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# Effect of Various Alkaline Activator Solutions on Compressive Strength of Fly Ash-Based Geopolymer Concrete

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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 negative environmental impacts of OPC effectively. In this experimental research, effects of different alkaline activator solutions and variations of associated parameters, including KOH concentration and Na<sub>2</sub>SiO<sub>3</sub>/KOH weight ratio, on the compressive strength of fly ash-based geopolymer concrete were investigated. The obtained results showed that using NaOH provided greater 3- and 7- day compressive strengths as well as faster hardening. Conversely, using KOH resulted in higher 28-day compressive strength. Additionally, simultaneous inclusion of 50% NaOH and 50% KOH resulted in decline of the compressive strength. Furthermore, the obtained results indicated that increasing the KOH concentration up to 14 M resulted in the highest compressive strength, while weight ratio of 1.5 for Na<sub>2</sub>SiO<sub>3</sub>/KOH was the optimum value to achieve highest 7-and 28-day compressive strengths.

**Keywords:** Geopolymer Concrete, Fly Ash, Alkaline Activator, Compressive Strength, NaOH

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## 1. INTRODUCTION

Concrete is the most consumed construction material after water, due to its special features including formability and availability of raw materials. As the demand for concrete rises, so does the consequent demand for Portland Cement (PC), as the main component of concrete [1]. But PC production has major environmental disadvantages, including high energy consumption and carbon dioxide (CO<sub>2</sub>) emissions [2]; for production of a ton of PC, approximately a ton of CO<sub>2</sub> would be released [3]. On the other hand, environmental pollution and the global warming phenomenon have become major concerns in developed countries [4]. Global warming is caused by the emission of greenhouse gases and among the greenhouse gases, CO<sub>2</sub> plays a major role in global warming with a 60% share [5]. The production process of PC is accounted for 7 to 10% of global CO<sub>2</sub> emissions [6]. Therefore, developing

an appropriate and workable substitution for PC is of great importance. In recent years, geopolymers have been introduced as environmentally friendly cementitious materials capable of reducing the negative environmental impacts associated with PC. Geopolymers were first developed by Davidovits, as a new family of binders of inorganic origin [7]. He utilized the name “poly(sialate)” to indicate the chemical composition of geopolymers, in which poly represented the polymeric nature and sialate was an abbreviation for the silicon-oxo-aluminate chain [8,9]. Geopolymers are inorganic alumino-silicate materials produced from raw materials, rich in silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>), in combination with an alkaline activator solution [10]. The geopolymerization process involves a substantially fast chemical reaction under alkaline condition on Si-Al minerals, that results in a three-dimensional

polymeric chain and ring structure consisting of Si-O-Al bonds [11]. Regarding civil engineering applications, Geopolymer Concrete (GPC) has showed enhanced physical and mechanical properties over conventional concrete, e.g. higher mechanical strengths [12,13], enhanced durability [14], higher resistance to elevated temperatures and fire [15-17], lower permeability, improved resistance to solvents and acids [18,19] and lower creep effects [20,21]. The raw material, 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 (GGBFS)). Fly ash is one of the raw materials. Fly ash is a by-product of the coal-fired power plant which can be one of the best raw-material candidates due to its proper structural nature. Fly ash is classified into two classes: C (high-calcium) and F (low-calcium). In this research, Class F fly ash was used as a raw material to make GPC specimens. The alkaline activator solution is another pillar of the geopolymerization process, playing an important role in the formation of crystalline structures of Si and Al, which is typically a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) or potassium silicate (K<sub>2</sub>SiO<sub>3</sub>) [22]. Considering the important role of alkaline activator solution in GPC, it seems necessary to study the impact of various alkaline activator solutions on the mechanical strength of GPC. In early research studies, Davidovits [23,24] used NaOH and KOH without incorporation of a silicate solution. Xu et al [25] also used NaOH and KOH without using silicate solution and found that KOH would result in better compressive strength. However, Palomo et al [18] revealed that between geopolymers made with NaOH and KOH without using silicate solution, specimens with NaOH would represent higher compressive strength. Most of these researchers pointed out the crucial role of the alkaline activator solution in the polymerization reaction and revealed that addition of a silicate solution to the NaOH and/or KOH solution would promote the polymerization rate. Cheng et al [17] reported that using a combination of NaOH and Na<sub>2</sub>SiO<sub>3</sub> solutions would result in higher compressive strength than using KOH and K<sub>2</sub>SiO<sub>3</sub>. Panagiotopoulou et al [26] utilized a combination of NaOH,

