- Technical Paper -

WORKABILITY AND COMPRESSIVE STRENGTH OF Na_2SiO_3-ACTIVATED GEOPOLYMER MORTAR CURED AT AMBIENT TEMPERATURE

Shaoqi HUANG[*1], Yukun ZHANG[*2], Yihan BAI[*3] and Lin AN[*4]

ABSTRACT

This study aims to investigate the most influential factors which dominate the flow-ability, setting time and compressive strength of Na_2SiO_3-activated geopolymer mortar cured at ambient temperature. Such factors include sodium silicate concentration, alkaline activator-to-binder ratio, and slag content. A Taguchi orthogonal array was adopted to conduct the experiment. Results show that sodium silicate concentration plays the most vital role in both workability and compressive strength among these above factors under the low alkaline environment.

Keywords: Na_2SiO_3-activated geopolymer mortar, low alkaline activation, Taguchi array, workability, cylinder compressive strength, S/N analysis

1. INTRODUCTION

Cement is the most widely used material in the infrastructure industry. However, the cement industry has been always among the largest CO_2 emission sources. Almost 5–7% of global CO_2 emissions are caused by cement plants, while 900 kg CO_2 is emitted to the atmosphere for producing one ton of cement [1]. In order to restrict the greenhouse effect, the use of alternative materials is on the rise and many research is being performed throughout the globe.

Geopolymer (GP) introduced by Davidovits in 1979 is made up of aluminosilicate materials with three-dimensional amorphous microstructures. The geopolymerization process takes place when the silica and alumina minerals or aluminosilicates are activated by the alkaline solution. Materials that are rich in aluminosilicates are calcined kaolinite and industrial waste such as fly ash (FA) and granulated blast furnace slag (BS). They are commonly activated by adding sodium hydroxide (SH) and sodium silicate (SS) [2]. While the industrial waste ashes are reutilized for GP production as the alkaline binder (AB), the amount of greenhouse gas emitted to the environment was lowered by 44–64% compared with the production of Ordinary Portland Cement (OPC). It is also attributed to curing GP at ambient temperature [3].

SH is user-hostile and must be implemented in mass applications with appropriate safety procedures. However, SS is not a caustic ingredient. So the concept of user-friendly GP by using Na_2SiO_3 solution alone, which means the low alkaline activation, has been proposed in recent years [4]. It is also a type of environment-friendly GP because of the lower emission of CO_2 and lower consumption of energy than using a highly alkaline mixed solution of NaOH and Na_2SiO_3.

Although researchers and industry can benefit from this kind of user-friendly GP material, its workability and compressive strength are still unclear. Therefore, it is urgent and indispensable to identify the basic properties of the new type of Na_2SiO_3-activated GP material for future research and application. This paper aims to reveal the most influential factor which dominates the flow-ability, setting time and 3d, 7d, and 28d compressive strength of Na_2SiO_3-activated GP mortar using SS as the unique alkaline activator (AA). An orthogonal experiment is designed to analyze the effects of SS/SS+Water (SS%, the concentration of SS), SS+Water/FA+BS (AA/AB) and BS content (BS%) on workability and compressive strength of GP mortar.

2. ORTHOGONAL EXPERIMENT

2.1 Materials

FA, BS, sodium metasilicate, sand and water were used to cast the GP mortar specimens. The physical properties and chemical components are shown in Table 1 and Table 2.

The major oxides in FA are mostly silica (SiO_2) and alumina (Al_2O_3) while the main components in BS are calcium oxide (CaO) and SiO_2. Most existing research added SS by diluting water glass, a type of solution with high viscosity which is very difficult to handle and solidifies easily in the air even in the sealed state [5]. The accuracy of the SS% cannot be guaranteed because water glass is a mixture of the compounds with the formula $Na_{2x}SiO_{2+x}$, where the SiO_2/Na_2O molar ratio is not a fixed value. Consequently, water glass was not used in this study. Besides, due to the low solubility of sodium

