XVI International Conference on Durability of Building Materials and Components
DBMC 2023, China
K.F. Li and D.P. Fang (Eds)

Optimal Amorphous Oxide Ratios and Multifactor Models for Binary Geopolymers from Metakaolin Blended with Substantial Sugarcane Bagasse Ash

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Abstract. *As a potential precursor, the utilization of sugarcane bagasse ash imparts enormous technical and environmental benefits to human society. However, its rich crystal content challenges the mix design of sugarcane bagasse ash-involved geopolymers. The present study is aimed to contribute toward the substantial utilization of sugarcane bagasse ash in geopolymers and develop a guideline for designing binary geopolymers from metakaolin and sugarcane bagasse ash. The experimental results show that when suitably designed, the compressive strength of metakaolin-sugarcane bagasse ash geopolymers satisfied the structural use in building engineering, and the sugarcane bagasse ash proportion could substantially reach up to 50%. Moreover, through a combination of mechanical, economic and environmental assessments, the optimal mixing proportions fall into the following ranges:* SiO_2/Al_2O_3*=4.63~5.60,* Na_2O/Al_2O_3*=1.5~2.0 and* H_2O/Na_2O*=8~10. Further, multi-factor models are proposed to regulate the mix design of binary geopolymers, with a* R^2 *value beyond 0.9.*

Keywords: *Binary geopolymers, sugarcane bagasse ash, mix design, multi-factor models.*

1 Introduction

Geopolymer is essentially produced by activating the aluminosilicate precursor under alkaline conditions. According to prior studies, metakaolin (MK), slag, fly ash, red mud, zeolite and sugarcane bagasse ash (SCBA) are found as some examples of eligible precursors (Albidah 2021). The market price for MK is about $300~$650/tonne, which is significantly higher than OPC, i.e., ~$125/tonne. On the other hand, sugarcane bagasse ash (SCBA) only costs $40~$60 per tonne. Besides, China has now been the third-largest sugarcane producer in the world (Zhang and Hou 2020). The annual production of SCBA also reaches up to 10 million tonnes (Franco-Luján et al.

2021). However, the disposal of SCBA has been a critical concern, due to the considerable production scale and the environmental restrictions (Bahurudeen and Santhanam 2014). Given this, the potential application of SCBA could resolve the above issue. Since SCBA contains both amorphous and crystalline silica, other aluminosilicates are usually coupled with it to produce the binary geopolymer systems. According to Yadav et al. (2020) replaced MK with 56% SCBA, and the associated binary geopolymer only registered a 25.32 MPa compressive strength. However, other mixtures with a poor mix design displayed extremely low compressive strength.

This study was undertaken to investigate the mechanisms underlying the effects of amorphous SiO_2/Al_2O_3, Na_2O/Al_2O_3, and H_2O/Na_2O molar ratios upon the performance of binary geopolymers. By combining environmental and economic indicators, their optimum range is found, which may be used to guide mixture design for binary MK-SCBA geopolymers. Furthermore, based on the least square method, multi-factor models are proposed to predict the compressive strength of binary MK-SCBA geopolymers.

2 Experimental Program

2.1 Materials and Mix Proportions

The amorphous oxides for MK and SCBA are shown in Table 1.

Table 1. Chemical compositions of employed MK and SCBA after removing non-reactive oxides

Groups	SiO_2 (wt.%)	Al_2O_3 (wt.%)	Fe_2O_3 (wt.%)	TiO_2 (wt.%)	CaO (wt.%)	K_2O (wt.%)	MgO (wt.%)	P_2O_5 (wt.%)	SO_3 (wt.%)	Cl (wt.%)	LOI (wt.%)
MK	44.02	45.9	2.93	0.41	0.49	0.33	0.16	0.15	-	-	0.44
SCBA	33.63	1.24	1.24	0.17	26.1	11.1	2.95	5.15	7.36	2.82	0.47

2.2 Mix Proportions and Sample Preparation

2.2.1 Mix proportions

The first series of MK-SCBA geopolymers was cast with the replacement of MK by SCBA from 0% to 100%. Then, with the ratio of MK to SCBA fixed at 1, a further three series were prepared by varying the molar ratios of SiO_2/Al_2O_3, Na_2O/Al_2O_3 and H_2O/Na_2O, respectively, as shown in Table 2. Note here that the mix design was based on the chemical compositions shown in Table 1.