KOH, and Na<sub>2</sub>SiO<sub>3</sub> solutions for geopolymerization reaction. They compared the obtained results with those for NaOH and Na<sub>2</sub>SiO<sub>3</sub> solutions and found that simultaneous application of NaOH and KOH would deteriorate the compressive strength. Regarding the influential factors on the compressive strength of GPC, Rashad [27] pioneered the investigation into the impact of alkaline solution concentration on the compressive strength of GPC. He revealed that in most of the cases, by increasing the alkaline solution concentration up to a certain point, the compressive strength would be enhanced. Sharma et al [28] reported that by increasing the NaOH concentration up to 16 M, the compressive strength increased, but with further increase to 18 M, no significant change was observed. Contrary, Patel et al [29] found that by increasing the NaOH concentration up to 12 M, the compressive strength would increase, and beyond that, the compressive strength would decrease. In another study, Petrus et al [30] studied the impact of the Na<sub>2</sub>SiO<sub>3</sub>/NaOH weight ratio on the compressive strength of GPC. They used 1, 1.5, 2, and 2.5 weight ratios and concluded that by increasing the weight ratio of Na<sub>2</sub>SiO<sub>3</sub>/NaOH from 1 to 1.5, the compressive strength of GPC would increase. The highest compressive strength was recorded for the weight ratio of 1.5 and by raising the ratio from 1.5 to 2.5, the compressive strength decreased significantly. Junaid et al [31] reported that increasing the weight ratio of Na<sub>2</sub>SiO<sub>3</sub>/NaOH would increase both the compressive strength and cost of production of GPC. Since the reported results regarding the impact of alkaline solution on the compressive strength of GPC are not uniform, this study aims at investigating and comparing the influences of various alkaline solutions on the compressive strength of fly ash-based GPC to provide insight into its developing practical applications. Although there is extensive research on the different aspects of utilizing a combination of NaOH and Na<sub>2</sub>SiO<sub>3</sub> solutions for producing GPC, the number of studies exploring KOH solution and combination of KOH and NaOH solutions is limited. Hence, in this experimental study, the impact of using NaOH and KOH combination in different ratios as alkaline activator solution, the concentration and weight ratio of Na<sub>2</sub>SiO<sub>3</sub>/KOH on the compressive strength of fly ash-based GPC, as well as their optimum amounts, will be studied.

## 2. MATERIALS AND METHODS

### 2.1. MATERIALS

The X-Ray Fluorescence (XRF) chemical analysis and image of the fly ash used in this study are given in Table 1 and Figure 1, respectively. NaOH with 98% purity, KOH with 90% purity and liquid Na<sub>2</sub>SiO<sub>3</sub> with SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio of 2, were used to prepare the alkaline activator solutions. Table 2 represents the chemical analysis of the Na<sub>2</sub>SiO<sub>3</sub>, NaOH, and KOH substances. The aggregates were obtained from quarries around Tehran. Aggregates with granular sizes of 7-10 mm was used as coarse aggregate (gravel), and < 4 mm sized aggregates were used as fine aggregate (sand). Fine and coarse aggregates were

sieved according to ASTM C33 [32]. The fineness modulus (using ASTM C136 [33]) and sand equivalent (using ASTM D2419 [34]) values of the fine aggregates were measured equal to 3.01 and 73, respectively. SSD specific gravity and water absorption tests were conducted on the coarse and fine aggregates using the ASTM C127 [35] and ASTM C128 [36] procedures, respectively, reported in Table 3 To reduce water content and improve workability of concrete, polycarboxylate-based Super Plasticizer (SP) was incorporated.



