Research

Geopolymer Concrete Based on Class C Fly ash Cured at Ambient Condition

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ABSTRACT

In recent years, geopolymers, as a new class of green cement binders, have been considered as an environmental-friendly alternative to Ordinary Portland Cement (OPC), which can potentially reduce the negative environmental impacts of OPC. Geopolymers are inorganic alumina-silicate materials produced from raw materials in combination with an alkaline activator solution. The alkaline activator solution is one of the pillars of the geopolymerization process, playing an important role in the formation of crystalline structures of Si and Al. Therefore, it seems necessary to study the impact of various alkaline activator solutions on the mechanical strength of Geopolymer Concrete (GPC). On the other hand, in most previous research in this regard, GPC based on Class F fly ash and high-temperature curing condition have been studied. Hence, in this research, Class C fly ash, and ambient curing conditions were used to make GPC. The obtained results indicated that in ambient curing conditions, using sodium hydroxide and sodium silicate results in higher compressive strength and lower permeability compared to potassium-based (potassium hydroxide and potassium silicate) and a combination of sodium potassium-based alkaline activator solutions. But, at elevated curing temperatures, a potassium-based activator provided higher compressive strength. Moreover, simultaneous inclusion of NaOH and KOH led to a decline the compressive strength. Furthermore, the obtained results indicated that increasing the NaOH and KOH concentration resulted in higher compressive strength. The optimal SiO_2/Na_2O ratio was 2 in the case of using 14M NaOH solution and 2.5 in the case of using 10M NaOH solution.

Keywords: Geopolymer concrete, Fly ash, Alkaline activator solution, Compressive strength, Resistance to acidic condition.

1. INTRODUCTION

Pollution and climate change due to global warming have become the most significant environmental concerns worldwide [1]. Greenhouse gas emissions are the main contributing factor to global warming, with carbon dioxide (CO_2) having the greatest share (65%) among other greenhouse gases [2]. The production process of Ordinary Portland Cement (OPC) is identified as one of the major sources of CO2 emission and energy consumption. OPC production accounts for approximately 5% of global energy consumption. Furthermore, the

Production of 1 ton of OPC releases approximately 1 ton of CO_2 into the environment [3] and consumes 1.5 tons of raw materials [4]. Therefore, it seems necessary to find an alternative to OPC. Pollution and climate change due to global warming have become the most significant environmental concerns worldwide [1]. Greenhouse gas emissions are the main contributing factor to global warming, with carbon dioxide (CO_2) having the greatest share (65%) among other greenhouse gases [2]. The production process of Ordinary Portland Cement (OPC) is

identified as one of the major sources of CO_2 emission and energy consumption. OPC production accounts for approximately 5% of global energy consumption. Furthermore, the production of 1 ton of OPC releases approximately 1 ton of CO_2 into the environment [3] and consumes 1.5 tons of raw materials [4]. Therefore, it seems necessary to find an alternative to OPC. The aluminosilicate source, also known by other names, such as raw material, geopolymerization source, and source material, plays the most important role in geopolymer types of cement, as the Si, and Al supplier. The aluminosilicate source, depending on required characteristics, cost, and availability, can be of natural origin (e.g. zeolite), synthetic (e.g. metakaolin), or waste materials (e.g. fly ash or granulated ground blast furnace slag) [1,20]. Fly ash is a by-product of the coal-fired power plant, which can be one of the best aluminosilicate source candidates due to its proper structural nature. Fly ash is classified into C (high-calcium) and F (low-calcium). Class C fly ash was used as an aluminosilicate source to make GPC specimens in this research. The alkaline activator solution is one of the two main constituents of geopolymers, playing a significant role in the formation of Al and Si crystals, and is normally chosen based on Na and K (solvent alkali metals) solutions. The most convenient alkali solution used in geopolymerization is a compound solution of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate (Na_2SiO_3) or potassium silicate (K_2SiO_3) [21,22]. Considering the important role of alkaline activator solution in geopolymer cement, it seems necessary to study the role and effectiveness of different alkaline activator solutions. In consequence, various research has been done by researchers in this field, some of which are briefly discussed below. In early research on geopolymers by Davidovits [23, 24], NaOH or KOH solution without silicate solution was used as the alkaline activator solution. They concluded that in this type of alkaline activator solution, KOH provides better results. Palomo et al. [18] compared NaOH and KOH in alkaline activators without silicate solution and concluded that using NaOH subjects has better results. Cheng et al. [14] found in their research that alkaline activator solution plays an important role in the polymerization reaction, and adding a silicate solution such as Na_2SiO_3 or K_2SiO_3 to NaOH or KOH solution can help increase the reaction rate and achieve better results. They also found that using a solution of NaOH and Na_2SiO_3 had better results than by means of a solution of KOH and K_2SiO_3. Rashed [4] decided in a study on geopolymers that, in general, in most cases, the compressive strength of GPC is increased through enhancing the concentration of NaOH solution to a certain concentration. In a study on metakaolin-based GPC, Moradikhou et al. [1] used a combination of NaOH and Na_2SiO_3 as an alkaline activator solution and concluded that increasing the concentration of NaOH to 14M subjects

to enhance the compressive strength of concrete. However, further proliferation in concentration up to 16M causes no significant change in compressive strength. This is while, in a similar study, Patel et al. [25] concluded that increasing the concentration of NaOH solution to 12M in metakaolin-based GPC increases the compressive strength, and increasing the concentration to more than 12M decreases the compressive strength. Regarding the weight ratio of silicate to hydroxide solution, Hardjito et al. [26] mulled over the GPC based on Class F fly ash and reported that the optimal weight ratio of Na_2SiO_3/NaOH solution was equal to 2.5 when using NaOH solution with a concentration of 14M. In contrast, Moradikhou et al. [22] did a similar study on GPC based on class F fly ash and determined the optimal weight ratio of Na_2SiO_3/NaOH solution in the case of 14M NaOH solution is 1.5. According to the aforementioned points, sodium-based alkaline activator solutions have been used in most articles and studies, and several types of research on sodium-based alkaline solutions and effective parameters of alkaline activator solution on compressive strength of GPC such as NaOH solution concentration, Na_2SiO_3 solution concentration, the ratio of Si_2O to Na_2O in Na_2SiO_3 solution, the weight ratio of Na_2SiO_3 solution to NaOH solution, as well as the optimization of these parameters have been implemented. Henceforth, they pave the way for more research. However, very little research has been done on KOH solution, combination of NaOH and KOH solution, the study of relevant parameters and their optimization, as well as comparison of these three different alkaline activator solutions. On the other hand, GPC is cured at temperatures of 60-90 ° C for 4-24 hours in most studies. Processing at ambient temperature can change the results of GPC mechanical strengths because, for example, the rate of reactivity the rate of dissolution of aluminosilicate sources in alkaline activator solution vary at different temperatures. Considering the fact that in practice, the use of concrete and mortar is done in ambient conditions and curing in the oven is only for the laboratory, the study of the role of different alkaline solutions in ambient temperature conditions (actual use conditions) is particularly significant. Therefore, this study tried to investigate the manufacturing of GPC by considering the practical cases in real conditions. Since the results of previous research in this field are contradictory and in addition, previous research has not considered the practical conditions of using GPC; such research is a step forward in the practical use of GPC in infrastructure construction. Hence, in this paper, the role of different alkaline solutions including NaOH, KOH, and combination of NaOH and KOH and Na_2SiO_3 and K_2SiO_3, some parameters related to alkaline activator solution and curing conditions on compressive strengths of GPC based on Class C fly ash and also, resistance to acidic condition and water absorption of GPC specimens, were deliberated.

2. MATERIALS AND METHODS

2.1. MATERIALS

According to ASTM C618 [27], the fly ash used is classified as Class C fly ash due to its chemical composition (high CaO content and $SiO_2+Al_2O_3+Fe_2O_3>$ 50%) . Table 1 summarizes the Class C fly ash's physical and chemical properties. NaOH with 98% purity, KOH with 90% purity, liquid Na_2SiO_3, and liquid K_2SiO_3, were used to prepare the alkaline activator solutions. The chemical analysis of these 4 substances is illustrated in Table 2. The aggregates were obtained from quarries around Tehran. Aggregates with granular sizes of 7-10 mm were used as coarse aggregate (sand), and < 4.75 mm sized aggregates were used as fine aggregate. Fine and coarse aggregates were sieved according to ASTM C33 [28]. SSD

specific gravity and water absorption tests were conducted on the coarse and fine aggregates using the ASTM C127 [29] and ASTM C128 [30] procedures, respectively, and gathered in Table 3. The fineness modulus (using ASTM C136 [31]) and sand equivalent (using ASTM D2419 [32, 33]) values of the fine aggregates were measured equal to 3.01 and 73, respectively. To reduce water content and improve the workability of concrete, a polycarboxylate-based Super Plasticizer (SP) with a specific gravity of 1.1 g/cm^3, was incorporated. Water consumption was also tapped water in Tehran.

