

# Effect of Cooling Rate on the Performance of Fired Geopolymer Paste

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**Abstract** - One of the major drawbacks of Ordinary Portland Cement (OPC) products; paste, mortar and concrete, is its performance under the effect of elevated temperatures, especially if it is suddenly cooled after exposure to fire. Seeking a durable fire-resistant material is highly demanded. In this paper, the effect of cooling rate on compressive strength and mineral composition of geopolymer paste (made from slag base material and also a combination of slag, red mud and/or meta-kaolin) is addressed. All the results are compared to OPC paste. The compressive strength of the geopolymers prior to firing shows significantly higher strength. After exposure to fire (up to 900°C), OPC and slag geopolymer paste has shown degradation in compressive strength regardless cooling rate. While, slag geopolymers with partial replacement had shown better performance with temperature increase regardless the cooling rate. In general, geopolymer pastes have shown formation of very stable mineral composition phases after exposure to elevated temperatures. It can be concluded that slag geopolymer pastes with partial replacement represent an excellent fire-resistant material.

## I. INTRODUCTION

Geopolymers are inorganic polymers that are produced by the reaction of aluminosilicate source materials (i.e. red mud, metakaolinite, fly ash, blast furnace slag, waste glass, rice husk ash, etc.) and high alkalinity aqueous solutions (mainly sodium and potassium based materials). The reaction via a polymerization mechanism forms a solid cementitious material[1].

Molecular structures of any binder material are stable at ambient temperatures. This stability is affected when the temperature conditions change. Exposure time and heating rates are also important parameters which may lead to micro cracks and failure of the material in fire or elevated temperatures. OPC binder goes through a degradation process called spalling, where the cracks take place at surface and the paste deteriorates and breaks into smaller pieces around temperatures of 300°C and 450°C [2-4].

Geopolymers are generally believed to provide good fire resistance due to their ceramic-like properties[5]. The previous studies that investigated the thermal properties of the slag geopolymers have reported that these materials possess low thermal shrinkage and good strength after exposure to high temperatures [6]. Other studies on fly ash geopolymer paste reported that it has high compressive strength prior firing but, after firing at 800°C, these geopolymers lose its strength and fail [7]. Another study stated that geopolymer beams can successfully retain about 67% of its original flexural strength after a simulated large fire [8]. It can be concluded from the literature that this subject is still in need to more investigation to accurately assess which type of geopolymer pastes is the most durable fire-resistant.

In this paper, Ground Granulated Blast Furnace Slag (GGBFS) geopolymer pastes were studied. Also, GGBFS base material was partially replaced by Red Mud (RM) and/or Meta-Kaolin (MK). A number of geopolymer mixes were chosen based on compressive strength results and their mineralogical compositions were assessed. The selected samples were also subjected to elevated temperatures (to simulate fire effect). After that, these samples were cooled even gradually in oven (after switching of the heater) or suddenly by soaking in water. The main objective of this paper is to investigate the effect of cooling rate; either gradual or sudden, on the mineralogical content and compressive strength of geopolymer pastes. Also, OPC samples were tested under the same procedure to compare the performance of geopolymer and OPC pastes under the effect of fire.

## 2. EXPERIMENTAL PROGRAM

### 2.1. Materials

#### 2.1.1. Base materials

The base materials used in the present study are GGBFS, MK and RM. These materials are available in the Egyptian market. GGBFS is an industrial by-product resulting from rapid water cooling of molten steel. This material is available in Iron and Steel Factory, Helwan Governate. Kaolin contains hydroxyl ions that are strongly bonded to the aluminosilicate framework and can only be altered by the temperature above 750 °C to be MK [9, 10]. At this high temperature, its atomic structure is rearranged to form partly ordered system with a great reaction potential to alkaline solutions. MK used in this study is obtained from an open quarry located in Sinai by Middle East Mining Company (MEMCO).

RM can be defined as defected and crushed fired clay bricks. RM used in this study is obtained from clay brick factories, Helwan Governate. The X-Ray Fluorescence (XRF) analysis was utilized to determine the oxide composition for these materials in addition to OPC. All these materials contain Aluminates (Al) and Silicates (Si) compounds with various amounts, as shown in Table (1). By inspecting the results of table (1), it is obvious that all base materials are rich in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in comparison to OPC.

Table 1: Oxide Composition (wt%) of the Raw Materials, X-ray Fluorescence (XRF) analysis.