Table 2. Mixing proportions for binary MK-SCBA geopolymers

Groups	S/A	N/A	H/N	MK (g)	SCBA (g)	Sodium silicate (g)	NaOH (g)	H_2O (g)	Sand (g)
MK100SCBA0	2.57	1	10	450	0	379.63	94.65	129.63	1350
MK75SCBA25	3.27	1.3	10	337.5	112.5	379.63	94.65	129.63	1350
MK50SCBA50	4.63	2.0	10	225	225	379.63	94.65	129.63	1350
MK25SCBA75	8.43	3.70	10	112.5	337.5	379.63	94.65	129.63	1350
MK0SCBA100	80.79	37.0	10	0	450	379.63	94.65	129.63	1350
S/A=3.65	3.65	2.0	10	225	225	177.06	130.59	235.50	1350
S/A=4.63	4.63	2.0	10	225	225	379.63	94.65	129.63	1350
S/A=5.60	5.60	2.0	10	225	225	582.19	58.71	23.75	1350
S/A=6.57	6.57	2.0	10	225	225	784.76*	22.77	0	1350
N/A=1.5	4.63	1.5	10	225	225	379.63	57.43	54.26	1350
N/A=2.0	4.63	2.0	10	225	225	379.63	94.65	129.63	1350
N/A=2.5	4.63	2.5	10	225	225	379.63	140.62	222.72	1350
H/N=8	4.63	2.0	8	225	225	379.63	94.65	56.73	1350
H/N=10	4.63	2.0	10	225	225	379.63	94.65	129.63	1350
H/N=12	4.63	2.0	12	225	225	379.63	94.65	202.53	1350

S/A=SiO_2/Al_2O_3; N/A= Na_2O/Al_2O_3; H/N=H_2O/Na_2O; *: 82.13 g of water was evaporated from the activator.

2.3 Cost and Embodied CO_2 Calculations

In order to evaluate the economic advantage of binary MK-SCBA geopolymers, a widely used composite index is calculated according to Eq. (1) (Cong et al. 2018):

$$I_c = \frac{C_t}{f_c'} \tag{1}$$

Wherein, I_c ($/m³·MPa) is the economic index; C_t is the total cost of binding materials to produce 1 m^3 of specimen ($/$m^3$). The compressive strength of the geopolymer at 28 days (MPa) is denoted by f'_c.

In this study, the environmental benefit of the binary MK-SCBA geopolymers is assessed in accordance with Eq. (2):

$$I_e = \frac{e_{CO_2}}{f_c'} \tag{2}$$

Here, I_e (kg/MPa·m^3) represents the environmental index; e_{CO_2} is the factored carbon emission coefficient, which equals the amount of CO_2 emissions per cubic meter of precursor (kg/m^3); and $f'c$ is the compressive strength of the geopolymer at 28 days.

3 Experimental Results and Analysis

3.1 Compressive Strength

Figure 1 presents the compressive strength of binary MK-SCBA geopolymers. The results showed that the compressive strength decreased significantly when the SCBA content exceeded 50% of the binary blend. This was evident from the two mixtures incorporating 75% and 100% SCBA in the precursor. Both consistently displayed extremely low strength (<10 MPa), which is lower than the minimum requirement for structural concrete, as specified in standard GB50010-2010 (i.e., 20 MPa). This decrease can be attributed to an increase in C-S-H formation due to the increase in CaO/SiO_2 ratio and a decrease in N-A-S-H formation due to the reduced Al_2O_3 fraction. Therefore, the authors fixed the MK-to-SCBA ratio at 1, so that each was 50% of the blend.

An increase in the SiO_2/Al_2O_3 ratio from 3.65 to 5.60 was found to improve strength. However, any further increase beyond 5.60 resulted in an unexpected decrease. On the one hand, increasing this ratio brings more silica species into the mixture, which in turn improves the degree of polycondensation and the ensuing strength development (Kong et al. 2008, Burciaga-Díaz and Escalante-García 2012). However, an excessive increase in the SiO_2/Al_2O_3 ratio beyond a certain value, here found to be 5.60, appears to degrade the microstructure of the geopolymer mixture due to the increased solid content.

An increase in the Na_2O/Al_2O_3 molar ratio results in a decrease in compressive strength, as shown in Figure 1(c). Once again, a workable range in terms of the Na_2O/Al_2O_3 ratio is noted to shift slightly toward the larger end (1.5~2.0), in comparison to the one recommended for the pure metakaolin system (0.8~1.2) (Davidovits 2018). This is partly due to a drop in the net alumina content in SCBA-MK systems. However, a drop in the alumina cannot be accompanied by a commensurate drop in the amount of Na_2O. To do this, the amount of water must also be reduced. But, this will adversely affect workability. On the other hand, retaining the same amount of water will reduce the alkalinity by diluting the Na_2O/H_2O ratio (Yi et al. 2020). The influence of the H_2O/Na_2O molar ratio on the strength of binary MK-SCBA geopolymers is presented in Figure 1(d). It is clear that the compressive strength dropped consecutively as the H_2O/Na_2O molar ratio increased.