Table 1. Physical and chemical properties of fly ash used

Content	Result	Unit
SiO_2	34.70	%
Al_2O_3	14.80	%
CaO	33.85	%
Fe_2O_3	15.10	%
TiO_2	0.48	%
K_2O	1.83	%
Na_2O	0.17	%
MnO	0.15	%
P_2O_5	0.05	%
L.O.I	1.10	%
SiO_2/Al_2O_3	2.34	-
Specific Gravity	2.22	g/cm^3
Fineness	3717	cm^2/g

Table 2. Chemical analysis of NaOH, KOH, Na_2SiO_3 and K_2SiO_3 solutions

NaOH			KOH			Na_2SiO_3			K_2SiO_3		
Chemical substance	Result	Unit	Chemical substance	Result	Unit	Chemical substance	Result	Unit	Chemical substance	Result	Unit
NaOH	98	%	KOH	90.7	%	SiO_2	30.00	%	SiO_2	30.50	%
Na_2CO_3	1	%	K_2CO_3	0.2	%	Na_2O	14.50	%	K_2O	14.50	%
NaCl	200	ppm	NaCl	0.006	%	Water	55.50	%	Water	55	%
Fe	6	ppm	Fe	0.2	ppm	ROM*	2.06	-	ROM**	2.1	-
SiO_2	15.7	ppm	NaOH	0.6	%	Appearance	Clear liquid		Appearance	**Clear liquid**	
Appearance	White flake		Appearance	White flake		*ROM: ratio of model (SiO_2/Na_2O)			**ROM: ratio of model (SiO_2/K_2O)**		

Table 3. Specific gravity and Water absorption of aggregates

Material	SSD Specific gravity (gr/cm^3)	Water absorption (%)
Coarse aggregates	2.62	**1.3**
Fine aggregates	2.59	**3.2**

2.2. Mix Design

2.2.1. Alkaline Activator Type

In this section, in order to investigate the effect of alkaline activator solution type on GPC compressive strength, 4 different types of alkaline activator solution were inspected, including:

1-NN: Na2SiO3 (SiO2/Na2O ratio = 2) + NaOH 10M
2-NK: Na2SiO3 (SiO2/Na2O ratio = 2) + KOH 10M
3-KN: K2SiO3 (SiO2/Na2O ratio = 2) + NaOH 10M
4-KK: K2SiO3 (SiO2/Na2O ratio = 2) + KOH 10M

In this regard, 3 mix designs were prepared, which are indicated in Table 4. To manufacture GPC specimens, initially, the alkaline activator solution, constituting of

NaOH, KOH, Na2SiO3, K2SiO3, SP, and the extra water (according to each mix design) are combined and allowed to cool for 24 hrs. In the mixing process, the aggregates and fly ash were first to dry mixed in the mixer for 3 minutes. Next, the alkaline activator solution was added, and the concrete was mixed for a further 2 minutes. Subsequently, three compressive (100x100x100 mm cubes) specimens (for each mix design) were molded and vibrated for 10 seconds on a vibrating table. Thus, the specimens were allowed to rest at laboratory ambient temperature. The specimens were subjected to the 7- and 28-day compressive strength test according to BS1881: Part116 [34].

Table 4. Mix designs related to the type of alkaline activator (kg/m^3)

Mix ID	Fly ash	NaOH 10M	KOH 10M	Na$_2$SiO$_3$	K$_2$SiO$_3$	Fine aggregates	Coarse aggregates	SP	Extra water
NN	400	80	-	120	-	860	860	6	**10**
NK	400	80	-	120	-	860	860	6	**10**
KN	400	-	80	-	120	860	860	6	**10**
KK	400	-	80	-	120	860	860	6	**10**

2.2.2. Concentration of Naoh and Koh

In this section, in order to investigate the effect of NaOH and KOH solutions on GPC compressive strength based on fly ash and optimization of this parameter, 8 mix designs were set, as detailed in Table 5. It should be noted that based on the results from previous sections,

NaOH+Na2SiO3 and KOH+K2SiO3 were selected as alkaline activator solutions. Similar compressive specimen production and testing procedure as Section 2-2-1 is followed.

Table 5. Mix designs related to NaOH and KOH concentration (kg/m3)

Mix ID	Fly ash	NaOH	KOH	Na$_2$SiO$_3$	K$_2$SiO$_3$	Fine aggregates	Coarse aggregates	SP	Extra water	NaOH concentration (M)	KOH concentration (M)
N10	400	80	-	120	-	860	860	6	10	10	-
N12	400	80	-	120	-	860	860	6	10	12	-
N14	400	80	-	120	-	860	860	6	10	14	-
N16	400	80	-	120	-	860	860	6	10	16	-
K10	400	-	80	-	120	860	860	6	10	-	**10**
K12	400	-	80	-	120	860	860	6	10	-	**12**
K14	400	-	80	-	120	860	860	6	10	-	**14**
K16	400	-	80	-	120	860	860	6	10	-	**16**

2.2.3. Concentration of Naoh and Koh

In this section, the effect of different combinations of NaOH and KOH solutions on the compressive strength of GPC based on fly ash was scrutinized. In this regard, 7 mix designs were set up, which are shown in Table 6. It should be noted that Na2SiO3 is cheaper and more available than K2SiO3 and the existence of Na2SiO3 with different SiO2/Na2O ratios and according to the results obtained from the previous sections, Na2SiO3 was used as the silicate solution in the continuation of the research. GPC specimens were made and tested exactly as in the previous sections.

Table 6. Mix designs related to NaOH / KOH ratio (kg/m^3)

Mix ID	Fly ash	NaOH 10M	KOH 10M	Na$_2$SiO$_3$	Fine aggregates	Coarse aggregates	SP	Extra water	NaOH/KOH ratio
N100	400	80	-	120	860	860	6	10	100/0
N80K20	400	64	16	120	860	860	6	10	80/20
N60K40	400	67	45	120	860	860	6	10	60/40
N50K50	400	40	40	120	860	860	6	10	50/50
N40K60	400	45	67	120	860	860	6	10	40/60
N20K80	400	20	90	120	860	860	6	10	20/80
K100	400	-	80	120	860	860	6	10	0/100

2.2.4. Sio2/Na2o Weight Ratio of Na2sio3 Solution

In this part, the effect of SiO2/Na2O weight ratio of Na2SiO3 solution on the compressive strength of GPC based on fly ash was studied. In this regard, NaOH solution and 3 types of Na2SiO3 solution with SiO2/Na2O ratios equal to 2, 2.5, and 3 were used. Similarly, in order to simultaneously dissect the effect of NaOH solution concentration and SiO2/Na2O ratio of Na2SiO3 solution, 2 concentrations of 10 and 14M were considered for NaOH solution. Hence, 6 mix designs were selected, which are indicated in Table 7. Similar compressive specimen production and testing procedure as pervious sections is followed.

Table 7. Mix designs related to SiO2/Na2O ratio (kg/m3)

Mix ID	Fly ash	NaOH	Na$_2$SiO$_3$	Fine aggregates	Coarse aggregates	SP	Extra water	SiO$_2$/Na$_2$O ratio of Na$_2$SiO$_3$	NaOH concentration (M)
N2-10	400	80	120	860	860	6	10	2	10
N2-14	400	80	120	860	860	6	10	2.5	14
N2.5-10	400	80	120	860	860	6	10	3	10
N2.5-14	400	80	120	860	860	6	10	2	14
N3-10	400	80	120	860	860	6	10	2.5	10
N3-14	400	80	120	860	860	6	10	3	14

2.2.5. Curing Condition

In this section, the effect of curing conditions on the compressive strength of GPC, was investigated. In this regard, curing temperature and curing time factors were studied. To investigate the effect of curing temperature on compressive strength, specimens made with 2 alkaline activator solutions, including: NaOH + Na2SiO3 (Na-based) and KOH + K2SiO3 (K-based), in different curing conditions, including ambient temperature and dry curing in the oven at a temperature of 40-90 ˚C, were cured for 24 hours. Then, in order to investigate the effect of curing time by determining the results of the previous step (curing temperature), the specimens were cured in the oven at 80 °C for 6, 12, 18, 24, 30, and 36 hours. After the curing process, the specimens were allowed to rest at laboratory ambient temperature. The specimens were subjected to the 3-, 7- and 28-day compressive tests. The mix designs of this section are divulged in Table 8, as well as fresh GPC images and GPC specimens in Figure 1.

