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Yazar(lar) (Author(s)): *Kasım MERMERDAŞ, Gailan PIRAZHN, Safie Mahdi OLEIWI, Esameddin MULAPEER*

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Effect of Alkali Activator Concentrations and Elevated Temperature Curing Regimes on The Strength of Fly Ash Based Geopolymer Mortar

Kasım MERMERDAŞ[1], Gailan PIRAZHN[2], Safie Mahdi OLEIWI[3,4], Esameddin MULAPEER[3]

[1]*Department of Civil Engineering, Harran University, Şanlıurfa, Turkey*
[2]*Civil Engineer, Comune di Velletri via orti Ginnetti, Rome, Italy*
[3]*Department of Civil Engineering, Hasan Kalyoncu University, Gaziantep, Turkey*
[4]*Department of Civil Engineering, Diyala University, Baqubah, Iraq*
e-posta: kasim.mermerdas@harran.edu.tr

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Abstract

Geopolymers have received considerable attention due to their properties and applications as environmentally friendly alternatives to ordinary Portland cement. Geopolymer mortar (GM) is an emerging alternative to ordinary Portland cement mortar (OPCM) and is produced via a polycondensation reaction between aluminosilicate source materials and an alkaline solution. As a relatively new material, many engineering properties of geopolymer mortar are still undetermined. In this study, the compressive strength, have been studied experimentally. A total of 12 geopolymer mix mortar were tested for the above-mentioned characteristics. The experimental data was analysed by an analysis of variance (ANOVA) utilizing MINITAB16 statistical software. This method establishes the magnitude of the total variation in the results and distinguishes the random variation from the contribution of each variable. Based on ANOVA results, all the level of significance values was determined to be less than 0.05 which indicates the independent variables are effective on compressive strength of geopolymer mortars.

Keywords: Geopolymer mortar, Fly ash, Alkaline solution, Compressive strength, ANOVA.

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Özet

Geopolimerler sahip oldukları özellikler ve uygulama alanları nedeniyle normal Portland çimentosunun yerini alabilecek çevre dostu bağlayıcı malzeme olrak ele alınabilmektedir. Normal Portland çimentosu harcına yeni bir alternatif olan geopolimer harcı, alüminosilikat kaynağı malzemeler ve bir alkali çözeltisi arasındaki polikondensasyon reaksiyonu yoluyla üretilir. Nispeten yeni bir malzeme olan geopolimer karışımların birçok mühendislik özelliği hala belirlenmemiştir. Bu çalışmada, geopolimer harçların basınç dayanımı deneysel olarak incelenmiştir. Bunun için için toplam 12 adet geopolimer karışım harcı test edilmiştir. Deneysel veriler, MINITAB17 istatistik yazılımı kullanılarak bir varyans analizi (ANOVA) ile değerlendirilmiştir. Bu yöntem, sonuçlarda toplam varyasyonun büyüklüğünü belirler ve her değişkenin katkısından rastgele değişimi ayırt eder. ANOVA sonuçlarına göre belirlenen önem seviyeleri 0.05 değerinden daha düşük çıkmış ve bu şekilde değerlendirilen bağımsız değişkenlerin basınç dayanımı üzerinde etkili oldukları görülmüştür.

Anahtar Kelimeler: Geopolimer harç; Uçucu Kül; Alkali çözelti, Basınç dayanımı, ANOVA.

1. Introduction

Around the world, the most widely used material in construction sector is concrete. In the production of concrete, cement plays the main role. In order to occupy the amount of cement needed for concrete production, huge amount of raw material and energy needed [1-2]. During the processes of cement production, some of harmful gases are released to the atmosphere causing pollution and greenhouse effect. Due to the increased demand for concrete, manufacture of cement has also been increased. According to the studies, it was estimated that the 2 billion tons of cement is manufactured annually. There is an approximate annual increase by 3% in production of cement. Since each tone of cement production release about 1 tone of CO_2 to atmosphere, due to combustion of fossil fuels and calcination of calcerous material in the kiln [3], it is one of the major causes of the greenhouse gas emission. The amount of CO_2 released to atmosphere due to cement production is about 7% of total emissions and CO_2 contributes about 65% of global warming.

