

Effect of Na₂O Content on Performance of Fly ash Geopolymers at Elevated Temperature

Kalyan Kr. Mandal, Suresh Thokchom and Mithun Roy

Abstract—The present paper reports results of an experimental program conducted to study performance of fly ash based geopolymer pastes at elevated temperature. Three series of geopolymer pastes differing in Na₂O content (8.5%, 10% and 11.5%) were manufactured by activating low calcium fly ash with a mixture of sodium hydroxide and sodium silicate solution. The paste specimens were subjected to temperatures as high as 900°C and the behaviour at elevated temperatures were investigated on the basis of physical appearance, weight losses, residual strength, shrinkage measurements and sorptivity tests at different temperatures. Scanning electron microscopy along with EDX and XRD tests were also conducted to examine microstructure and mineralogical changes during the thermal exposure. Specimens which were initially grey turned reddish accompanied by appearance of small cracks as the temperature increased to 900°C. Loss of weight was more in specimens manufactured with highest Na₂O content. Geopolymer paste specimen containing minimum Na₂O performed better than those with higher Na₂O content in terms of residual compressive strength.

Keywords—Compressive strength, EDX, Elevated temperature, Fly ash, Geopolymer, Scanning electron microscopy, XRD

I. INTRODUCTION

ALKALI activated geopolymer composites have become very popular in the last few decades due to the reported properties form its environment friendliness. Among the family of geopolymer, fly ash based geopolymer is gaining more attention which is due to the fact that fly ash is available abundantly throughout the world as a waste from thermal power plants. Previous research in geopolymer have pointed out about its high early strength, high resistance to acid and sulphate attack, less creep and drying shrinkage as well as greater stability at high temperatures. Though there are quite a number of literatures available on geopolymer, those dealing with geopolymer manufacture with fly ash are very few. Husem [1] studied effects of high temperature on compressive and flexural strength of ordinary and high performance concrete and concluded the superior performance of high performance concrete over ordinary portland concrete. Effect

of rate of heating, duration of exposure to maximum temperature and role of graphite powder was investigated by Culfik and Ozturan [2]. The author indicated that high performance mortar lost almost all of their initial compressive strength at high temperature. Geopolymer possesses high early strength, better durability and has no dangerous alkali – aggregate reaction [3]. Geopolymer manufactured from low calcium fly ash by activation with various alkaline solutions have shown excellent performance against acids and sulphate [4-13]. Wallah and Rangan [8] investigated long term properties of fly ash based geopolymer concrete based on acid exposure, sulphate attack, creep and shrinkage. The author concluded that fly ash based geopolymer has excellent durability. Bakharev [4, 9] also showed that geopolymer materials manufactured from fly ash perform much better than OPC counterparts in acid and sulphate environment. An investigation of effect of elevated temperature curing on properties of alkali activated slag was conducted by Bakharev, Sanjayan and Cheng [14]. Behaviour of geopolymer paste and concrete at elevated temperature were found to be different due to differential thermal expansion between aggregate and pastes [15]. Specimen size and aggregate size have been identified as the two main factors that govern geopolymer behaviour at elevated temperatures of 800°C [16]. Bakharev [17] reported that geopolymer materials have low thermal stability and stated that these were unsuitable for refractory insulation application. However, due to limited number of studies on performance of geopolymer at high temperature, it is still felt necessary to carry out more investigations in order to arrive to a concrete conclusion.

The present experimental investigation was to study effect of Na₂O(alkali) content on the performance of fly ash based geopolymer paste specimens at elevated temperature exposure. Geopolymer pastes manufactured with varying alkali content of 8.5%.10% and 11.5% were subjected to elevated temperature up to 900°C and its performance was evaluated on the basis of weight loss, strength loss, volumetric shrinkage and sorptivity after temperature exposure. In addition, mineralogical changes due to elevated were studied by XRD. Investigation of microstructure as well as micro-probe analysis was performed using Scanning electron microscopy (SEM) and EDX.

