

Development of High Thermal Stability Geopolymer Composites Enhanced by Nano Metakaolin

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Abstract: This paper deals with study of thermal stability of geopolymer composites enhanced by nano metakaolin materials (NMK) and exposed to high firing temperature up to 1000 °C. The main geopolymer made up of water cooled slag having various kaolin ratios. The activators used are Na₂SiO₃ and NaOH in the ratio of 3:3. The thermo-physical, micro-structural and mechanical properties of the geopolymers before and after the exposure to elevated temperatures of 300, 500, 600 800 and 1000 °C have been investigated. The fire shrinkage of the geopolymer specimens increased by increasing temperature up to 1000 °C. Also, the fire shrinkage increased slowly up to 500 °C. The mechanical strength of geopolymer specimens increased with temperature up to 500 °C. The good thermo-physical and mechanical properties for these geopolymer composites increase the possibility of vast application of these eco-friendly materials in construction sectors.

Key words: firing shrinkage, geopolymer composites, slag, kaolin, nano metakaolin.

1. Introduction

The geopolymerization technology introduced as an ideal and novel environmentally-friendly process for producing supplementary materials to ordinary Portland cement (OPC) in 1980s, by professor Joseph Davidovits that possessing higher mechanical and durability properties. The geopolymers synthesizing technology is based on the relatively simple alkaline activation of a source material which is rich in silicon (Si) and aluminum (Al) in amorphous form at relatively low temperature (Davidovits, 1999). Geopolymers have superior resistance to thermal shrinkage when exposed to temperatures up to 1000 °C compared to Portland cements (Palomo et al., 1999; Duxson et al, 2005 ; Duxson et al., 2007; Rahier, 1996) very little attention has been given to the wider issue of ambient temperature drying shrinkage (Barbosa & MacKenzie, 2003-a). Unlike Portland cement, water is not incorporated directly into the geopolymer gel product. Only a small percentage of the mixing water remains as interstitial water in the geopolymer gel shrinkage (Barbosa & MacKenzie, 2003-b). This fact, combined with the high water requirement to mix geopolymer pastes, means that there is a large excess of unbound or free water, which can evaporate from the hardened paste under low relative humidity conditions at ambient temperature (Rahier, 1996). Despite the lack of chemically bound water, it still plays an important role in structural stability. Excessive water loss under relatively normal environmental conditions can result in extensive shrinkage cracking of specimens (Barbosa & MacKenzie, 2003-a). The previous studies that investigated thermal properties of fly ash materials possessed low thermal shrinkage and good strength maintenance after exposure to high temperatures (Bakharev, 2006; Kong & Sanjayan, 2008; Kong & Sanjayan, 2010; Rickard et al., 2010). The FA geopolymers in these papers were directly heated from room temperature up to the elevated temperature of 800 °C or further up to 1200 °C, without studying the changes in the geopolymer phase composition and microstructure occurred at temperatures ranged from about 600-800 °C. Recently, these changes have been highlighted via dilatometric analysis

(Rickard et al., 2012; Provis et al., 2009). However, these studies were focused substantially on the effect of the silicate phase concentration exist in the FAs sources and/or geopolymers which lacks to the micro-structural and mechanical analysis. Also, all the designed alkali activated fly ash based systems, not depending on initial curing condition, displayed a higher resistance to high temperature with respect to traditional cementitious binders, which are affected by very high strength loss at high temperature such as 800 °C (Messina et al., 2018).

Adding nano silica have good effect and improve residual compressive strength of both sodium and potassium activators synthetized geopolymers at elevated temperatures. The potassium activator synthetized geopolymers containing nano silica exhibited higher residual compressive strength at elevated temperatures above 400 °C than its sodium based counterparts (Shaikh & Haque, 2018).

The main objective of the current study is to address the thermo-physical, mechanical and the macro/micro-structural changes that the geopolymer products experience after exposing to different elevated temperatures of 300, 500, 600, 800 and 1000 °C to enhance the understanding about this new type of building materials.

