DOI: 10.31276/VJSTE.63(1).21-29

Composition of ground granulated blast-furnace slag and fly ash-based geopolymer activated by sodium silicate and sodium hydroxide solution: multi-response optimization using Response Surface Methodology

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Received 13 August 2020; accepted 10 November 2020

Abstract:

Geopolymers are a class of new binder manufactured by activating aluminosilicate source materials in a highly alkaline medium. This binder is considered "environmentally friendly" due to the recycling of industrial waste sources such as fly ash and blast furnace slag. However, in order to be widely used, this binder has to ensure both quality and economic efficiency. This paper focuses on the optimization of the composition of ground granulated blast-furnace slag and fly ash-based geopolymers activated by sodium silicate and sodium hydroxide solutions. Statistical models are developed to predict the compressive strength and cost of 1 ton of binder using Response Surface Methodology (RSM). In this regard, the effects of three principal variables (%Na_2O, M_s and %GGBS) were investigated in which: %Na_2O - mass ratio of Na_2O in the alkali-activated solution and total solids; M_s - mass ratio of SiO_2 and Na_2O in the activated solution; %GGBS - mass ratio of ground granulated blast-furnace slag (GGBS), and total binder. Quadratic models were proposed to correlate the independent variables for the 28-d compressive strength and cost of 1 ton of binder by using the Central Composite Design (CCD) method. The study reveals that M_s has a minor effect on the strength of mortar in comparison with %Na_2O and %GGBS. The optimized mixture proportions were assessed using the multi-objective optimization technique. The optimal values found were %Na_2O=5.18%, M_s=1.16, and %GGBS=50%, with the goals of maximum compressive strength, the largest amount of fly ash, and reasonable cost for one ton of binder. The experimental results show that the compressive strength of the samples ranged between 62.95-63.54 MPa and were consistent with the optimized results (the variation between the predicted and the experimental results was obtained less than 5%).

Keywords: **alkali-activated slag, fly ash, geopolymer, GGBS, optimization, Response Surface Methodology.**

Classification number: **2.3**

Introduction

Alkali-activated binders were first investigated in the 1940s by Purdon's research [1] with the use of GGBS activated with NaOH solution. In 1991, Davidovits developed and patented binders obtained from the alkaline activation of metakaolin named "Geopolymer" [2]. The chemistry of geopolymers are different from Portland cement (OPC). It is well known that OPC is a fine powder obtained by grinding a mixture of clinker, which is made by heating limestone, clay, and other materials such as fly ash with a few percent of gypsum ($CaSO_4.2H_2O$) or anhydrite ($CaSO_4$) to a high temperature (approximately 1450°C). The main binding product, which is derived from the hydration of clinker with water, is calcium silicate hydrate gels known as "C-S-H" gels. The formation of C-S-H, which is an apparently amorphous phase of variable composition, is principally responsible for strength development and matrix formation in Portland cement.

Unlike Portland cement, an alkali-activated binder can be synthesized by exposure of aluminosilicate materials to concentrated alkaline hydroxide (NaOH, KOH) and/or alkali silicate (Na_2SiO_3) solutions, which are then curing at room temperature or slightly elevated temperature [2]. Source materials for alkali-activated binder synthesis should be rich in silicon and aluminium. These could be natural minerals such as kaolinite or metakaolin or one with an empirical

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formula containing Si, Al, and oxygen. Alternatively, by-product materials such as fly ash, silica fume, slag, rice husk ash, and red mud could also be used as source materials. The choice of precursor for making an alkali-activated binder depends on factors such as availability, cost, type of application, and specific demand of end users.

According to Roy (1999) [3] and Palomo, et al. (1999) [4], source materials for alkali-activated binder synthesis can be classed into two groups:

- 1st group: aluminosilicate materials such as metakaolin and class F fly ash produce N-A-S-H gel, also called poly(sialates) gel or "geopolymer" when activated by an alkaline solution.

- 2nd group: alkali-earth enriched aluminosilicate materials such as blast furnace slag and class C fly ash produce C-(A)-S-H gel like hydrated calcium silicate gel with high amounts of tetracoordinated Al in its structure, as well as Na^+ ions in the interlayer spaces when activated by an alkaline solution.

Several authors suggested that blending these two groups may produce both N-A-S-H and C-S-H gels in the matrix. Puertas, et al. (2011) [5] studied the hydration products of a geopolymer paste made by a mixture of 50% fly ash and 50% slag activated with 10 M NaOH and cured at 25°C using XRD, FTIR, and MAS-NMR analysis. They found that the main reaction product in these pastes is a hydrated calcium silicate, like C-S-H gel, with high amounts of tetracoordinated Al in its structure as well as Na^+ ions in the interlayer spaces. Yunsheng, et al. (2007) [6] reported that a geopolymer synthesized by 50% metakaolin and 50% slag activated with water glass at 20°C had both N-A-S-H and C-(A)-S-H gels forming within its matrix.