*1 Graduate School of Civil Engineering, University of Kyoto, JCI Member
*2 Graduate School of Civil Engineering, University of Kyoto, JCI Student Member
*3 Graduate School of Civil Engineering, University of Kyoto
*4 Associate Prof., Dept. of Civil Engineering, University of Kyoto, Dr.E., JCI Member

Table 1 Raw materials

Raw materials	Origin or Properties
Sand	Standard sand for the strength test of cement, water absorptivity: 0.42%, bulk density: 1.76kg/L, solid volume percentage: 66.7%
FA	produced by Hekinan Thermal Power Station of Chubu Electric Power Corporation (JIS A6201-Ⅱ), density: 2.34g/cm^3, specific surface area: 3680cm^2/g
BS	produced by Nippon Steel & Sumikin Esment Chubu Corporation (Esment, JIS A 6206 granulated blast furnace slag 4000), density: 2.89g/cm^3, specific surface area: 4120cm^2/g
Water	Tap water
Sodium metasilicate	Na_2SiO_3 9H_2O, sodium metasilicate nonahydrate produced by Osaka Keisou Corporation, Na_2O (wt%): 21.7, SiO_2 (wt%): 20.9, molar ratio: Si/Na=1.04

Table 2 Chemical components of Sand, FA and BS

Components (%)	ig.loss (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
Sand	0.0	98.4	0.4	0.40	0.20	0.00	0.01	0.01	---
FA	8.4	46.7	23.6	7.8	1.7	1.4	0.8	1.1	0.7
BS	3.5	29.1	14.7	0.5	35.6	7.0	0.3	0.2	4.5

metasilicate, it is impossible to prepare the solution of alkaline activator with relatively high concentration by dissolving the sodium metasilicate powder. Therefore, sodium metasilicate was added as solid powder in this study.

2.2 Design of Taguchi Orthogonal Array

The priority when designing a Taguchi array is to devise the factors and levels. In this experiment, SS% was set to represent the concentration of sodium silicate; AA/AB was termed as the ratio of Liquid to Binder which is similar to OPC mortar; the BS content represents the ratio of BS to the alkaline binder.

Determination of levels was based on the results of pre-experiment and relevant existed literatures [6] [7]. In most of the existing research, it is common to add 30%BS into the fly-ash based GP activated by SH+SS and to cure the specimen with high temperature such as 60℃ to obtain good early compressive strength [2]. In this study, higher BS content was necessary, considering the low alkaline environment without using NaOH and ambient curing condition. Besides, according to the pre-experiments, the GP mortar with appropriate flow-ability and setting time can be obtained while the value of SS% is in the range of 25%~35%. Meanwhile, the value of AA/AB and BS% can be determined in the range of 45%~50% and 30%~60% respectively. According to the related literatures and in-situ experience, the SS% and AA/AB may have more influence than AB-to-sand ratio, and it is possible to obtain ideal flow-ability, setting time and strength when AB-sand ratio is in the range of 0.3-1.0. So a fixed alkaline binder-to-sand ratio of 0.55 was used in this experiment. Factors and levels of Taguchi orthogonal array are shown in Table 3. Based on the factors and levels, L9(3^3) was selected as the Taguchi array. The array and proportions of GP mortar are shown in Table 4.

Table 3 The information of Factors and Levels

Levels	**Factors**		
	SS% (wt%)	(AA/AB)	BS% (wt%)
	A	B	C
1	25.0	0.450	30.0
2	30.0	0.475	45.0
3	35.0	0.500	60.0

Table 4 Proportions of Taguchi orthogonal array

Number	Factors and Levels			Unit mass (kg/m^3)				
	SS%	(AA/AB)	BS%	Water	SS (solid)	FA	BS	Sand
	A	B	C					
1	1	1	1	236	79	490	210	1273
2	1	2	2	249	83	385	315	1264
3	1	3	3	263	88	280	420	1252
4	2	1	2	221	95	385	315	1279
5	2	2	3	233	100	280	420	1261
6	2	3	1	245	105	490	210	1244
7	3	1	3	205	110	280	420	1271
8	3	2	1	216	116	490	210	1263
9	3	3	2	228	123	385	315	1249