It is known that many concrete structures being vulnerable to corrosive environment, deteriorate after exposure time of about 20-30 years. Based on similar facts, researchers have considered developing more durable materials for structures which have green properties and better service life. Therefore, construction materials with geopolymer binders that use waste materials such as fly ash have been developed to become an alternative to cement based ones [4-5].

Large amount of fly ash generated worldwide from thermal power plant and lead to the problem of waste management. Alkali activated alumino-silicate based binder system alternative to conventional concrete is called "Geopolymer concrete". Geopolymer concrete includes geopolymer binder and aggregate. This material is ideal for building and repairing infrastructure and for manufacture of pre-casting units. The new product that called geopolymer has properties of using waste materials on its production and saves up to 80% of CO_2 emission, gaining high final strength in a short time, better resistance to freezing and thawing, high resistance to sulphates, corrosion etc. [6].

Davidovits in 1978 was the first researcher that introduces the term "Geopolymer" and described as a member family of mineral binders with an amorphous microstructure and has chemical composition similar to zeolites [7]. Davidovits [8] used waste materials or by product materials such as slag, husk ash and fly ash that has an aluminum (Al) and silicon (Si) with an alkaline activator to produce a binder. The word "geopolymer" was used to depict another cementitious material which has ceramic-like properties. Geopolymer could be created by joining a pozzolanic compound or aluminosilicate source material with highly alkaline solutions. The reaction of Al_2SiO_5 with alkali polysilicates produces a shapeless to semi-crystalline three-dimensional structure of polymeric sialate (Si-O-Al-O) bonds create are inorganic materials that polycondense practically identical to natural polymers called geopolymer.

Sialate tetrahedral arrangements, alkali silica-oxo-aluminate abbreviation, the Figure 1 clarify calcium, sodium, lithium or potassium being the alkali [7]

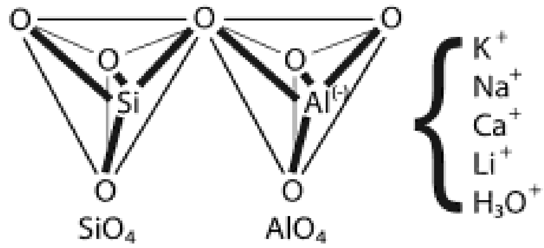

Figure 1. Sialate tetrahedral arrangements [7]

The geopolymer binder is a low-CO_2 cementious material. It doesn't depend on the calcination of limestone that produces CO_2. This innovation can set aside to 80% of CO_2 emissions created by the cement and aggregate industries.

Furthermore, it can be considered that the geopolymer is an environmentally friendly product, has better properties compared to conventional ordinary Portland cement. Through a research, Rattanasak and Chindaprasirt [9] used fly ash as a base material to produce geopolymer concrete, with 3 different concentration of alkaline activator made by NaOH (5, 10 and 15M) with Na_2SiO_3, used heat curing at constant temperature at 65 oC for 48 hours. By using different methods of analyses SEM, FT-IR and DSC thermogram, they indicated that the fly ash has a good reactivity and give good degree of geopolymerization. For that study, it was determined that concentration of 10M is the best for alkaline activation in geopolymer production.

The aim of this study is to determine the interaction between molarity of NaOH, Na_2SiO_3/NaOH ratio and the applied accelerated curing regime. In order to monitor the effect of parameters, the strength development of geopolymer mortar has been evaluated. Moreover, statistical evaluation of the test results were conducted by means of analysis of varience using a software called Minitab 17.

2. Experimental study

2.1. Materials

In this research dry FA (ASTM low calcium, Class F) was used as the base materials, obtained from local power plant. The table below show the chemical and physical properties of FA used in research was obtained as a demonstrated (Table 1)

Table 1. Chemical and physical properties of FA

Physical and chemical analysis (%)	FA
CaO	2.2
SiO_2	57.2
Al_2O_3	24.4
Fe_2O_3	7.1
MgO	2.4
SO_3	0.3
K_2O	3.4
Na_2O	0.4
Loss on ignition	1.5
Specific gravity	2.25
Specific surface area (m^2/kg)	379

In this study a mix of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) solution was chosen alkaline activator. They were selected based on the activation of sodium because it was cheaper than potassium. Sodium hydroxide used has technical grade in the form of flakes (3 mm), with a specific gravity of 2.130, 98% purity, and PH 14. The molar mass is 40 g / mol and the materials were obtains from a local supplier.

