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MICROSTRUCTURAL ANALYSIS OF FLY ASH BASED GEOPOLYMER EXPOSED TO ELEVATED TEMPERATURES

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Abstract: Many research work related to geopolymer are being carried out in the recent years because of its better environment friendly status than ordinary Portland cement. This paper attempts to study the microstructural behaviour of fly ash based geopolymer after exposed to elevated temperatures. FTIR, XRD, TGA and SEM analysis has been carried out on geopolymer mortar/paste specimens after they were exposed to 200°C, 400°C, 600°C and 800°C. Based on the present study, the mechanism of early strength loss and the subsequent strength gain of geopolymer during temperature exposure have been established. The difference between the mass loss characteristics of geopolymer paste and OPC mortar specimen when exposed to elevated temperatures has been identified. It has also been established that, the geopolymer will have lower crack width compared to OPC specimen when they are exposed to elevated temperatures.

Keywords: Geopolymer, Fly ash, High temperature, FTIR, XRD, SEM

INTRODUCTION

Cement is the commonly used binding material in mortar and concrete. However during the production of cement almost the same mass of greenhouse gas is also released to the atmosphere [1, 2]. So an alternative material that can replace cement in concrete and mortar will reduce the generation of greenhouse gas to a great extent. One of such promising material is geopolymer.

Geopolymer (GP) is a binding material formed by alkali activation of amorphous alumina-silicate materials under warm atmosphere [3]. Even though exact reaction mechanism for the formation of geopolymer is not clearly known [4], most accepted reaction mechanism has three stages namely dissolution, hydrolysis and condensation [5-7].

The source materials (alumino-silicate) may be natural minerals, such as kaolinite, calcined kaolinite (metakaolin) and clays [5,8,9,10]. Alternatively, industry waste products such as fly ash, slag, red mud, rice-husk ash and silica fume may be used as source material for the synthesis of geopolymers [11-18].

The alkali component as an activator is a compound from the elements of first group in the periodic table. The commonly considered activators are NaOH, Na₂SO₄,

water glass, Na₂CO₃, K₂CO₃, KOH, K₂SO₄ or a little amount of cement clinker and combination of alkalis [19].

Large quantity of fly ash generated in thermal power industry faces disposal issue. Only a small percentage of fly is utilized for construction purposes and remaining quantity is disposed in ash ponds or lagoons. Deposition of the fly ash in storage places can have negative influence on water and soil because of its granulometric and mineral composition as well as morphology and filtration properties [20]. Therefore use of fly ash for making geopolymer has dual benefit to atmosphere.

There are many factors which influence the mechanical properties of geopolymer concrete [3,21,22]. Microstructural analysis shows that, amorphisity and particle size of source material, Si/Al ratio etc. in geopolymer influences the mechanical properties of geopolymer concrete [23, 24, 25].

Structures are likely to expose high temperature due to accident or due to functional cause. There is much information regarding the strength loss characteristics of Portland cement concrete after exposure to high temperatures [26-31]. However only few information is available related to the engineering properties of geopolymer after exposure to elevated temperatures

and particularly with respect to the microstructural aspects.

It has been reported that strength loss characteristics of fly ash based geopolymer paste, mortar and concrete after exposure to elevated temperature are different [32]. However, a clear understanding about this behaviour is possible only with a microstructural analysis. Hence present study attempts to understand some of the microstructural behaviour of geopolymer after they are exposed to elevated temperatures.

EXPERIMENTAL PROGRAM

Materials

Low calcium fly ash (ASTM Class F) obtained from a thermal power station (India) has been used for the present study. The chemical composition of fly ash is presented in Table 1. The fly ash used had a specific gravity of 1.9.