2.3 Experiments

In this study, SS was mixed with binders (fly ash and slag) and sand in dry condition. Water was poured to the raw materials after mixing the SS powder with other solid mass. Materials were mixed with low speed for 30 seconds and then a high speed was used to mix for 30 seconds. After waiting for 90 seconds, the fresh mortar was mixed with a high speed for 60 seconds. After the mixing work had been finished, the flow-ability of fresh mortar was measured according to the method from JIS R5201. And cylinder specimens with 5Φ×10cm were made for compressive strength. Initial setting time and final setting time were tested according to the method from JIS R5201.

After demolding, all the GP mortar specimens were cured in ambient temperatures of 20±0.5℃ and relative humidities of 60±0.2%. 3d, 7d and 28d compressive strength were tested according to the JIS A1108.

3. RESULTS AND ANALYSIS

3.1 Mean Square Deviation (MSD) and the Signal to Noise Ratio (S/N)

A set of nine proportions of GP mortar are proposed according to the Taguchi L9 array. This specific arrangement of factors and levels allow us to analyze each factor separately. Analyzing MSD and S/N is to find the most important factor which dominates the flow-ability, setting time, compressive strength for 3d, 7d and 28d respectively, and which is the optimal level for each factor.

The first step is to isolate each factor with an average response, Y, for each level. The mean response, for each factor, is the tally of case responses. It can be represented by Y, for the cases containing that factor. According to the L9 array, the Y can be calculated by averaging the sum of measured values on the same level of each factor. For example, the three cases that contained level 1 for factor A are case 1, case 2 and case 3. So the mean value of level 1 for factor A is (242+247 +250)/3=246.3 which can be represented as Y_{A1}.

The next step is to calculate the MSD. The appropriate formula is selected according to the objective of the experiment. If the maximum setting is required, the MSD formula for "bigger is better", B-Type, is shown as Eq.1:

$$MSD = \frac{\frac{1}{Y_{An,1}^2}+\frac{1}{Y_{An,2}^2}+\cdots+\frac{1}{Y_{An,n}^2}}{n} \quad (1)$$

where,

n: number of replications

$Y_{An,n}$: mean value of the nth experiment for the n level of factor A.

The formula for "smaller is better", S-type, is shown as Eq.2:

$$MSD = \frac{Y_{An,1}^2+Y_{An,2}^2+\cdots+Y_{An,n}^2}{n} \quad (2)$$

The formula for "nominal is better", N-type, is shown as Eq.3:

$$MSD = \frac{(Y_{An,1}-Y_0)^2+(Y_{An,2}-Y_0)^2+\cdots+(Y_{An,n}-Y_0)^2}{n} \quad (3)$$

where,

Y_0: target value of Y.

In this study, n=1 as the experiment wasn't replicated.

The last step is to calculate the S/N. The MSD is a stepping stone to calculate the signal to noise ratio (S/N). The different MSD formula permits a common analysis for any situation by comparing S/N values. A higher S/N value indicates a stronger influence on the response. S/N can be calculated by using the formula shown as Eq.4:

$$S/N = -10\log(MSD) \quad (4)$$

It is the magnitude of the S/N difference that indicates the influence level of each factor. The larger the difference between S/N for each factor's levels, the bigger the difference value (D-v) is and the more that factor influences the results. If there is little difference, then it can be said that there is little difference in response for either level selected. When no other considerations suggest a level, the level with a higher S/N value is more appropriate.