To obtain the solution of (NaOH), the flakes were dissolved in water by proper amount depending on the chemical proportions to get proper molarity of the solution. The main purpose of the research is the effect of NaOH on the strength of geopolymer mortar. Therefore different concentrations of NaOH were obtained. Solid mass of sodium hydroxide in solution varied depending on the concentration of the solution in terms of the molarity M. For example, sodium hydroxide solution concentration 8M consists 262 grams of solid sodium hydroxide (in flake or pellet form) per liter of the solution, where 40 is the molecular weight of sodium hydroxide. Similarly, the mass of solidy sodium hydroxide measuring per kilogram of solution are 10M: 313 grams, 12M: 361 grams, 14M: 404 grams, 16 M: 444 grams. Note that the mass of solids as sodium hydroxide is only part of the mass of the sodium hydroxide solution, and water is the main ingredient. The chemical composition of a solution of sodium silicate Na2O = 14.7%, SiO2 = 29.4%, and 55.9% of the water mass. The other characteristics of a solution of sodium silicate are specific gravity 1.48 and viscosity at 20 ^oC, 400 CP

Aggregate were used in research was provided from local river quarry (river sand), just fine aggregate was used (0-4 mm), sieve of size (4 mm) was used to obtain aggregate grade from (0-4 mm). Aggregate was stored in laboratory specified gravity of aggregate obtained according to ASTM by using a sample of aggregate and weigh of 250 gram by using clean water and glass can. The specific gravity was 2.64.

To provide the workability of the mortar polycarboxylate ether type chemical admixture was used by amount of 6 % of FA weight in all mixtures.

2.2. Mix Proportions

Twelve mixtures were prepared by varying Na_2SiO_3/NaOH ratio and molarities (Table 2). The binder and the sand were first mixed together in a rotary mixer for about 2 min. The alkaline liquid was then added to the dry materials and the mixing was continued for further 5 min to produce the fresh mortar.

The fresh mortar was compacted to achieve mortar with less air voids. The molds were covered by plastic film to avoid evaporation of alkaline solution. For each mortar mixture, set of 12 specimen by dimension of (50x50x50) mm cube were cast to determine the compressive strength.

Table 2. Mix proportions of the geopolymer mixtures

NaOH : Na_2SiO_3 ratio	Molarity	Na_2SiO_3 solution (kg/m^3)	F A (kg/m^3)	River sand aggregate (kg/m^3)	NaOH solution (kg/m^3)	Superplasticizer (kg/m^3)
2	6	225	600	1295.747	75	36
2	8	225	600	1291.544	75	36
2	10	225	600	1286.95	75	36
2	12	225	600	1281.953	75	36
2	14	225	600	1276.511	75	36
2	16	225	600	1271.271	75	36
3	6	225	600	1295.747	75	36
3	8	225	600	1291.544	75	36
3	10	225	600	1286.95	75	36
3	12	225	600	1281.953	75	36
3	14	225	600	1276.511	75	36
3	16	225	600	1271.271	75	36

3. Test results and discussions

Compressive strength of GM specimens exposed to different curing regimes were shown in Figure 2a through Figure 2f. Moreover, strength development of the GMs with increasing the time was comparatively illustrated in Figure 3. The effect of molarity on compressive strength of geopolymer mortar have revealed that the increase in molarity, resulted in enhancement of compressive strength for Na_2SiO_3/NaOH =2 except for high molarity levels (14M and 16M). For Na_2SiO_3/NaOH =3, there was a steady increase in compressive strength for all molarities.

It can be observed that the mix with molarity 12M demonstrated higher strength than the other mixtures for Na_2SiO_3/NaOH=2, while for the other group 16m mix had the highest strength development. The highest strength in 12M mix at the end of curing period of of 72 hrs for Na_2SiO_3/NaOH=2, however 52 MPa was obtained for the other group. The lowest strength in 16M mix at the age 72 hrs is found to be lower than mix with molarity 12M for Na_2SiO_3/NaOH =2. However, for 2h of curing no significant change was observed for both groups.

