

Review of Geopolymer Behaviour in Thermal Environment

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Abstract. This paper presents a review of the thermal resistance of geopolymers towards the fire and elevated temperature. Geopolymers are one of the new class materials, emerging in far-reaching potential in fire and thermal resistance areas. The review includes the thermal performance of geopolymers before and after the thermal exposure. An overview on the recent progress of the geopolymers in high-temperature application is discussed in detail to keep pace with the development in this field. The characterization of geopolymers before and after the thermal treatment in term of microstructural, and crystallographic are also reviewed.

1. Introduction

The exponential increase of articles on geopolymers provides a better understanding on the applicability of geopolymers as a prominent alternative to the traditional cement which leads to a revolution in civil engineering. Geopolymer, is a state-of-the-art inorganic material that has been found displaying enhanced performances in thermal stability and fire resistance. In the urgent necessity to enhance the thermal or fire resistance, geopolymers present an enormous potential product such as geopolymer concrete, coating, lining and composite matrix to combat the problems.

There are several specific properties of geopolymers which lead to particular suitability in the high temperature application such as tunnel fire resistance, furnace lining, wall panel and thermal insulation. Davidovits [1] had emphasised the ceramic-like properties henceforth the formation of several crystalline aluminosilicate phases with the potentially high melting point up to 1100°C. These physiochemical characteristics believed as pivotal to preserve the structural integrity upon heating at high temperatures. It is in the sense that the chemical composition of the raw materials itself, admixtures, aggregates and alkaline used determine the production of geopolymers with a longer life cycle.

Be that as it may, it must be emphasised that even though geopolymers are incombustible materials, it still undergoes allowable strength deteriorations with increasing exposing temperature. Any construction materials, mainly ordinary Portland cement (OPC) will end its life cycle or undergo a significant strength loss at elevated temperatures (500-550°C) due to dehydration of OPC systems with formation of calcium oxide. During the rehydration, calcium hydroxide is formed, which is a



high-end process leading to the formation of thermal cracking henceforth it degrades in strength irreversibly [2, 3].

Thermal expansion, thermal conductivity, strength retention, spalling and melting point are the critical macroscopic characteristics when assessing the suitability of the high-temperature performance of geopolymers. Hlavacek et al. [4] recognised there are high shrinkage and sintering effect associated with the elevated temperature resistance. In the microstructural point of view, the thermal analysis of the geopolymer for instances the thermodynamics, dehydration, phase stability and morphology are those of the major concern. Thus, this paper summarises the thermal performances as well as the effect of extent heating rates to the structural evolution and phase stability of geopolymeric materials.

2. Evolution of geopolymer during thermal exposure

The physical evolution of geopolymer during thermal exposure are of the major concern used to assess the behaviour after firing geopolymers sample. Geopolymers molecular structures particularly MK-based geopolymers are stable even when exposed at temperatures above 700°C is in many cases far superior to Portland cements [5-8]. Temperature condition change in term of the exposure time and heating rates are one of the ultimate factors that affecting the molecular structure henceforth entirely concerned in the material deterioration. But then, the benchmarks used to assess fire resistance could be defined differently according to their applications.

Considering the fire endurance assessment of geopolymers, the evolution of geopolymer during thermal exposure is of interest. On the basis, geopolymers undergo phase changes, namely thermal shrinkage, crystallisation, thermal conductivity and mechanical strength when exposed to fires. The responses of geopolymers towards the elevated temperature hereafter lead to microstructural stresses. This causes a major decline in the mechanical properties of the geopolymers. Microstructural variations as a results of high-temperature exposure can be analysed through differential thermogravimetry (DTG)/TG, Fourier transform infrared (FTIR), and X-ray diffraction analyser (XRD).

According to the study conducted by Barbosa and MacKenzie [6], geopolymers based on potassium sialate displayed extremely superior thermal stability. These geopolymers displayed high degree of thermal stability with no sign of melting up to 1000°C. Beyond these, few data have been compiled to have an insight into the microstructure change of such geopolymer concrete and mortar after thermal exposure.

2.1. Visual appearance

Serious damage of cracking and spalling of concrete structure are the major drawback of OPC concrete when it was subjected to rapid heating rates. Additional thermal stresses induced the explosive spalling commonly causes severe cracking within concrete's structure. According to Hertz and Kristian [9], spalling of concrete occurs due to the high internal stresses caused by water evaporation or temperature gradients inside the concrete. Referring to (figure 1), after 119min of ISO 834 fire, sudden explosive spalling leading to a loss of 60 mm of concrete consequently lower strength [10].