Table 8. Mix designs related to curing condition (kg/m3)

Mix ID	Fly ash	NaOH	KOH	Na$_2$SiO$_3$ [*]	K$_2$SiO$_3$ [**]	Fine aggregates	Coarse aggregates	SP	Extra water	KOH concentration (M)	NaOH concentration (M)
Na-based	400	80	-	120	-	860	860	6	10	-	14
K-based	400	-	80	-	120	860	860	6	10	14	-

[*]SiO$_2$/Na$_2$O=2   [**]SiO$_2$/K$_2$O=2

Figure 1. Images of fresh GM and GM compressive specimen

2.2.6. Water Absorption and Weight Loss under Acidic Condition

In the last part of the research, the effect of alkaline activator type on weight loss under acidic conditions and water absorption of GPC specimens were studied. The water absorption capacity of the GPC specimens was studied following the ASTM C642 [35] procedures. Hence, 3 compressive cube specimens were considered for N, NaK, and K mix designs (Table 9). The 28-day specimens, after the production process similar to section 2-2-1, were initially placed in a 105 ˚C oven to reach a stable dry weight and then weighted (m0). The specimens were then placed in a water tank for 3 days. They were then taken out and, after drying the surface water, were weighted again (m). The 3-day water absorption capacity (W) is calculated by Eq. (1):a

$$W = \frac{m-mo}{mo} \times 100 \qquad \text{Eq. (1)}$$

Also, to test the chemical resistance of GPC specimens, the 28-day specimens of N, NaK, and K mix designs were placed in a solution of water and sulfuric acid at a pH equal to 1 for 28 days. Then, a weight loss test was taken from specimens.

Table 9. Mix designs related to the Water absorption and weight loss under acidic condition (kg/m^3)

Mix ID	Fly ash	NaOH 10M	KOH 10M	Na$_2$SiO$_3$	K$_2$SiO$_3$	Fine aggregates	Coarse aggregates	SP	Extra water
N	400	80	-	120	-	860	860	6	**10**
NaK	400	40	40	120	-	860	860	6	**10**
K	400	-	80	-	120	860	860	6	**10**

3. RESULTS AND DISCUSSION

3.1. Effect of Alkaline Activator Solution Type on Compressive Strength of Gpc

Figure 2 shows the effect of alkaline activator solution type on the mean compressive strength of Class C fly ash-based GPC. The 7- and 28-day compressive strength of the NN specimen, which was made of NaOH and Na2SiO3 solution, was measured as 35.3 and 50.4 MPa, respectively. The 7-day and 28-day compressive strengths of the KK (KOH+K2SiO3) specimen, were 18.4 and 33.9 MPa, respectively. According to the results, the specimen made with Na-based activating solution (NaOH+ Na2SiO3), offered a much higher compressive strength than the specimen made with K-based activator solution (KOH+K2SiO3), so the use of Na-based activator resulted in maximum compressive strength.
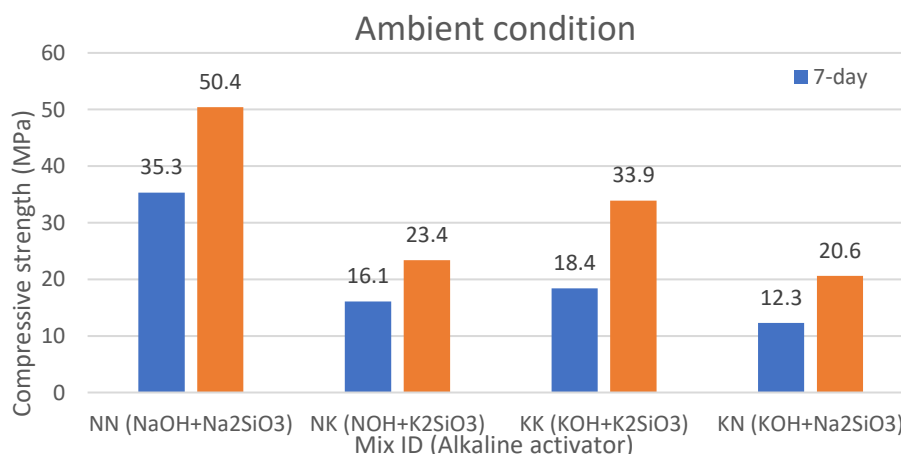

Figure 2. Effect of alkaline activator type on 7 and 28-day compressive strength of GM

Table 10 shows the changes in the specimens' early strength (the level of strength obtained at 7-days). The results revealed that the use of Na-based activator solution upsurges early strength. Na-based specimen obtained a higher percentage of its final strength (28 days) at 7 days of age compared to the specimen made with K-based solution. Moreover, the early strength of KN and NK specimens improved in comparison with K-based specimens but were less than Na-based specimens.

Table 10. Effect of alkaline activator solution type on lateral and early strength of GPC

Mix ID	Alkaline activator type	28-day compressive strength (MPa)	28-day strength above KK mix (%)	Level of 28-day strength obtained at 7-days (early strength) (%)	Early strength above KK mix (%)
NN	$NaOH + Na_2SiO_3$	50.4±0.5	-	70	-
NK	$NaOH + K_2SiO_3$	23.4±1.1	-53	68	-3
KK	$KOH + K_2SiO_3$	33.9±1	-33	54	-23
KN	$KOH + Na_2SiO_3$	20.6±0.6	-59	59	-16

These results may be related to differences in the mechanism of reactions of Na and K. The mechanism of action of alkaline activator solution breaks the structure of silica and alumina of aluminosilicate source, formins silicon and aluminum ions and makes geopolymer gel, within 3 stages of dissolution, the partial orientation of the mobile precursor, and reloading of particles from the initial solid phase are implemented [36, 37]. The type of alkaline activator plays a very important role in the development of the geopolymer production process. In most previous studies in this regard, high-temperature curing conditions (60-90 °C) have been practiced to process GPC specimens. The researchers concluded that potassium leads to the formation of larger oligomer silicates due to its larger atomic radius, which $Al(OH)_4^-$ prefers and attaches to. Therefore, more geopolymer is formed in the case of using K-based activator solution, subjects to the formation of a stronger and more compact system than Na-based activator solution [38], which results in lower 3- and 7-day compressive strength, slower hardening, and higher 28-day compressive [22]. On the other hand, in Na-based activator solution, NaOH has the ability to dissolve more minerals in concentrations similar to KOH and NaOH. This leads to a higher reaction rate of Na^+ compared to K^+ [39,40]. Attributable to the same high rate of reaction Na^+, in the case of using Na-based activator, higher 7-day compressive strength and faster hardening than K-based, obtained [22]. However, it should be noted that these results are achieved in the case of curing at high temperatures and providing the necessary energy. In this study, ambient temperature conditions are used, and as can be seen, the results of this study are different from the previous ones. This could be due to Less Active K^+ for the sake of the larger ionic size of K^+ compared to Na^+ [39] as well as the lower solubility of Si and Al in K-based activator solution than Na-based at similar molar concentrations [40]. Therefore, more energy is needed in the case of using a K-based activator, so the use of ambient temperature conditions in this study did not provide the essential energy for effective K^+ activity. As a result, the specimen made with a K-based activator provided both lower lateral compressive strength and lower early strength compared to Na-based activator. In fact, for this reason, the early compressive strength of the specimen increased by replacing part of K^+ with Na^+ in the NK, KN specimens. These results differ from the results of previous research [1,20,22], which may be due to differences in processing conditions. According to the results obtained from this section, two alkaline activator solutions $(NaOH+Na_2SiO_3)$ and $(KOH+Na_2SiO_3)$ were selected to continue the research process.

