FTIR, and NMR spectroscopy. Following [111], the stability of composites against thermal was investigated through TGA and DTA, thermal expansion and thermal conductivity amid $30\text{--}800\text{ }^{\circ}\text{C}$. for temperature. The good-quality thermal attitude of the paste of geopolymer had demonstrated a small noticeable shrinkage of $<1\%$; while the geopolymer with conventional sand displays the growth of at 2.5% . Although a filler has undergone thermal reactivity was not essentially unfavourable and might help to the strength.

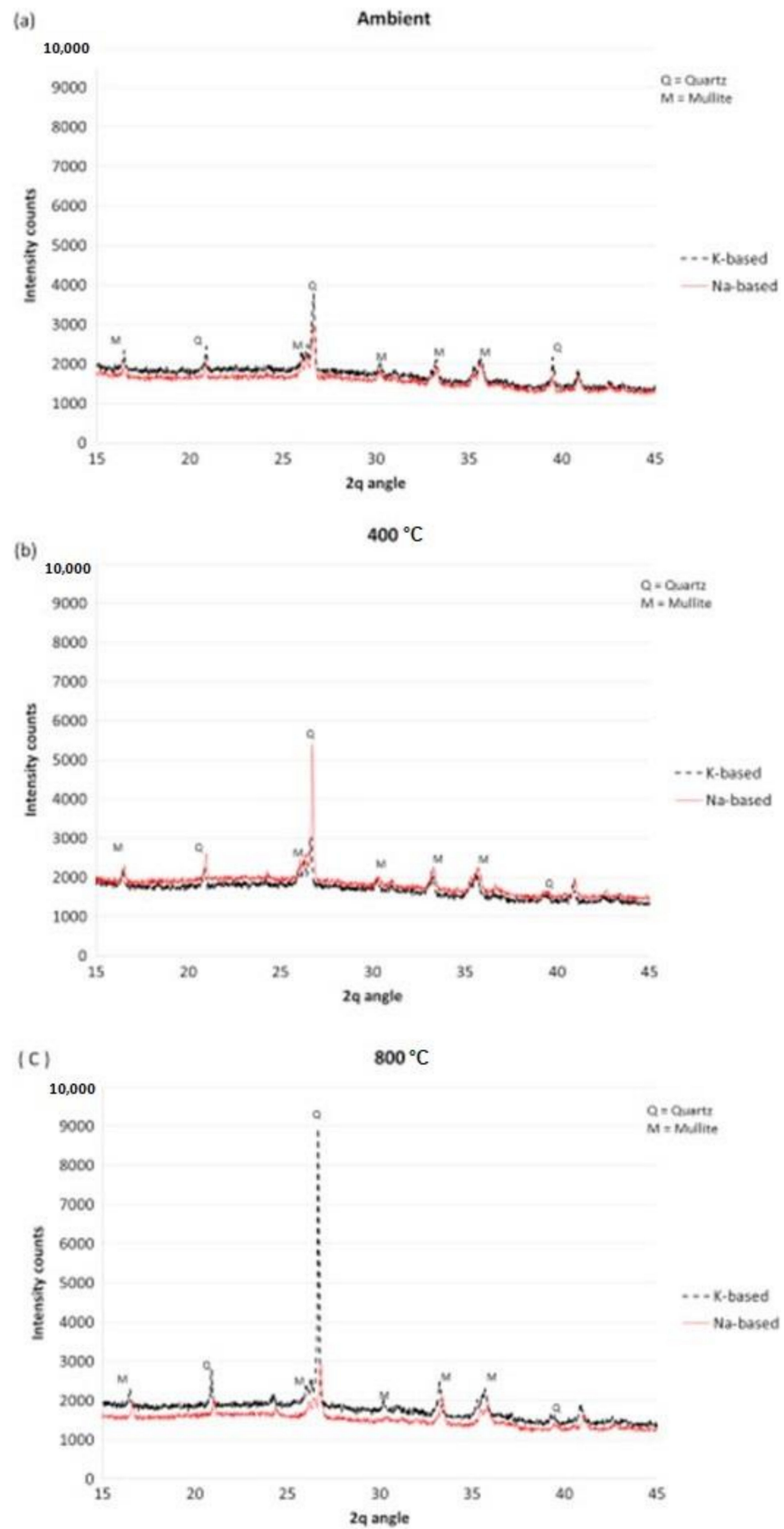


Figure 5. XRD analysis of Na- and K-based fly ash geopolymer (a) ambient, (b) at 400 °C and (c) at 800 °C temperatures [102].