2. Geological setting of kaolin deposit

The studied kaolin raw material was delivered from quarry of the Middle East Mining Company (MEMCO) (6 km west of Gebel Gunna in the central Sinai, Egypt). The kaolinitic sandstone beds in the quarry belong to the Naqus Formation of the Early Paleozoic age (El Nagar, 2016). These rocks are partially covered in some parts by windblown sands and some gravel. These loose sands and detrital materials belong to the recent age.

The studied quarry face section attains about 5.5 m thick (Fig. 1). The quarry bed is completely composed of kaolinitic sandstone; whitish, very fine grain, compact and hard. The Figure 1 illustrate the lithostratigraphic columnar section of the interface studied quarry of Naqus Formation, west of Gebel Gunna, Sinai, Egypt.

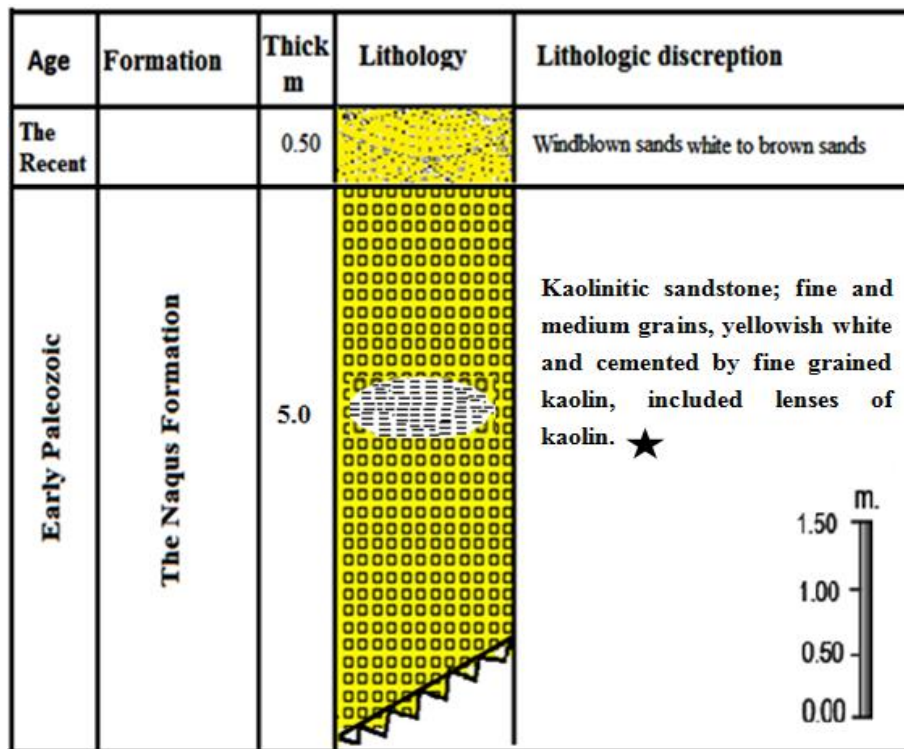


Fig. 1. Lithostratigraphic columnar section of the interface studied quarry of Naqus Formation, west of Gebel Gunna, Sinai. ★ Refers to the bed of samples collected.

3. Materials and Methods

3.1 Materials

Materials used in this work are kaolin collected from Sinai, West of Gebel Gunna, Egypt; water cooled slag also called ground granulate blast furnace slag (GGBFS) sourced from Iron and Steel Factory- Helwan, Egypt. Commercially sodium hydroxide (NaOH) with purity 98 % in the form of pellets and sodium silicate (Na_2SiO_3) are used as alkali activators. Nano-metakaolin Particles were prepared in the lab from the kaolin raw by firing at 800 °C for 2 hr with heating rate of 5 °C /min. The chemical composition of the starting raw materials are tabulated in Table (1). Also, the used dose of NMK was chosen at 3% from total weight based on the literatures (El Nagar, 2016).