3.2. Effect of Naoh and Koh Concentration on Compressive Strength of Gpc

The results of the study of the effect of NaOH solution concentration on compressive strength are presented in Figure 3, and the results of this experiment for KOH solution are divulged in Figure 4. According to the results, the lowest 7- and 28-day compressive strengths were 32.1 and 45.8 MPa in the case of using Na-based activator, related to 10M NaOH. By increasing the concentration of NaOH solution from 10 to 16M, the 7- and 28-day compressive strength also increased. The results were similar for the KOH solution. The lowest compressive strengths of 7 and 28 days were measured in 10M KOH solution at 18.2 and 30.8 MPa. By increasing the concentration of KOH solution to 16M, the compressive strength increased and reached its maximum value. Increasing the molar concentration of hydroxide solutions increases the pH. Also, more amounts of SiO2 and Al2O3 of aluminosilicate source are dissolved in the alkaline activator solution, resulting in higher amounts of geopolymer gel formation, leading to higher compressive strength [41]. Consequently, the compressive strength also increased significantly through growing the concentration of NaOH and KOH solutions to 16M.
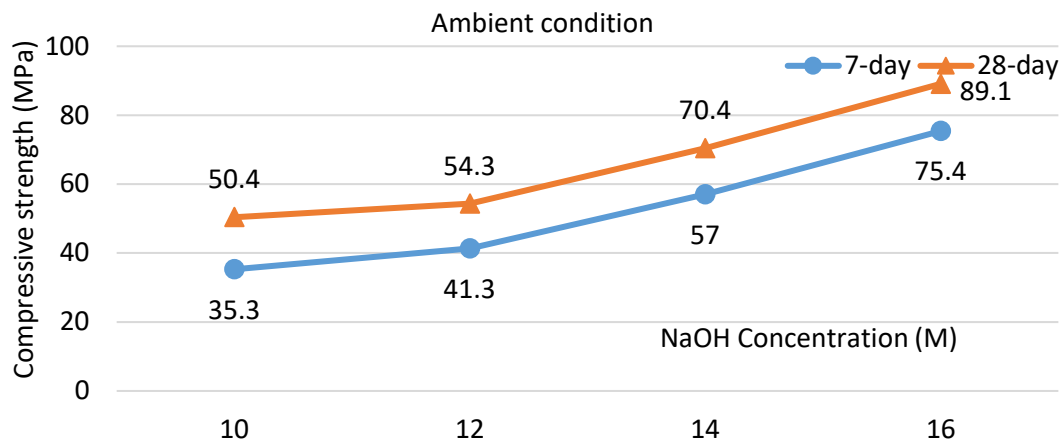
Figure 3. Effect of NaOH concentration on 7 and 28-day compressive strength of GPC
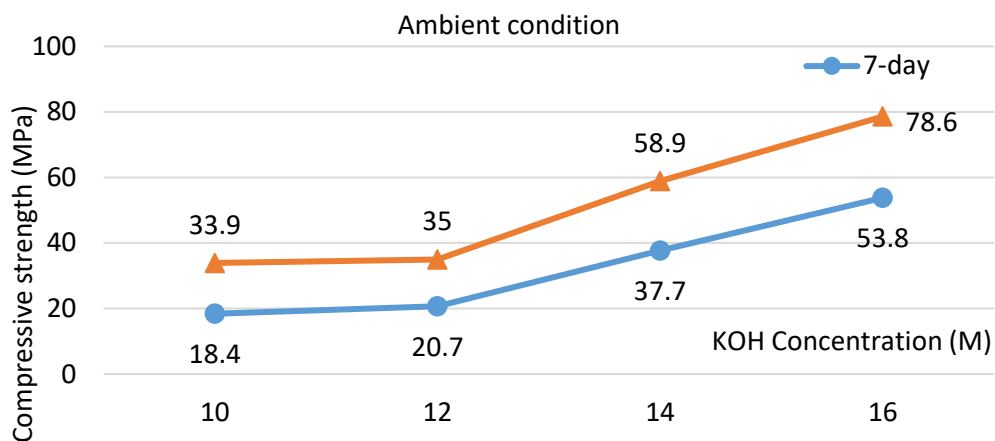

Figure 4. Effect of KOH concentration on 7 and 28-day compressive strength of GPC

On the other hand, an increasing trend in the acquisition of early strength of GPC was observed by increasing the concentration of NaOH and KOH solutions (Tables 11 and 12). This could be related to the acceleration of the geopolymerization process with NaOH and KOH solutions concentration [22]. It should be considered that the results obtained from this section are different from some of the results of previous research. Moradikhou et al. [1] scrutinized the role of NaOH solution concentration on GPC compressive strength. The researchers used a combination of NaOH and Na2SiO3 solution as the alkaline activator solution and concluded that increasing the concentration of NaOH solution to 14 mol improves

the compressive strength, but further increasing the concentration to 16 mol decreases the compressive strength. The researchers used 80 °C curing conditions to process the specimens, which could be the main reason for the difference in results. Patel et al. [42] obtained similar results. In another study, Esparham et al. [22] also premeditated the effect of the concentration of NaOH solution on the compressive strength of GPC. They also used a heat curing regime at 90 °C to cure the specimens and concluded that increasing the concentration from 10 to 14M increased the compressive strength by 23%, but no significant change in compressive strength was detected with a further increase in concentration from 14 to 16M.

Table 11. Effect of NaOH concentration on lateral and early strength of GPC

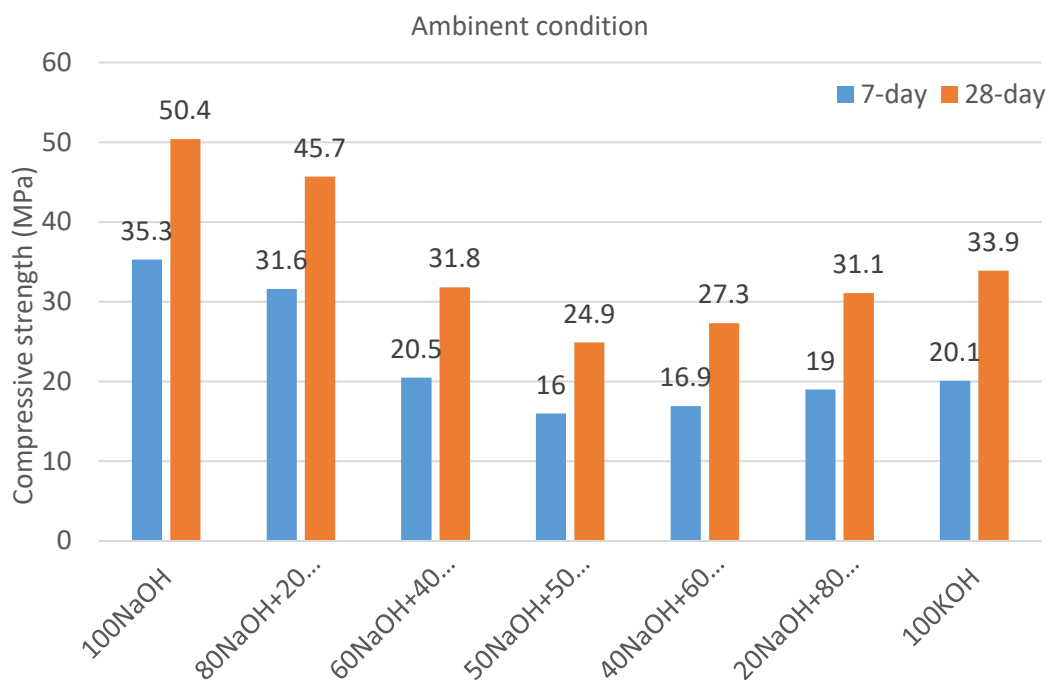| NaOH concentration	28-day compressive strength (MPa)	28-day strength above 10 M (%)	Level of 28-day strength obtained at 7-days (early strength) (%)	Early strength above 10M (%)
10M	45.8±0.8	-	70	-
12M	49.3±09	+8	76	+9
14M	64±0.8	+40	81	+16
16M	81±1.1	+77	84	+20

Table 12. Effect of KOH concentration on lateral and early strength of GPC

KOH concentration	28-day compressive strength (MPa)	28-day strength above 10 M (%)	Level of 28-day strength obtained at 7-days (early strength) (%)	Early strength above 10M (%)
10M	33.9±1	-	54	**-**
12M	35±0.6	+3	59	**+10**
14M	58.9±0.8	+74	64	**+19**
16M	78.6±0.6	+132	68	**+26**

3.3. Effect of Combination of Naoh and Koh on Compressive Strength of Gpc

The obtained results for the effect of the combination of NaOH and KOH solutions on the compressive strength of GPC, are presented in Figure 5.

Figure 5. Effect of combination of NaOH and KOH on 7 and 28-day compressive strength of GPC

The results demonstrated that the combination of NaOH and KOH solutions reduced the compressive strength of the specimens compared to both 100% NaOH and 100% KOH solution, and the higher the replacement percentage, the lower the compressive strength was measured (Table 11). Thus, the lowest 7-and 28-day compressive strength was observed in the specimen made of 50% NaOH solution and 50% KOH solution at the rate of 16 and 24.9 MPa. These results can also be due to differences in the mechanisms of Na and K. As mentioned in Section 3.1, KOH tends to perform a condensation reaction and the formation of large oligomer silicates due to the larger atomic radius, while NaOH is capable of dissolving more inorganic components than KOH, which leads to faster reaction rate for Na^+ than for K^+. The high reactivity of Na+ could not be balanced with the tendency of K+ towards condensation reaction [40]. This can well explain the declining trend of the compressive strength of GPC by increasing the substitution level of NaOH and KOH from 20 to 50%; that is, by increasing the substitution level, the interference in the reactivity of Na^+ and K^+ would increase. On the other hand, it can be seen that in specimens where the amount of NaOH solution is predominant (NaOH solution content ≥50%) according to Table 13, adding KOH solution not only lessens the compressive strength of the specimens compared to 100% NaOH solution, but also diminishes the early strength. Nonetheless, the results are the opposite. In specimens with a predominant amount of KOH solution (KOH solution ≥50%), the addition of NaOH solution increases the early strength of the specimens to a 100% KOH solution, and as the percentage of NaOH increases, the early strength of the specimens also upsurges, which can also lead to the differences in Na and K reaction maps are related.