Previous studies on alkali-activated slag/fly ash binders show that their mechanical properties are influenced by many factors such as precursor materials, type, dosage of alkali-activated solution, and curing conditions [7-9]. However, experimental design methods in these studies stop at univariate analysis or combine simple multivariate with orthogonal design to determine the optimal value through a limited number of experiments. Response Surface Methodology (RSM) allows one to determine the optimal condition of multiple factors accurately and takes into account the effects of these factors and their interactions with one or more response variables with reliability. Some authors have used RSM to optimize the composition of alkali-activated binders. Research by Pinheiro, et al. (2020) [10] focused on predicting equations for compressive and flexural strength at 7 d and 28 d based on three input variables (activator index, precursor index and sodium hydroxide concentration). The ideal composition obtained for the alkaline cement was a mixture constituted by 75% sodium silicate and 25% sodium hydroxide, 50% slag and 50% fly ash, and a sodium hydroxide concentration equal 10 M. This mixture achieved 8.70 MPa of flexural strength and 44.25 MPa of compressive strength. Besides, other authors have used a two-input-variable model in their research. For example, Mohammed, et al. (2019) [11] focused on the mass ratio of GGBS and total binder and the mass ratio of sodium metasilicate anhydrous and total solid. In addition, Rivera, el al. (2019) [12] studied SiO_2/Al_2O_3 and Na_2O/SiO_2 molar ratios with a fixed ratio of fly ash and slag. These studies selected compressive strength as the target function to optimize the binder composition. However, a product requires not only good features but also a reasonable cost. Therefore, using cost for one ton of binder as an objective function is necessary.

Additionally, most previous studies have selected input parameters when preparing the alkali solution as the mass ratio of sodium silicate to sodium hydroxide (SS/SH=1.5/1-2.5/1) and the molarity of sodium hydroxide solution (8-14 M). These studies all use sodium silicate liquid with a silica modulus (SiO_2/Na_2O) of 2.0 while the water glass produced in Vietnam and some other countries has silica moduli ranging from 1.5 to 2.7. Therefore, preparation in this manner is detrimental to practical application because the quality of the concrete can be very different with different types of water glass.

In this study, by using RSM, statistical models are developed to predict the compressive strength and cost for one ton of binder. For better quantification when preparing the alkali solution, this study selected input parameters $\%Na_2O$ and M_s, in which: $\%Na_2O$ - mass ratio of Na_2O in the alkali-activated solution and total solids (FA, GGBS and solids in alkali solution); M_s - mass ratio of SiO_2 and Na_2O in the activated solution. Therefore, liquid sodium silicate, sodium hydroxide, and added water were blended in different proportions providing the required M_s and $\%Na_2O$. Additionally, the precursor index was characterized by the input parameter of %GGBS - mass ratio of GGBS and total binder (FA, GGBS). The effects of these principal variables ($\%Na_2O$, M_s and %GGBS) and their interactions were investigated. Thus, the optimal compositions of ground granulated blast-furnace slag and fly ash-based geopolymers (AAFS) were determined through optimization analysis.

Materials and experimental program

Materials

Fly ash: most of the thermal power plants in Vietnam uses poor quality coal, resulting from the high loss on

ignition (LOI) fly ash products (LOI>6%). Therefore, research on the use of FA with a high LOI content (this FA is not allowed to be used as mineral additives for cement) will bring great economic benefits. In this inquiry, 3 types of class F fly ash, according to the Vietnamese national code TCVN 10302:2014 [13], were used as the main binder. The chemical constituents were identified by X-ray fluorescence (XRF) and displayed in Table 1. These FAs with different LOI were obtained from the Hai Phong (HP) Thermal Power Plant (LOI=11.32%), Pha Lai (PL) Thermal Power Plant (LOI=10.93%), and Formosa (FO) Thermal Power Plant (LOI=1.83%). These three FA types were selected to evaluate the effect of LOI on compressive strength.

Ground granulated blast-furnace slag: ground granulated blast-furnace slag was used as the secondary binder in this study. GGBS was obtained from Hoa Phat Steel Joint Stock Company with finesses and chemical constituents displayed in Table 1. The partial replacement of FA with GGBS was expected to produce high strength samples under room temperature curing condition.

Table 1. Chemical composition of FA and GGBS (percentage by weight).