Oxide Composition	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	SO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Other Oxides
OPC	64.50	21.70	6.30	1.86	0.28	1.77	3.40	0.19
GGBFS	33.07	36.59	10.01	6.43	1.39	3.52	1.48	4.88
RM	1.35	73.05	13.41	1.46	1.62	0.74	6.35	0.98
MK	0.14	55.01	40.94	0.34	0.09	0.00	0.55	1.15

### 2.1.2. Activator solution.

Sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) and Sodium hydroxide (NaOH) based alkali activators were used for activating the geopolymerization process. Na<sub>2</sub>SiO<sub>3</sub> is a white viscous liquid. Its chemical composition is 8.9% Na<sub>2</sub>O, 28.7% SiO<sub>2</sub> and 62.5% H<sub>2</sub>O (by weight). NaOH is on form of white pellets with 99% purity. NaOH solution was prepared at desired molarity (12 molar) and kept in air for one day prior to mixing. Tap water was used throughout the synthesis process. The ratio of Na<sub>2</sub>SiO<sub>3</sub> to NaOH solution ranged from 1:3 to 6:1 by weight.

### 2.2. Specimen preparation and curing

For all geopolymer mixes, the proportion of solution to binder (W/G) ratio was 20% by weight in order to obtain acceptable workability. At first, GGBFS was utilized in order to prepare geopolymer mixtures (denoted as “S”) with activators ratios ranged from 1:3 to 6:1. After that, the “S” mixture that possessed the highest compressive strength was selected. The “S” mixture content of GGBFS material was partially replaced by other base materials. The replacement ratio ranged from 1 to 15% (by weight) for MK and the samples were denoted as “K” samples and from 5 to 100% (by weight) for RM and the samples were denoted as “R” samples. Additional samples were prepared by replacing 10% RM and 5% MK instead of GGBFS “SRK”. Also, reference samples of OPC were prepared with W/C of 0.24 in order to give the same workability of geopolymer pastes.

All the base materials were first mixed together by hand for about 5 minutes. Then, the alkaline liquid was added and the mixing was continued for further 10 min. to produce the fresh paste. The fresh paste was casted in cubes of size 70x70x70 mm, compacted and vibrated for 2 min. The excess paste was removed and the molds were wrapped for one day by plastic film to avoid evaporation of water. After demolding, the specimens were cured in water. One day before testing, the specimens were left to air-dry condition in the laboratory with the temperature and humidity of 27°C and 70%, respectively.

### 2.3. Test procedure

All the prepared samples were tested in compression according to ASTM: C109/C109M-13. Then, five different mixes (from S, K, R, RKS and OPC) were chosen according to the highest compressive strength. The crushed samples were grinded to 25 µm using HERZOG and were exposed to X-ray diffraction technique (XRD) to determine their mineralogical composition. Another set of samples were exposed to different firing temperatures for 2 hours at 200, 400, 500 and 900°C. Half of the samples were left to cool gradually in oven. The other half of the samples were suddenly cooled by emerging in water. These samples were tested in compression to study the effect of cooling rate on their compressive strength. The mineralogical composition of the samples that were fired to 900°C was detected by X-ray diffraction.

## 3. RESULTS AND DISCUSSION

### 3.1. Compressive Strength

Table 2 shows the compressive strength of “S” samples with various activator ratios in ambient conditions. By inspecting the values in table 2, it can be concluded that the sample S3 gives the highest compressive strength over the other samples. By plotting these results (figure (1)), the high early gain in compressive strength can be noticed (about 65% of the compressive strength at 28 days).

Table 2: Effect of activator ratio on compressive strength in ambient conditions.

Mix	Activator ratio Na <sub>2</sub> SiO <sub>3</sub> :NaOH	f <sub>c</sub> (MPa)		
		3 days	7 days	28 days
S1	1:3	20.9	29.8	49
S2	1:1	22.4	40.1	54.3
S3	3:1	43	46.4	61
S4	5:1	24	25.3	40.7
S5	6:1	21.1	24.3	34.2

Sample S3, as the highest compressive strength was chosen. The slag in this sample was replaced by RM and by MK by various ratios as shown in tables 3 and 4, respectively. The activator ratio was kept at 3:1. Table 3 depicts that the highest compressive strength was obtained in sample R2 (replacement ratio= 10%). Also, compressive strength gains at 7 days reached about 90% of its compressive strength at age 28 days. For the other samples, this ratio varied between 55 to 110% which means that number of samples suffered strength loss at 28 days. Moreover, sample R7 which corresponds to the full replacement of S by RM shows the least compressive strength in comparison to other R mixes.

Figure 1: Effect of activator ratio on compressive strength of “S” samples in ambient conditions.