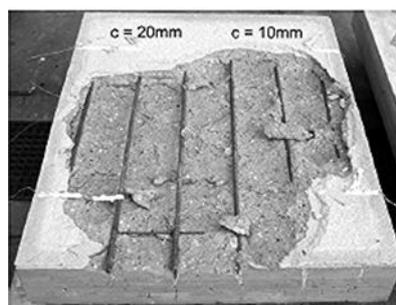


Figure 1. Explosive spalling that occur to High Performance Concrete (HPC) [10].

The violent breaking off of OPC concrete fragments at high temperatures provide as an essential input in the development of sustainable construction materials which is geopolymer. Sakkas et al. [11] reported that FeNi slag- based geopolymers shows little no crack on the surface after subjected to a propane flame with temperature higher than 1100°C for 120 min. Referring to X-ray diffractograms, there is an oxidation of magnetite to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) when thermally treated at 500°C, whereas the red colour is formed when it is treated to 1000°C which transforms maghemite to hematite. Simultaneously, new aluminosilicate phases such as albite and olivine were formed [12, 13].

Physical evolution of fly ash geopolymer after firing was perceived to have a reddish in colour with diversifying degree (figure 2 and figure 3). The degree of red tinge was observed to be corresponding to the iron content in each different type of fly ash. The higher amount of iron oxide which is 16.4% (figure 2) cause remarkable change in colour than fly ash that consist 4.1% of iron oxide (figure 3). Even so, the inferior amount of iron oxide prevent macro cracking due to dimensional stability and preferred particle connectivity associated with sintering [14].

The improvement in the interconnectivity through sintering could increase the mechanical strength; in some cases can be more than five times the strength at ambient temperature [15, 16]. According to Rickard et al. [17], sintering can be defined as the “heal” of crack induced during the dehydration phase (phase in which water escaping caused the structural damage) and hence improve the mechanical properties of the materials. However, severe macro crack was observed for fly ash geopolymer (figure 2) and the crack healed as the temperature is was increase to 900°C and 1000°C. This was attributed to the dimensional instability caused by the heterogeneous melting [14].

Saker et al. [18] reported that fly ash based geopolymer shows a significant colour change when subjected to ISO 834 [19] fire curve in gas fired furnace. In companion to OPC concrete when subjected to same temperature profile as geopolymer, it did not display much change in colour, but greyness of the cement faded. Colour change in OPC is due to the higher reduction of moisture. Whereas the reddish tinge from the geopolymer concrete at 1000°C was because of the high iron oxide content on the fly ash and oxidised [18, 20].

Susceptible surface cracking and spalling was observed on OPC after the high temperature ranges starting 600°C. It is mainly due to the large amount of differential strain and thermal gradient which cause the pore pressure to exceed the tensile stress of the structure element. The relative less cracking and spalling of geopolymer concrete allowed it to be considered for use in high- temperature application such as furnace.

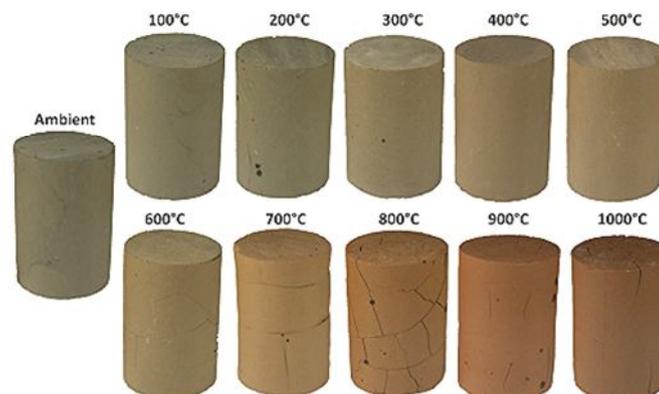


Figure 2. Fly ash geopolymer (16.4% iron oxide) fired under various temperatures [14].



Figure 3. Fly ash geopolymer (4.1% iron oxide) fired under various temperatures [14].

On the other hand, after heating to 800°C and 1000°C the geopolymer mortar prepared by using calcined ore- dressing tailing of bauxite and ground granulated blast furnace slag showed visible cracks of 0.25 ± 0.1 mm [21]. Similar cracks were observed for fly ash geopolymers containing high concentration of iron oxide and α - quartz [22]. Visual inspection indicated that larger sample generates more cracks compared to smaller one caused by the thermal differential during heating. The differential of oxidised and non- oxidised regions contributed to the cracking in the samples.