**Figure 1.** The fly ash used in this study

**Table 1.** XRF chemical analysis of class F fly ash

Chemical substance	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	TiO <sub>2</sub>	Na <sub>2</sub> O	MnO	P <sub>2</sub> O <sub>5</sub>
% Weight	70.7	21.1	1.13	3.90	0.77	1.09	0.92	0.26	0.05	<b>0.05</b>

**Table 2.** Chemical analysis of NaOH and Na<sub>2</sub>SiO<sub>3</sub> solutions

NaOH			KOH			Na <sub>2</sub> SiO <sub>3</sub>		
Chemical substance	Result	Unit	Chemical substance	Result	Unit	Chemical substance	Result	Unit
NaOH	98	%	KOH	90.7	%	SiO <sub>2</sub>	30.00	%
Na <sub>2</sub> CO <sub>3</sub>	1	%	K <sub>2</sub> CO <sub>3</sub>	0.2	%	Na <sub>2</sub> O	14.50	%
NaCl	200	ppm	NaCl	0.006	%	Water	55.50	%
Fe	6	ppm	Fe	0.2	ppm			
SiO <sub>2</sub>	15.7	ppm	NaOH	0.6	%			
Appearance	White flake		Appearance	White flake		Appearance	<b>Clear liquid</b>	

**Table 3.** Specific gravity and water absorption of aggregates

Material	SSD Specific gravity (gr/cm <sup>3</sup> )	Water absorption (%)
Coarse aggregates	2.62	<b>1.3</b>
Fine aggregates	2.59	<b>3.2</b>

## 2.2. EXPERIMENTAL PROGRAM

### 2.2.1. Part I

To conduct the first part of the study, focusing on investigating the influence of different alkaline solutions on

the compressive strength of GPC, 5 alkaline solutions were prepared:

- N: 100% NaOH and sodium silicate
- K: 100% KOH and sodium silicate
- N50K50: 50% NaOH + 50% KOH and sodium silicate
- N75K25: 75% NaOH + 25% KOH and sodium silicate
- N25K75: 25% NaOH + 75% KOH and sodium silicate

Concentration of all the NaOH and KOH solutions was 14 M and the weight ratio of sodium silicate solution to hydroxide solution (NaOH or KOH or NaOH+KOH) was 1.5. Furthermore, the weight ratio of the alkaline

solution/fly ash and fine/coarse aggregate ratio in preparing the first series of specimens were 0.5 and 1, respectively. [Table 4](#) represents mix designs of the specimens for the first part of the study.

**Table 4.** Mix designs of part I

Mix ID	Fly ash	NaOH	KOH	Na <sub>2</sub> SiO <sub>3</sub>	Coarse aggregates	Fine aggregates	SP	Extra water	Unit
N	400	80	-	120	850	850	8	10	Kg/m <sup>3</sup>
N50K50	400	40	40	120	850	850	8	10	Kg/m <sup>3</sup>
N75K25	400	60	20	120	850	850	8	10	Kg/m <sup>3</sup>
N25K75	400	20	60	120	850	850	8	10	Kg/m <sup>3</sup>
K	400	-	80	120	850	850	8	10	Kg/m <sup>3</sup>

To manufacture GPC specimens, initially, the alkaline activator solution, constituting of NaOH (14M), KOH (14M), Na<sub>2</sub>SiO<sub>3</sub>, 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 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. The specimens were cured in the oven (90 °C) for 24hrs. 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 strength test according to BS1881: Part116 [\[37\]](#).

### 2.2.2. Part II

In the second part of the study, the effect of KOH concentration on compressive strength of GPC based on fly ash was studied. Hence, 3 mix designs were prepared in which concentration of KOH varied (10, 12, and 14 M) and the weight ratio of Na<sub>2</sub>SiO<sub>3</sub>/KOH was kept constant, equal

to 1.5. The mix designs of this section are presented in [Table 5](#) GPC specimens of this section were made and cured similar to the previous step. Then, specimens were subjected to the 3-, 7- and 28-day compressive strength test according to BS1881: Part116 [\[37\]](#).

**Table 5.** Mix designs of part II

Mix ID	Fly ash	KOH	Na <sub>2</sub> SiO <sub>3</sub>	Coarse aggregates	Fine aggregates	SP	Extra water	Unit	KOH concentration (M)
FK10	400	80	120	850	850	8	10	Kg/m <sup>3</sup>	10
FK12	400	80	120	850	850	8	10	Kg/m <sup>3</sup>	12
FK14	400	80	120	850	850	8	10	Kg/m <sup>3</sup>	14

### 2.2.3. Part III

In the last part of this research, to study the effect of Na<sub>2</sub>SiO<sub>3</sub>/KOH weight ratio on compressive strength of GPC specimens, 5 mix designs were set in which the concentration of KOH was kept constant at 14 M, and the weight ratio of Na<sub>2</sub>SiO<sub>3</sub>/KOH varied (1, 1.5, 2, 2.5, and 3).