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II. EXPERIMENTAL

A. Materials

Low calcium Class F fly ash used in the present experimental program was sourced from Kolaghat Thermal Power Plant near Kolkata, India. It had a mineral and chemical composition as in Figure 1 and Table-1. X-ray diffractogram of the fly ash showed amorphous phases with inclusions of semi crystalline phases such as mullite, quartz and hematite. About 75% of particles were finer than 45 micron and Blaine's specific surface was 380 m²/kg. Laboratory grade sodium hydroxide in pellet form (98 percent purity) and sodium silicate solution (Na₂O= 8%, SiO₂ =26.5% and 65.5% water) with silicate modulus ~ 3.3 and a

bulk density of 1410 kg/m³ was supplied by Loba Chemie Ltd,India. A mixture of sodium hydroxide and sodium silicate solution having Na₂O in the mix as 8.5% to 11.5% of fly ash was prepared one day ahead and used as the activating solution to manufacture the geopolymer paste. Water to fly ash ratio was maintained at 0.32.

TABLE I CHEMICAL COMPOSITION OF FLY ASH BY XRF

| Chemical composition | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | TiO ₂ | CaO | MgO | K ₂ O | Na ₂ O | SO ₃ | P ₂ O ₅ | LOI* |
|----------------------|------------------|--------------------------------|--------------------------------|------------------|------|------|------------------|-------------------|-----------------|-------------------------------|------|
| Percentage | 56.01 | 29.8 | 3.58 | 1.75 | 2.36 | 0.30 | 0.73 | 0.61 | Nil | 0.44 | 0.40 |

* Loss on ignition

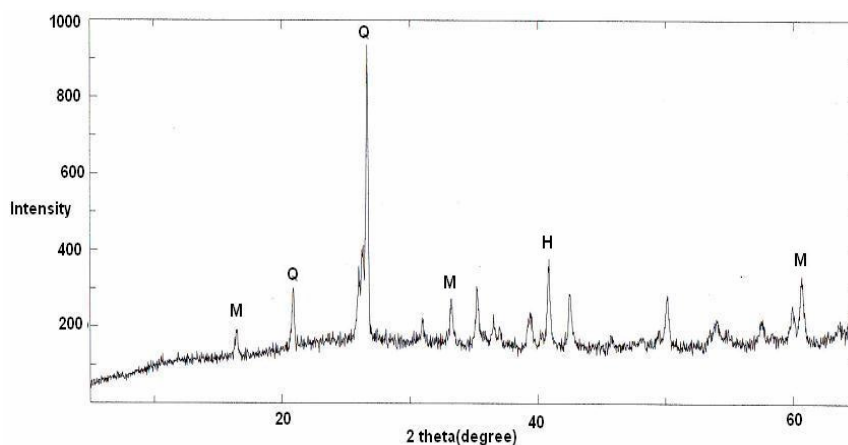


Fig. 1 X-ray diffractogram of fly ash, M-Mullite; Q- Quartz; H- Hematite

A. Preparation of specimen

Low calcium fly ash was first mixed with required quantity of activator solution in a Hobart mixer for 5 minutes to produce a uniform mix. The geopolymer mix exhibited a thick sticky nature with good workability. The mix was then transferred into 50 mm cube moulds and vibrated for 2 minutes to expel any entrapped air. Specimens were cured

along with the moulds in an oven for a period of 24 hours at 85°C and allowed to cool inside the oven before being removed to room temperature. The details of the samples used in the present study are given in the Table.2. The compressive strength determined at 7 days was found to be 36.51 MPa, 36.60 MPa and 37.33 MPa for specimens manufactured with 8.5%, 10% and 11.5% Na₂O content respectively.

TABLE II DETAILS OF TEST SPECIMENS

| Spec. ID | Na ₂ O content (%) | Water to Fly ash ratio | Curing temp. and duration | 7days comp. strength (MPa) |
|----------|-------------------------------|------------------------|---------------------------|----------------------------|
| GP 8.5 | 8.5 | | 85°C | 36.51 |
| GP 10 | 10 | 0.32 | and | 36.60 |
| GP 11.5 | 11.5 | | 24 hours | 37.33 |

A. Test procedure

After 7 days from manufacture, the geopolymer paste specimens were exposed at elevated temperatures of 300, 600 and 900°C and were held at these temperatures for a period of 2 hours. The specimens were allowed to cool inside the furnace before removing them for further tests. An optical microscope was used to observe the surface for cracks and such other changes after temperature exposure. Measurements of weight were performed immediately after removal from the furnace. Dimensional shrinkage after each exposure was measured with the help of a vernier caliper and volumetric strain was obtained. Three specimens from each series were used for determination of water sorptivity. Before the test, such specimens were painted with water proof paint all around in order to allow unidirectional flow of water into the specimen. XRD tests were conducted on powdered samples in a Rigaku Miniflex XRD machine. Microstructure changes at various exposure temperatures along with micro-probe analysis was performed in a JEOL JSM 6360 scanning machine fitted with Inca Oxford EDX analyzer.