3.2 Analysis of Experiment Results

Table 5 Results of experiments

Case Number	Flow (mm)		Setting Time		Compressive Strength (N/mm^2)		
	Measured Value	Average	Initial (min)	Final (h)	3d	7d	28d
1	241×243	242	75	10.0	11.7	13.6	12.3
2	246×248	247	105	10.5	18.3	20.5	22.9
3	250×249	250	171	7.4	18.2	19.2	24.6
4	225×220	223	52	3.9	24.1	32.1	37.3
5	224×220	222	63	4.2	26.4	31.9	35.6
6	248×252	250	89	5.5	20.3	22.1	22.3
7	182×186	184	46	3.4	31.1	44.1	46.6
8	231×222	226	50	2.7	24.4	25.7	27.4
9	235×233	234	54	3.7	32.4	33.4	38.6

Table 6 MSD and S/N of flow value (mm)

Factor	Level	Sum of Level	Y	MSD		S/N (dB)	
				B-Type	N-Type	B-Type	N-Type
A	A1	739	246.3	1.65E-05	39.7	47.8	-16.0
	A2	695	231.7	1.86E-05	68.9	47.3	-18.4
	A3	644	214.7	2.17E-05	640.1	46.6	-28.1
D-v	---					1.2	12.1
B	B1	649	216.3	2.14E-05	561.7	46.7	-27.5
	B2	695	231.7	1.86E-05	68.9	47.3	-18.4
	B3	734	244.7	1.67E-05	190.4	47.8	-13.4
D-v	---					1.1	14.1
C	C1	718	239.3	1.75E-05	0.5	47.6	3.1
	C2	704	234.7	1.82E-05	28.1	47.4	-14.5
	C3	656	218.7	2.09E-05	453.7	46.8	-26.6
D-v	---					0.8	29.7

※ Y_0 is equal to 240 based on the Japanese Public Building Renovation Standard Specification when we use the equation (3) to calculate the MSD of N-type.
※ D-v represents the difference value (maximum - minimum) of S/N.
※ The red numbers represent the biggest values of D-v.

MSD and S/N are calculated to analyze the influence of factors on workability and compressive strength of Na_2SiO_3-activated GP mortar, based on the results of experiments shown in Table 5. The MSD values, S/N values, and D-v are shown in Table 6, Table 7 and Table 8 for flow value, setting time and compressive strength respectively.

According to Table 6, the most influential factor for the flow-ability of GP mortar is factor A and C because of their biggest difference value of B-Type and N-Type of S/N respectively. Moreover, in the D-value of B-Type, factor B is closed to the factor A. Thus, SS% and AA/AB are the dominant factors for the flow-ability of Na_2SiO_3-activated GP mortar at B-type. Furthermore, since the largest S/N value of B-Type for factor A, B and C is A1, B3 and C1 respectively, if the higher flow value is required, the best group is A1B3C1. In addition, based on the S/N values of N-Type, the best group for getting flow value close to the ideal flow value (240mm) is A1B3C1. According to the results of verification tests, with group A1B3C1, the flow value of 244mm can be obtained. Besides, it can also lead to initial setting time of approximately 80min, final setting time of 8.4h and 20N/mm^2 compressive strength at 28 days.

Table 7 MSD and S/N of setting time (min/h)

Factor	Level	Sum of level		Y		MSD				S/N (dB)			
						S-Type		N-Type		S-Type		N-Type	
		I	F	I	F	I	F	I	F	I	F	I	F
A	A1	351	27.8	117	9.3	13689	85.9	3249	1.6	-41.4	-19.3	-35.1	-2.1
	A2	204	13.7	68	4.6	4624	20.7	64	11.9	-36.7	-13.2	-18.1	-10.8
	A3	150	9.7	50	3.2	2500	10.5	100	22.7	-34.0	-10.2	-20.0	-13.6
D-v	---									7.4	9.1	17.0	11.5
B	B1	173	17.3	58	5.8	3325	33.1	5	5.0	-35.2	-15.2	-7.4	-7.0
	B2	218	17.4	73	5.8	5280	33.4	160	4.9	-37.2	-15.2	-22.1	-6.9
	B3	314	16.5	105	5.5	10955	30.4	1995	6.2	-40.4	-14.8	-33.0	-7.9
D-v	---									5.2	0.4	25.6	1.0
C	C1	214	18.1	71	6.0	5088	36.5	128	3.8	-37.1	-15.6	-21.1	-5.8
	C2	211	18.1	70	6.0	4947	36.3	107	3.9	-36.9	-15.6	-20.3	-5.9
	C3	280	15.0	93	5.0	8711	24.8	1111	9.1	-39.4	-14.0	-30.5	-9.6
D-v	---									2.5	0.6	10.2	3.8

※ Y_0 for initial and final setting time is 60 min and 8h respectively, referred to the JIS R5213 and results in Table.4.
※ I and F represent the initial setting time and final setting time respectively.