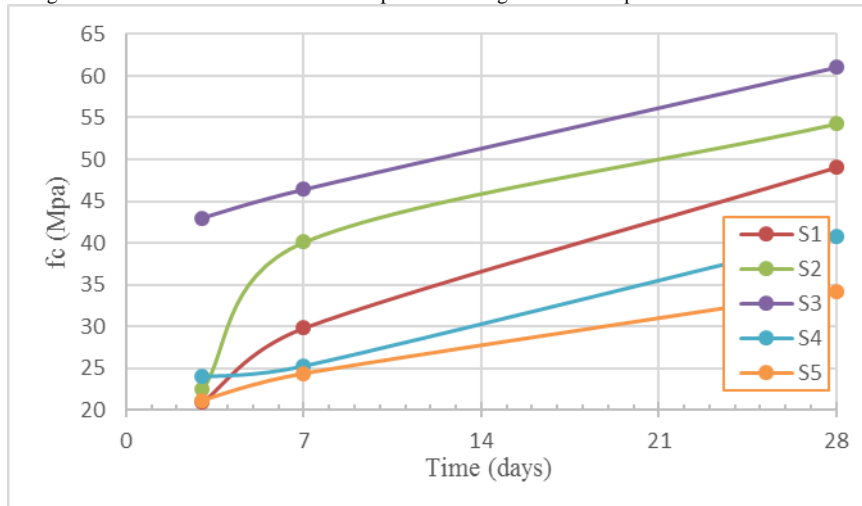


Table 3: Effect of RM replacement on compressive strength at ambient temperature.

Mix	Replacement ratio (RM : Total Base Material Weight)	f <sub>c</sub> (MPa)		f <sub>c7</sub> :f <sub>c28</sub>
		7 days	28 days	
R1	5%	27.4	51.2	0.54
<b>R2</b>	<b>10%</b>	<b>64.7</b>	<b>73.0</b>	<b>0.87</b>
R3	15%	54.1	53.6	1.01
R4	20%	46.2	46.4	1.00
R5	30%	43.4	46.2	0.94
R6	50%	39.3	35.6	1.10
R7	100%	16.4	27.4	0.60

Table 4 shows that the highest compressive strength was achieved in sample K3 (replacement ratio= 5%). Also, the compressive strength ratio between 7 and 28 days ranged from about 0.75 to 0.90. This ratio tends to increase with the increase in MK replacement ratio.

Table 4: Effect of MK replacement on compressive strength at ambient temperature.

Mix	Replacement ratio (MK : Total Base Material Weight)	f <sub>c</sub> (MPa)		f <sub>c7</sub> :f <sub>c28</sub>
		7 days	28 days	
K1	1%	39.6	50.9	0.78
K2	3%	49.6	65.8	0.75
<b>K3</b>	<b>5%</b>	<b>52.2</b>	<b>70.3</b>	<b>0.74</b>
K4	7%	47.9	62.4	0.77
K5	10%	46.8	57.5	0.81
K6	15%	43.6	49.0	0.89

Table 5 gives a summary of the chosen samples to be exposed to firing in addition to OPC and SRK samples. As concluded from tables 2, 3 and 4 samples S3, R2 and K3 had shown highest compressive strength. It is obvious that the partial replacements of GGBS by RM, MK or a combination of them leads to higher compressive strengths. Also, all geopolymer samples showed higher strength than OPC with the same water ratio.

Table 5: Chosen samples for firing exposure.

Mix	OPC	S3	R2	K3	RKS
fc (MPa) at 28 days	40.6	61.0	73.0	70.3	75.5

Two sets of the chosen samples were prepared to be exposed to elevated temperatures at age of 28 days. The first set was left to cool gradually in oven after switching the heater off and the second set was suddenly cooled in water. The results of the two sets are shown in table 6.

Table 6: Effect of firing on compressive strength of the chosen samples (MPa).

Mix	Firing temperature (°C)					Firing temperature (°C)				
	Gradually Cooled Set					Suddenly Cooled Set				
	Ambient	200	400	500	900	Ambient	200	400	500	900
OPC	40.6	35.2	30.7	18.1	16.8	40.6	40.0	36.8	34.0	0
S3	61.0	72.5	76.2	53.1	44.8	61.0	63.1	58.2	53.7	53.4
R2	73.0	75.2	78.3	69.7	101.2	73.0	63.5	70.6	71.4	82.0
K3	70.3	72.7	74.0	77.0	85.0	70.3	58.0	63.7	65.8	72.6
RKS	75.5	77.2	78.2	82.6	140.5	75.5	64.8	66.2	69.2	102.6

It can be noted from table 6 that OPC and S samples showed loss of compressive strength with temperature increase regardless the rate of cooling. On the contrary, R, K and RKS samples showed strength enhancement with temperature increase. Figure 2 shows the degradation of OPC samples after firing at 900°C due to the sudden immersion in water (sudden wet cooling). It is obvious that the major strength loss took place after temperatures of 400 to 500 °C. Also, OPC samples spalled and lost all its strength at 900°C under the effect of sudden cooling (see figure 3).