The lowest Na_2SiO_3 content is detected from the samples with Na_2SiO_3/NaOH ratio of 2.0 in the (M14 and M16). This ratio composed the poorest strength development among the other ratios at all tested ages and thus presents the lowest geopolymerization reaction. Although, at the highest Na2SiO3 solution from the samples with a Na_2SiO_3/NaOH mass ratio of 3, the geopolymer exhibits relatively poor strength development at the tested ages in the M6, M8, M10 and M12. The strength development in the specimens with Na_2SiO_3/NaOH mass ratios of 3.0 and 2.0 mention the complexity of the geopolymerization regression and the significance of the concentration of the alkaline activator constituents.

The general linear model analysis of variance (GLM-ANOVA) is used to evaluate the mean discrepancy among data groups which have been classified on independent factors. The interaction term in a GLM-ANOVA gives an information that the effect of one of the independent variables on the dependent variable is the same for all values of other independent variable. The main aim of this statistical method is to find out if an interaction is available among independent factors on the dependent variable. In this study GLM-ANOVA is used to understand whether there is an interaction among Na_2SiO_3/NaOH ratio, Molarity of NaOH solution, and curing periods of GMs, where compressive strength development of GM is the dependent variables.

Table 3 indicates that the critical parameters Na_2SiO_3/NaOH ratio, Molarity of NaOH solution, and curing time are statistically effective on the compressive strength development of GM mortars with 5% level of significance (p<5%). The contribution of each factor on the variation can be found by proportioning the sequential sum of squares values. This shows that the curing time and molarity are more dominant factors than Na_2SiO_3/NaOH ratio.