[Table 6](#) illustrates the mix designs of this section. GPC specimens of this section were made and cured similar to the previous parts. The specimens were then subjected to the 3-, 7- and 28-day compressive strength test according to the BS1881: Part116 [\[37\]](#).

**Table 6.** Mix designs of part III

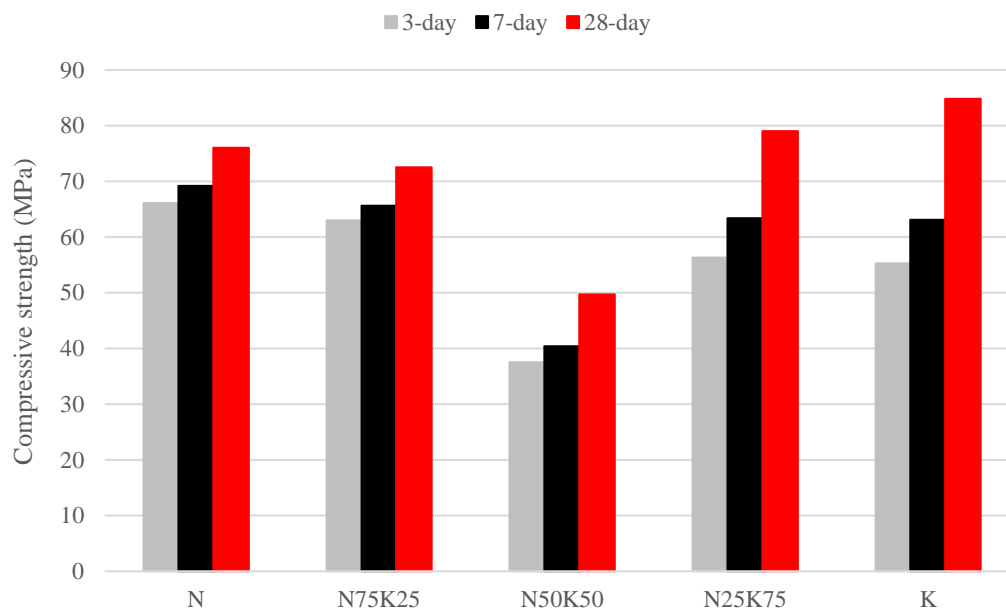
Mix ID	Fly ash	KOH	Na <sub>2</sub> SiO <sub>3</sub>	Coarse aggregates	Fine aggregates	SP	Extra water	Unit	Na <sub>2</sub> SiO <sub>3</sub> /KOH weight ratio
FK1	400	100	100	850	850	8	10	Kg/m <sup>3</sup>	1
FK1.5	400	80	120	850	850	8	10	Kg/m <sup>3</sup>	1.5
FK2	400	66	134	850	850	8	10	Kg/m <sup>3</sup>	2
FK2.5	400	57	143	850	850	8	10	Kg/m <sup>3</sup>	2.5
FK3	400	50	150	850	850	8	10	Kg/m <sup>3</sup>	3

### 3. RESULTS AND DISCUSSION

#### 3.1. EFFECT OF ALKALI ACTIVATOR SOLUTION TYPE ON COMPRESSIVE STRENGTH

Figure 2 shows the effect of alkaline activator solution type on the mean compressive strength of fly ash-based GPC. The 3-, 7- and 28-day compressive strengths of mix N (100% NaOH), were measured as 66.1, 69.2 and 76 MPa, respectively. The 3-, 7- and 28-day compressive strengths of mix K (100% KOH), were 55.5, 63.1 and 84.4 MPa, respectively. Mix N gained approximately 91% and 87% of its 28-day compressive strength at 7 and 3 days,

respectively. These numbers for mix K were approximately 75% and 66%, respectively. Comparison of these two types of alkaline activator solutions indicated that mix N provided greater 3- and 7- day compressive strengths as well as faster hardening/strength gaining capacity. On the other hand, a greater 28-day compressive strength was observed in mix K over mix N, i.e. around 10%.