Table 1. The chemical composition of fly ash

Parameter	Content % by mass)
SiO ₂	59.70
Al ₂ O ₃	28.36
Fe ₂ O ₃ +Fe ₂ O ₄	4.57
CaO	2.10
Na ₂ O	0.04
MgO	0.83
Mn ₂ O ₃	0.04
TiO ₂	1.82
SO ₃	0.40
Loss of ignition	1.06

A mixture of NaOH and Na₂SiO₃ solution (SiO₂= 34.64%, Na₂O=16.27%, water 49.09%) was used as alkali solution in the present investigation. NaOH pellets of 98% purity were used to make sodium hydroxide solution. The specific gravity of alkali liquid solution, having Na₂SiO₃/NaOH (molarity 10) ratio 2.5 was 1.54.

Mixture proportioning for GP specimens

Geopolymer paste or mortar was prepared for the microstructural analysis based on a mixture proportion for geopolymer concrete that gave maximum compressive strength. The mixture proportion of GP concrete which gave maximum compressive strength had aggregate content by volume (70%), the ratio of fine aggregate to total aggregate (0.35), ratio of alkali to fly ash by mass (0.55), molarity of NaOH (10), ratio of Na₂SiO₃ to NaOH (2.5) ratio of water to geopolymer solid (0.25).

Details of this study has been reported elsewhere [3].

For preparing specimens for Scanning Electron Microscope (SEM) analysis, mortar from GP concrete prepared based on the proportion as stated above was separated and used. Specimens for Fourier Transform Spectroscopy (FTIR), X-ray Diffraction (XRD) analysis and Thermogravimetric (TGA) analysis were prepared with fly ash and alkali in the proportion that has been arrived in the case of GP concrete.

Casting of GP specimens

Mortar specimens of size 10 mm diameter and 10 mm thick were prepared using aluminium tubes for SEM analysis.

GP paste specimens were prepared in a small steel container for FTIR, XRD and TGA analysis.

The specimens were kept in an oven for 24 hours at 100°C for temperature curing. After temperature curing, specimens were demoulded and kept at room temperature till they were tested.

Mixture proportioning for OPC specimens

OPC mortar specimens were prepared for SEM analysis based on a mixture proportion for OPC concrete that gave almost the same compressive strength as that of GP concrete. The detail of study has been reported elsewhere [3].

For preparing specimens for Scanning Electron Microscope (SEM) analysis, mortar from OPC concrete prepared based on the proportion stated was separated and used.

Casting of OPC specimens

Mortar specimens of size 10 mm diameter and 10 mm thick were prepared using aluminium tubes for SEM analysis. After 24 hours (kept in laboratory condition), the specimens were demoulded and immersed in water till they were tested.

Heating and cooling of specimens

GP and OPC specimens (except for TGA analysis) were heated in an electric furnace to 200°C, 400°C, 600°C and 800°C. The rate of heating was kept at 5.5°C per minute. After attaining the target temperature, specimens were kept at the same temperature for 1hour to ensure that the specimens attain a uniform temperature throughout. The heated specimens were then cooled down to room temperature by air cooling.

RESULTS AND DISCUSSIONS

FTIR analysis

Figure 1 shows the comparison of FTIR spectrum of fly ash with that of GP paste at ambient temperature. FTIR spectrum of fly ash has four distinct bands identified as h, g, f and d in the figure. The wave number corresponding to 1088 cm⁻¹ (d) and 460 cm⁻¹ (h) represents the Si-O/Al-O stretching vibration and in plane bending vibration respectively.

The wave number 795 cm⁻¹ (f) indicates the tetrahedral linkage of Si-O-Al and 553 cm⁻¹(g) indicate octahedral linkage of Al [9, 33- 35].

The peak area and peak height in the FTIR spectrum are frequently used in quantitative assessment of geopolymer reaction [Peak area]. The FTIR spectrum of geopolymer paste shows higher peaks corresponding to wave numbers 795 cm⁻¹ (f), 1088 cm⁻¹(d) and 460 cm⁻¹(h) as against the FTIR of fly ash. This phenomena indicates an increase in chain length and formation of alumino-silicate compound due to polymerisation [36].