III. RESULTS AND DISCUSSION

A. Physical appearance

The typical photograph showing the physical appearance with regard to changes in colour at different temperatures is shown in Figure 2. Colour of paste sample changed from grey (before temperature exposure) to light reddish as the temperature was increased to 900°C. In most of the specimens, small micro cracks began to appear at 300°C and it gradually increased with temperature. At 900°C these cracks were spread over a larger area and extended deep into the specimen. Images of specimen surfaces as seen through an optical microscope are given in Figure 3 to Figure 5. It was observed that Geopolymer paste specimen containing lower Na₂O exhibited cracks of minimum size. In contrast, cracks observed in specimens of higher Na₂O content were larger and deeper. GP8.5 specimen manufactured with 8.5% Na₂O did not show visible cracks even after exposure at elevated temperature of 900°C (Figure 3). However, geopolymer paste specimens of GP10 and GP11.5 having higher alkali (Na₂O)



Fig. 2 Photograph of GP8.5 specimen at different temperatures

content of 10% and 11.5% performed poorly with regard to physical changes. Cracks extending along the surface as well as deep into the specimen were observed in such specimens.

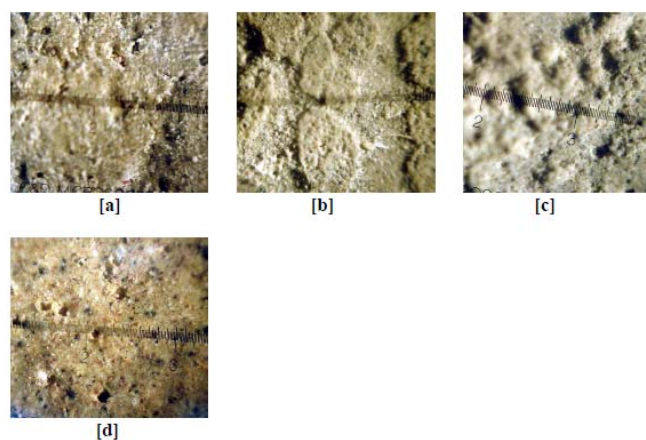


Fig. 3 Surface image of GP8.5 specimen at different temperatures as seen through optical microscope

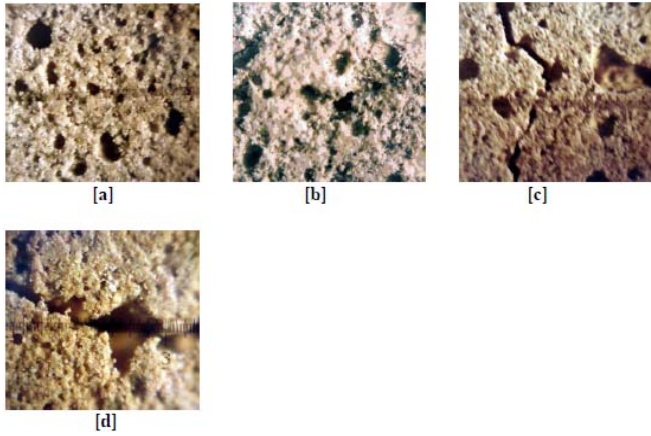


Fig. 4 Surface image of GP10 specimen at different temperatures as seen through optical microscope

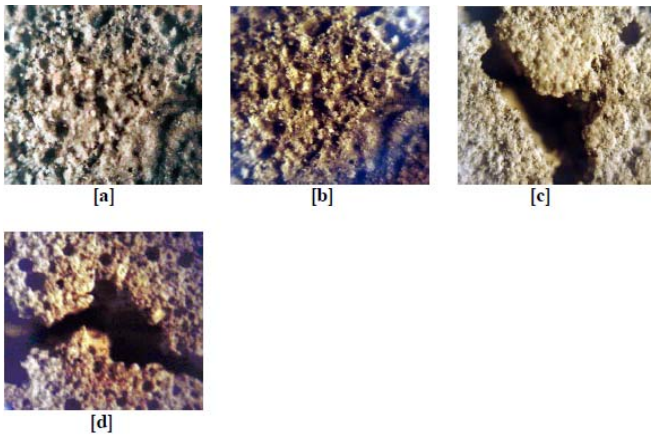


Fig. 5 Surface image of GP11 specimen at different temperatures as seen through optical microscope