Table 1. Chemical composition of the used raw materials (mass).

Material	Kaolin	Nano meta-kaolin	GGBFS
SiO_2	49.86	56.14	36.59
Al_2O_3	34.10	38.21	10.01
Fe_2O_3	0.30	0.38	1.48
CaO	0.09	0.07	33.07
MgO	0.26	0.37	6.53
SO_3	0.59	0.18	3.52
K_2O	0.02	0.00	0.74
Na_2O	0.03	0.02	1.39
TiO_2	0.88	1.14	0.52
MnO_2	0.01	0.00	3.44
P_2O_5	0.35	0.26	0.10
Cl ⁻	0.00	0.00	0.05
LOI	13.44	3.13	0.00
Total	99.92	99.89	99.69
Notes			BaO=5.00

3.2 Experimental

3.2.1 Preparation of activator solution

The alkaline solution was prepared by dissolving NaOH pellets in water and then added to the required amount of water glass. After the solution was cooled down, the nano-kaolin powder was stirred for 15 minutes. The binders were first dry mixed together. Then, the prepared activator solution was added on the powder and mixed for 5 minutes.

3.2.2. Casting and molding

The mix was poured in steal molds of 2.5 cm side length cube and vibrated for 30 second using a vibrating table. All mixes were left to cure at ambient temperature for 24 hours, and then subjected to curing temperature of 38 °C and 100% relative humidity in a controlled humidity chamber. Compressive strength was measured at 28 days before firing. Compressive strength tests were carried out using five tones German Bruf pressing machine with a loading rate of 100 kg/min determined according to ASTM-C109-07 (2012), as follows:

$$C = W/A$$

Where, C= Compressive strength of the specimen, kg/cm². W= Total load at which failure occurs, kg. A= Calculated area of the bearing surface, cm².

As a confirmatory tool, thermo-gravimetric (TGA) analysis was used. The thermal analyses were carried out using computerized DT-50 thermal analyzer (Shimadzu Co., Kyoto, Japan). The heating rate was 20 °C /min. The heating temperature was up to 1000 °C for TGA under nitrogen atmosphere (30 ml/min). The microstructure of specimens was studied using SEM Inspect S (FEI Company, Netherland). The studied mixes composition shown in Table (2).

Table 2. The studied mix design of geopolymer composites specimens.

Mix	Kaolin, %	Slag, %	NMK, %	NaOH, %	Na ₂ SiO ₃ , %
G1	50	50	3	3	3
G2	20	80	3	3	3
G3	-	100	3	3	3

3.3 Fire shrinkage

At the age of 28 days, the geopolymer specimens were dried at 105 °C for 24 hrs, then fired at temperatures of 300 °C, 500 °C, 600 °C, 800 °C and 1000 °C for 2 hrs with a heating rate of 5 °C/min. Afterwards, the geopolymer specimens were left to cool inside the furnace to room temperature. Then, fire shrinkage test for the fired specimens was measured according to the following equation.

Firing shrinkage% was calculated for each test specimen using the following formula Norsker, 1987):

$$\text{Average of Firing Shrinkage \%} = (\text{DL}-\text{FL})/\text{DL} * 100$$

Where: DL means dried length and FL is fired length.

4. Results and discussion

4.1. Firing shrinkage

Fire shrinkage results of dried geopolymer specimens (G1, G2 and G3) fired at 300, 500, 600, 800 and 1000 °C are shown in (Table 3) and plotted against temperature degrees in Fig. (2).

It can be seen that the firing shrinkage increases for the geopolymer specimens with temperatures higher than 300 °C and up to 1000 °C is which can be related to water evaporation from the geopolymer structure in a phenomenal called the 'vapors effect' as discussed elsewhere (Abdulkareem et al., 2013).

Table 3. Fire shrinkage of dried geopolymer specimens fired at 300, 500, 600, 800 and 1000°C.