**Figure 2.** Effect of the alkaline activator solution type on GPC compressive strength

The obtained results showed that simultaneous inclusion of 50% NaOH and 50% KOH resulted in decline of the compressive strengths compared to the N and K specimens (approximately 35% compared to N and 42% compared to K). Whereas, the 3-, 7- and 28-day compressive strengths of N50K50 specimens were 37.5, 40.4 and 49.7 MPa, respectively. Also, 3-, 7- and 28-day compressive strengths were measured as 56.3, 63.4 and 71 MPa, respectively for N25K75 specimens and 63, 65.6 and 72.5 MPa, for N75K25 specimens respectively.

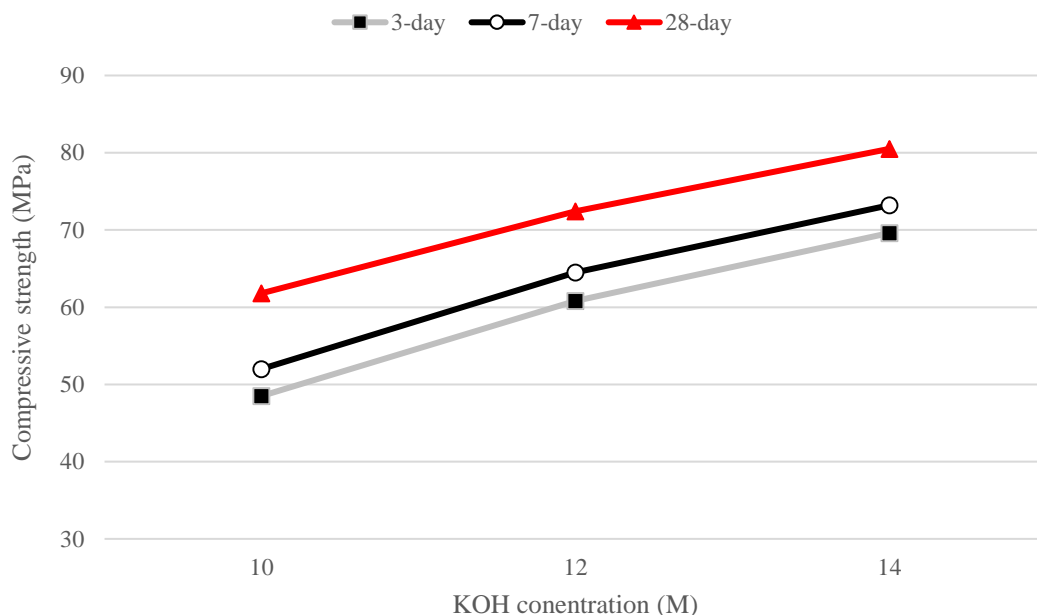
To explain the observed trends, the performance mechanism of the alkaline solution should be considered. There are three steps for generating the silica and aluminum ions in the raw material, dissolution, and formation of the geopolymer paste by utilizing alkaline activator solution: (i) dissolution, (ii) partial orientation of the mobile pre-material, and (iii) reloading of the particles from the solid phase [13]. The type of the alkaline activator has a significant influence on the advancement of the geopolymerization process. Due to the larger atomic radius, KOH generates larger silicate oligomers than NaOH, and Al(OH)<sub>4</sub> has the tendency to attach to these larger silicate

oligomers. Hence, by using KOH, more geopolymers are produced, leading to a stronger and more compact microstructure [38], which will result in low 3- and 7-day compressive strengths, slow hardening rate, and high 28-day compressive strength in comparison with NaOH. On the other hand, at the same concentration, NaOH is capable of dissolving more inorganic components than KOH, which leads to faster reaction rate for Na<sup>+</sup> ions over K<sup>+</sup> [25,26]. Due to the higher reaction rate of Na<sup>+</sup>, higher initial compressive strength and more rapid hardening would be observed by using NaOH. However, simultaneous inclusion of NaOH and KOH (N50K50) would reduce the compressive strength of GPC noticeably. This could be attributed to the different performances of NaOH and KOH during the geopolymerization process. The high reactivity of Na<sup>+</sup> in the dissolution of Si and Al presented in the aluminosilicate source is very strong and could not be balanced with the tendency of K<sup>+</sup> ions towards condensation reaction [26]. This interference phenomenon reduces with the decrease in the percentage of NaOH and KOH combination from 50-50 to 25-75 and thus the N25K75 and N75K25 specimens provided greater compressive strength than the N50K50 specimen.