B. Scanning electron microscopy (SEM) and EDX

SEM micrographs along with EDX spectra at the indicated spots (A, B, C and D) for GP8.5 specimen at different temperatures are shown in Figure 6. Before exposure to elevated temperature, the microstructure appears to be amorphous (Fig.6 [A1]). EDX spectra at the particular spot A identified with arrowhead showed presence of oxygen (O), sodium (Na) and carbon (C). As the temperature was increased to 300°C, some disturbances in the microstructure occurred with formation light coloured substances. EDX examination of such a formation (spot B) indicated presence of many elements like oxygen, iron (Fe), sodium, aluminium(Al) and silicon(Si) among others. Further increase in temperature resulted in initiation of melting and flow inside the specimen as observed in SEM micrographs of specimens for 600°C and 900°C. Due to melting inside the specimen, the microstructure appears to be continuous thereby filling most of the pores. Figure 7 gives the SEM micrographs and corresponding EDX spectra at selected spots for GP10 and GP11.5 specimens. Though, melting was common at 900°C, specimen with highest Na₂O(GP11.5) content showed almost

complete melting and flowing as compared specimen with lowest Na₂O(GP8.5) content. However, such melting did not disturb the shape of the specimens. EDX spectrum of GP8.5 at 900°C showed presence of titanium (Ti), magnesium (Mg) and calcium (Ca) in addition to Al, Fe, O, Si etc. Most of these elements were also found in GP10 specimen at 900°C. While Al, Si, O and Ca were indicated in the EDX spectrum of GP11.5 at the same temperature, Ti and Fe were absent.