Figure 2: Effect of cooling rate on compressive strength of OPC samples.

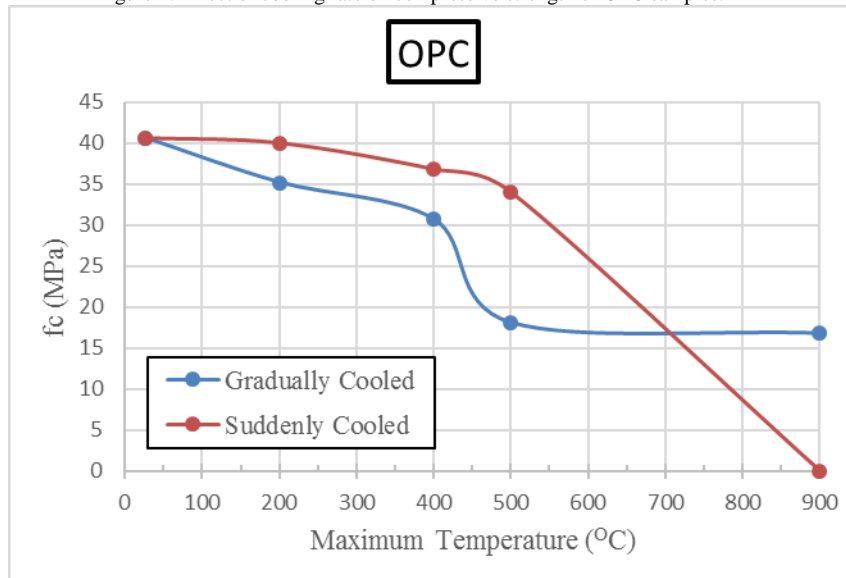
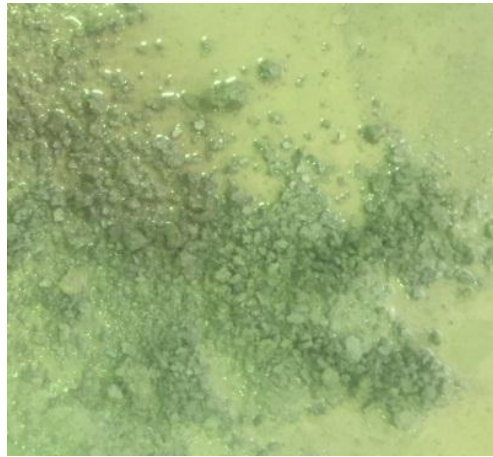


Figure 3: Spalling of suddenly wet cooled OPC samples after firing at 900°C.



For S3 samples, it is obvious from figure 4 that the gradual cooling has enhanced the compressive strength of all samples exposed to firing up to 400°C but at higher temperatures strength loss takes place. While the case of sudden cooling shows a slight increase in strength at lower temperature but with the increase of firing temperature the samples shows stability in its compressive strength. Figure 5 shows the sample after firing at 900°C and sudden wet cooling. On the contrary to OPC samples, S3 samples show higher resistance to severe heating and cooling conditions. The cracks of the sample are obvious and can be noticed by naked eye.

Figure 4: Effect of cooling rate on compressive strength of S3 samples.

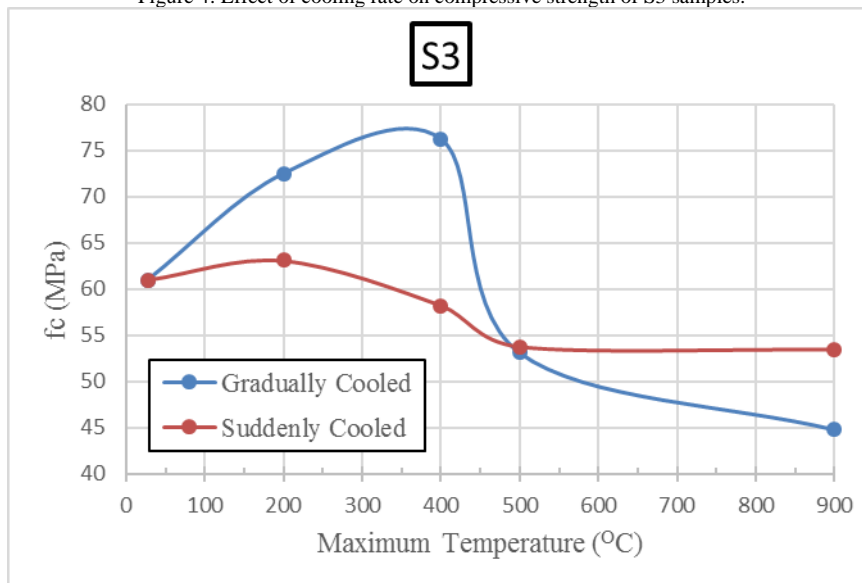


Figure 5: S3 sample after firing at 900°C and sudden wet cooling.