Chemical oxide	FA from HP	FA from PL	FA from FO	GGBS
SiO_2	49.31	47.45	53.48	36.15
Al_2O_3	21.68	20.55	28.84	10.59
Fe_2O_3	8.76	5.17	4.73	0.35
CaO	1.27	8.3	4.12	39.13
MgO	1.62	1.6	2.31	7.59
SO_3	0.42	0.81	0.32	1.47
K_2O	4.36	3.84	1.25	0.95
Na_2O	0.13	0.24	0.85	0.2
TiO_2	0.98	0.76	1.8	0.54
MnO	0.08	0.05	0.04	2.25
P_2O_5	0.13	0.14	0.26	<0.01
LOI	11.32	10.93	1.83	-
Specific gravity (g/cm^3)	2.24	2.24	2.15	2.85
Blaine fineness (cm^2/g)	2935	2863	3617	3503

Alkali-activated solution: alkali-activated solution includes sodium hydroxide (NaOH) in powder form of 99% purity and sodium silicate as a solution (Na_2SiO_3), or called waterglass, with 6.7% SiO_2, 9.84% Na_2O and 63.46% H_2O by weight. Liquid sodium silicate, sodium hydroxide, and added water were blended in different proportions providing the required M_s and $\%Na_2O$.

Experimental design

Input variables: the composition of alkali-activated binder includes FA, GGBS, and an alkali solution. The water-to-solids ratio and the sand-to-solids ratio were constant at 0.35 and 3.0 respectively. Therefore, the input parameters were selected as $\%Na_2O$, M_s, and %GGBS. The surveyed domain, coded value, and the real value are shown in Table 2.

Table 2. Surveyed domain, the coded value and the real value of input variables.

Input variables	- Alpha	Lower limit	Center point	Higher limit	+ Alpha
	(-1.6818)	*(-1)*	*(0)*	*(+1)*	*(+1.6818)*
$\%Na_2O$	1.64%	3%	5%	7%	8.36%
M_s	0.83	1	1.25	1.5	1.67
%GGBS	7.96%	25%	50%	75%	92.04%

Experimental design: Design Expert software has been used for the experimental design. Based on the Central Composite Design (CCD) for three independent variables, the mix design formulations of the alkali-activated pastes were randomly selected. The results of this work are the 28-d compressive strength and cost for one ton of binder. The software developed $(2^3+2x3+6)=20$ mixtures for these responses with five randomized duplications. The five duplications are the central points used by the software to improve the experiment's accuracy against any likely errors. Thus, for three types of fly ash (HP, PL and FO), the number of mixtures is 3x20=60. The composition of mortar specimens are shown in Table 3.

Mixing procedure, curing and testing of specimens: the mixing and preparation of the specimens used to investigate strength development was done according to the European code EN196-1 [14] with the exception that the water-to-binder ratio (w/b) was not 0.50. A water/solid ratio (w/s) of 0.35 was used instead of the w/b ratio when preparing the geopolymer mortars to give more consistent workability due to the high quantity of solid (Na_2O and SiO_2) contained in the alkaline activator. According to EN 196-1, 40x40x160 mm prism specimens were cast. The test apparatus and measurement of the flow diameter is shown in Fig. 1. After 24 h, hardened mortars were removed from the moulds and cured in water until the test period. At 28-d age, three sets of the specimens were used to conduct the compressive strength test. Each compressive strength, R_{28}, is the average of six experimental results.

Fig. 1. Flow test apparatus and measurement of the flow diameter [15].

Results and discussion

Statistical models of 28-d compressive strength and the cost for 1 ton of binder

The effects of the three input variables (%Na_2O, M_s, and %GGBS) and their interactions with the responses (the 28-d compressive strength and the cost for one ton of binder) were conducted by a quadratic function as follows:

$$Y_i = \beta_o + \sum_{i=0}^{k} \beta_i X_i + \sum_{i=0}^{k} \beta_{ii} {X_i}^2 + \sum_{i,j=0}^{k} \beta_{ij} X_i X_j$$

where Y represents the response value, X represents the input variable, β_o is the interception coefficient, β_i is the coefficient of the linear effect, β_{ii} is the coefficient of the quadratic effect, and β_{ij} is the coefficient of the interaction effect.

The software Design Expert version 11 was used for multiple regression analysis of the obtained experimental data. An F-test was employed to evaluate the statistical significance of the quadratic polynomial. The multiple coefficients of correlation, R, and the determination coefficient of correlation, R^2, were calculated to evaluate the performance of the regression equation.

The mixture proportions and the test results of the 60 prepared mixtures to derive the CCD models are summarized in Table 3.

Table 3. Composition of mortar specimens and the experimental results.