Table 13. Effect of NaOH and KOH combination on lateral and early strength of GPC

NaOH/KOH ratio	28-day compressive strength (MPa)	28-day strength above 100% NaOH (%)	Level of 28-day strength obtained at 7-days (early strength) (%)	Early strength above 100% NaOH (%)
100%NaOH	50.4±0.5	-	70	-
80%NaOH+20%KOH	45.7±0.9	-9	69	-2
60%NaOH+40%KOH	31.8±0.7	-37	65	-7
50%NaOH+50%KOH	24.9±0.8	-50	64	-9
NaOH/KOH ratio	**28-day compressive strength (MPa)**	**28-day strength above 100% KOH (%)**	**Level of 28-day strength obtained at 7-days (early strength) (%)**	**Early strength above 100% KOH (%)**
100%KOH	33.9±1	-	59	-
80%KOH+20%NaOH	31.1±0.6	-8	61	+3
60%KOH+40%NaOH	27.3±0.9	-19	62	+5
60%KOH+40%NaOH	24.9±0.8	-26	64	+8

3.4. Effect of the Weight Ratio of Sio2/Na2o of Na2sio3 Solution on Compressive Strength of Gpc

The compressive strength test results using 14M NaOH in Figure 6 and 10M NaOH are presented in Figure 7. The results indicate that the highest 7- and 28-day compressive strength was obtained in Na_2SiO_3 solution with the weight ratio of $SiO_2/Na_2O = 2$ in the case of using 14M NaOH solution (57 and 70.4 MPa). Increasing the SiO_2/Na_2O ratio of Na_2SiO_3 solution to 2.5 and 3 reduced the compressive strength by 3 and 4%, respectively. In the case of using 10M NaOH solution, the specimen's 7- and 28-day compressive strength made with Na_2SiO_3 solution

with $SiO_2/Na_2O = 2$ were 35.3 and 50.4 MPa, respectively. Unlike the use of 14M NaOH solution, increasing the SiO_2/Na_2O ratio of Na_2SiO_3 solution to 2.5 increased the compressive strength by approximately 7% and achieved the maximum compressive strength at 7 and 28 days (38.4 and 54.1 MPa). By further increasing the SiO_2/Na_2O ratio of Na_2SiO_3 solution to 3, the compressive strength decreased by roughly 10% compared to the optimal state (2.5).
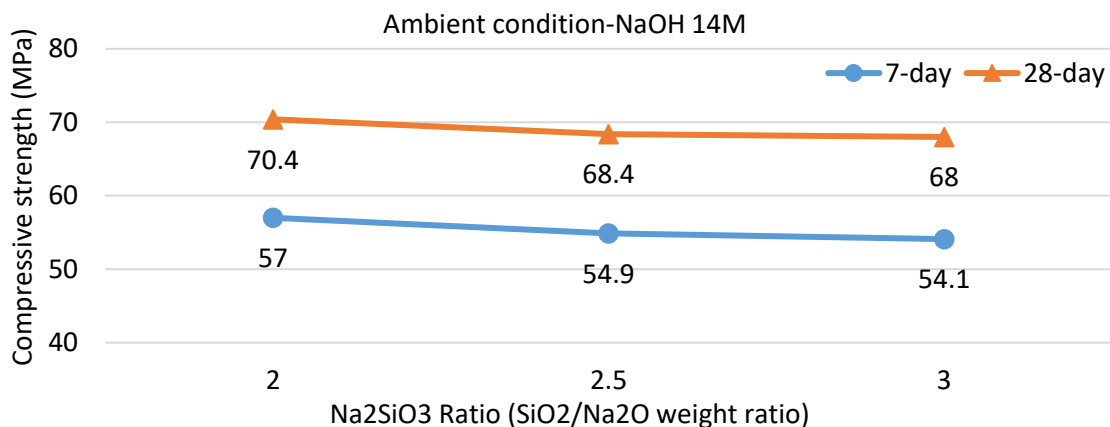
Figure 6. Effect of SiO_2/Na_2O of Na_2SiO_3 solution on compressive strength of GPC (NaOH concentration=14M)
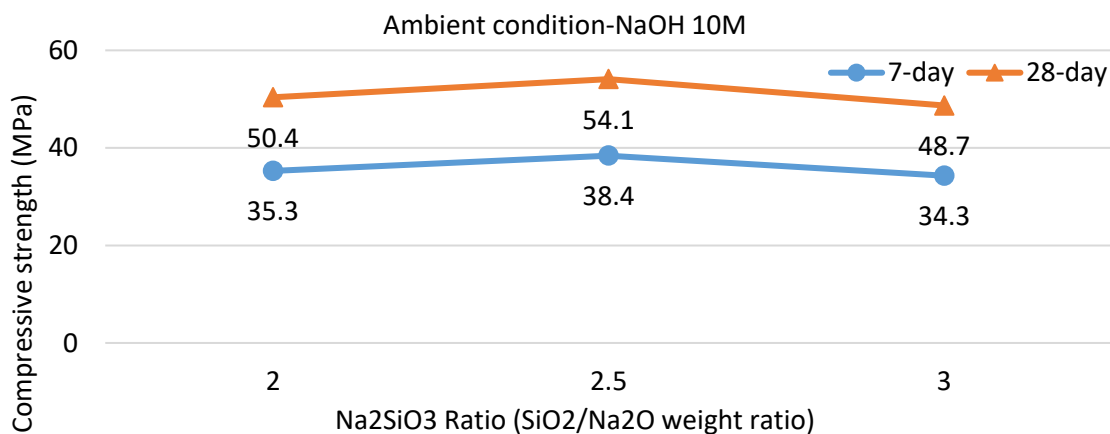
Figure 7. Effect of SiO_2/Na_2O of Na_2SiO_3 solution on compressive strength of GPC (NaOH concentration=10M)

The role of alkaline activator solution, especially NaOH or KOH, is to dissolve Si and Al in the aluminosilicate source, produce SiO_4 and AlO_4 and yield a geopolymer gel. Adding a silicate solution such as Na_2SiO_3 or K_2SiO_3 to the alkaline activator solution increases the amount of SiO_4 and the geopolymerization reaction rate, due to the presence of soluble Si. Consequently, it improves the compressive strength of GPC. Meanwhile, adding a small amount (less than the optimal ratio) of soluble Si and accordingly lowering the amount of SiO_4 reduces the compressive strength. On the other hand, adding an extra amount (more than the optimal ratio) also reduces the compressive strength because the amounts of SiO_4 are produced, in this case excessive, whereas the amount of AlO_4 in the composition is constant (or limited) [38, 43]. As a result, the compressive strength decreases as the Si/Al ratio deviates from the optimal range. But the optimal amount of Si in the solution can depend on several factors, and the first one is the SiO_2/Na_2O ratio of the Na_2SiO_3 solution. Naturally, Na_2SiO_3 solution with a higher SiO_2/Na_2O ratio has higher amounts of SiO_2 as well as soluble Si. The next factor that can affect the optimal SiO_2/Na_2O ratio of Na_2SiO_3 solution is the concentration of NaOH solution. As observed in the previous sections, the degree of dissolution of the Si presented in the aluminosilicate source is directly related to the concentration of NaOH solution. The use of higher concentrations of NaOH solution increases the solubility of Si of the aluminosilicate source and produces higher amounts of soluble Si. In this case, the use of Na_2SiO_3 solution with a high SiO_2/Na_2O beard can lead to a decrease in compressive strength due to excessive increment of soluble Si. In fact, this issue can be the reason for the difference in the results of optimizing the SiO_2/Na_2O ratio of Na_2SiO_3 solution in two states of NaOH 10M and 14M in this study. The results of this study presented that in the case of using 10M NaOH solution, the optimal amount of SiO_2/Na_2O is 2.5, and it is 2 in the case of using 14M NaOH solution. These results differ from the results of previous research [1,20,25,33], which may be due to differences in processing conditions.