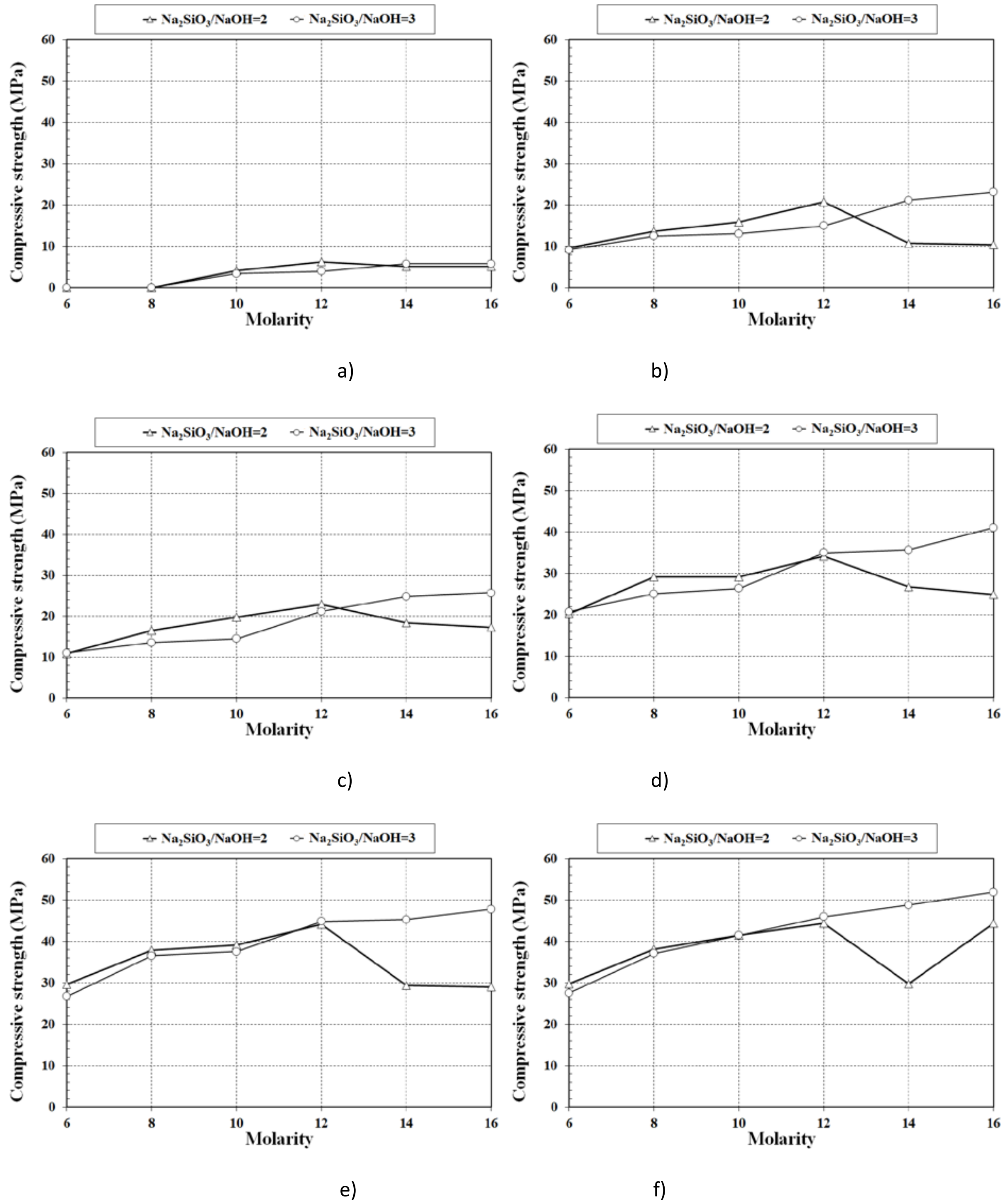

Figure 2. Compressive strength of GMs exposed to accelerated cruring regimes of a) 2h, b) 6h, c) 8h, d) 24h, e) 48h and f)72 h

It can be observed that the mix with molarity 12M demonstrated higher strength than the other mixtures for Na_2SiO_3/NaOH=2, while for the other group 16m mix had the highest strength development. The highest strength in 12M mix at the end of curing period of of 72 hrs for Na_2SiO_3/NaOH=2, however 52 MPa was obtained for the other group. The lowest strength in 16M mix at the age 72 hrs is found to be lower than mix with molarity 12M for Na_2SiO_3/NaOH =2. However, for 2h of curing no significant change was observed for both groups.

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Table 3 indicates that the critical parameters $Na_2SiO_3/NaOH$ ratio, Molarity of NaOH solution, and curing time are statistically effective on the compressive strength development of GM mortars with 5% level of significance (p<5%). The contribution of each factor on the variation can be found by proportioning the sequential sum of squares values. This shows that the curing time and molarity are more dominant factors than $Na_2SiO_3/NaOH$ ratio.

Table 3. General linear model analysis of varience (GLM-ANOVA results)

Source	**DF**	**Adj SS**	**Adj MS**	**F-value**	**P-value**	**Significance**
$Na_2SiO_3/NaOH$ ratio	1	112	112.03	6.36	0.014	**YES**
Molarity	5	1124.2	224.84	12.76	0.000	**YES**
Curing time	5	12141.9	2428.37	137.81	0.000	**YES**
Error	60	1057.2	17.62			
Total	71	14435.3				

The equations of compression strength were generated based on the control factors and their interactions. General Regression Analysis: y versus x_1, x_2, x_3