According to Zhang et al. [23], the breeding of cracking was contributed by the inhomogeneous distribution of binders and aggregates in the geopolymer concrete specimens. The preparation of specimen caused the floating upward of geopolymer binder and sinking downward of coarse aggregates. The exorbitant inhomogeneity between both unintended layers in the geopolymer concrete specimens, exacerbated the problem of crack. Therefore, according to Perera et al. [24], it was practical to cure under controlled relative humidity with mild heating between 40°C to 60°C to obtain crack free state.

2.2. Thermal shrinkage

Thermal shrinkage or expansion can be the basic response that causes failure in a fire. It is evaluated through the volumetric changes of geopolymers that occurs during given high temperature. Some studies proved that thermal incompatibility between geopolymer and aggregates renders them to thermal expansion. Thermal shrinkage is caused by the evaporation of water and hydroxyl groups OH which consequently weakens the geopolymer's structure system. Rahier et al.[25] studied the synthesis of dehydroxylated clay suspended in alkali sodium silicate solution at low-temperature curing denoted as "low temperature inorganic polymer glass (LTIPG)". The LTIPG material shrunk about 5% attributed to the evaporation of water at 250°C after polymerization. However, the evaporation of water can occur at room temperature as well.

Rovnanik et al.[26] claimed that the shrinkage alkali-activated slag (AAS) is comparable to the shrinkage of OPC with a maximum of only 6.6% at 1200°C. It was reported that the increase in shrinkage for AAS is 5% between 40°C to 1000°C sequentially dominates the mass loss and the decrease in bulk density. This was attributed to the moisture loss and the liberation of water from the structure as a result of the thermal shrinkage which unfortunately weakens the geopolymer structure. The dissimilarity of density of structure, as well as the large number of micro-cracks in conjunction to the increased in the total porosity rapidly changed the morphology of AAS paste when the material is heated up to 800°C (figure 4).

On the basis, thermal shrinkage can be categorised into four characteristic regions which are the structural resilience, dehydration, dehydroxylation and sintering. Pore parameter of mortar before and

after heating, closely affecting the thermal properties of geopolymers. The expansion and shrinkage as results of the thermal exposure were caused by the dehydration, dehydroxylation, phase transformation of quartz and viscous sintering. Ye et al.[21] acquiesced in the results that the porosity accumulate momentarily after exposing to 400°C and reaches maximum at 1000°C. However, at 1200°C, there was almost 2% reduction in porosity due to the viscous flow and surface tension joint action.

Previous studies [21, 22, 27-29] observed that the dependence of bulk density under thermal exposure is not erratic, it actually undergoes several obstructing processes. First is the weight loss which derives from the density loss. Next is the shrinkage in the temperature ranging from ambient temperature to 800°C, followed by the sintering at the higher temperature that causes yield in the density. Later, is the expansion of quartz, engendering in a density loss. Also, the amount of shrinkage due to firing can be measured by using Vernier callipers as an average shrinkage using at least three samples.

Recent work by Duxson et al. [29] elucidated the physical evolution of geopolymeric materials derived from metakaolin and synthesised with sodium, mixed- alkali and potassium activating solutions (Na- NaK- K) during thermal exposure. According to the results, K- geopolymer implied prominent influence to the thermal shrinkage with the increasing of Si/Al ratios. This was attributed to the densification caused by reduction in porosity during dehydroxylation and sintering. Besides, according to previous literature geopolymers prepared using K-containing activators with a high Al/Si ratio remained their thermal stability up to 1300- 1400°C [6]. It is pronounced that the geopolymer specimen experienced recrystallization to feldspar leucite and kalsilite at 1000°C. This statement was further supported by Barbosa et al. [6], who stated that potassium geopolymers with low Al/Si ratio show significant large-grained in consistency and porous when heated >1200°C. The reduction of shrinkage in length and diameter when the geopolymer prepared using K activators was also concurred by Bakharev and Tatiana [28].

2.3. Crystallisation

The structural changes of fly ash geopolymers under thermal exposure were quite complex due to the influence of secondary phases in precursor for instances quartz, mullite, unburnt carbon, magnetite and other various iron species.