Run	Input variables			Composition of mortar specimens (gam)						28-d Compressive strength (MPa)			Cost for 1 ton of binder
	%Na_2O	*M_s*	*%GGBS*	*Sand*	*GGBS*	*FA*	*Na_2SiO_3 (liquid)*	*NaOH (powder)*	*H_2O (extra)*	*HP-R_{28}*	*PL-R_{28}*	*FO-R_{28}*	
1	3%	1	75%	1350	317.3	105.8	51.9	11	124	28.1	30.5	36.1	$49.86
2	8.36%	1.25	50%	1350	182.7	182.7	180.9	26.2	40.9	49.4	46.3	51.2	$112.58
3	7%	1	75%	1350	290.3	96.8	121.2	25.7	79.4	62.8	64.1	65.2	$93.43
4	5%	1.67	50%	1350	195	195	144.5	11.2	64.2	55.5	55.8	52.0	$80.47
5	1.64%	1.25	50%	1350	216.7	216.7	35.5	5.1	134.7	0.0	0.0	0.0	$32.45
6	5%	1.25	50%	1350	199.7	199.7	108.2	15.7	87.6	56.8	62.1	60.2	$72.52
7	5%	1.25	92.04%	1350	367.6	31.8	108.2	15.7	87.6	59.1	68.3	63.5	$78.93
8	5%	1.25	7.96%	1350	31.8	367.6	108.2	15.7	87.6	5.9	14.3	12.9	$66.10
9	5%	0.83	50%	1350	204.4	204.4	71.8	20.2	111	58.5	55.8	46.2	$64.56
10	3%	1	25%	1350	105.8	317.3	51.9	11	124	6.5	9.8	0.0	$41.79
11	5%	1.25	50%	1350	199.7	199.7	108.2	15.7	87.6	59.4	58.9	56.8	$72.52
12	5%	1.25	50%	1350	199.7	199.7	108.2	15.7	87.6	62.1	62.5	60.7	$72.52
13	7%	1.5	25%	1350	92.8	278.4	181.7	18.2	40.4	29.9	40.3	36.0	$99.45
14	5%	1.25	50%	1350	199.7	199.7	108.2	15.7	87.6	62.1	61.6	59.8	$72.52
15	3%	1.5	75%	1350	312.2	104.1	77.9	7.8	107.3	25.4	37.4	32.1	$55.48
16	7%	1	25%	1350	96.8	290.3	121.2	25.7	79.4	28.7	36.1	32.0	$86.04
17	7%	1.5	75%	1350	278.4	92.8	181.7	18.2	40.4	63.0	70.4	62.3	$106.54
18	5%	1.25	50%	1350	199.7	199.7	108.2	15.7	87.6	58.7	62.2	59.8	$72.52
19	5%	1.25	50%	1350	199.7	199.7	108.2	15.7	87.6	56.6	60.3	60.2	$72.52
20	3%	1.5	25%	1350	104.1	312.2	77.9	7.8	107.3	1.5	1.5	1.3	$47.53

The ANOVA response models for 28-d compressive strength of HP, PL and FO specimens are shown in Table 4-6, respectively. The model's F-values of 75.1, 188.8, and 188.0 for HP, PL, and FO mixtures, respectively, show that the models are significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate the model terms are significant and those greater than 0.1000 indicate the model terms are not significant. The resulting p-values in Tables 4-6 show that factors like $\%Na_2O$ and %GGBS were important at a confidence level of 95% and thus were accepted as crucial parameters on the test results. However, M_s has a minor effect on the 28-d compressive strength in comparison with $\%Na_2O$ and %GGBS. This result is consistent with the study of Prusty and Pradhan (2020) [16]. The model's quality could be assessed on the basis of lack of fit, for example, the smaller lack of fit value indicates the worthiness of the models. The lack of fit for the F-value was 4.05, 4.92, and 4.83 in the models of HP, PL, and FO mixtures, respectively, implies that there was 7.54, 5.25, and 5.44% chance that the lack of fit for an F-value this large could occur due to noise. The lack of fit for the p-value in all models was larger than 0.05, which indicates "not significant" and thus implies good fitness for all the model's responses.

Table 4. ANOVA response models for 28-d compressive strength of HP specimens.

Source	Sum of squares	Degrees of freedom	Mean Square	F-value	p-value	Remark
Model	10102.5	9	1122.50	75.11	<0.0001	significant
A-$\%Na_2O$	2806.7	1	2806.65	187.79	<0.0001	
B-Ms	9.4	1	9.43	0.63	0.4456	
C-%BFS	3302.5	1	3302.49	220.97	<0.0001	
AB	0.2	1	0.21	0.01	0.9077	
AC	58.9	1	58.86	3.94	0.0753	
BC	10.4	1	10.35	0.69	0.4247	
A^2	2627.3	1	2627.27	175.79	<0.0001	
B^2	62.5	1	62.49	4.18	0.0681	
C^2	1663.7	1	1663.66	111.32	<0.0001	
Residual	149.5	10	14.95			
Lack of fit	119.9	5	23.97	4.05	0.0754	not significant
Pure error	29.6	5	5.92			
Cor total*	10252.0	19				

*Cor total: totals of all information corrected for the mean.

Table 5. ANOVA response models for 28-d compressive strength of PL specimens.