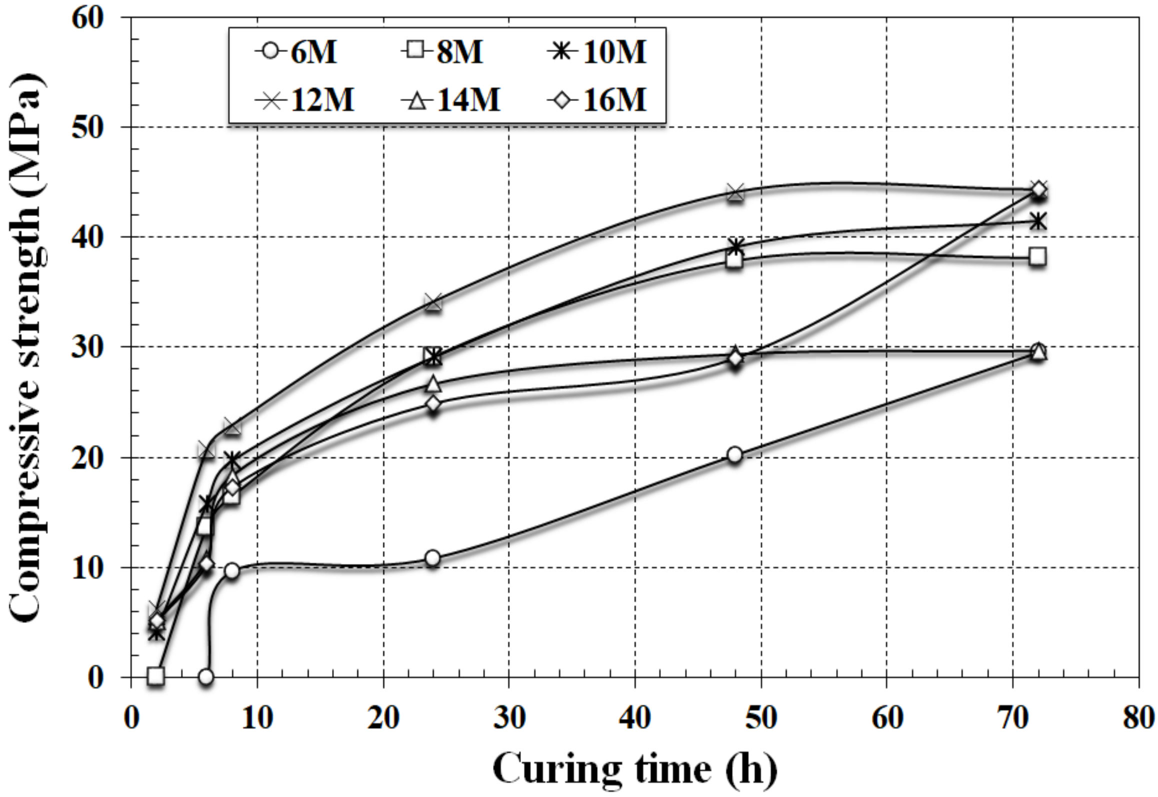
Regression Equation:

$$Y = -5.71084 + 2.91764 X_1 + 0.450419 X_2 + 0.899768 X_3 \quad (1)$$

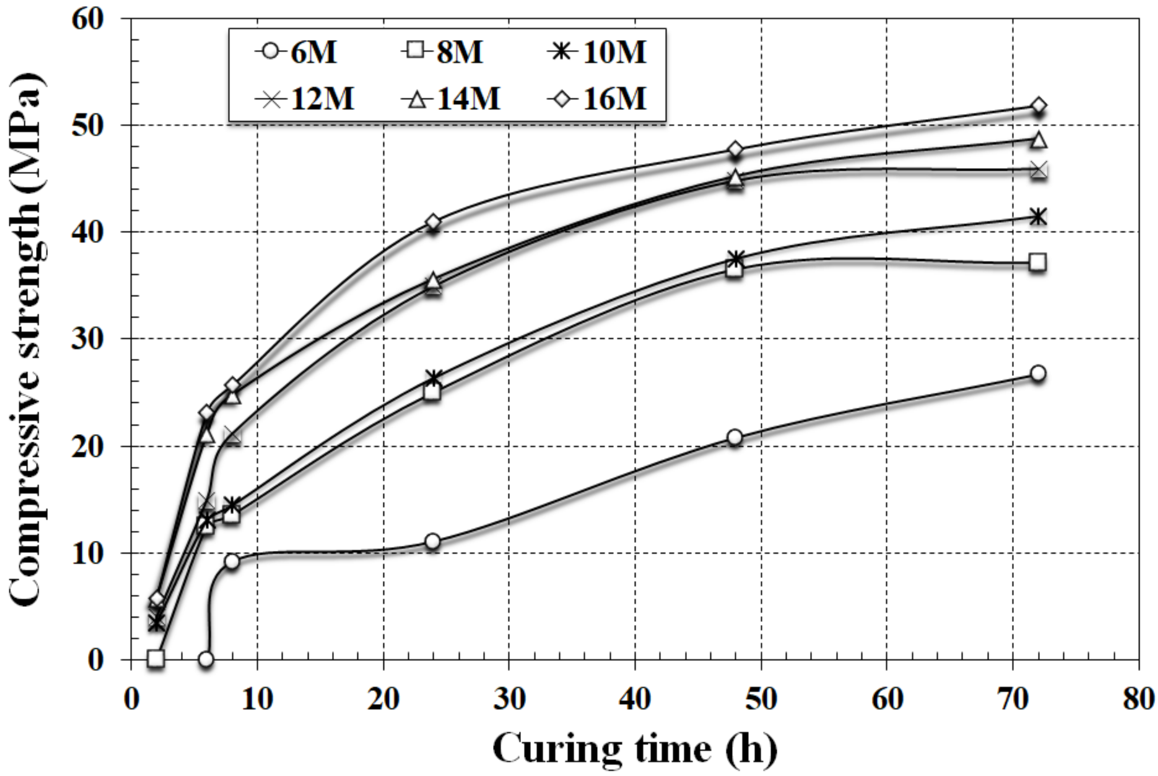
Table 4. demonstrates regression equation of the analysis of variance (ANOVA). The data can be collect from table the coefficients SE- coefficients for all factors over responses. P value more than 0.050 indicate that $Na_2SiO_3/NaOH$ rate (X_1), can be ignored. While for other parameters the P value is less than 0.050.