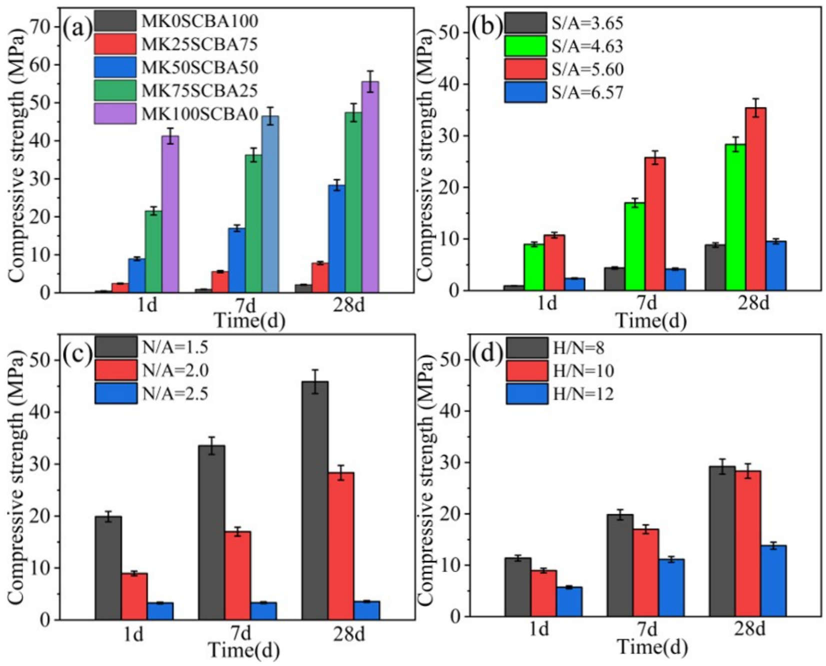

Figure 1. Compressive strength for binary MK-SCBA geopolymers made with varying (a) SCBA proportion, (b) SiO_2/Al_2O_3, (c) Na_2O/Al_2O_3 and (d) H_2O/Na_2O ratios

3.2 Economic and Environmental Assessment

The details of the variables as used for the economic and environmental assessments are presented in Table 3. Figure 2 presents the economic and environmental indexes for various binary MK-SCBA geopolymer systems. One sees that when the MK replacement is within 50%, both economic and environmental indexes are low, whereas any further increase beyond the above value yields a considerable rise in these two indexes. The reason for this is that the binary MK-SCBA geopolymer has a very low compressive strength when the SCBA content exceeds 50%. However, it should be emphasized here that when suitably designed, the binary MK-SCBA geopolymer, when properly designed, has been found to have superior engineering properties, economic benefits and environmental friendliness. In this respect, the optimum mixes are obtained when the respective proportions fall within the following ranges: SiO_2/Al_2O_3=4.63~5.60, Na_2O/Al_2O_3=1.5~2.0 and H_2O/Na_2O=8~10, as evident from Figure 2(b)-(d).

Table 3. Economic and environmental parameters for various raw materials

Variables	MK	SCBA	Sodium	NaOH	H_2O
Cost ($/t)	450	40	571	330	0.62
e_{CO2} (kg/t)	93	0	545	228	0.91

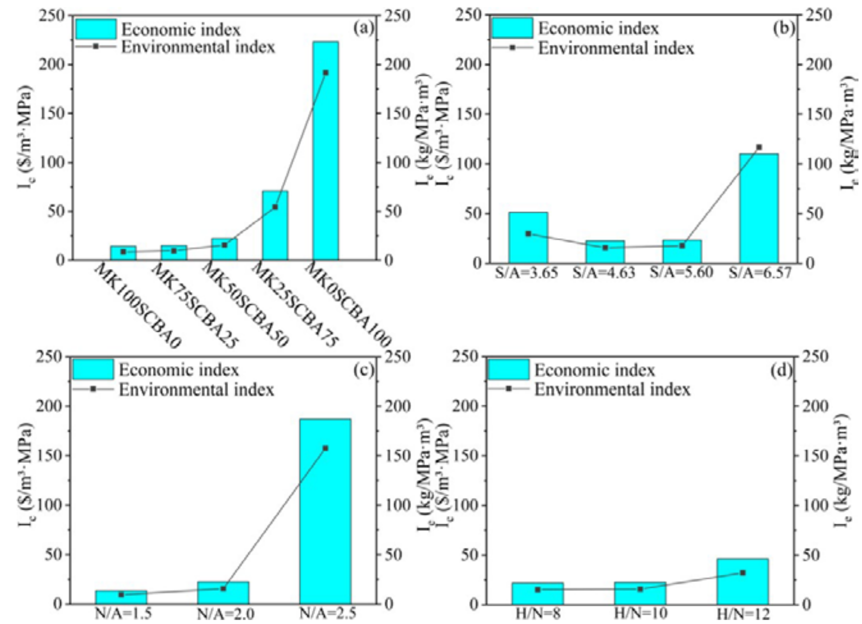

Figure 2. Economic and environmental indexes for MK-SCBA geopolymers made with varying (a) SCBA proportion, (b) SiO_2/Al_2O_3, (c) Na_2O/Al_2O_3 and (d) H_2O/Na_2O ratios