According to Table 7, the biggest difference value of S-Type and N-Type for initial setting time belong to factor A and B respectively. So the most important factor for faster initial setting is factor A while the most influential factor for getting the appropriate initial setting time approached to the OPC (60min) is factor B. If the quick setting effect is required, it is possible to choose the group A3B1C2. Group A2B1C2 is expected to get the ideal initial setting time (60min), which is similar to that of OPC. For the final setting time, whether it is S-Type or N-Type, factor A has the largest difference value of

S/N. It is to say that factor A is the dominant factor regardless of its contribution on decreasing the final setting time or getting the final setting time approached to the OPC paste. Due to the biggest value of S/N in each factor, the group A3B3C3 has the shortest final setting time while the final setting time of group A1B2C1 is close to the ideal final setting time (8h), which is approached to OPC paste. In this study, the mix proportion of 25.0% SS%, 47.5% AA/AB and 30% BS% is expected to obtain the ideal initial setting time of 75min and the final setting time of 8.7h, with flow value of 242mm and 20N/mm^2 compressive strength at 28 days, according to the results of verification tests.

Table 8 MSD and S/N of compressive strength (N/mm^2)

Factor	Level	Sum of Level			Y			MSD (B-Type)			S/N (dB) (B-Type)		
		3d	7d	28d	3d	7d	28d	3d	7d	28d	3d	7d	28d
A	A1	48.1	53.3	59.8	16.0	17.8	19.9	3.89E-03	3.17E-03	2.52E-03	24.1	25.0	26.0
	A2	70.7	86.1	95.2	23.6	28.7	31.7	1.80E-03	1.21E-03	9.93E-04	27.5	29.2	30.0
	A3	87.9	103.2	112.6	29.3	34.4	37.5	1.16E-03	8.45E-04	7.10E-04	29.3	30.7	31.5
D-v	---										5.2	5.7	5.5
B	B1	66.8	89.8	96.2	22.3	29.9	32.1	2.01E-03	1.12E-03	9.73E-04	27.0	29.5	30.1
	B2	69.0	78.1	85.9	23.0	26.0	28.6	1.89E-03	1.48E-03	1.22E-03	27.2	28.3	29.1
	B3	70.9	74.7	85.5	23.6	24.9	28.5	1.79E-03	1.61E-03	1.23E-03	27.5	27.9	29.1
D-v	---										0.5	1.6	1.0
C	C1	56.4	61.4	62.0	18.8	20.5	20.7	2.83E-03	2.39E-03	2.34E-03	25.5	26.2	26.3
	C2	74.8	86.0	98.8	24.9	28.7	32.9	1.61E-03	1.22E-03	9.22E-04	27.9	29.1	30.4
	C3	75.6	95.2	106.8	25.2	31.7	35.6	1.57E-03	9.93E-04	7.89E-04	28.0	30.0	31.0
D-v	---										2.5	3.8	4.7

MSD and S/N values of compressive strength are shown in Table 8. According to Figure 1, regardless of compressive strength of 3d, 7d and 28d, the most influential factor is A. Furthermore, the difference values of factor B are very small, so AA/AB has less influence on the development of strength than the other two factors. Group A3B1C3 is able to obtain the best compressive strength in every case.