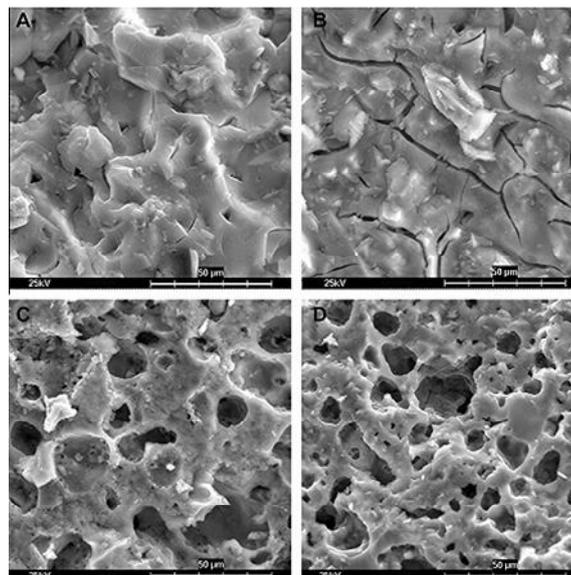


Figure 4. The micrographs of AAS paste treated at a room temperature (A) and after exposure to 600°C (B), 800°C (C) and 1200°C (D) [26].

The high-temperature exposure increased the predisposition towards the liberation and oxidation of iron species which accounted for the formation of stable crystalline phase [22]. Heah et al. [30] and Bakharev [28] studied the thermal properties of fly ash geopolymers, and they reported that the increase in iron oxide species, such as hematite, after high-temperature exposure. Comparatively, for metakaolin geopolymers, the crystallisation of dense sodium aluminosilicate phases namely nepheline was formed when exposed to temperature 800°C [31].

Figure 5 presents the phase composition of fly ash geopolymers with iron oxide content of 16.4%. This fly ash geopolymers showed relatively broad humps of amorphous with the crystalline components originated from fly ash. Analysis of XRD pattern indicated a slightly increased concentration of hematite after heating to 500°C. This was the typical characteristic of aluminosilicates matrix after the geopolymerization at high-temperature.

The drop of amorphous phases from 66% to 43% at 1000°C might due to the crystallisation into nepheline ($\text{NaAlSi}_3\text{O}_8$) and anorthoclase ($\text{NaAlSi}_3\text{O}_8$). Mineral phases of quartz, hematite and maghemite were likely reduced in intensity. These phases have higher melting points than 1000°C (studied temperature range) which is mullite, 1830°C [32] and quartz (β - cristobalite), 1713°C. This reflected that mullite and quartz are the unique sintering agents [33].

2.4. Mechanical strength at elevated temperature

There is considerable on- going interest in adopting geopolymers in construction industry especially concerning the residual strength of the material after exposure to high temperature or fire. In general, the mechanical strength and microstructural analysis of all geopolymers have very distinct properties both before and after exposed to heating. Rickard et al.[8, 14, 16, 17, 34] supported that the main mechanism for the mechanical strength gain or losses is anticipated to dehydration damage, dimensional stability, sintering and melting. The mechanism that corporated to the reduction in mechanical strength is accord well with the formation of cracking too.

An earlier qualitative study by Perera et al. [24] showed that the strength of geopolymers decrease linearly with the increase in porosity. Porosity of geopolymers was highly dependent on the amount of water extant in the original precursors followed by the weight loss due to the curing conditions. According to Bakharev [28], geopolymer materials prepared with sodium containing activators deteriorate rapidly in strength as it reaches 800°C, which is connected to the intense amount of build-up pore in the structures.

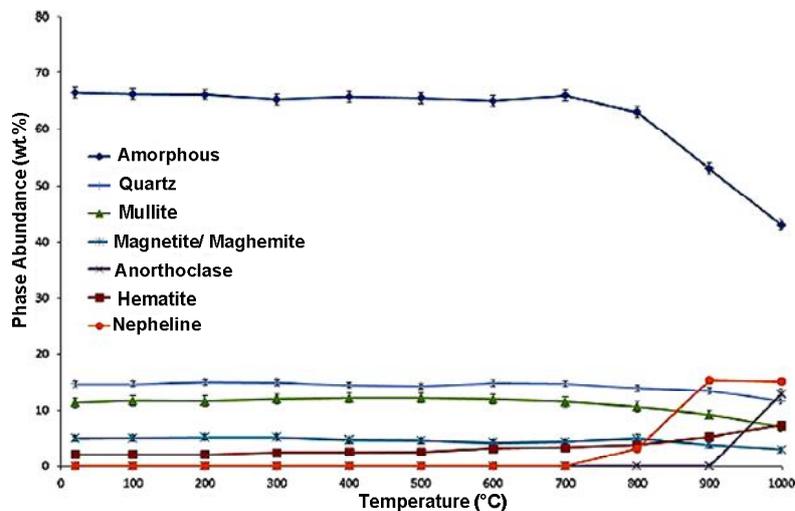


Figure 5. Fly ash geopolymer (16.4% iron oxide) fired under various temperatures [14].