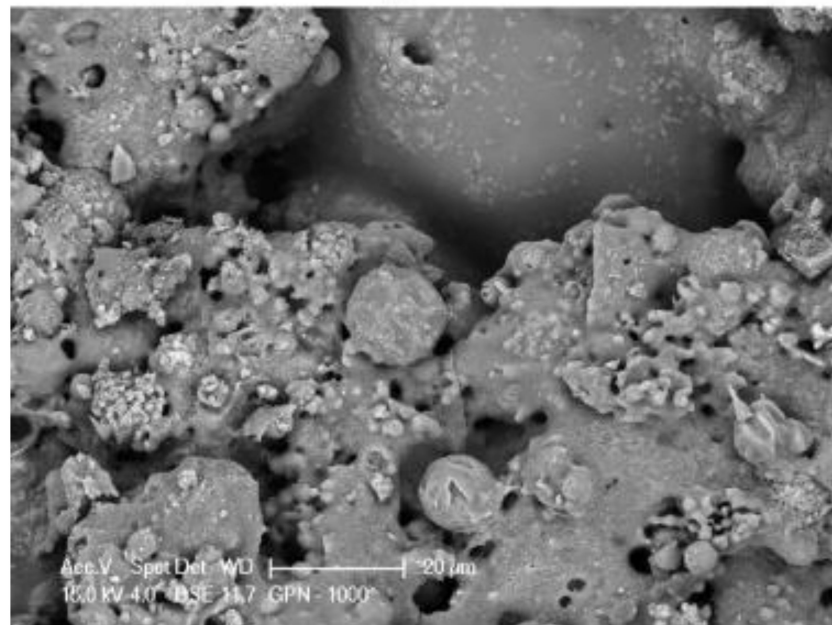


Figure 6. SEM images of geopolymer concrete after 1000 °C fire exposure [83].

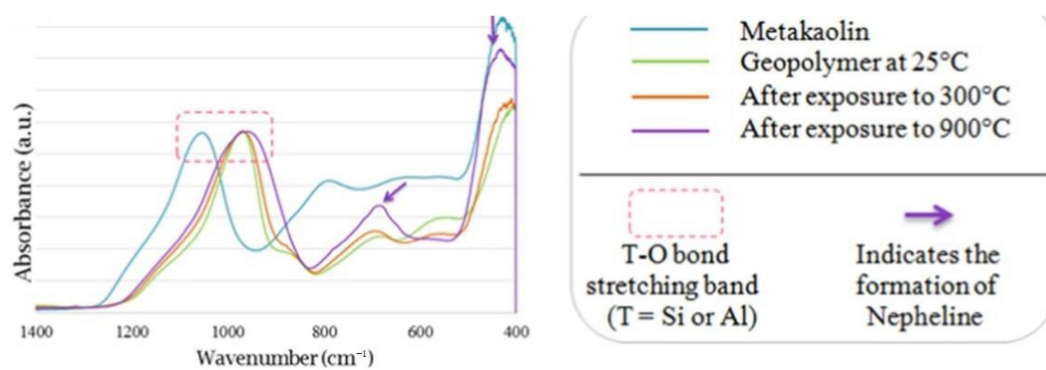


Figure 7. FTIR analysis of geopolymers before and after fire exposure [108].