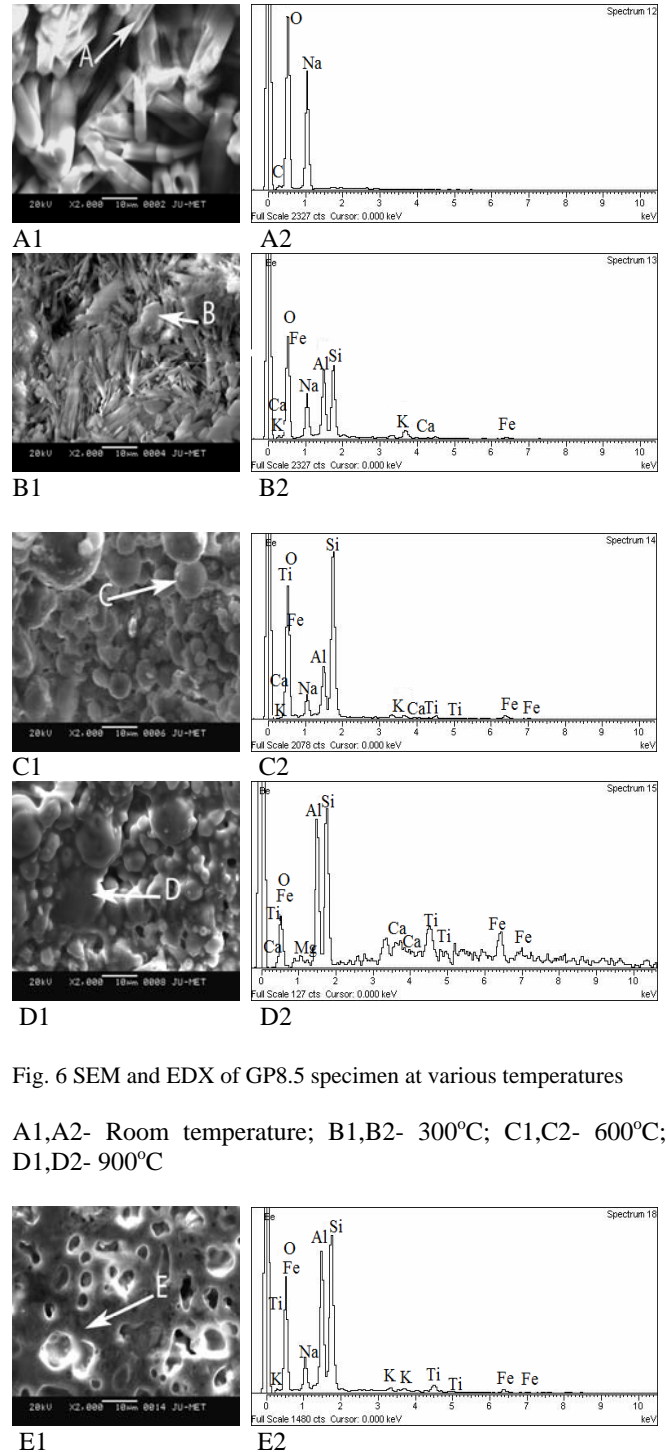


Fig. 6 SEM and EDX of GP8.5 specimen at various temperatures

A1,A2- Room temperature; B1,B2- 300°C; C1,C2- 600°C; D1,D2- 900°C

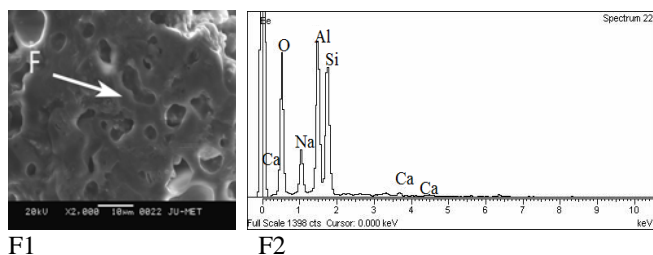


Fig. 7 SEM and EDX of GP10 and GP11.5 at 900°C E1,E2- GP10; F1,F2- GP11.5

C. X-ray diffractogram

Powdered sample of specimens were used for XRD tests for unexposed as well as for those exposed at different temperatures. X-ray diffractogram for GP8.5 specimen before exposure and after elevated temperature exposure is presented in Figure 8. Diffractogram for an unexposed GP8.5 specimen showed traces of amorphous aluminosilicate gel and semi-crystalline hydroxy-sodalite were observed in addition to residue of unreacted fly ash, quartz, mullite and hematite. On heating the specimen at higher temperature, new traces of nepheline (AlNaSiO_4) and albite ($\text{NaAlSi}_3\text{O}_8$) were observed. However, peaks of sodalite and hematite disappeared at elevated temperatures. At 900°C, peaks of albite dominated the diffractogram of GP8.5 specimen. Another X-ray diffractogram in Figure 9 shows the traces for GP8.5, GP10 and GP11.5 after exposure to 900°C. More peaks of albite could be noticed in GP8.5 specimen while nepheline is predominant in GP10 and GP11.5 specimens. A closer observation of the traces reveals that more peaks had disappeared in the GP11.5 specimen which contained maximum Na_2O of 11.5%. It can then be concluded that fly ash based geopolymer manufactured with higher alkali content (Na_2O) does not perform well at elevated temperatures.