Tempertaure degree °C	Fire Shrinkage, %		
	G1	G2	G3
300	0.016	0.013	0.005
500	0.018	0.017	0.016
600	0.042	0.040	0.021
800	0.044	0.045	0.024
1000	0.048	0.045	0.027

It is generally considered that there are three types of water exist in the hardened geopolymer products: physically bonded water, chemically bonded water and hydroxyl groups OH. The physical bonded water and chemically bonded water evaporate between 20 °C to 100 °C, and between 100°C to 300 °C, respectively.

When the temperature reaches above 300°C, the dehydroxylation of OH groups happens with the subsequent polycondensation into siloxo bond Si-O-Si, linking neighboring geopolymeric micelles. It is proven that more than 70% of the reactions water is physically bonded water, which evaporates below 100 °C without causing any internal stress and remarkable shrinkage.

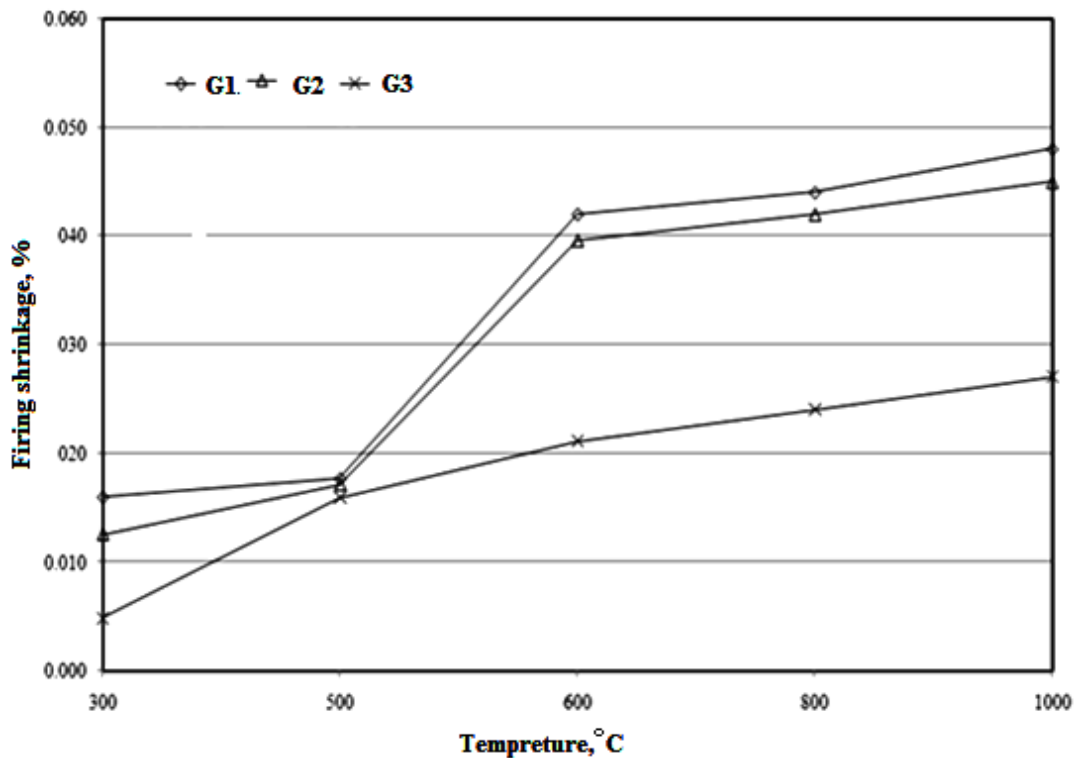


Fig. 2. Firing shrinkage of dried geopolymer specimens of various compositions exposed to 300, 500, 600, 800 and 1000°C.