### 3.2. EFFECT OF KOH CONCENTRATION ON COMPRESSIVE STRENGTH

The obtained results for the effect of KOH concentration on mean compressive strength of GPC specimens are represented in [Figure 3](#). As it is evident, the lowest 3-, 7- and 28-day compressive strengths, equal to 48.5, 52 and 61.8 MPa, were recorded for the mix FK10, in which the KOH concentration was 10M. According to the obtained results, by increasing the KOH concentration from 10 to 14 M, the 3-, 7- and 28-day compressive strengths increase around 42, 39 and 30%, respectively. Increasing the molarity of the

alkaline solution would result in more dissolution of the raw materials. This is because at higher concentrations, the  $Al_2O_3$  and  $SiO_2$  substances of the raw materials dissolve in the activator solution quicker and consequently, more geopolymer gel will be produced, leading to higher compressive strength [29]. As a result, the concentration of 14 mol was measured as the optimum concentration of the KOH solution.

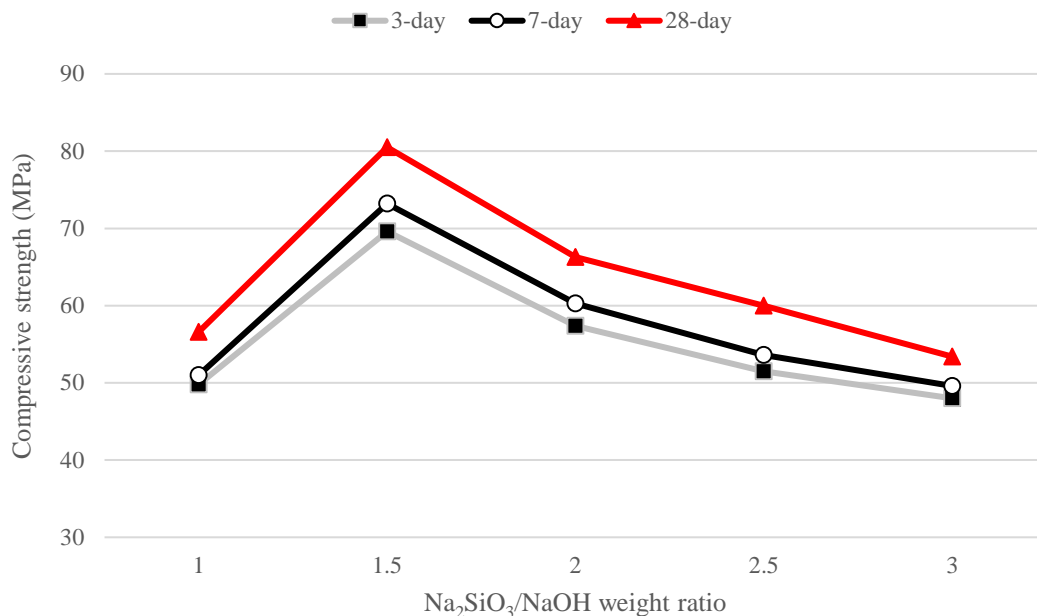


**Figure 3.** Effect of KOH concentration on GPC compressive strength

### 3.3. EFFECT OF THE WEIGHT RATIO OF $Na_2SiO_3/KOH$ ON COMPRESSIVE STRENGTH

The results related to the effect of  $Na_2SiO_3/KOH$  weight ratio on mean compressive strength of GPC are illustrated in [Figure 4](#). For  $Na_2SiO_3/KOH$  weight ratio of 1, the 3-, 7 and 28- day compressive strengths, are equal to 49.8, 51 and 56.6 MPa, respectively. By increasing the ratio from 1 to 1.5, all 3, 7, and 28-day compressive strengths increased significantly (around 40%) and reached 69.6, 73.2, and 80.5 MPa, respectively. Further increase of this ratio up to 3, resulted in substantial decrease in compressive strength, so that for  $Na_2SiO_3/KOH$  weight ratio equal to 3, 31, 32, and 36% decline in 3-, 7- and 28-day compressive strengths was observed compared to the weight ratio of 1.5. As a result, the  $Na_2SiO_3/KOH$  weight ratio of 1.5 was considered as the optimal ratio with regard to compressive strength in this study. Addition of a silicate solution such as  $Na_2SiO_3$  or  $K_2SiO_3$  to the alkaline activator solution increases the  $SiO_4$  content and the geopolymerization reaction rate and consequently increases the compressive strength of the GPC due to increases in soluble Si.

The alkaline activator solution, especially NaOH or KOH, dissolves the Si and Al within the aluminosilicate source and consequently, provides the  $SiO_4$  and  $AlO_4$  needed to form the geopolymer gel. Addition of a silicate solution such as  $Na_2SiO_3$  or  $K_2SiO_3$  to the alkaline activator solution, increases the  $SiO_4$  content and the geopolymerization reaction rate and consequently increases the compressive strength of the GPC due to increases in soluble Si. At lower  $Na_2SiO_3/KOH$  weight ratios (lower than the optimum ratio), the compressive strength decreased due to the lower dissolution of Si and consequently, lower  $SiO_4$  content. Furthermore, at higher  $Na_2SiO_3/KOH$  weight ratios (higher than the optimum ratio), the compressive strength of GPC decreased as well, which would be attributed to the excessive formation of  $SiO_4$ , while the  $AlO_4$  content was constant (the amount of  $AlO_4$  was limited) [30,38], i.e., when the Si/Al ratio was not in the range of its optimum value, the compressive strength of GPC decreased.