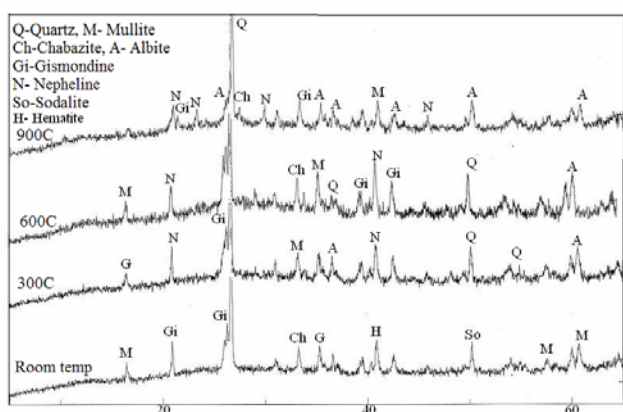


Fig. 8 X-ray diffractogram of GP8.5 specimen

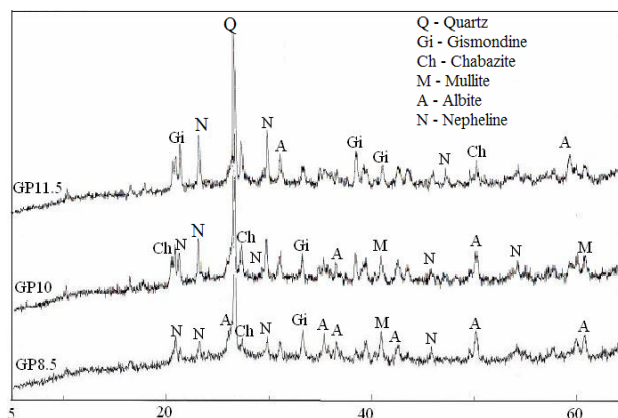


Fig. 9 X-ray diffractogram of geopolymer specimens after exposure to 900°C

D. Shrinkage

Variation of volumetric shrinkage with temperature for the three series of Geopolymer paste specimens is shown in Figure 10. At 300°C, volumetric strain measured was in the range of 6.4% for specimen with 8.5% Na_2O to 13.04% for specimen containing 11.5% Na_2O . In all the specimens, there was no appreciable change in volumetric shrinkage between 300°C till 600°C. Further increase in temperature to 900°C caused rapid increase in volumetric strain in all the specimens. This might be connected to melting and subsequent evaporation of unreacted alkali and silicate at higher temperatures. Increase in shrinkage showed a relation with Na_2O content in the mix. Geopolymer paste specimen with higher alkali resulted in greater shrinkage than those with lower alkali content at all the exposure temperatures. Specimen prepared by activation with 11.5% Na_2O when exposed to 900°C caused a volumetric strain of 19.15%. At the same temperature specimens of 8.5% and 10% Na_2O resulted in shrinkage of 16.8% and 17.84% respectively.

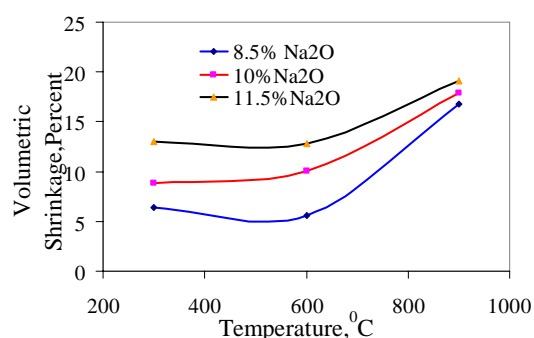


Fig. 10 Variation of volumetric shrinkage of geopolymer specimen with temperature

E. Weight loss

Loss of weight of specimen after exposure to various temperatures was measured immediately after removal from

the oven. Figure 11 presents the weight loss recorded by different geopolymer paste specimens at various exposure temperatures. Geopolymer paste specimens exhibited rapid loss in weight till 300°C. Thereafter, further increase in temperature from 300°C to 900°C did not cause appreciable loss in weight. At 300°C, GP8.5 specimen showed a weight loss of 15.21%, which is rather high. But, subsequent heating up to 900°C caused a loss of 16.35% showing a very little increase in weight loss over that of 300°C. Though, weight loss was observed in the entire specimen, the ones which are manufactured by activation with higher Na₂O content recorded greater loss. Weight loss is due to evaporation of chemical water as well as due to melting and evaporation of unreacted excess alkali. Since paste specimens of GP10 and GP11.5 would have more unreacted excess alkali, these specimens have shown greater loss in weight than GP8.5 specimen.