However, many micro pores will be produced owing to the empty space left by the water evaporation. The remaining 30% water, chemically bonded water and hydroxyl groups OH, accounting for up to 90% of the total shrinkage when the samples are heated from 20 °C to 500 °C (Perera et al., 2007). Above 500 °C further shrinkage takes place due to densification and/or volume changes as a result of crystallization and subsequent melting. Davidovits estimated that the evaporation of the free water is not the cause of the damaging stresses except a very small shrinkage, although the free water contributes about 60% of the total water content in the geopolymer structure (Davidovits, 1988).

However, the remaining 40% of the water content evaporation is contributing about 90% of the total shrinkage at high temperatures. The main reason for the shrinkage when the samples are exposed to the 500 °C may be caused by the loss of the chemically bonded water and hydroxyl groups OH. It can be noticed from the pattern all mixes possess shrinkage values lower than 0.02 % for temperature lower than 600°C, also increase replacement of slag by kaolin results in the increase of shrinkage values due to the low reactivity of kaolin leading to the increase of physical water content. We can also notice that mix without kaolin has the lowest values of shrinkage due to the formation of dense structure that hinder the evaporation of water by all its type.

4.2 Thermo-gravimetric (TGA) analyses

Thermograms of geopolymer specimens at firing temperatures (0 °C, 500 °C and 1000 °C) are illustrated in Fig. (3). Comparing the TGA patterns with firing temperatures, the geopolymer specimens (G1) gave a total weight loss of 13.91%, 7.20% and 1.10 % at 0 °C, 500 °C and 1000 °C, respectively. Also, geopolymer specimens (G2) gave a total weight loss of 11.19 %, 5.32% and 0.34 % at 0 °C, 500 °C and 1000 °C, respectively. It is noticeable the geopolymer specimens (G3) gave a good stability and a lower weight loss of 11.68 %, 3.30 % and 0.81 % at 0 °C, 500 °C and 1000 °C respectively, as compared with G1 and G2 because of the lower intensity of the formed zeolite structure.