3.5. Effect of Curing Condition on Compressive Strength of Gpc

Figure 8 illustrates the effect of curing temperature on the compressive strength of GPC. Under the ambient temperature curing condition, Na-based specimens' 3-, 7- and 28-day compressive strengths were 50.7, 57, and 70.4 MPa, respectively. The obtained results indicated that the use of heat curing significantly increased the compressive strength compared to curing at ambient temperature and this increase in compressive strength was more noticeable in 3- and 7-day compressive strengths.
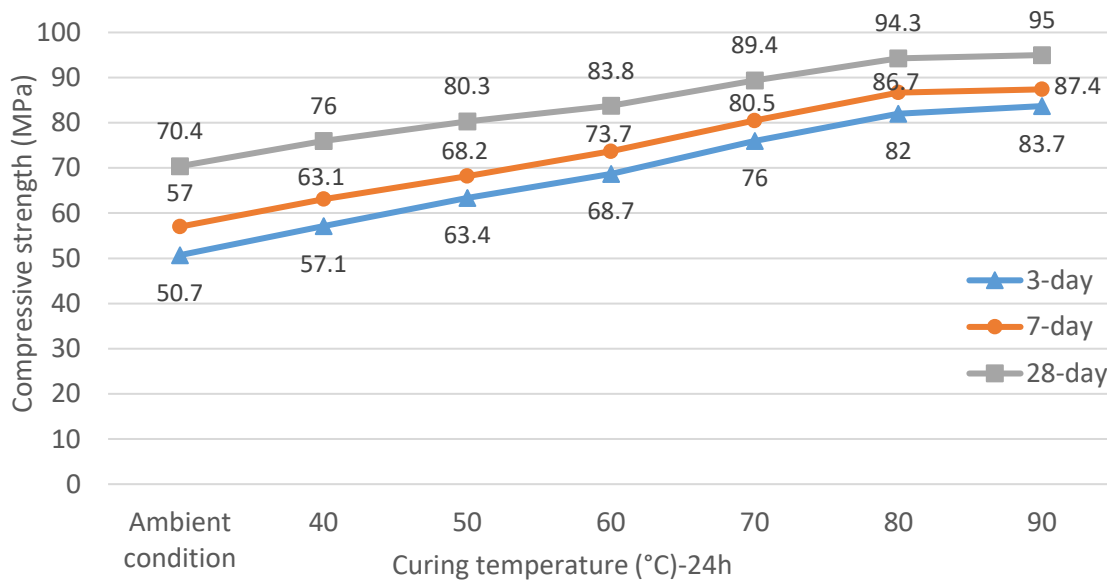
Figure 8. Effect of curing temperature on compressive strength of Na-based GPC

According to Figure 8 and Table 13, increasing the curing temperature from ambient temperature to 80 °C resulted in 62, 52, and 35% increase in 3- , 7- and 28-day compressive strengths of Na-based GPC specimens. With further increase of temperature up to 90 °C, no significant changes in compressive strength were observed compared to 80 °C. The results also showed that the changes in compressive strength were more noticeable in the temperature range of 60-80 °C. On the other hand, as the curing temperature increased, the GPC specimens gained a higher percentage of their 28-day compressive strength at 3 and 7 days. Specimens cured at ambient temperature achieved 72% and 81% of their 28-day compressive strength in 3 and 7 days, while these numbers were 87% and 92%, for the specimens cured at 80 °C (Table 14).

Table 14. Effect of curing temperature on lateral and early strength of Na-based GPC

Curing temperature (°C)	28-day compressive strength (MPa)	28-day strength above ambient condition (%)	Level of 28-day strength obtained at 7-days (%)	Level of 28-day strength obtained at 3-days (%)
Ambient condition	70.4±0.7	-	81	72
40	76±1.4	8	83	75
50	80.3±1.3	14	85	79
60	83.8±1.1	19	88	82
70	89.4±1.3	27	90	85
80	94.3±1.2	34	92	87
90	95±1	35	92	88

The results related to the effect of curing temperature on the compressive strength of K-based GPC specimens, are presented in Figure 9. The 3-, 7- and 28-day compressive strengths of K-based specimens were 30.6, 37.7, and 58.9 MPa, respectively. Similar Na-based GPC specimens, the use of heat curing resulted in increasing the compressive strength of the specimens, but on the contrary, an improvement in the compressive strength of the K-based GPC specimens was observed by increasing the curing temperature to 90 °C, so that it increased the 3-, 7- and 28-day compressive strengths by 143, 116 and 77% compared to the ambient temperature. Furthermore, similar Na-based GPC specimens, increase in compressive streng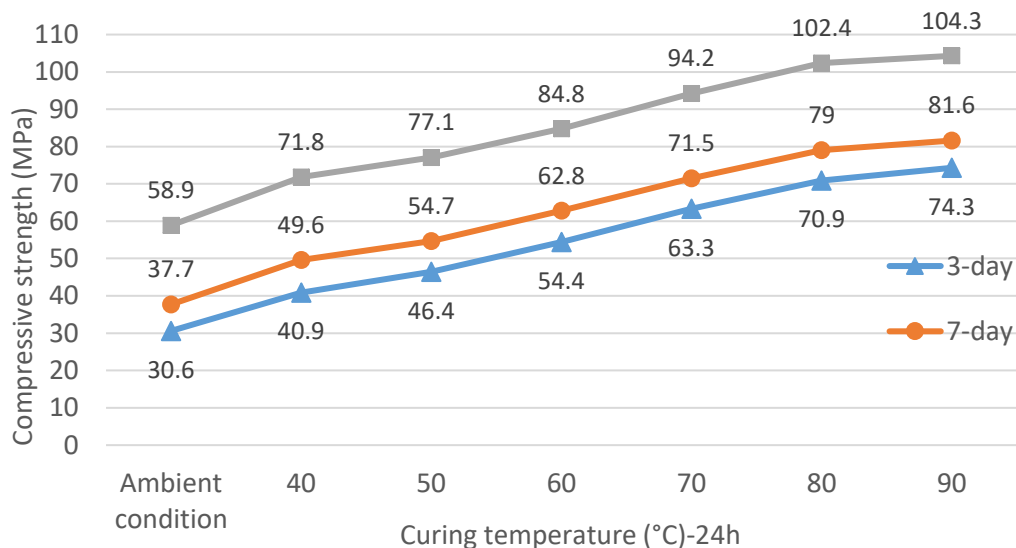th was more noticeable in 3- and 7-day compressive strengths, but in K-based specimens, changes in compressive strength at a temperature range of 40-80°C were noticeable (Table 15).

Figure 9. Effect of curing temperature on compressive strength of K-based GPC

Table 15. Effect of curing temperature on lateral and early strength of K-based GPC

Curing temperature (°C)	28-day compressive strength (MPa)	28-day strength above ambient condition (%)	Level of 28-day strength obtained at 7-days (%)	Level of 28-day strength obtained at 3-days (%)
Ambient condition	58.9±0.8	-	64	52
40	71.8±1	22	69	57
50	77.1±0.9	31	71	60
60	84.8±1.3	44	74	64
70	94.2±1.2	60	76	67
80	102.4±1.5	74	77	69
90	104.3±1.8	77	78	71

Summarizing the results showed that increasing the curing temperature up to 80 °C caused a relative increase in the lateral compressive strength and a significant increase in the early strength of GPC specimens. Increasing the curing temperature greatly accelerates the formation of the geopolymer gel and the process of gaining strength, especially when high-molarity alkaline activators such as this paper (14M), are used. Increasing the curing temperature provides the energy needed to overcome the barriers to continued later-age geopolymerzation that are

presented by high-molarity activators [44]. Another reason could be the increase in the dissolution rate of Si and Al presented in fly ash with increasing curing temperature [45,46]. Moreover, comparing the two types of alkaline activator solution, the results indicated that compressive strength improvement with increasing curing temperature is more noticeable in K-based specimens. Additionally, according to Figure 10, the compressive strength of the Na-based specimens at ambient temperature was much higher than that of K-based specimens. As the temperature increased to nearly 60 °C, the difference in the

compressive strength of the two types of alkaline activators decreased. In the temperature range of 60-90 °C, the trend was reversed, and the K-based specimens provided a greater compressive strength. This can be attributed to the lower K activity due to the larger K^+ ionic size compared to Na^+ [39] as well as the lower dissolution of Si and Al in the K-based activator solution compared to the Na-based at similar molar concentrations [40]. Consequently, K^+ needs more energy to function efficiently, which is provided by increasing the curing temperature.