Compressive strength of R2 samples had shown better performance, in general, for temperatures greater than 500°C regardless the cooling rate. Its strength increased by about 39% and 12% at 900°C for gradual and sudden cooling, respectively (figure 6). Figure 7 shows the sample, after firing at 900°C and sudden wet cooling, with no apparent cracks on surface which depicts very high compressive strength and durability.

Figure 6: Effect of cooling rate on compressive strength of R2 samples.

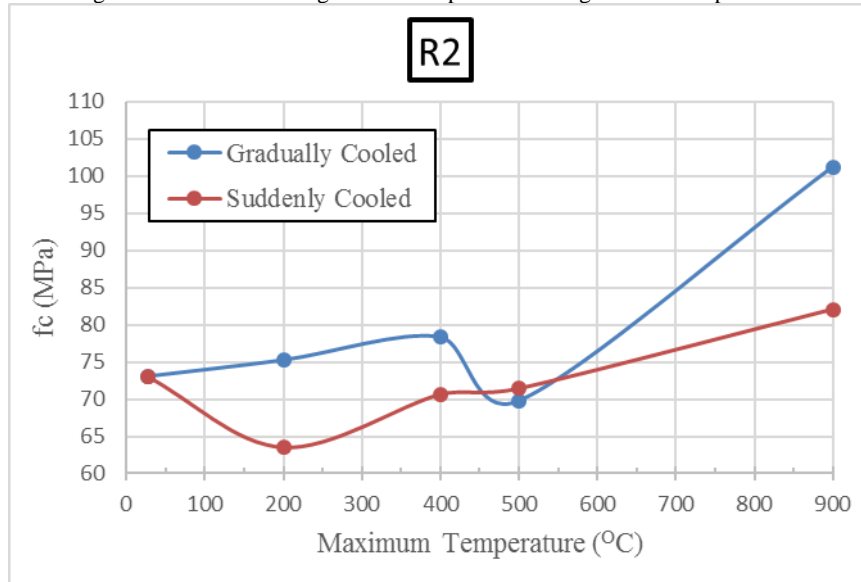


Figure 7: R2 sample after firing at 900°C and sudden wet cooling.



For samples K3, the gradual cooling guaranteed continuous enhancement of the compressive strength in a linear-like fashion. While sudden cooling degraded the strength and the enhancement took place after 200°C firing temperature. The increase in the compressive strength reached minimal values for sudden cooling at firing temperature of 900°C compared to ambient compressive strength. On the contrary, it reached about 21% for gradual cooling at firing temperature of 900°C (figure 8). Figure 9 shows the sample K3, after firing at 900°C and sudden wet cooling. Same remarks of R2 can be concluded that there are no apparent cracks on surface which refers to higher durability.

Figure 8: Effect of cooling rate on compressive strength of K3 samples.