Table 4. Coefficients of regression equation

Term	Coef.	SE Coef.	T	P
Constant	5.71084	5.32448	-1.0727	0.287
X1	2.91764	1.73978	1.6770	0.098
X2	0.45042	0.03411	13.2033	0.000
X3	0.89977	0.25468	0.001	0.001



a)



b)

Figure 3. Effect of Molarity on compressive strength of GMs with Na_2SiO_3/NaOH ratios of 2 and b) 3

4. **Conclusions**

The results of the study carried out on FA-based geopolymer concrete are reported in the paper. The following conclusions are drawn from the study:

- The results illustrate that the investigated combination of the constituents of GMs provided the strength values as high as 50 MPa at 90°C curing temperature.
- The molarity increase resulted in increase of compressive strength with ratio of Na_2SiO_3/NaOH=2 excepting 14M and 16M.
- While with ratio of Na_2SiO_3/NaOH solution 3 the molarity increases, compressive strength demonstrated enhancement for all molarities.
- The statistical analysis have indicated that three critical parameters, namely, Na_2SiO_3/NaOH ratio, Molarity of NaOH solution, and curing time, dealt with this study are statistically significant for compressive strength development.
- Variation of the data for different cases highlighted the fact that by increasing the test parameters, such as type of base material and levels of elevated curing temperatures, further studies can be performed on the subject. This can provide an opportunity to develop optimum mixes and prediction models.

Note:

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References

[1] Vijai, K., Kumutha, R., & Vishnuram, B. G. 2010. Effect of types of curing on strength of geopolymer concrete. International Journal of the Physical Sciences, **5,** 1419-1423.

[2] Silverstrim, T., Martin, J., Rostami, H. 1999. Geopolymeric FA cement. Geopolymer International Conference (pp. 107-108). Saint-Quentin, France: Institut Geopolymere.

[3] Hardjito, D., Rangan, B. V. 2005. Development and properties of low-calcium fly ash-based geopolymer concrete, Perth, Australia, Curtin University of Technology.

[4] Worrell, E., & Galitsky, C. 2008. Energy efficiency improvement and cost saving opportunities for cement making. Washington, D.C., Environmental Protection Agency.

[5] Manjunath, G. S., Radhakrishna, Giridhar, C., Jadhav, M. 2011. Compressive strength development in ambient cured geopolymer mortar, International Journal of Earth Sciences and Engineering, **4**, 830-834.

[6] Mermerdaş, K., Algın, Z., Oleiwi, S.M., Nassani D.E. 2017. Optimization of lightweight GGBFS and FA geopolymer mortars by response surface method. Construction and Building Materials, 139 (2017) 159–171

[7] Davidovits, J. 1976. Solid phase synthesis of a mineral block polymer by low temperature polycondensation of aluminosilicate polymers, International Symposium on Macromolecules. Stockholm, Sweden: International Union of Pure and Applied Chemistry.

[8] Davidovits, J. 1989. Plenary lecture and round table discussion: The greenhouse effect - A challenge for science, Symposium on Chemical Thermodynamics, Calorimetry and Thermal Analysis. Basel, Switzerland.

[9] Rattanasak U, Chindaprasirt P. 2009 Influence of NaOH solution on the synthesis of F A geopolymer. Mineral Engineering, 22,1073–1078.