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COMPRESSIVE STRENGTH OF FLY ASH GEOPOLYMER PASTE DESIGNED BY TAGUCHI METHOD

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ABSTRACT

Geopolymers are a type of inorganic polymeric material which have emerged as one of the environmentally sustainable properties materials. In this paper, Taguchi method was used to design of fly ash based geopolymer mixtures. Oven curing temperature, sodium silicate to sodium hydroxide (NaOH) ratio, and NaOH concentration were considered as main factors. By utilizing the Analysis of Signal to Noise ratio, the Analysis of Mean, and the Analysis of Variance, these controllable factors have been optimized and percentage contribution of each factor on compressive strength was also determined. It is concluded that NaOH concentration has the most influence on compressive strength. The optimum suggested condition for producing fly ash based geopolymer is NaOH concentration of 16 M, sodium silicate to sodium hydroxide ratio of 1.5, and oven curing temperature of 70°C. To validate the accuracy of mentioned situation, the specimen was produced, and tested at 7 days. The compressive strength of mentioned condition was higher than that for other 16 specimens.

Keywords: Geopolymer, Fly ash, Compressive strength, Taguchi method

INTRODUCTION:

Concrete is the most used construction material around the world, and cement is one of its most important components. Manufacturing cement does need huge amount of energy. Besides, one tone of carbon dioxide is released during the production of per ton of cement (Gartner, 2004). In recent decades, sustainable development is one of the most significant concepts in scientific researches. Hence concrete technology experts investigate for supplementary cementious materials to produce concrete with minimum impact on environment and satisfying durability.

Geopolymer is a kind of inorganic polymer produced by the reaction of aluminosilicate materials with alkaline solutions (Kong et al., 2007, Damtoft et al., 2008). Geopolymer has shown many excellent properties such as high early strength, good resistance against acid and sulfate attacks, and good performance in high temperature (Wang et al., 1995, Hardjito et al., 2004, Bakharev, 2005a, Hu et al., 2008, Kong and Sanjayan, 2008). One remarkable point about geopolymer is elimination of cement usage (Van Deventer et al.), and 44-64% reduction of greenhouse gas emission (McLellan et al., 2011). Besides, some of wastes and by-products such as fly ash and blast furnace slag are appropriate sources of aluminosilicate which are used to produce geopolymer (Olivia and Nikraz, Lloyd and Rangan, 2010). As geopolymers made from mentioned materials need less amount of sodium silicate to be activated, they have lower environmental impact in comparison to other types of geopolymers (Habert et al., 2011).

Vast numbers of researches have been done on alkaline activated slag; however, more researches are needed for fly-ash based one (Fernández-Jiménez and Puertas, 2001, Fernández-Jiménez et al., 1999, Wang et al., 1995, Pan and Sanjayan, 2012). Although several works have been carried out on geopolymers, there is not specific description about effects of various factors on geopolymer properties. Some of the significant factors are aluminosilicate source type, curing temperature, alkaline solutions characteristics, and alkaline solutions to fly ash ratio. Assaying all parameters may not be possible in a single work, but by a proper design method, one can investigate some of them.

Developing an experiment scheme in different conditions is known as Design of Experiment (DOE). Taguchi experiment design is a presented method utilized to optimize the variables since it efficiently reduces experiments' time and costs. In author knowledge, there are few works of using Taguchi method to design of geopolymer mixtures. Riahi et al. considered oven curing time, oven curing temperature, and NaOH concentration as main factors. By applying L9 Taguchi array, they found that oven curing time is not a significant factor (Riahi et al., 2012). Nazari et al.(Nazari et al., 2012a) considered 6 main factors including NaOH concentration, sodium silicate to NaOH weight ratio, oven curing time and temperature, alkali activator to solid ratio, and water curing regime time, with 4 levels for each one. Results of the optimal mixtures showed the dominant positive effect of NaOH concentration on compressive strength.

There are different opinions about effects of NaOH concentration on compressive strength of geopolymer (Chindaprasirt et al., 2007, Rattanasak and Chindaprasirt, 2009, Nazari et al., 2011, Nazari et al., 2012a). Besides, Hardjito et al. reported that increasing sodium silicate to NaOH ratio improves the compressive strength of low calcium fly ash based geopolymer, (Hardjito et al., 2004) while Chindaprasirt et al. contradicted this opinion (Chindaprasirt et al., 2007). Anyhow, addition of sodium silicate to sodium hydroxide solution improves the reaction between raw materials and the solution (Xu and Van Deventer, 2000). Besides, curing temperature is found to have effect on compressive strength (Nazari et al., 2011).