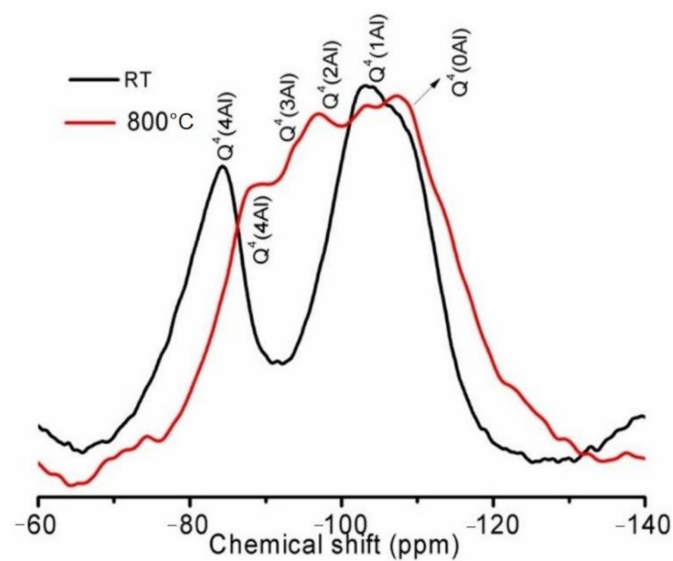


Figure 8. NMR analysis of geopolymer composites [111].

7. Conclusions and Discussion

To sum up, the scientometrics review of the fire and thermal resistance behaviour of geopolymer concretes as structural materials found competent enough to make certain not only the safety and security of lives and properties but also to promote them as more durable and sustainable construction materials for future. Their outstanding mechanical and durability performances at elevated temperatures pilot to put them into a cut-throat position against OPC-concrete in the infrastructure and construction industries. During the past couple of decades, geopolymer concrete has created a centre of attention and strong interests across the globe on account of their benefits of lower energy cost, higher initial strength, brilliant durability and sustainability as well as a unique fireproof structural material on account of their ceramic-like characteristics plus intrinsic inorganic structure. Not merely have that, their thermo-chemistry and their behaviour at lofty temperatures are known to be reducible destructive as compared to their OPC-counterparts. What is more, they do not experience decomposition of the binder phase as found in the case of OPC-system at towering temperature exposure which proves their chemical stability. Heat-cured geopolymer concrete using precursors like Metakaolin and low calcium F type fly ash is believed to be a model edifice material for precast geopolymeric concrete structures. Nowadays, the use of GP-materials as a heat resistant cement and concrete in tunnels, high-rise buildings, fire-proof panels, refractory, foundries, aeroplanes, ships, etc. is found increased due to their extraordinary resistance against thermal and fire. On the basis of the report of several concrete researchers, the present review concludes that geopolymers are found stable chemically at elevated temperature exposure, i.e., they do not undergo breakdown of a chemical structure as met within the case of OPC hydration product. Higher temperature exposure causes thermal shrinkage or expansion which in turn responsible for macro cracking. It is significant to control the water quantity in geopolymer mixture in the interest to regulate the strength and spalling resistance and thermal deformation. Moreover, thermal deformations are influenced by the type of alkali activator solutions like Potassium (K) or Sodium (Na). Thermal shrinkage is found to trim down through the use of Potassium as compared to Sodium as Alkali Cation. The review of reports of experimental and field observations for a degree of cracking, spalling and loss of strength within the geopolymer concretes subsequent to exposure at elevated temperature and incidences of occurrences of disastrous fires escorted to conclude for an indication of their resistance against such severely catastrophic conditions on mechanical attributes such as mechanical-compressive strength, flexural behaviour, elastic modulus; durability-thermal shrinkage; chemical stability; the impact of thermal creep on compressive strength; and microstructure properties—XRD, FTIR, NMR, SEM as well as physicochemical modifications of geopolymer composites and the results obtained are quite encouraging. Every bit of reports sees eye to eye for these marvellous construction materials which are found performing superior to their OPC-counterparts. For these reasons, geopolymer composites can be positioned at the epicentre of an innovative and essential switch-over from contemporary OPC to the novel innovative green construction composites of the days to come with “Go Green, Live Green” concept.

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Abbreviations

GHG = Green House Gases, GPC = Geopolymer concrete, RC = Reinforced concrete, OPC = Ordinary Portland cement, POFA = Palm Oil Fuel Ash, PFP= Passive fire protection.

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