Source	Sum of squares	Degrees of freedom	Mean square	F-value	p-value	Remark
Model	9795.5	9	1088.39	188.80	<0.0001	significant
A-$\%Na_2O$	2715.3	1	2715.27	471.01	<0.0001	
B-Ms	6.1	1	6.06	1.05	0.3293	
C-%BFS	3625.6	1	3625.56	628.92	<0.0001	
AB	37.4	1	37.41	6.49	0.0290	
AC	0.3	1	0.28	0.05	0.8296	
BC	17.7	1	17.70	3.07	0.1103	
A^2	2829.2	1	2829.22	490.78	<0.0001	
B^2	87.8	1	87.77	15.23	0.0030	
C^2	831.2	1	831.17	144.18	<0.0001	
Residual	57.7	10	5.76			
Lack of fit	47.9	5	9.58	4.92	0.0525	not significant
Pure error	9.7	5	1.95			
Cor total	9853.1	19				

Table 6. ANOVA response models for 28-d compressive strength of FO specimens.

Source	Sum of squares	Degrees of freedom	Mean square	F-value	p-value	Remark
Model	9719.0	9	1079.89	188.02	<0.0001	significant
A-$\%Na_2O$	3306.7	1	3306.73	575.75	<0.0001	
B-Ms	4.9	1	4.87	0.85	0.3789	
C-%BFS	3263.0	1	3263.03	568.14	<0.0001	
AB	18.6	1	18.60	3.24	0.1021	
AC	6.8	1	6.84	1.19	0.3006	
BC	1.8	1	1.80	0.31	0.5874	
A^2	2319.0	1	2319.02	403.78	<0.0001	
B^2	276.1	1	276.07	48.07	<0.0001	
C^2	976.3	1	976.25	169.98	<0.0001	
Residual	57.4	10	5.74			
Lack of fit	47.6	5	9.52	4.83	0.0544	not significant
Pure error	9.9	5	1.97			
Cor total	9776.4	19				

Table 7 shows the model for the cost of 1 ton of binder. The model's F-value of 1505.28 implies the model is significant. The resulting p-value shows that all factors were important. However, $\%Na_2O$ has a significant effect on the cost for one ton of binder in comparison with M_s and %GGBS.

Table 7. ANOVA response models for the cost of 1 ton of binder.

Source	Sum of squares	Degrees of freedom	Mean square	F-value	p-value	Remark
Model	8664.81	3	2888.27	1505.28	<0.0001	significant
A-%Na_2O	8150.72	1	8150.72	4247.90	<0.0001	
B-Ms	327.55	1	327.55	170.71	<0.0001	
C-%BFS	186.53	1	186.53	97.22	<0.0001	
Residual	30.70	16	1.92			
Lack of fit	30.70	11	2.79			
Pure error	0.0000	5	0.0000			
Cor total	8695.51	19				

The cost for one ton of binder and the 28-d compressive strength of GGBS-FA geopolymer mortar for the HP, PL, and FO mixtures can be predicted using the analysis of variance (ANOVA). The relationships and influence between the variables (%Na_2O, M_s and %GGBS) and their responses were achieved through variance analysis and are presented in Eqs. (1), (2), (3), and (4).

$$R_{28} \text{ of HP} = -155.763 + 37.8043 * \%Na_2O + 69.2449 * M_s + 1.84237 * \%GGBS + 0.325 * \%Na_2O * M_s + 0.05425 * \%Na_2O * \%GGBS + 0.182 * M_s * \%GGBS - 3.37552 * \%Na_2O^2 - 33.3171 * M_s^2 - 0.017191 * \%GGBS^2 \quad (1)$$

$$R_{28} \text{ of PL} = -146.623 + 36.485 * \%Na_2O + 67.8557 * M_s + 1.55059 * \%GGBS + 4.325 * \%Na_2O * M_s + 0.00375 * \%Na_2O * \%GGBS + 0.238 * M_s * \%GGBS - 3.50285 * \%Na_2O^2 - 39.4861 * M_s^2 - 0.0121511 * \%GGBS^2 \quad (2)$$

$$R_{28} \text{ of FO} = -253.679 + 44.231 * \%Na_2O + 188.911 * M_s + 1.93268 * \%GGBS - 3.05 * \%Na_2O * M_s - 0.0185 * \%Na_2O * \%GGBS + 0.076 * M_s * \%GGBS - 3.17133 * \%Na_2O^2 - 70.0289 * M_s^2 - 0.0131689 * \%GGBS^2 \quad (3)$$

$$\text{Cost of 1 ton of binder} = -20.7913 + 12.215 * \%Na_2O + 19.5896 * M_s + 0.14783 * \%GGBS \quad (4)$$

It should be noted that Eq. (4) was established based on the unit price of material as shown in Table 8. Therefore, Eq. (4) is of reference only because the unit price of the material can change over time, for example, by taxes or transportation distance.