In this work, curing temperature, sodium silicate to NaOH ratio and NaOH concentration, each at four levels, are considered as main factors for the Taguchi design. 16 suggested series were produced. Then obtained results were examined by the Analysis of Mean and the Analysis of Variance to determine optimum condition and percentage of participation of mentioned factors on low calcium fly ash based geopolymer compressive strength.

EXPERIMENTAL PROCEDURE

Materials

Fly-ash used in the synthesis of geopolymers is from coal-fired power stations with chemical compositions as shown in Table 1. Fig. 1 shows X-ray diffraction (XRD) pattern of the FA. The average particle size obtained for FA was 4 μm with the BET specific surface of 41 m2/g. NaOH and sodium silicate (SiO2/Na2O=3.1) solutions are used as alkaline activator. After diluting NaOH solution to have concentrations of 4, 8, 12, and 16 M, the solution is left in ambient condition to lose its excess heat to avoid accelerating in setting time.

Alkali activator to fly-ash weight ratio was 0.4 for all mixtures since it has been shown that its range between 0.35 to 0.45 does not affect compressive strength significantly (Nazari et al., 2012a). The mixing was done in laboratory room condition at approximately 25℃. At first, specific amounts of fly ash and NaOH were mixed for 5 minutes. Next, sodium silicate was added to the blend and mixed for more 5 minutes. The mixtures were cast in 50 mm edge cubic molds. The molds were half-filled, vibrated for 20 seconds, filled to the top and vibrated for 20 more seconds and sealed with the lid. All specimens were precured for 24 hours at room temperature as this precuring has positive effect on compressive strength (Bakharev, 2005b). Then the specimens cured for 24 hours at a specific temperature. After mentioned curing, specimens were unmolded, and were kept in isolated chamber with humidity of 60-70% in laboratory room till the test day. Totally 16 series of geopolymer (T1-T16) were prepared for compressive strength test. The tests were carried out on three samples of each series. Besides, Ordinary Portland Cement (OPC) paste was produced as a control mix.

Table 1: Chemical composition of FA and OPC (wt.%)

Material	SiO2	Al2O3	Fe2O3	CaO	Na2O	K2O	MgO	TiO2
FA	60.01	31.05	3.45	0.84	0.08	1.04	0.68	1.605
OPC	20.83	4.34	2.21	65.34	0.36	0.63	2.17	0.257