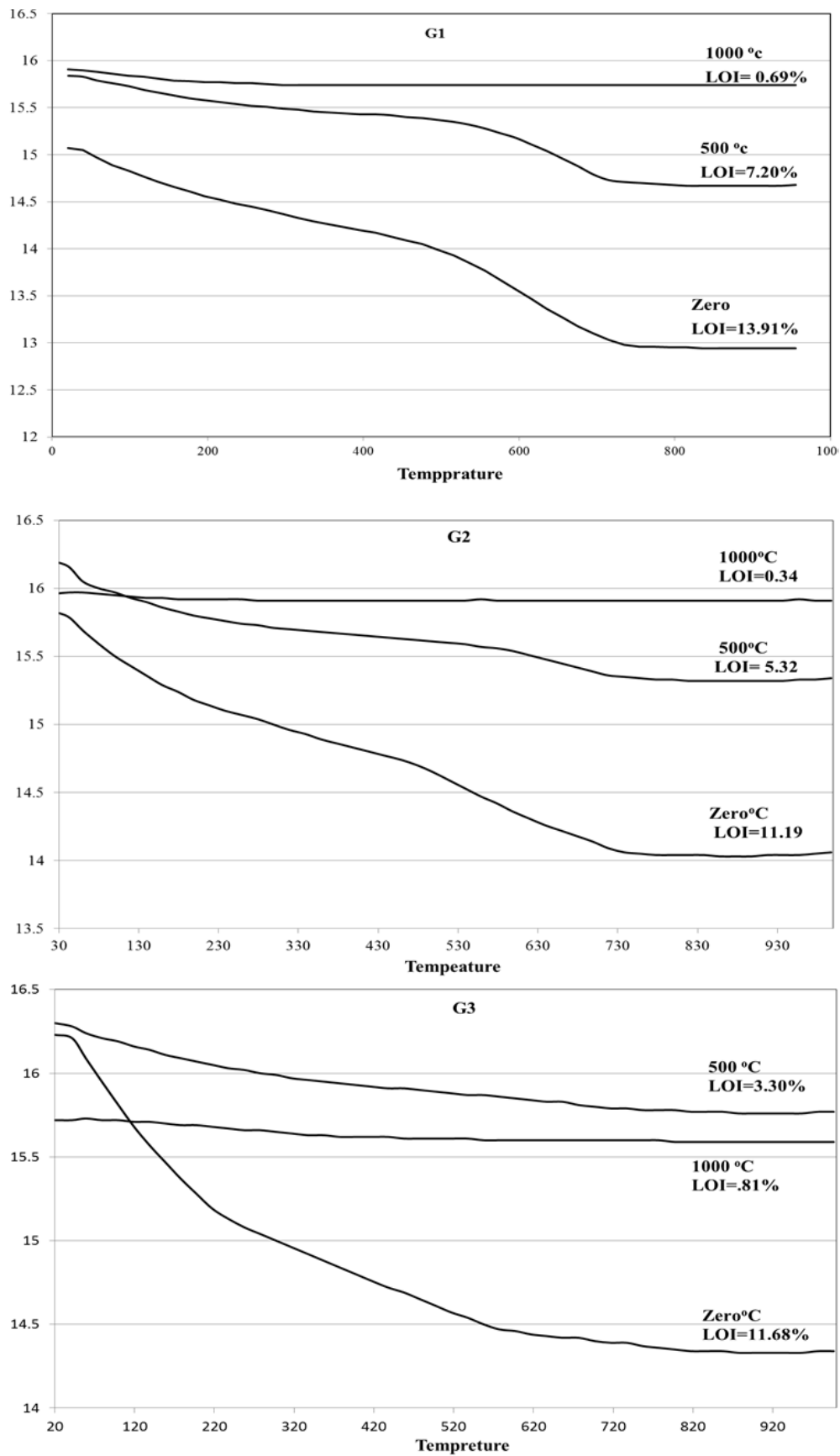


Fig. 3. Thermo-gravimetric graphs of geopolymer specimens of mixes G1, G2 and G3 fired at 0 °C, 500 °C and 1000 °C.

4.3. Scanning Electron Microscope

From previous works a possible explanation for geopolymer shrinkage and cracking is the generation of high capillary pressures between wet and dry areas of the micro pore network, which has been reported to initiate crack propagation in the microstructure. Attempts to avoid shrinkage and crack propagation have focused on modifying the pore structure to minimize capillary porosity, and controlling water loss during curing (Perera et al., 2007; Bell & Kriven, 2008).

The SEM micrographs geopolymer composite fired at 1000 °C and having various ratios of kaolin are represented in Fig (4), where as elucidated before from shrinkage data, the mix specimen which has high ratio of kaolin exposed to high deterioration as the lower reactivity of kaolinite material facilitate the evaporation of water and so increase the gaps and cracking between interacting particles Fig (4a).

On lowering the kaolin content to 20% results in somehow lower cracking depth as well as cohesion between geopolymer ingredient further increases in slag content G3 leads to extra enhancement and stability of the matrix against high temperatures leading to formation of dense structure where formed calcium silicate hydrate leads to formation of matrix free of wide cracks but only some micro cracks formed.