Figure 10. Comparison of the effect of curing temperature on 28-day compressive strength of Na-based and K-based GPC specimens

The results of the study of the effect of curing time on the compressive strength of Na-based and K-based GPC specimens, are shown in Figures 11 and 12, respectively. Similar to the curing temperature, the increase in curing time due to providing the required energy accelerated the

alkali activation reaction and increased the production of geopolymer gel, resulting in a significant increase in the 3- and 7-day compressive strengths and a relative increase in 28-day compressive strength.
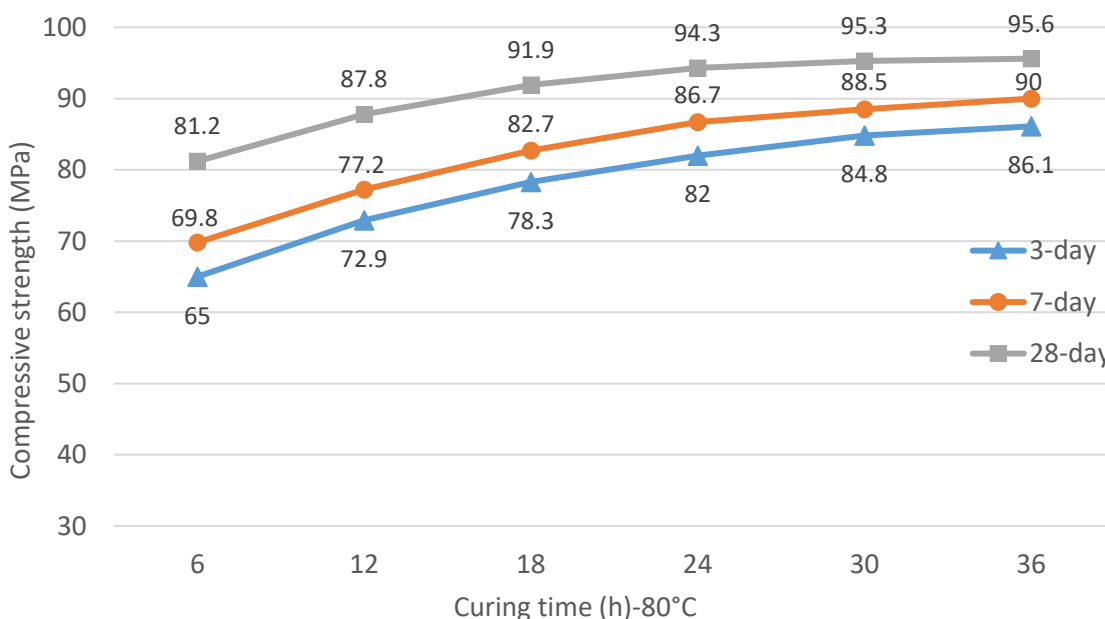
Figure 11. Effect of curing time on compressive strength of Na-based GPC
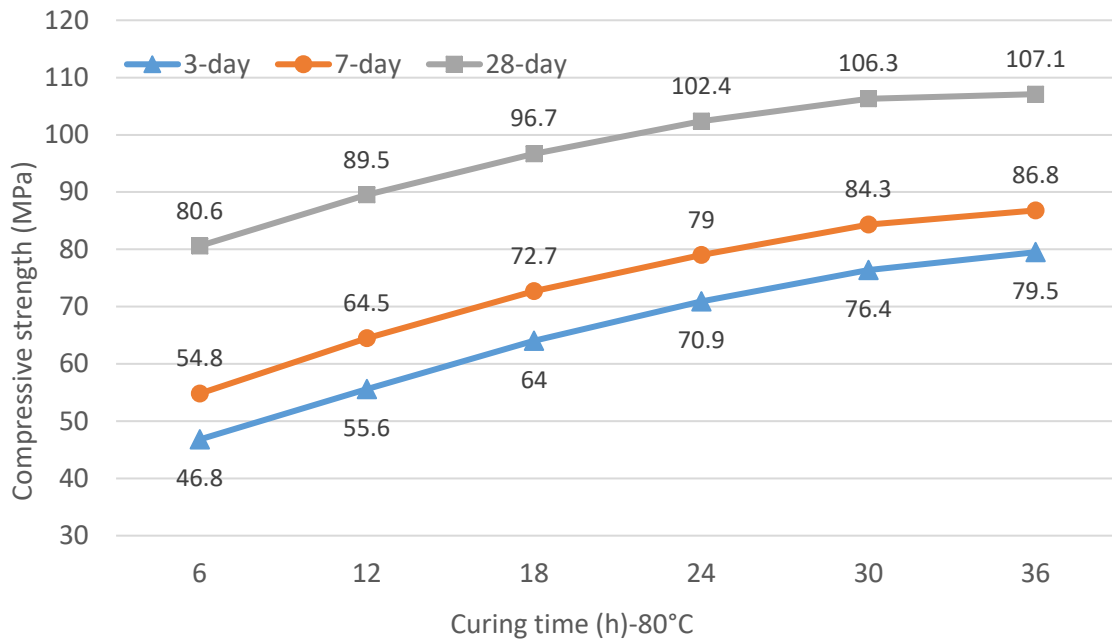
Figure 12. Effect of curing time on compressive strength of K-based GPC

In the case of Na-based specimens, increasing the curing time from 6 to 24 hours caused a 27, 24, and 15% increase in 3- and 7-day compressive strengths. Moreover, the specimens also gained a higher percentage of their lateral compressive strength at 3 and 7 days. However, with a further increase of curing time to 36 hours, no significant change in the compressive strength of the specimens was observed. Table 16 shows the early strength of Na-based specimens at different curing times. In the case of K-based specimens, with increasing curing time from 6 to 30 hours, the 3-, 7- and 28-day compressive strengths increased approximately 63, 54, and 32%. Also, these specimens gained a higher percentage of their lateral compressive strength at 3 and 7 days (Table 17).

Table 16. Effect of curing time on lateral and early strength of Na-based GPC

Curing time (h)	28-day compressive strength (MPa)	28-day compressive strength above 6h (%)	Level of 28-day strength obtained at 7-days (%)	Level of 28-day strength obtained at 3-days (%)
6	82.1±1.2	-	86	80
12	87.8±0.9	7	88	83
18	91.9±1.5	12	90	85
24	94.3±1.2	15	92	87
30	95.3±1.4	16	93	89
36	95.6±1.1	16	94	90

Table 17. Effect of curing time on lateral and early strength of K-based GPC

Curing time (h)	28-day compressive strength (MPa)	28-day compressive strength above 6h (%)	Level of 28-day strength obtained at 7-days (%)	Level of 28-day strength obtained at 3-days (%)
6	80.6±1.5	-	68	58
12	89.5±1.3	11	72	62
18	96.7±1.6	20	75	66
24	102.4±1.5	27	77	69
30	106.3±1.4	32	79	72
36	107.1±1.7	33	81	74

Regarding the comparison of the effect of curing time on Na-based and K-based specimens, the results of Figure 13 showed that although increasing the curing time improved the compressive strength, increasing the curing time was more effective on K-based specimens. Also, Na-based specimens at the curing time of 6 hours provided more compressive strength than K-based specimens, but with increasing curing time from 12 to 36 hours, K-based specimens offered higher compressive strength.
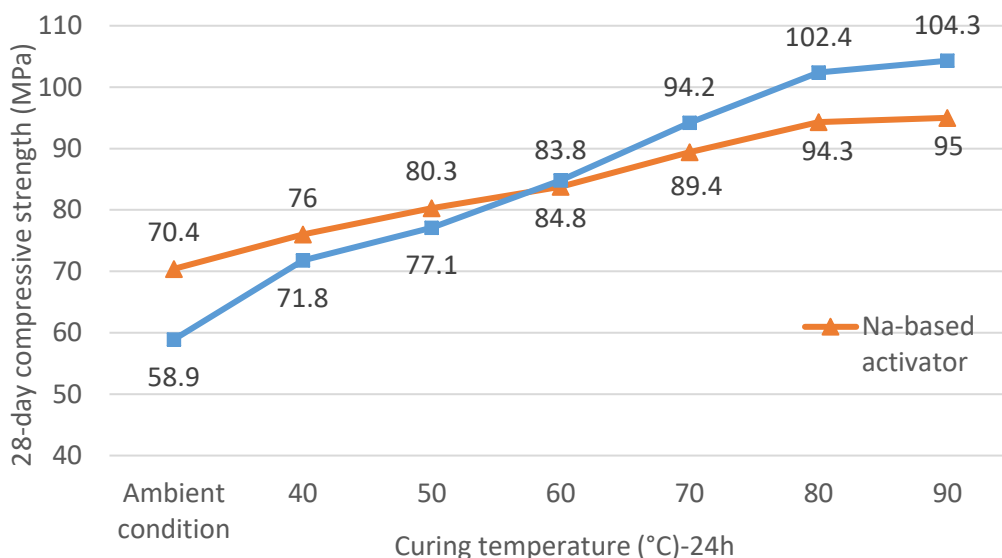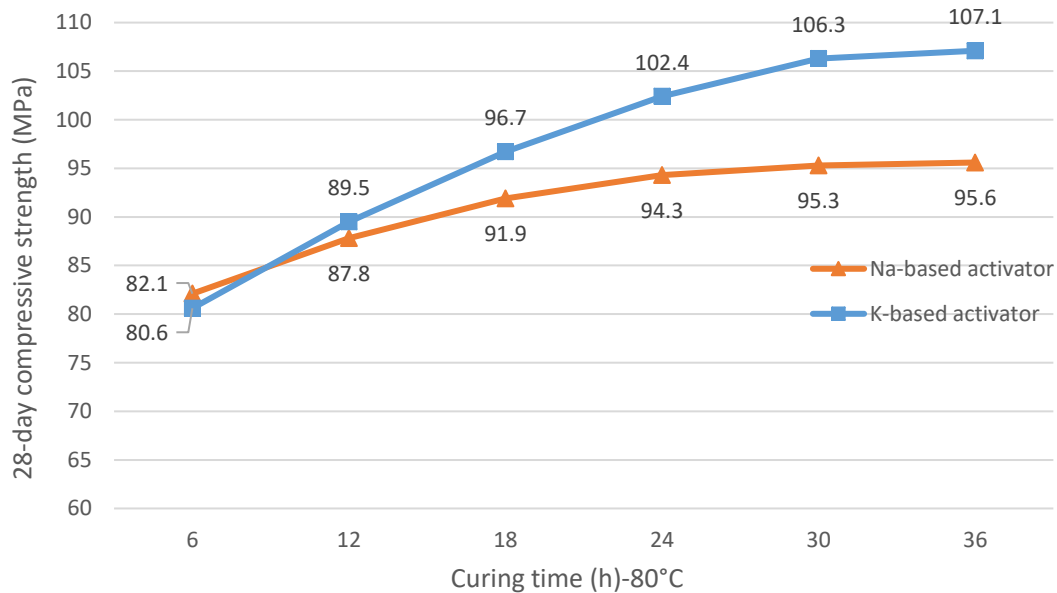
Figure 13. Comparison of the effect of curing time on 28-day compressive strength of Na-based and K-based GPC specimens