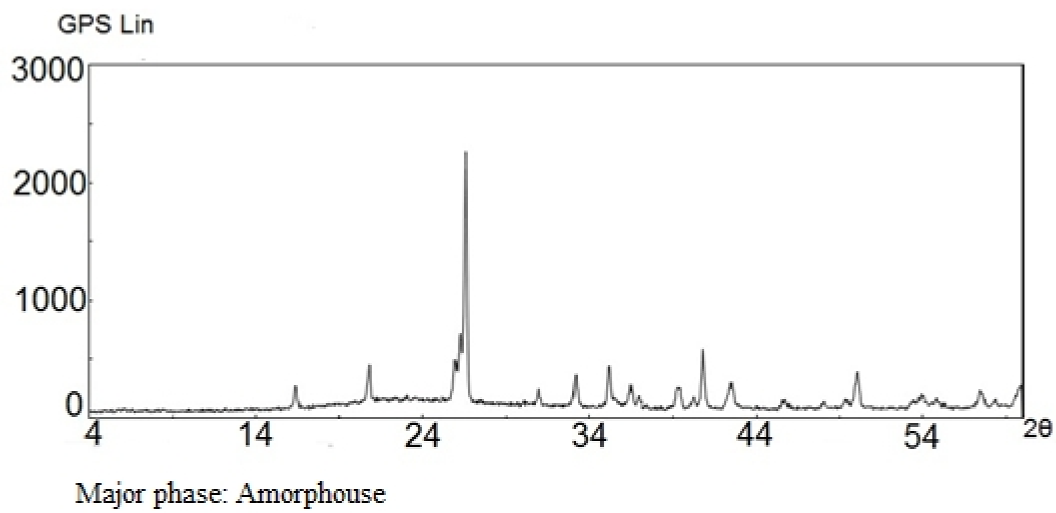

Figure 1: XRD pattern of FA used in this study

Experiment design

In this study, orthogonal arrays, i.e. OA16 (3^4) developed by Taguchi to represent a full factorial experiment is used. The details of factors' levels and components of each mixture (T1-T16) are shown in Table 2 and Table 3, respectively. Primary tests were implemented to identify effective range of considered factors. It was observed that oven curing temperature under 40℃ did not provide necessary condition for geopolimerization, and mentioned temperature above 70℃ were not economically acceptable. Besides, it has been shown that increasing curing temperature over than 75℃ decreases the compressive strength in some cases (Nazari et al., 2011, Nazari and Riahi, 2012, Nazari et al., 2012b).The same results were observed about NaOH concentration less and more than 4 and 16 M respectively. In addition, sodium silicate to NaOH ratio less than 0.5 or more than 3.5 did not provide appropriate workability. Therefore, curing temperature (40, 50, 60, 70℃), sodium silicate to NaOH ratio by weight (0.5, 1.5, 2.5, 3.5), and NaOH concentration (4, 8, 12, 16 M) were considered as main factors.

Table 2: The introduced levels for each factor in Taguchi experiment design

Factor	Description	Level 1	Level 2	Level 3	Level 4
A	Curing Temperature (℃)	40	50	60	70
B	Sodium silicate/NaOH	0.5	1.5	2.5	3.5
C	NaOH concentration (M)	4	8	12	16

Table 3: Test conditions

No.	Alkaline activator/FA	Curing temperature(℃)	Sodium silicate/NaOH	NaOH concentration(M)
T1	0.4	40	0.5	4
T2	0.4	40	1.5	8
T3	0.4	40	2.5	12
T4	0.4	40	3.5	16
T5	0.4	50	0.5	8
T6	0.4	50	1.5	4
T7	0.4	50	2.5	16
T8	0.4	50	3.5	12
T9	0.4	60	0.5	12
T10	0.4	60	1.5	16
T11	0.4	60	2.5	4
T12	0.4	60	3.5	8
T13	0.4	70	0.5	16
T14	0.4	70	1.5	12
T15	0.4	70	2.5	8
T16	0.4	70	3.5	4
OPC	0.4	20		

ANALYSIS

Optimum condition

An analysis of the signal-to-noise (S/N) ratio is used to evaluate the experimental results. Three types of S/N ratio analysis are applicable: (1) Lower is Better (LB), (2) Nominal is Better (NB) and (3) Higher is Better (HB). Since the highest compressive strength is targeted in this study, the S/N ratio with HB characteristic was applied, which is defined by Eq. (1):

$$\frac{S}{N} = -10\log\left(\frac{1}{N}\sum_{i=1}^{n}\frac{1}{Y_i^{2}}\right) \quad (1)$$

Where n is the number of repetitions under the same experimental conditions and Y represents the result of measurement, i.e. Y is the FA based geopolymer paste compressive strength.

To determine the optimal conditions, the Analysis of Mean (ANOM) statistical approach is adopted. The values of the S/N ratio were substituted into Eq. (2) and the mean of the S/N ratios of a certain factor in the ith level, is calculated.

$$(M)_{Factor=I}^{Level=i} = \frac{1}{n_{Ii}}\sum_{j=1}^{n_{Ii}}\left[\left(\frac{S}{N}\right)_{Factor=I}^{Level=i}\right]_j \quad (2)$$

In Eq. (2), n_{Ii} represents the number of appearances of factor I in the level i, and $\left[\left(\frac{S}{N}\right)_{Factor=I}^{Level=i}\right]_j$ is the S/N ratio of factor l in level i, and its appearance sequence in **Error! Reference source not found.** is the jth. As the same, the mean of the S/N ratios of the other factors in a certain level is determined. Therewith, the S/N response table is obtained, and the optimal conditions are established. The confirmation experiments on solidification under these optimal conditions are carried out, finally.

Percentage of contribution

In addition to ANOM, the Analysis of Variance (ANOVA) statistical method is also used to analyze the influence of each controllable factor on the geopolymer compressive strength. The contribution percentage of each factor, ρ_f, is given by:

$$r_F = \frac{SS_F - (DOF_F V_{ER})}{SS_T} \times 100 \quad (3)$$

In Eq. (3), DOF represents the degree of freedom for each factor, which is obtained by subtracting one from the number of the level of each factor (L=4, DOF=4-1). The total sum of squares, SST, is given by:

$$SS_T = \sum_{j=1}^{m}\left(\sum_{j=1}^{n} Y_i^{2}\right)_j - mn(\overline{Y}_T)^2 \quad (4)$$

Where $\overline{Y}_T$ is defined by Eq.(5), m represents the number of experiments carried out (m=16) and n represents the number of repetitions under the same experimental conditions (n=3).