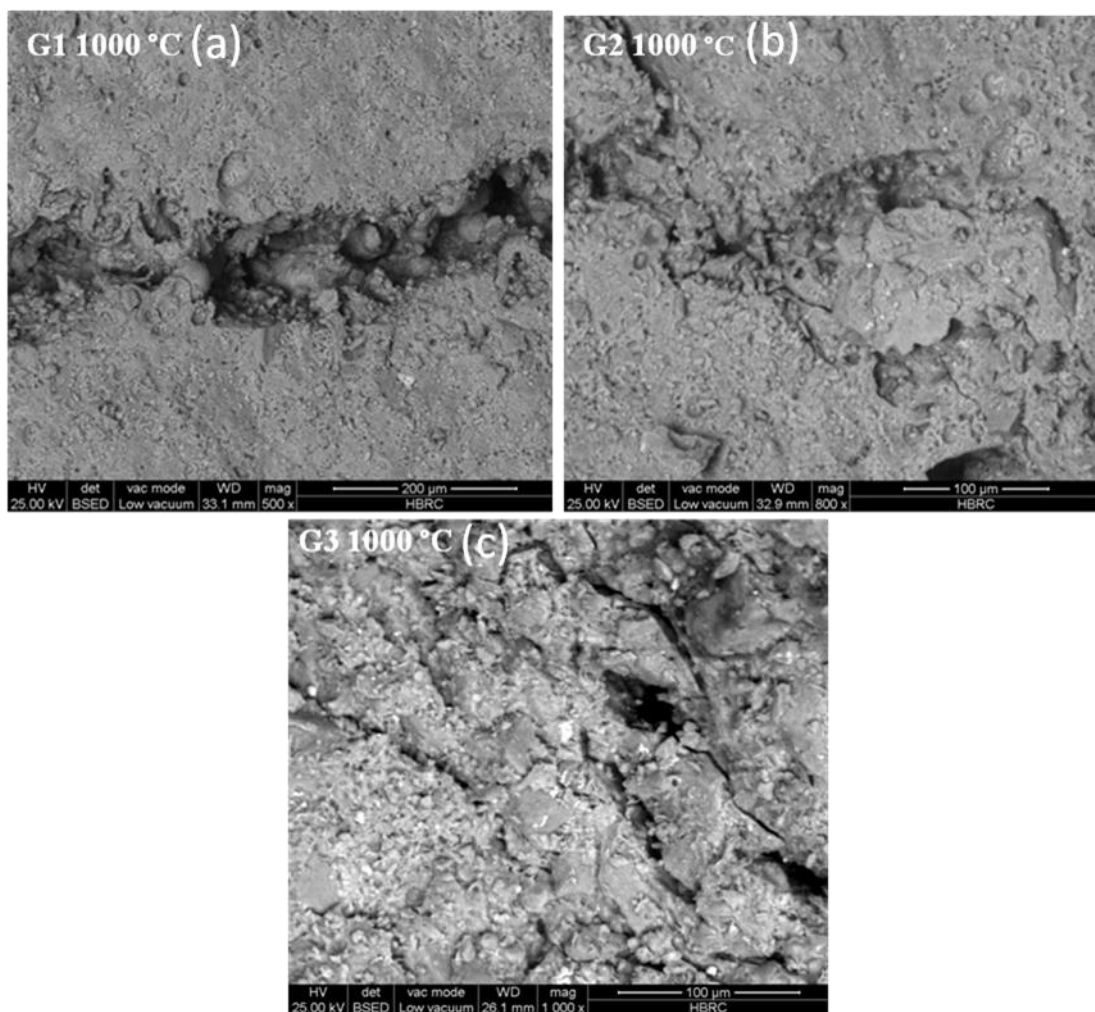


Fig. 4. SEM micrographs of geopolymer specimens after exposure to 1000 °C.

4.4. Compressive strength

Compressive strength of geopolymer specimens was increased with increasing firing temperature up to 500 °C. Generally, this increasing is mainly related to the hydrothermal reaction and inter-autoclaving effect. The increase in strength is noticeable dramatically at 500 °C in both G2 (composed of 80% water cooled slag and 20% kaolin) and G3 (composed only of water cooled slag) as shown in Fig. 5.

The data presented in Fig. (2) very closely reflect the trends in Fig. (5), implying a strong correlation between firing shrinkage and changes in mechanical properties, so the firing shrinkage increase slowly up to 500 °C in the most specimens. On the other hand the compressive strength increase up to 500 °C, due to the microstructure is partially resisting further shrinkage. Explanation for these observations is that the shrinkage mechanism causes a uniform physical contraction in the gel microstructure which, brings about an increase in strength (Kuenzel et al., 2012).