3.3 Multi-factor Models

The principal theory behind multi-factor modelling is the Ordinary Least Square (OLS) method. Recall that, the mechanical properties of geopolymers are dependent on the compositional oxide ratios. Also, the MK replacement is noted to play an important role in this study. So that, the three oxide ratios, namely SiO_2/Al_2O_3, Na_2O/Al_2O_3 and H_2O/Na_2O, and the SCBA proportion and the age of specimen, t are chosen as the main explanatory variables. According to the experimental results (Figure 1), a monotonic correlation is observed between the compressive strength of binary MK-SCBA geopolymer and MK replacement, Na_2O/Al_2O_3 and H_2O/Na_2O. And there exists an optimum value for SiO_2/Al_2O_3, i.e. 5.6, to yield the maximum compressive strength. Hence, a parabolic correlation is assumed. Hence, a preliminary multi-factor model without considering coupling is described as Eq. (3). Subsequently, the mutual combinations between various explanatory variables are taken into account, and the associated coupled multi-factor model is updated as Eq. (4).

$$y = [0.01309 R_{S/A}^2 + (-2.47382) R_{N/A} + (-0.76487) R_{H/N} + (-0.0667) R_{BA} + 20.88234]\sqrt{t} \tag{3}$$

$$y = [(-2.07794) R_{S/A}^2 + 21.19702 R_{N/A} + (-0.76487) R_{H/N} + (-2.70804) R_{BA} + 0.3244 R_{S/A} R_{BA} + (-43.61948)\frac{R_{S/A}}{R_{N/A}} + (-0.74489) R_{N/A} R_{BA} + 0.04335 R_{S/A} R_{N/A} R_{BA} + 0.91919(\frac{R_{S/A} R_{BA}}{R_{N/A}}) + 124.09505]\sqrt{t} \tag{4}$$

The results predicted from the multi-factor models are compared with the experimental data in Figure 3. It can be seen that even without coupling between the explanatory variables, the associated model registers a fair determination coefficient R^2, i.e., 0.715, and this value is then improved up to 0.913 for the coupled multi-factor model.

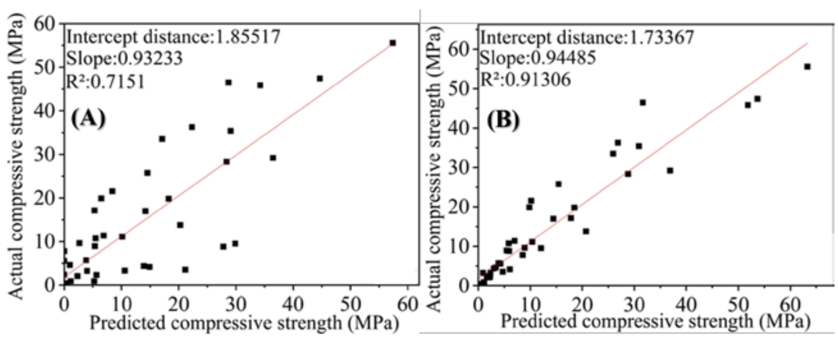

Figure 3. Comparing predicted results with actual compressive strength data

4 Conclusions

- The prominent crystallinity of SCBA indicates that it may not serve as a sole precursor for geopolymers. However, when coupled with metakaolin and suitably designed, the binary MK-SCBA geopolymer displays superior mechanical strength. Therefore, for structural applications, the maximum SCBA replacement of MK should not exceed 50%, so that adequate compressive strength as specified by governing standards may be met.
- The mixtures made with SiO_2/Al_2O_3=4.63~5.60, Na_2O/Al_2O_3=1.5~2.0 and H_2O/Na_2O=8~10 have the highest compressive and flexural strength in the respective series. More importantly, these mixtures also show the lowest economic and environmental indices across the examined mixtures. Taken together, they provide the optimum

compositional range to produce MK-SCBA geopolymers with a substantial SCBA content.

- The proposed multi-factor models capture the effects of principal oxide ratios and the SCBA content in the design of the binary MK-SCBA geopolymers with a substantial SCBA content. When the mutual interactions between the different variables are taken into account, the coefficient of determination is increased from 0.715 to 0.913.

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