The FTIR spectra of GP paste shows an increased peak in the wave number corresponding to water molecule (3430 cm^{-1}) when compared to fly ash. New band (1635 cm^{-1}) showing formation of water molecule is also visible in the FTIR of GP paste. These bands are due to weakly bound water molecule which were adsorbed on the surface or trapped in the large cavities between the geopolymeric products [37]. Wave number corresponding to the 1453 cm^{-1} (c) and 870 cm^{-1} (e) represent the presence of Na_2CO_3 and that might be formed due to the carbonation of unreacted sodium silicate and /or sodium hydroxide [9].

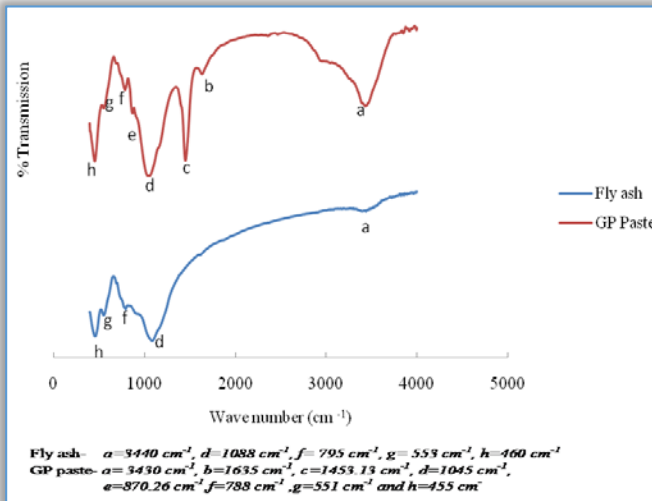


Figure 1. FTIR diagram of fly ash and geopolymer paste
The FTIR spectrum analysis of GP paste exposed to elevated temperatures is presented in Figure 2. Figure 3 shows the enlarged view of FTIR in Si-O-Si and Si-O-Al region (h to d - wave number 460 cm^{-1} to 1088 cm^{-1}). Figures 2 and 3 shows a substantial reduction of the peak in Si-O-Al and Si-O-Si regions at a temperature exposure of 200°C , indicating a reduction in their bonding force and decrease in chain length [23, 38].

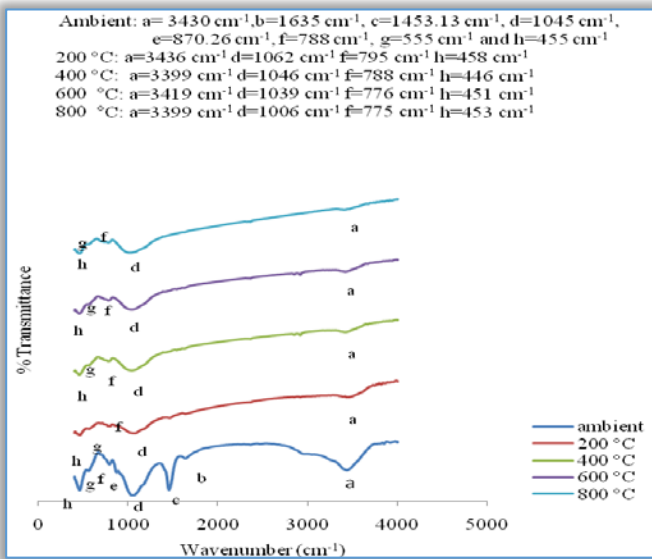


Figure 2. FTIR diagram of geopolymer paste after exposure to elevated temperatures

Figure 2 shows that, the band representing water molecule (hydroxyl groups) in GP paste (3440 cm^{-1}) showed a marked decrease in its peak at a temperature exposure of 200°C and further increase in exposure temperature do not cause significant decrease in these peaks. This means that, most of the weakly bound water molecules that were either adsorbed on the surface or trapped in the large cavities between the geopolymeric products get expelled at about 200°C . The combined result of the above may lead to a reduced strength in GP concrete products during the initial heating process.