Table 8. Unit price of material.

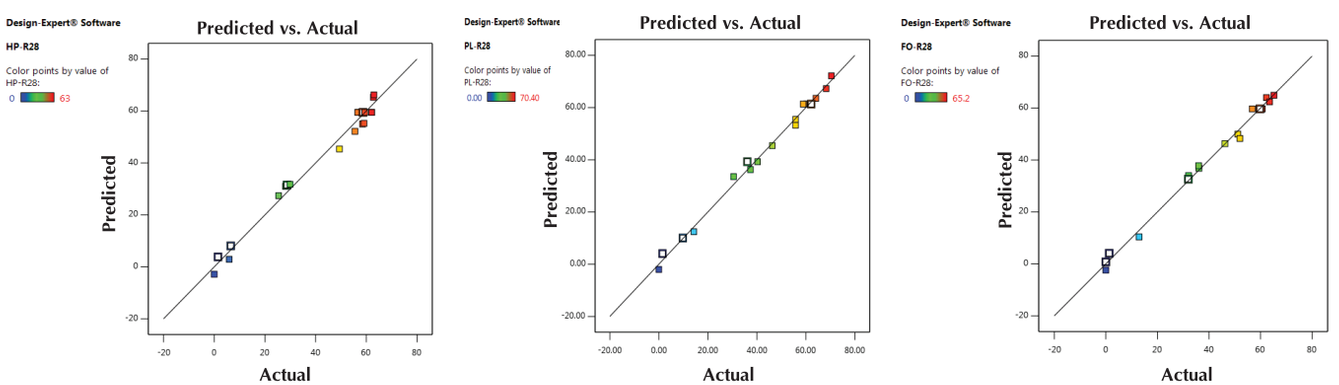
Materials	GGBS	FA	Sodium silicate liquid	Sodium hydroxide
Unit price* (USD per ton)	21.49	4.30	171.90	567.25

Note: unit price includes taxes and transportation costs.

Table 9 shows high R^2 values of 0.985, 0.994, and 0.964 for the 28-d compressive strength models of the HP, PL, and FO mixtures, respectively, which indicate a good measure of the correspondence between the predicted and experimental results. The predicted R^2 values are in reasonable agreement with the adjusted R^2 as the differences are less than 0.2. All models have sufficient precision values of more than 4, indicating that the models could be used to navigate the design space. The predicted vs actual results are plotted in Fig. 2 and show that the predicted response model was precise. The points were fitted smoothly to a straight line, which indicates a good relationship between experimental and predicted outcomes in the established models.

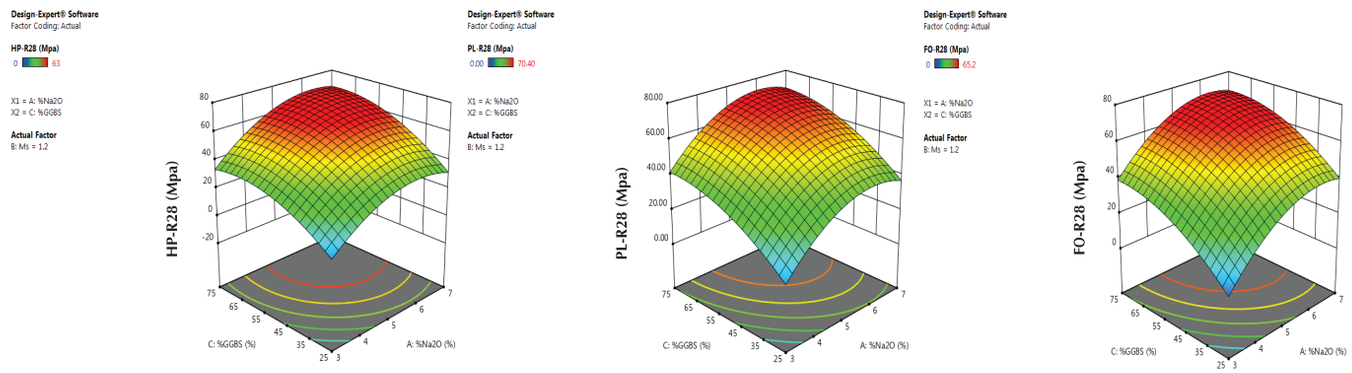
Table 9. Validation properties of response model.