**Figure 4.** Effect of Na<sub>2</sub>SiO<sub>3</sub>/KOH on GPC compressive strength

#### 4. CONCLUSION

In this experimental study, impact of different alkaline solutions, (namely NaOH and KOH solutions accompanied by Na<sub>2</sub>SiO<sub>3</sub> silicate solution) variation of KOH concentration and variation of weight ratio of Na<sub>2</sub>SiO<sub>3</sub>/KOH on the compressive strength of fly ash-based GPC were assessed. The following conclusions can be drawn based on the current experimental study:

1- The alkaline solution of KOH with Na<sub>2</sub>SiO<sub>3</sub> would result in lower 3- and 7- day and higher 28-day compressive strengths than using NaOH and Na<sub>2</sub>SiO<sub>3</sub> solutions, due to the slower reactivity of K<sup>+</sup> than that of Na<sup>+</sup> and its tendency to the condensation reaction. Conversely, using NaOH and Na<sub>2</sub>SiO<sub>3</sub> solutions as the alkaline activator, result in higher 3- and 7-day compressive strengths and faster hardening compared to NaOH and Na<sub>2</sub>SiO<sub>3</sub>, due to the further dissolution of Si and Al in NaOH and faster reactivity of Na<sup>+</sup> than K<sup>+</sup> ions.

2- Simultaneous application of NaOH and KOH, along with Na<sub>2</sub>SiO<sub>3</sub>, as the alkaline solution, decreased 3-, 7- and 28-day compressive strengths of GPC due to the interference in Na<sup>+</sup> and K<sup>+</sup> reactivity.

3- In the case of using KOH and Na<sub>2</sub>SiO<sub>3</sub> as the alkaline activator solution, by increasing the KOH concentration up to 14 M, the 3-, 7- and 28-day compressive strengths improved, which was probably due to the increased dissolution of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> of the raw materials.

4- The optimum weight ratio of Na<sub>2</sub>SiO<sub>3</sub>/KOH in this study was obtained to be 1.5, leading to the highest 3-, 7- and 28-day compressive strengths. By increasing this weight ratio up to 3, a 31, 32, and 36% decline in the 3-, 7- and 28-day compressive strengths was observed, respectively, attributed to the extra formation of SiO<sub>4</sub> and the non-optimum Si/Al ratio.

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**AUTHORS CONTRIBUTION**

This work was carried out in collaboration among all authors.

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**CONFLICT OF INTEREST**

The author (s) declared no potential conflicts of interests with respect to the authorship and/or publication of this paper.

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