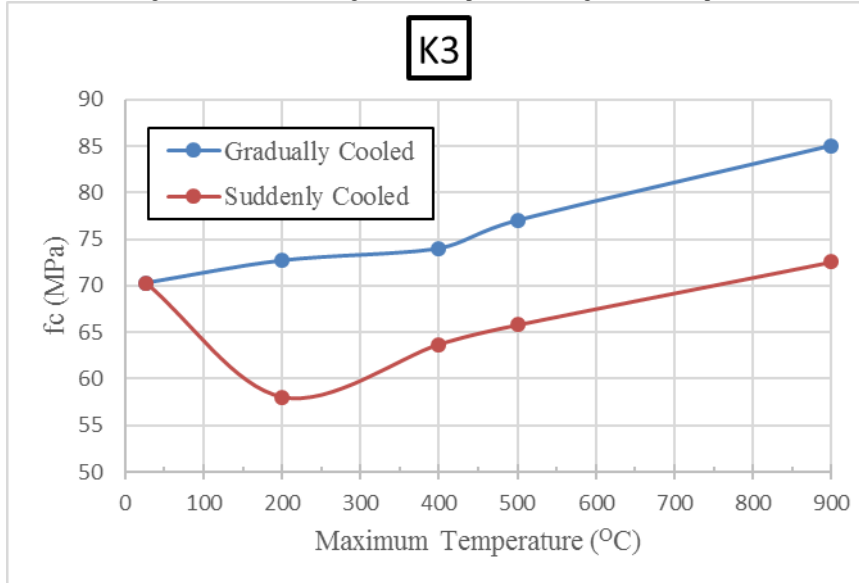
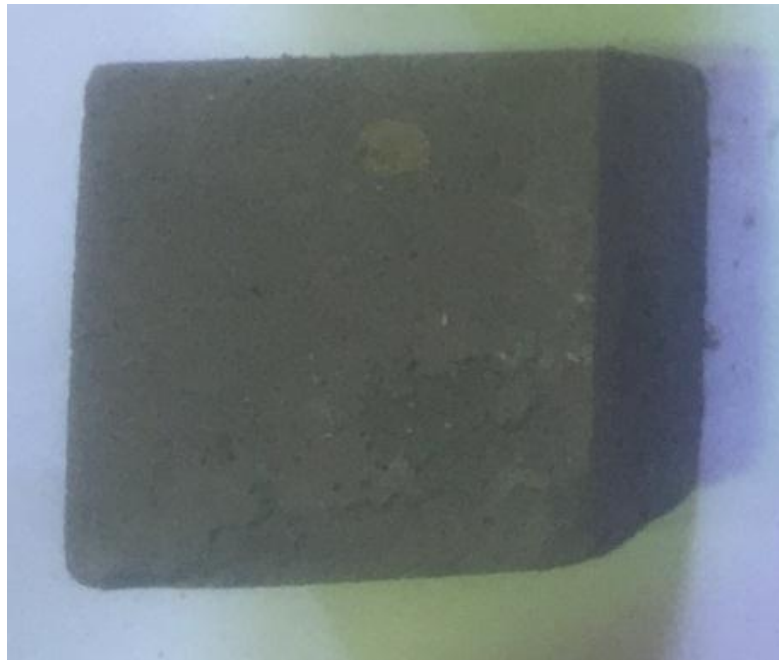


Figure 9: K3 sample after firing at 900°C and sudden wet cooling.



RKS samples performance was totally stable against firing, regardless cooling rate, at temperatures up to 500°C. The samples showed a significant increase in compressive strength at 900°C; about 86% and 36% in comparison to ambient compressive strength for gradual and sudden cooling, respectively (figure 10). Figure 11 shows the sample, after firing at 900°C and sudden wet cooling. Again, no apparent cracks on surface assure the very high strength and durability of RKS samples.

Figure 10: Effect of cooling rate on compressive strength of RKS samples.

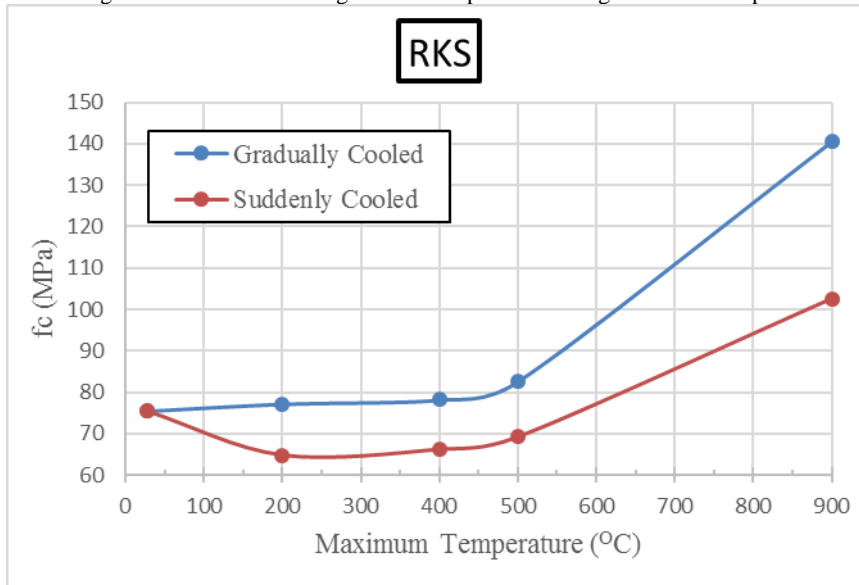
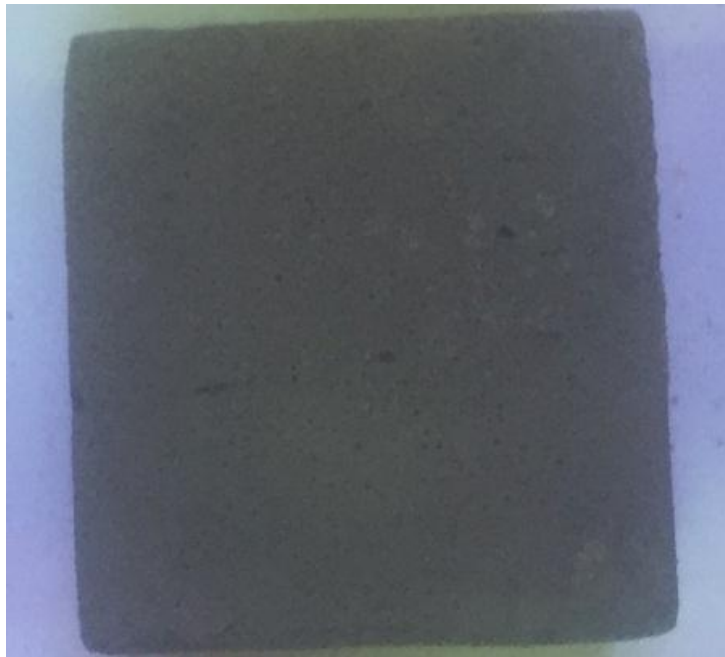