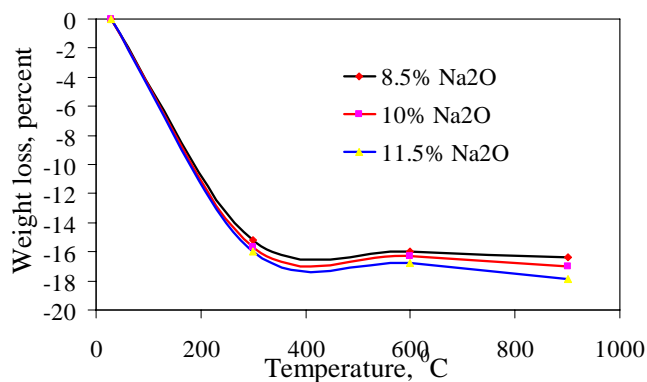


Fig. 11 Weight loss of geopolymer specimen with temperature

F. Residual compressive strength

Residual compressive strength after elevated temperature exposure was determined on the basis of 7 days compressive strength. The variation of residual strength for the geopolymer paste specimens with temperature is shown in Figure 12. Up to 300°C, all the specimens did not show much loss in strength. The minimum residual strength at this temperature was noticed in GP11.5 with a value of 79.5%. On further increase in temperature till 600°C, while GP10 and GP11.5 exhibited a rapid loss in strength; GP8.5 specimen almost maintained its compressive strength. However, at 900°C, there was a sudden drop in strength in all specimens. The final residual strength after exposure to 900°C was 58.89%, 30.93% and 23.47% for GP8.5, GP10 and GP11.5 respectively. The results show better performance in specimen with lower Na₂O content at elevated temperature.

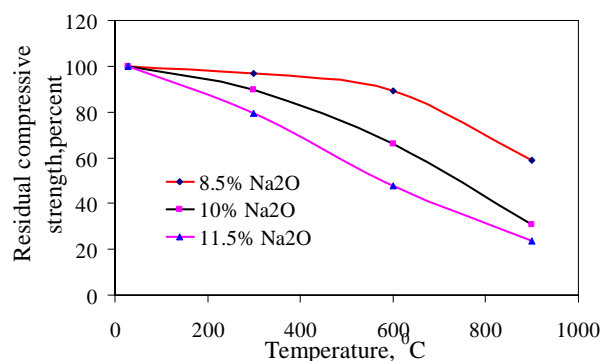


Fig. 12 Variation of residual compressive strength of geopolymer specimen with temperature

G. Sorptivity

Figure 13 presents the evolution of water sorptivity of the geopolymer paste specimens with exposure temperature. For all specimens, the trend was almost similar. Sorptivity of specimens increased with temperature till up to 300°C, after which there was no appreciable change up to 600°C. On further increase in exposure temperature to 900°C, sudden drop of sorptivity was observed in all specimens. Before

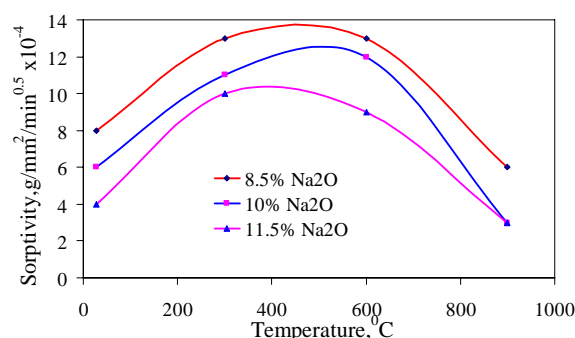


Fig. 13 Variation of water sorptivity of geopolymer specimen with temperature

exposure to elevated temperature, the sorptivity measured was 8×10^{-4} , 6×10^{-4} and 4×10^{-4} g/mm²/min^{0.5} for GP8.5, GP10 and GP11.5 respectively. However, after exposure to 900°C, the sorptivity values of the specimens dropped to 6×10^{-4} , 3×10^{-4} and 3×10^{-4} g/mm²/min^{0.5} for the geopolymer paste specimens manufactured with Na₂O content of 8.5%, 10% and 11.5% respectively.

IV. CONCLUSION

Based on the results obtained in the experimental investigation, the following conclusions have been made.

1. Colour of geopolymer specimens gradually changed from grey to light brown as the exposure temperature increased.
2. Volumetric shrinkage due to elevated temperature was

- observed to be sudden after 600°C till 900°C.
- Loss of weight was rapid till 300°C and beyond that, there was no appreciable loss in weight of the specimens.
 - Specimens showed similar trend in evolution of residual strength. However, specimen with highest Na₂O content recorded maximum loss in strength after exposure to elevated temperature.
 - Formation of new peaks identified as albite and nepheline were observed in the X-ray diffractogram of exposed geopolymer specimens.
 - When exposed to elevated temperature, specimens showed a completely disrupted microstructure.

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Geopolymer specimens manufactured by activation of class F fly ash with Na based alkaline activators remained physically stable without structural disintegration under exposure to elevated temperature. However, performance of specimens with lesser alkali content was noticeably better in elevated temperature exposure.

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