From the analysis results, it can be seen that the SS% played a vital role in strength achievement. This can be explained by that the OH^- ion acts as a catalyst in the chemical reaction and accelerates the dissolution of alumino-silicate species and Na^+ ion acts as charge balancing cation in the matrix [8]. At low SS contents, because of the low OH^- concentration, less Si^{4+} and Al^{3+} ions dissolved, resulting in the formation of a weak polymeric network which had lower strength. Hence, a lower compressive strength is obtained at lower SS%.

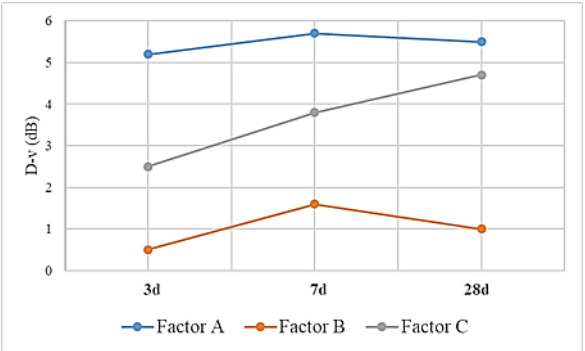

Fig.1 D-v of compressive strength

According to Figure 1, the difference value of factor C increases with the curing time. It can be confirmed that slag content makes more contribution to the development of compressive strength as curing time goes on. The reason is that the hydration reaction continues in the slag for a longer period. The influence on compressive strength with slag addition is attributed to the formation of gel phases (C-S-H and A-S-H) and compactness of microstructure [9]. Moreover, as the hydration reaction in the slag lasts for a long time, a continuous dehydration in the specimen occurs which in turn results in shrinkage cracks [8]. These cracks influence the compressive strength of the specimen. Thus, the slag content has more ability to influence the compressive strength of Na_2SiO_3-activated GP mortar with time.

4. CONCLUSIONS

For investigating the properties of GP with low alkaline activation, an L9 Taguchi orthogonal array was adopted and nine proportions of GP mortar were designed using sodium silicate as the only alkaline supply. More than 30% granulated blast furnace slag was added in order to get relatively high early-age compressive strength. The alkaline binder-to-sand ratio was fixed at 0.55. No extra admixture was added to the mortar. And the specimens were cured in ambient temperature. Furthermore, several verification experiments were done to test the properties of the specimens with the proposed proportions. The results can be summarized as follows:

- Both sodium silicate concentration (SS%) and alkaline activator-to-binder ratio (AA/AB) are the major influencing factors on flow-ability. Better flow-ability can be achieved by reducing the concentration of sodium silicate, increasing alkaline

activator-to-binder ratio and reducing slag content slightly. The flow value, 244mm, closed to the ideal value, can be obtained by using the mix proportion of 25.0% SS%, 50.0% AA/AB and 30% BS%. Besides, it can also lead to initial setting time of approximately 80min, final setting time of 8.4h and around 20N/mm^2 compressive strength at 28 days.

- Sodium silicate concentration (SS%) is the most influential factor in initial and final setting time. The higher sodium silicate concentration leads to the faster setting of GP paste. In this study, the mix proportion of 25.0% SS%, 47.5% AA/AB and 30% BS% is expected to obtain the ideal initial setting time of 75min and the final setting time of 8.7h, with flow value of 242mm and 20N/mm^2 compressive strength at 28 days.
- Sodium silicate concentration (SS%) is also the primary influencing factor of 3d,7d,28d compressive strength. Increasing sodium silicate concentration up to 35.0% and adding slag more than 45% of the total binder can achieve compressive strength of mortar over 40N/mm^2 at 28 days with flow value of 220 mm and initial setting time of about 50min which are close to the target value.
- The slag content (BS%) is found to play an increasingly important role in the development of the compressive strength and achieve almost the same level of importance with sodium silicate concentration (SS%) at 28 days.

Na_2SiO_3-activated GP mortar is found to be a suitable material for in-situ production, as it may achieve reasonably high compressive strength at 46N/mm^2 with no necessity of heat curing. However, the microstructure of this kind of Na_2SiO_3-activated GP mortar is still unclear. The crystal phase and amorphous phase also need to be revealed.

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