This result related to the increase of vitreous component in water cooled slag which enhance the geopolymer activation and so increase the yield of the reaction product. Moreover, using 50% kaolin along with water cooled slag (G1) gave a higher fire shrinkage and low thermal stability as compared with other geopolymer specimens. However, the viscous sintering process occurred in the geopolymer matrix at the temperature range from 800 °C to 1000 °C led to strength gain (Tai Tran-Thanh et al., 2016) especially in specimen G3.

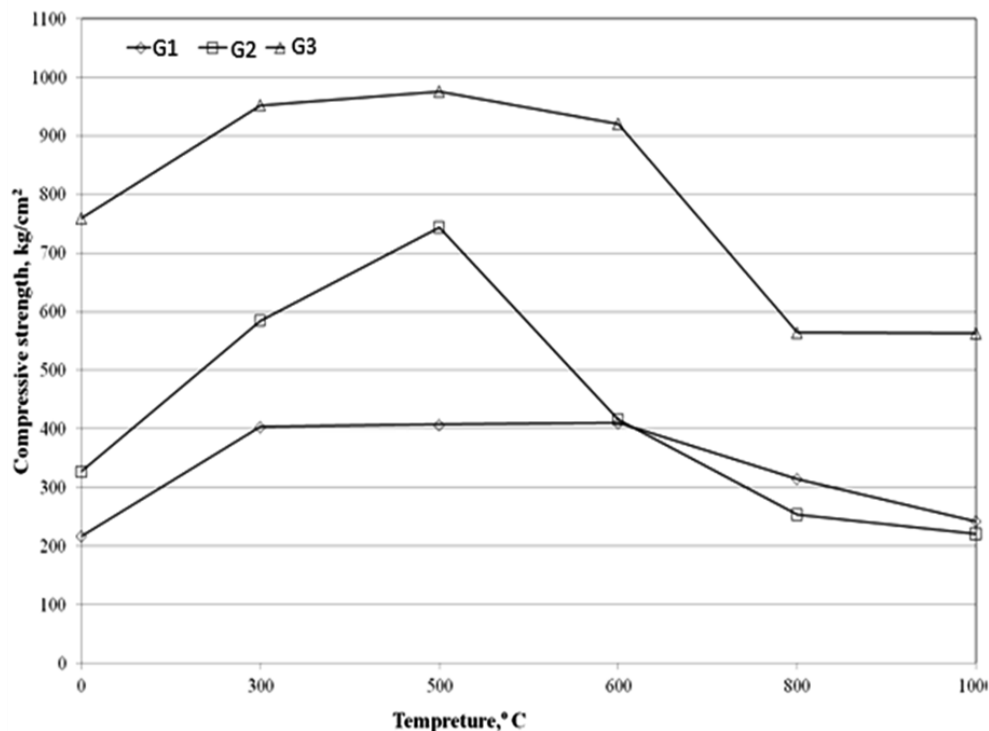


Fig. 5. Compressive strength of geopolymer specimens (G1, G2, G3) after exposure to 0°, 300°, 500°, 600°, 800° and 1000 °C.

On the other hand, all specimens have promising mechanical properties up to 500 °C, which may be attributed to the effect of nano metakaolin filling the voids, producing denser geopolymer, and/or it may be attributed to the fact that the nano-composite specimens had higher amounts of geopolymer gel and amorphous content.

5. Conclusion

- 1- The firing shrinkage increases of the geopolymer specimens after exposed to temperatures higher than 300 °C and up to 1000 °C.
- 2- The firing shrinkage increase slowly up to 500 °C in the most geopolymer specimens, and possess lowest values for mixes without kaolin leading to the formation of dense compacted geopolymer.
- 3- The micrographs showed the increasing of the voids content as well as wide micro cracks within in the paste microstructure with decreasing in slag content, while mix without kaolin has highest cohesive and denser structure at 1000 °C.
- 4- Compressive strength of geopolymer specimens increased with increasing firing temperature up to 500 oC, then strength decrease up to 1000 °C.
- 5- The studied geopolymer mixes with their highly thermal stability favors their applications in construction sectors.

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