According to Bakharev [35], fly ash geopolymers with sodium containing activator had very small average pore size of about 4.5 nm and caused these materials to have low permeability. The high stresses in the pore wall developed movement of uncombined water and therefore greater degradation with rising temperature contributed from the collapse of fine pores and extent of shrinkage. As stated above, the loss of water after exposure to temperatures up to 1200°C led to more pores (figure 6) in the structure and consequently lessen the strength [36].

This trend was supported by Duxson et al. [37] whereby the microstructure of the material that contains a less dense gel and nanometer size pore improves the thermal performance and finally increases the compressive strength. This can be achieved by increasing the silicate concentration in the activating solution, successively leads to a massive increase in densification of the material up to temperature between 600°C to 900°C [8].

The high- strength geopolymers exhibited poor thermal properties, whereas the relatively low initial strength geopolymers exhibited impressive thermal properties. The unexposed fly ash geopolymer with early strength of 100 MPa exhibited severe macro cracking when heated to 600°C but retained its minimum strength of 2 MPa. Attractively, beyond 700°C, the strength improved to 15 MPa until reaching 1000°C. The SEM image revealed that at elevated temperature exposure the sintering of geopolymers produced a more homogenous and exceptional connection between the microstructure [14].

The exposure at elevated temperature caused changes in the phase composition and hence the mechanical strength of the geopolymers. This was supported by Bernal et al. [38] for slag geopolymers synthesised with high- modulus activators. When the slag geopolymer was exposed to the temperature of 1200°C, the compressive strength increased by 40% compared to the unexposed geopolymers. This was attributed to the formation of crystalline phases such as akermatite and gehlenite.

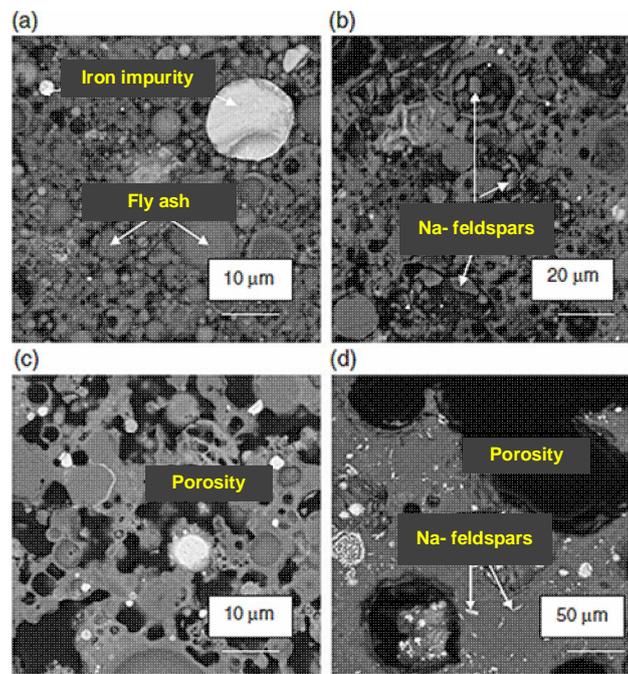


Figure 6. SEM micrograph of fly ash geopolymer using Na alkaline activators for unexposed sample (a), exposed to elevated temperature, 800°C (b), 1000°C (c) and 1200°C (d).

3. Conclusions

In this paper, the thermal behaviour of geopolymers was reviewed. With the global scarcity towards development of new materials with improved thermophysical properties and the necessary issues of reutilising of industrial by-products, alkali-activated binders so-called geopolymers, materials with very high fire resistance ratings is necessary for the long-term basis. Increased demands and reduced supply of Portland cements as common construction materials require industries to participate in employing geopolymers through the dissolution and polycondensation of aluminosilicate sources in highly alkaline solution. As the literature has shown, geopolymers is an alternative fire resistance construction materials that can be adopted. Finally, geopolymerization methods are encouraged to be realised applying either in existing structures or as novel technologies.

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