$$\bar{Y}_T = \sum_{j=1}^{m} \left(\sum_{i=1}^{n} Y_i\right)_j /(mn) \qquad (5)$$

The factorial sum of squares, SSF, is given by:

$$SS_F = \frac{mn}{L} \sum_{k=1}^{L} (\bar{Y}_k^F - \bar{Y}_T)^2 \qquad (6)$$

Where $\bar{Y}_k^F$ is the average value of the measurement results of a certain factor in the kth level. Additionally, the variance of error, V_{Er} is given by:

$$V_{ER} = \frac{SS_T - \sum_{F=A}^{D} SS_F}{m(n-1)} \qquad (7)$$

RESULTS AND DISCUSSION

Fig. 2 shows the average compressive strength of 16 suggested experiments at age of 7-days. The highest compressive strength (61.2 MPa) is related to T14 with oven curing temperature of 70℃, sodium silicate to NaOH ratio of 1.5 and NaOH concentration of 12 M. Results show as expected, NaOH concentration has significant effect on compressive strength since the lowest compressive strength results are related to T11, T1, and T6 (3.6, 4.5, 4.5MPa) respectively with NaOH concentration of 4 M. However, low compressive strength of some other specimens such as T3 and T2 (7.7 and 8.5 MPa), proves that NaOH concentration is not the only factor influencing compressive strength of geopolymer since NaOH concentrations were 12 and 8 M in mentioned series respectively. Besides, considering T1 to T4 in Table 4 shows that in low temperature, increasing NaOH concentration up to 16 M has not remarkable effect on compressive strength of geopolymer. As shown in Table 4, T8 and T5 cured in same temperature, and NaOH concentration of T8 (12 M) is more than T5's (8 M). Nevertheless, lower compressive strength of T8 in comparison to T5 shows negative effect of increasing sodium silicate to NaOH ratio from 0.5 to 2.5 on compressive strength. Meanwhile, as seen in Fig. 2 for T4, T8, T12, and T16 series, regardless of effect of other factors, sodium silicate to NaOH ratio of 3.5 influences the compressive strength negatively. It is noted that by increasing the NaOH concentration and sodium silicate to NaOH ratio, the workability of mixtures decreased (Chindaprasirt et al., 2007). As shown in Fig. 2, compressive strength of 6 series including T7, T9, T10, T13, T14, and T15 is close or more than OPC‘s.

Contribution of mentioned factors on compressive strength of geopolymer is quite complex and evaluating those needs a precise method. Therefore, an analysis of the Signal-to-Noise (S/N) ratio, the Analysis of Mean, and the Analysis of Variance are used for this purpose. Table 4 shows S/N ratio of each experiment calculated according to Eq. (1) and the boldface refers to the maximum value of S/N ratio among the 16 tests related to T14. Then, the values of the S/N ratio were substituted into Eq. (2) and the mean of the S/N ratios of a certain factor in the ith level, $(M)_{Factor=I}^{Level=i}$, was obtained. The boldface in Table 5 refers to the maximum value of the mean of the S/N ratios of a certain factor among four levels which indicate the optimum conditions for the compressive strength of fly ash based geopolymer. Therefore, the optimum proportions to obtain the highest 7-days compressive strength are as follows: Curing temperature of 70℃, sodium silicate to NaOH ratio of 1.5 and NaOH concentration of

16 M. This mixture was produced and Table 6 shows characteristics of optimum mixture in comparison to T14. The value of S/N ratio under optimum condition is slightly more than T14 which is because of increasing the NaOH concentration to 16 M.