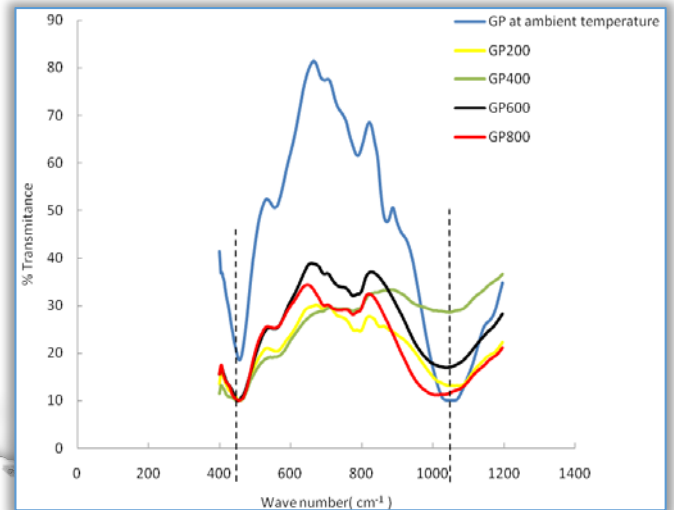


Figure 3. Enlarged view of FTIR diagram

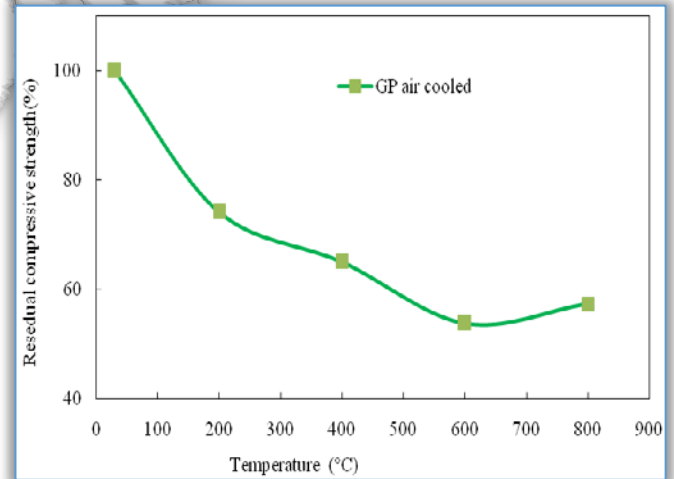


Figure 4. Variation of residual compressive strength of GP concrete with temperature exposure

Also, while the FTIR spectrum of GP paste shows marginal reduction in the peak intensities over the Si-O-Al and Si-O-Si region (h-d) for the temperature exposure between 200°C and 600°C , the peak intensity corresponding to Si-O-Si linkage increases slightly beyond 600°C , confirming the polymerization of initially unreacted materials beyond 600°C and this may lead to increase in the compressive strength of GP concrete product beyond 600°C temperature exposure. Typical variation of compressive strength of GP concrete after exposure to temperatures is presented in Figure 4

and this figure confirms the hypothesis of early strength loss and subsequent strength gain of GP concrete when exposed to elevated temperatures.

XRD Analysis

Figure 5 shows the XRD diagram of fly ash and geopolymer paste at ambient temperature. The amorphous phase in GP paste, as per XRD analysis was 78% while that in fly ash was 41%. This is to say that the geopolymer is more amorphous than the fly ash used in it and this observation is consistent with the observations reported elsewhere [25].