Response	28-d compressive strength			Cost for 1 ton of binder
	for HP mixture	*for PL mixture*	*for FO mixture*	
Standard deviation	3.87	2.4	2.4	1.39
Mean	41.5	44.91	42.41	72.16
C.V. %	9.32	5.35	5.65	1.92
R^2	0.9854	0.9941	0.9941	0.9965
Adjusted R^2	0.9723	0.9889	0.9888	0.9958
Predicted R^2	0.9074	0.9583	0.9617	0.9934
Adequate precision	25.2553	43.6859	39.7157	132.6476



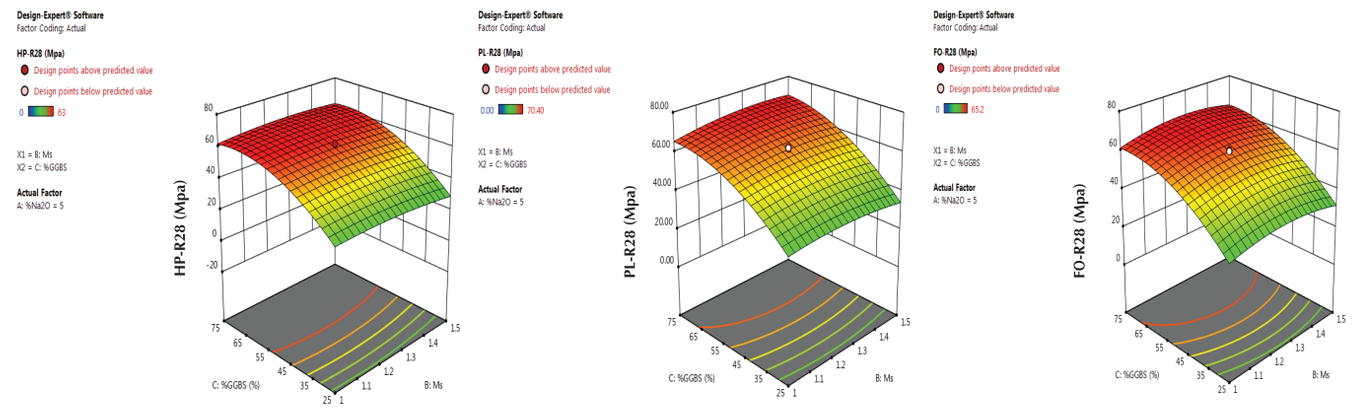
(A) (B) (C)

Fig. 2. Predicted vs actual plot of 28-d compressive strength models for the (A) HP mixture, (B) PL mixture, and (C) FO mixture - effect of %GGBS and %Na_2O.



(A) (B) (C)

Fig. 3. 3D surface plots of 28-d compressive strength models for the (A) HP mixture, (B) PL mixture, and (C) FO mixture - effect of %GGBS and %Na_2O.



(A) (B) (C)

Fig. 4. 3D surface plots of 28-d compressive strength models for the (A) HP mixture, (B) PL mixture, and (C) FO mixture - effect of %GGBS and M_s.

Three-dimensional surface plots were generated for the pairwise combination of the three factors while keeping one constant. The graphs are given here to highlight the roles played by the various factors in the 28-d compressive strength. Fig. 3 shows the effect of %GGBS and %Na_2O while Fig. 4 shows the effect of %GGBS and M_s on the 28-d compressive strength of mortar. It is noteworthy that the sources of FA with different LOI have minor effect on the compressive strength of mortar. In other words, although fly ash is obtained from different factories, it is only necessary to ensure that the class F fly ash is in accordance with the Vietnamese national code TCVN 10302:2014 and contains less than 12% of LOI. With those two conditions met, it can be used to make a high strength alkali-activated binder. It is also noteworthy that M_s has a very small effect when compared to the other factors (%Na_2O and %GGBS). This result opens up a promising research direction; instead of the standard combination of sodium silicate and sodium hydroxide, 100% sodium silicate can be used as an activator. With the properties that exist in powder form ($Na_2SiO_3.5H_2O$) and are not heat generating like sodium hydroxide, we can pre-mix $Na_2SiO_3.5H_2O$ with FA and GGBS in the appropriate ratio for bagging to use as traditional cement.

Optimizations

Although alkali-activated binders are considered to have many good properties and are environmentally friendly, it has not been widely used as Portland cement due to its high cost. Therefore, an optimisation of binder composition should be performed to ensure both high strength and reasonable cost. Furthermore, most of the thermal power plants in Vietnam use poor quality coal, which results in high-LOI fly ash products (LOI>6%). Therefore, the increased use of FA with high LOI content (this FA is not allowed to be used as mineral additives for cement), the more environmental and economic benefits. Based on the purpose of optimisation, the characteristic goals of the factors and their response for the multi-response optimization process are shown in Table 10.

Table 10. Definitions for the factors and the responses in the optimization process.