Figure 11: RKS sample after firing at 900°C and sudden wet cooling.



### 3.2. Mineralogical Composition

X-ray diffraction test was used to determine mineral content of the chosen samples. Two cases were thoroughly inspected; 1- before firing and 2- after fired at 900°C and suddenly cooled. For OPC samples (figure 12), the disintegration in phases of cement especially in CSH which disappeared with firing and the sharp reduction of calcium hydroxide in firing can be noticed. The last reaction may be considered the responsible of releasing CO<sub>2</sub> gas which lead to increase in the internal pressure and caused large cracks and spalling.

All geopolymer samples had shown formation of very stable phases as quartz. These phases are highly resistant to firing. Moreover, there were no gas emissions during the firing. Figures 13 and 14 shows scans of the mineral compositions of slag and slag with partial replacement of meta-kaolin and red mud before and after firing.



Figure 12: Mineral Composition of OPC before and after firing.

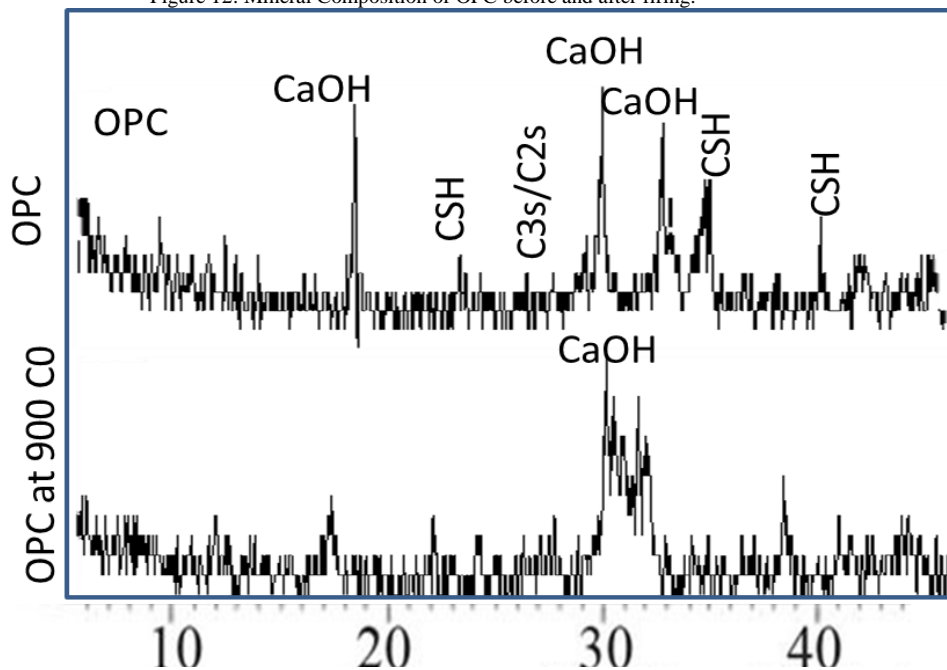


Figure 13: Mineral Composition of slag geopolymer before and after firing.