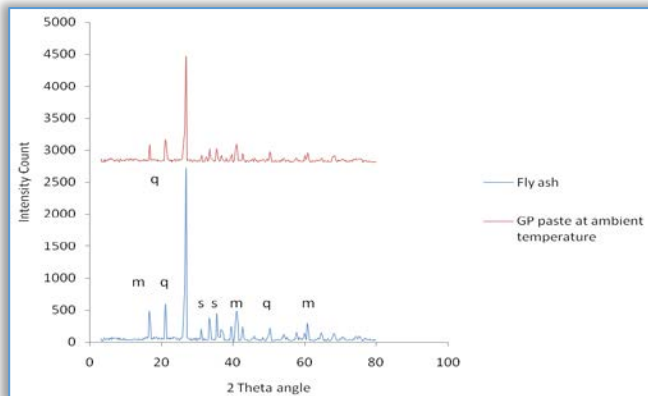


Figure 5. XRD diagram of fly ash and geopolymer paste at ambient temperature

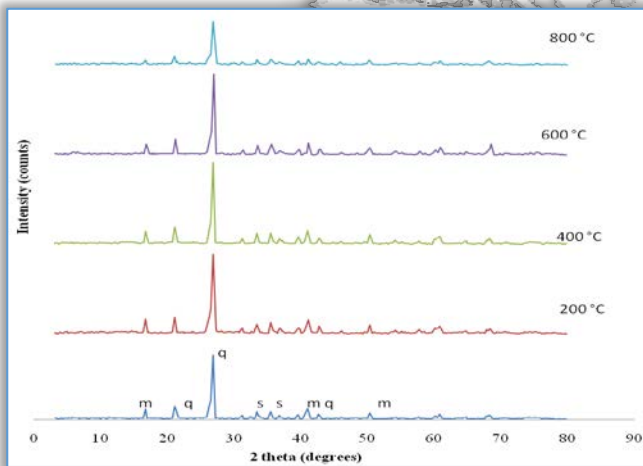


Figure 6. XRD diagram of geopolymer paste after exposed to elevated temperatures

Furthermore, from Figure 5 it is clear (existence of the peaks of Quartz, Mullite and Sellmanite) that, complete dissolution of fly ash due to alkali activation has not taken place at ambient temperature. Figure 6 shows the XRD diagram of GP paste after exposure to elevated temperatures.

From Figure 6, it could be seen that the crystalline materials present in the GP paste has not under gone significant change in its phase up to an exposure temperature of 600°C. However, at 800°C, the crystalline phase got further changed to amorphous phase. This new amorphous content further undergoes polymerization and may cause increased strength in the GP paste.

TGA Analysis

Figure 7 shows the result of the Thermo gravimetric Analysis (TGA) of GP paste.

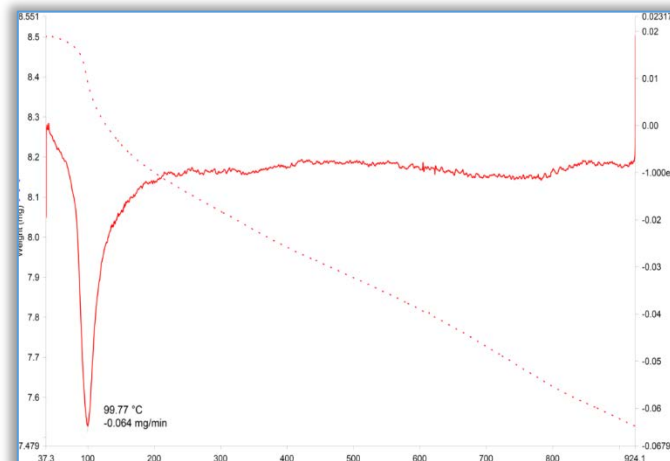


Figure 7. TGA of geopolymer paste exposed to elevated temperatures

A rapid mass loss at 100°C could be seen from Figure 7. Further, the rate of mass loss is more or less constant beyond a temperature of about 200°C. Hence it could be stated that, most of the free water and weakly adsorbed water within the geopolymer paste escape at a temperature below 200°C. This observation is in line with the published literatures [39]. The FTIR analysis presented also justifies the said behaviour. It may further be noted that, the mass loss of OPC specimen at elevated temperature is different from that of GP specimen, primarily due to the difference in the chemical and structural change of OPC specimen at elevated temperatures.

It has been reported elsewhere [40] that the TGA of OPC has three rapid mass loss stages like loss of water due to dehydration of C-S-H between 100°C and 200°C; dehydration of portlandite causing rapid weight loss between 450°C and 500°C; and the decarbonation of Ca_2CO_3 at 750°C.