Factors and response	1st goal	2nd goal	Lower	Upper
A:%Na_2O	is in range	is in range	3	7
B:Ms	is in range	is in range	1	1.5
C:%GGBS	is in range	minimize	25	75
HP-R_{28}	maximize	maximize	0	63
PL-R_{28}	maximize	maximize	0	70.4
FO-R_{28}	maximize	maximize	0	65.2
Cost	none	minimize	31.076	113.248

Based on the purpose of optimization, the numerical optimization solutions are presented in Table 11. According to those results, for the 1st goal, the optimal values were %Na_2O=6.15%, M_s=1.30, and %GGBS=73% with predicted 28-d compressive strengths of 69.84, 74.06, and 71.07 MPa. For the 2nd goal, the optimal values were %Na_2O=5.18%, M_s=1.16, and %GGBS=50% with predicted 28-d compressive strengths of 60.69, 61.84 and 60.19 MPa.

To validate the appropriateness of the optimization results and the entire response model, an additional set of investigations were carried out using the optimized mixture proportions. The experimental results were consistent with predicted results with errors between them less than 5% as shown in Table 11. However, the specimens containing 73% GGBS (for the 1st goal) a microcracking network developing on the surface was visible (Fig. 5). This phenomenon was also found in the study of Zawrah, et al. (2018) [17] with samples containing more than 70% GGBS. This result may have contributions from the high autogenous and drying shrinkage of the alkali-activated slag (AAS). Thomas, et al. (2012) [18] proposed a hypothesis that this effect was due to part of the greater chemical shrinkage of the alkali

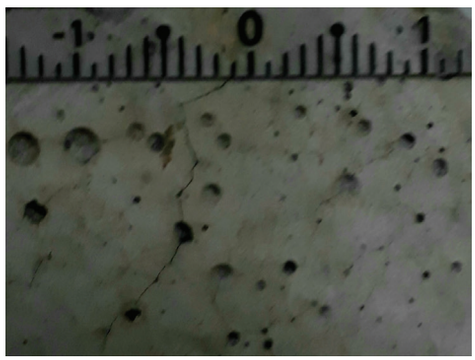


Fig. 5. A visual micro cracking network developing on the surface of the specimens containing 73% GGBS.

activated slag. Additionally, the effect of autogenous shrinkage may be exacerbated by the fact that incorporating GGBS yields a lower permeability of the AAS samples, which prevents excess water into the specimens during saturated curing, which leads to differential stresses that can cause cracking. This phenomenon was not observed in the samples containing 50% GGBS (for the 2nd goal). It is said that the higher replacement of GGBS with fly ash, the lower shrinkage of AAFS mortars [19] and also lower compressive strength.

Conclusions

This study focused on the effects of the input variables %Na_2O, M_s, and %GGBS as well as the interaction between them on the target responses of 28-d compressive strength and the cost for one ton of binder. The following conclusions were drawn:

- Although fly ash can be obtained from different factories, it is only necessary to ensure that the class F fly ash in accordance with the Vietnamese national code TCVN 10302:2014 and contains less than 12% of LOI. Then, it

Table 11. Optimization results and model verification.

Optimization goal	Response	%Na_2O	M_s	%GGBS	Predicted results	Experimental results	Error (%)
1st Goal	28-d compressive strength for HP mixture (MPa)	6.15	1.30	73	69.84	71.75	2.73%
	28-d compressive strength for PL mixture (MPa)				74.06	73.99	-0.10%
	28-d compressive strength for FO mixture (MPa)				71.07	72.71	2.30%
	Cost of 1 ton of binder (USD)				$90.59		
2nd Goal	28-d compressive strength for HP mixture (MPa)	5.18	1.16	50	60.69	62.95	3.72%
	28-d compressive strength for PL mixture (MPa)				61.84	63.54	2.75%
	28-d compressive strength for FO mixture (MPa)				60.19	63.11	4.85%
	Cost of 1 ton of binder (USD)				$72.49		

can be used to make high strength alkali-activated binder. Moreover, the sources of FA with different LOI have minor effects on the compressive strength of mortar.

- M_s has a very small effect compared to the other factors (%Na_2O and %GGBS). This result opens up a promising research direction; instead of the standard combination of sodium silicate and sodium hydroxide, 100% sodium silicate may be used as an activator.

- The optimal values were %Na_2O=5.18%, M_s=1.16, and %GGBS=50% with the goals of maximum compressive strength, the largest amount of fly ash, and reasonable cost. The experimental results show that the compressive strength of the samples were between 62.95 and 63.54 MPa and consistent with the optimized results (the variation between the predicted and the experimental results was less than 5%).

For future work, with emphasis on the properties that exist in powder form ($Na_2SiO_3.5H_2O$) and the lack of heat generation like sodium hydroxide, research will be conducted to pre-mix $Na_2SiO_3.5H_2O$ with FA and GGBS in an appropriate ratio for bagging for use as a traditional cement.

ACKNOWLEDGEMENTS

This study is a part of the national project KC08.21/16-20. The authors would like to admit the program KC08/16-20, Ministry of Science and Technology, Vietnam for the research financial support.

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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