3.6. Effect of Alkaline Activator Type on Water Absorption and Weight Loss under Acidic Condition of Gpc

Figure 14 illustrates the water absorption and weight loss results under acidic condition tests of GPC specimens. Also, the SEM analysis images of GPC specimens are represented in Figure 15. The water absorption capacity of N, NaK, and K mix designs was measured approximately 4.7, 5.5and 5%, respectively. Also, weight loss under acidic conditions N, NaK, and K mix designs was

measured approximately 3.3, 4.1, and 3.7%, respectively. By observing the results of Figure 14 and Figure 15, water absorption capacity and weight loss in an acidic condition of N mix design were less compared to other specimens, mainly due to the higher density of the geopolymeric matrix structure in this mix design.
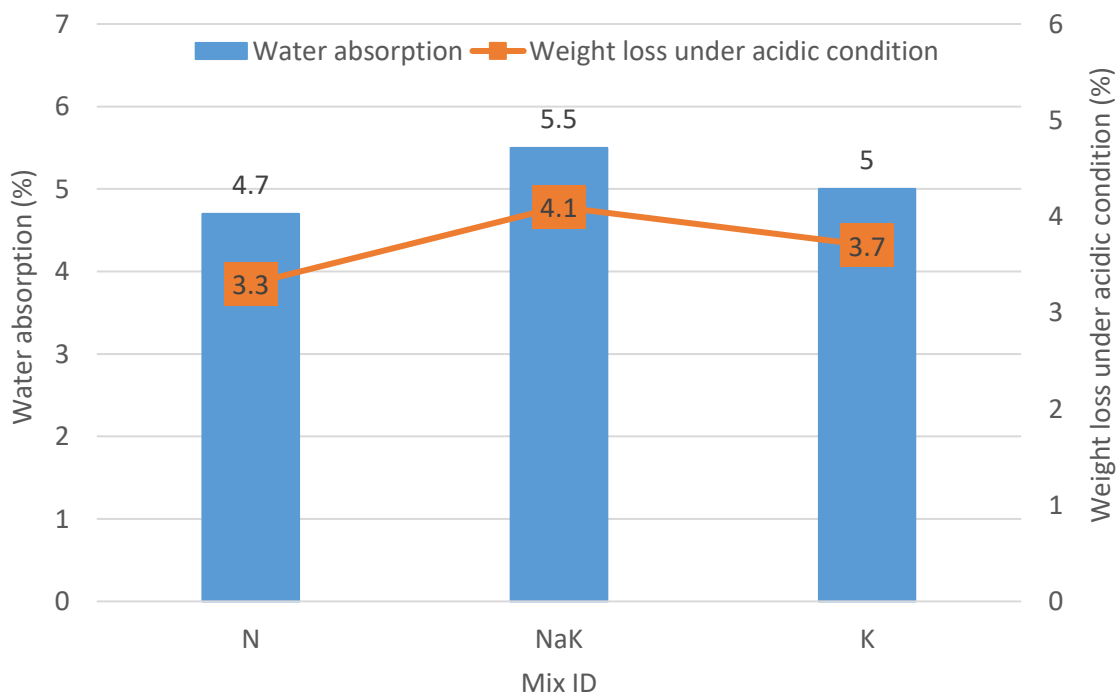
Figure 14. Water absorption and weight loss under acidic condition of N, NaK and K mix designs

a)

b)

c)
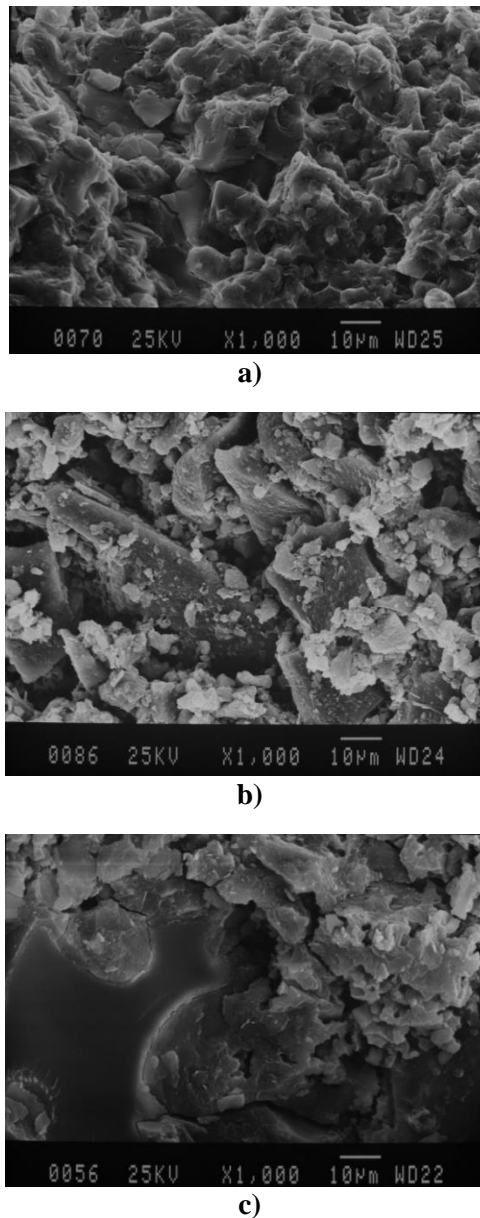
Figure 15. SEM analyze of N (a), NaK (b) and K (c) mix designs

4. CONCLUSION

In this comprehensive experimental study, the role of different alkaline solutions type, some parameters related to alkaline solution and curing conditions on compressive strengths and also, resistance to acidic condition and water absorption of GPC based on Class C fly ash, were deliberated. The following conclusions can be drawn based on the results of the current experimental studies:

- The type of alkaline activator solution is one of the parameters affecting the compressive strength of GPC. At ambient temperature, the use of Na-based activator (NaOH+Na2SiO3) leads to greater lateral compressive strength and early strength than the K-based activator (KOH+K2SiO3) due to the higher reactivity of Na+ compared to K+ and higher dissolution of Si and Al in NaOH solution in comparison with KOH solution.

- The curing condition is another parameter influencing the compressive strength of GPC. Higher curing temperatures and times result in higher early and lateral compressive strength, accelerating the geopolymerization reaction and geopolymer gel formation. K-based activators achieve greater early and lateral compressive strength at elevated curing temperatures than Na-based activators due to providing the energy needed for efficient K+ reactivity.

- In addition, the concentration of NaOH and KOH solutions potentially affects the compressive strength of GPC. Increasing the concentration from 10 to 16M cusses a 77% improvement in GPC compressive strength (in the case of using NaOH solution) and 132% (in the case of using KOH solution) as a result of the rise in the

dissolution of Si and Al (presented in fly ash) by the alkaline activator solution.

- Using the combination of NaOH and KOH solutions reduces the compressive strength of GPC because of the interference of the reactive affinity of Na+ and K+. Moreover, increasing the replacement ratio of NaOH and KOH solutions from 20-80 to 50-50 % significantly diminished the compressive strength.

- The SiO2/Na2O ratio of the Na2SiO3 solution is another parameter influencing the compressive

strength of GPC. The optimal amount depends on various factors, including the concentration of the hydroxide solution. The optimal SiO2/Na2O ratio of Na2SiO3 solution is 2 in the case of using 14M NaOH solution and 2.5 in the case of using 10M NaOH solution.

- The use of Na-based activator solution to make GPC leads to the formation of a denser geopolymer matrix than the K-based activator, resulting in lower water absorption and weight loss under acidic conditions.

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