SEM analysis

The SEM Image study was carried out on GP mortar and OPC mortar taken from their respective concrete samples. The SEM images of GP mortar and OPC mortar specimens were taken after they were exposed to 200°C, 400°C, 600°C and 800°C and air cooled to ambient temperature. These images are compared in Figure 8. From Figure 8 it could be observed that, at a temperature exposure of 200°C, GP mortar specimen experiences very low crack width (400 nm), compared to the crack width of cement mortar (2.33 μm).

As the exposure temperature increases, both GP and OPC specimen develops wider crack. However, even at 800°C, the crack width of GP specimen is (6.19 mm) lower compared with OPC specimen (16.67).

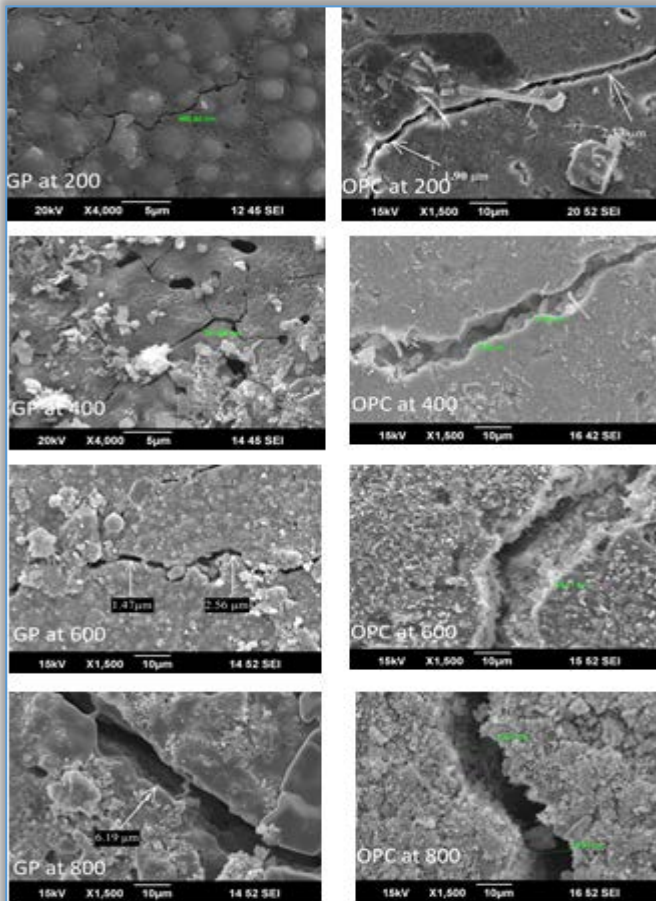


Figure 8. SEM image of GP and OPC mortar after exposure to elevated temperatures

CONCLUSIONS

Following conclusions could be derived based on the experimental study conducted on geopolymer paste and mortar.

- The geopolymer concrete, when exposed to elevated temperatures, experiences a higher rate of strength loss up to 200°C and gains its strength beyond 600°C.
- The higher rate of strength loss in the early heating period of geopolymer is contributed due to the reduction in bonding force and decrease in chain length in Si-O-Al and Si-O-Si bond.
- The strength gain of geopolymer beyond 600°C temperature exposure is primarily due to the polymerization of initially unreacted materials.
- The materials with crystalline phase in geopolymer tends to change to amorphous phase at temperature above 600°C and undergoes further polymerization; leading to improved strength properties.
- There is a rapid mass loss in geopolymer at 100°C due to the expulsion of most of the water (free and weakly adsorbed) from the geopolymer. Further, the rate of mass loss beyond 200°C is more or less constant.
- The mass loss characteristic of geopolymer is different from the mass loss characteristics of OPC paste. The OPC paste undergoes rapid mass loss at

three stages when exposed to elevated temperatures (at about 100°C, 450°C and 750°C).

- The crack developed in geopolymer mortar during early heating period is very much less compared to that of OPC mortar. Even at elevated temperatures, the geopolymer mortar develops only lesser crack width than OPC mortar. In the present study, at 200°C, OPC mortar developed a crack width of about 5.8 times that of geopolymer mortar and at 800°C, the corresponding figure is about 2.7.

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