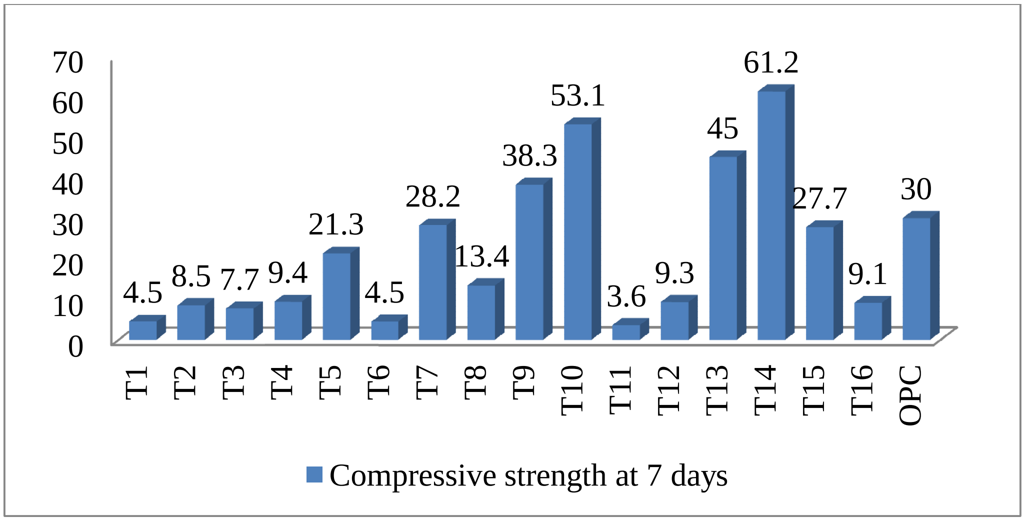

Figure 1: Compressive strength of geopolymers at 7 days (MPa)

Table 4: S/N ratio of the tests.

Design No.	Temperature (℃)	Sodium silicate/ NaOH	NaOH concentration (M)	Y1	Y2	Y3	S/N
1	40	0.5	4	4	4.1	4.4	12.37
2	40	1.5	8	9.3	8.4	9	18.96
3	40	2.5	12	7.6	8.4	7.2	17.71
4	40	3.5	16	10	9.2	9	19.44
5	50	0.5	8	16.4	17.4	18.7	24.82
6	50	1.5	4	5	4.1	4.5	13.04
7	50	2.5	16	28	27.2	29.4	28.99
8	50	3.5	12	13.2	14	13	22.53
9	60	0.5	12	37.8	39	38	31.65
10	60	1.5	16	53.3	52	54	34.50
11	60	2.5	4	3.2	3.6	3.9	10.96
12	60	3.5	8	8.5	10.4	9	19.28
13	70	0.5	16	44	46	44.8	33.05
14	70	1.5	12	60.8	62.8	60	**35.73**
15	70	2.5	8	29.7	27	26.4	28.82
16	70	3.5	4	8	9.2	10.1	19.06

Table 5: S/N ratio response table

Factor/level	j=1	j=2	J=3	j=4	M
A/1	12.37	18.96	17.71	19.44	17.12
A/2	24.82	13.04	28.99	22.53	22.35
A/3	31.65	34.50	10.96	19.28	24.10
A/4	33.05	35.73	28.82	19.06	**29.16**
B/1	12.37	24.82	31.65	33.05	25.47
B/2	18.96	13.04	34.50	35.73	**25.56**
B/3	17.71	28.99	10.96	28.82	21.62
B/4	19.44	22.53	19.28	19.06	20.08
C/1	12.37	13.04	10.96	19.06	13.86
C/2	18.96	24.82	19.28	28.82	22.97
C/3	17.71	22.53	31.65	35.73	26.91
C/4	19.44	28.99	34.50	33.05	**28.99**

Table 6: S/N ratios of the optimum conditions and confirmation tests

Design No.	Temperature	Sodium silicate/ NaOH	NaOH concentration	Y1	Y2	Y3	S/N
Omptimum mixture	70	1.5	16	62	61.5	63	35.87
14	70	1.5	12	60.8	62.8	60	35.73

By substituting Y_T, SS_F, SS_T and V_{ER} in Eq.3, contribution percentage of each factor, r_f, is calculated. According to Table 7, NaOH concentration has the most contribution on compressive strength. Similar result is reported in other investigations (Nazari et al., 2012a). Curing temperature is in the second rank and sodium silicate to NaOH ratio has the minimum effect on compressive strength of fly ash based geopolymer. The error gained in Table 7 is probably because of other factors influencing compressive strength which we did not consider such as different curing condition and silicate sodium module.

Table 7: Percentage of contribution ρ(f)

Factor	ρ(f)
A: Curing temperature (℃)	25.74
B: Sodium silicate to NaOH ratio (By weight)	18.48
C: NaOH concentration (M)	28.83

CONCLUSION

The obtained results from this study indicates that increasing NaOH concentration from 4 to 12 molar improves the compressive strength significantly; however, the effect of increasing NaOH concentration of 12 to 16 M on compressive strength is negligible. Moreover, oven curing temperature does not improve the compressive strength significantly for fly ash based geopolymer paste with NaOH concentration of less than 8 M. Besides, comparison of fly ash based geopolymer paste with OPC one, it can be inferred that for substitution OPC paste with geopolymer, the following preparation is needed: NaOH concentration more than 8 M, sodium silicate to NaOH ratio between 0.5 and 2.5, and curing temperature more than 50℃.

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