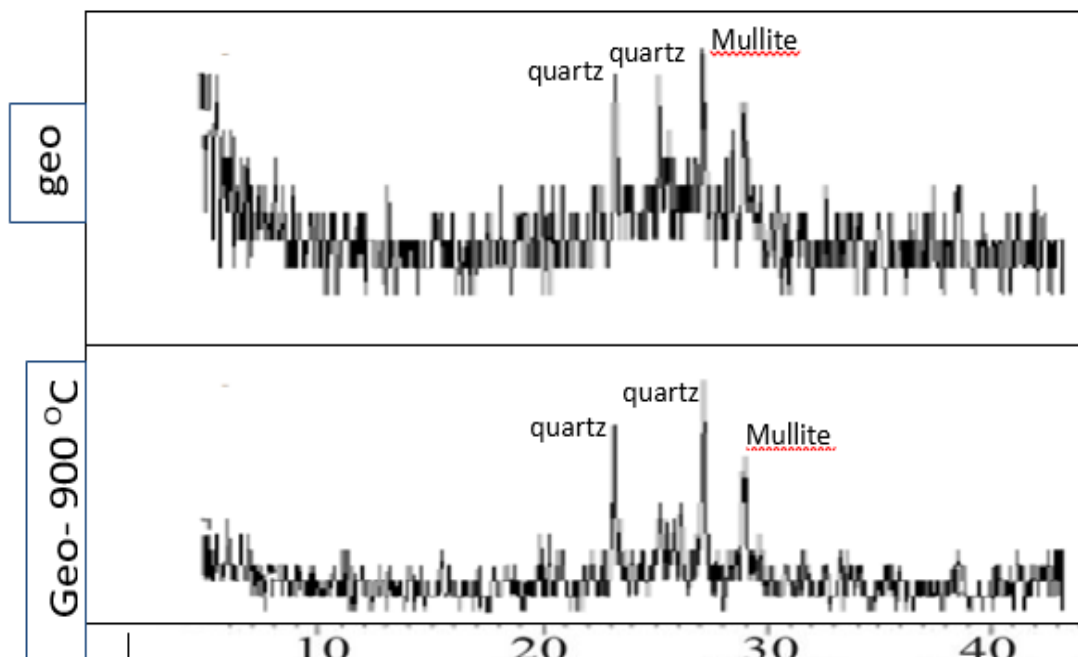
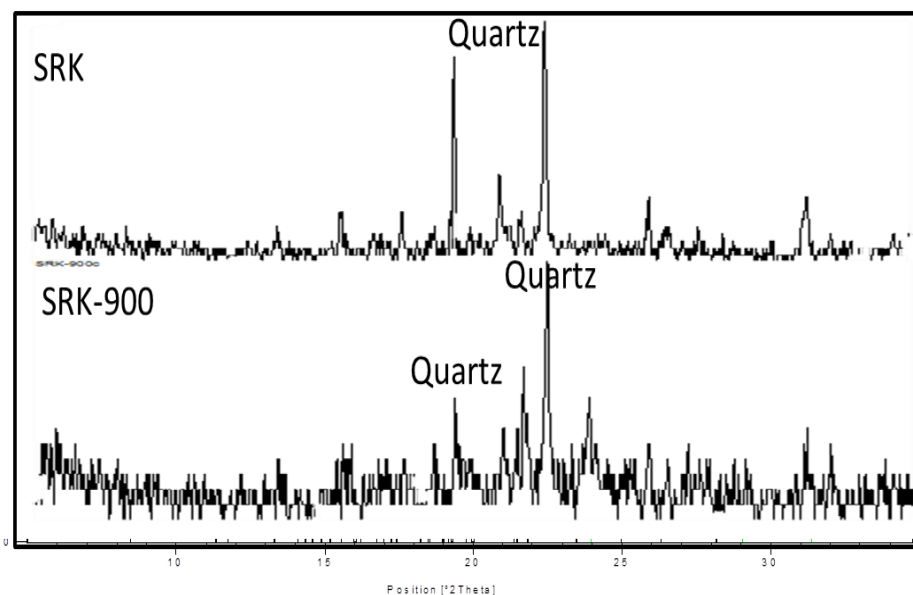


Figure 14: Mineral Composition of SRK geopolymer before and after firing.



#### 4. CONCLUSIONS

The current work has shown that geopolymer has high specifications compared to OPC. The combination of slag, red mud and meta-kaolin gives the highest compressive strength. Also, slag geopolymers with partial replacement of red mud and meta-kaolin have shown enhanced performance when subjected to elevated temperatures. Moreover, its compressive strength increased regardless the cooling rate. OPC paste has shown destruction in its mineral composition under fire effect and sudden cooling. This led to spall of samples. On the contrary, slag geopolymer has shown formation of very stable phases which are highly resistant to firing. In general, the effect of sudden cooling is more hazardous to geopolymer pastes than gradual cooling. It can be concluded that slag geopolymer with partial replacement of red mud and meta-kaolin had shown the most favorable characteristics. Slag geopolymer with partial replacement of red mud and meta-kaolin can be considered an excellent fire-resisting material that not only has very stable mineral composition but also gains strength when exposed to fire.

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