Optimisation of Limestone Calcined Clay Cement Based on Response Surface Method

G. Huang, Y. Zhuge, T. Benn, and Y. Liu

Abstract Limestone calcined clay cement (LC3) is a new type of cement that contains Portland cement, calcined clay, and limestone. Compared with traditional cement clinker, LC3 reduces CO_2 emissions by up to 40%, and is a promising technology for the cement industry to achieve its emission target. We used a numerical approach to predict the optimum composition of LC3 mortar. The experiments were performed using central composite rotational design under the response surface methodology. The method combined the design of mixtures and multi-response statistical optimization, in which the 28-day compressive strength was maximized while the CO_2 emissions and materials cost were simultaneously minimized. The model with a nonsignificant lack of fit and a high coefficient of determination (R^2) revealed a well fit and adequacy of the quadratic regression model to predict the performance of LC3 mixtures. An optimum LC3 mixture can be achieved with 43.4% general purpose cement, 34.16% calcined clay, 20.6% limestone and 1.94% gypsum.

Keywords Limestone calcined clay cement · Optimum LC3 mixture · Response surface method · Value-added recycling

1 Introduction

Concrete is the most widely used construction material, and as an essential component, Portland cement (PC) production accounts for approximately 8% of annual anthropogenic greenhouse gas emissions [1]. Because there is no viable economic alternative to concrete, cement consumption is ever-growing. Currently, using supplementary cementitious materials (SCMs) to achieve a partial clinker replacement is the most effective strategy to reduce cement production. Nevertheless, the shortage of traditional SCMs (e.g., fly ash and slag) requires exploration of other types of cementitious materials [2].

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Recently, researchers have worked on limestone calcined clay (LC3) cement, which consists of PC, calcined clay (metakaolin: MK), and limestone (LS). Such a combination of ingredients allows higher clinker replacement and leads to the development of a denser microstructure that gives LC3 excellent mechanical and durability performance [3]. Because LC3 cement has various components, the single-factor method is mainly used in the design of material proportions in LC3 cement, but this can only obtain an optimal mix design for a single performance and cannot achieve multi-objective optimization. In comparison, the response surface method (RSM) is especially advantageous for designing a competitive and more sustainable blended cement binder [4].

In this study, central composite rotation design (CCRD) in RSM was performed. The content of MK, LS and gypsum (GYP) was taken as the variables. The 28-day compressive strength, CO_2 emission, and materials cost were used as response values. The mathematical model was established by analysis of variance (ANOVA) to determine the interaction of various variables and model accuracy. The multi-objective optimization of LC3 mortar was achieved using the numerical-functional optimization model.

2 Methods

2.1 Materials

LS, MK, GYP, and general-purpose cement (GPC) were used to create the LC3 binder mixtures (Table 1). MK was obtained after calcination of kaolin clay at 800 °C for 2 h. The LS, MK and GYP were ground using a horizontal roller mill. Concrete sand with a particle size ranging from 75 to 2.36 mm and a specific density of 2.64 was collected from ResourceCO Australia. A polycarboxylate-based superplasticizer was used to maintain the same consistency for all mixtures (between 185 and 195 mm). Mortar samples with a binder to aggregate ratio of 1:2.75 were cast in accordance with ASTM C305.

2.2 Design of Mixtures

CCRD is the most suitable technique in RSM to obtain a highly effective mathematical experiment design and develop a functional relationship between the variables and responses [5]. For the binder design of LC3 cement, MK content (x_1), LS content (x_2) and GYP content (x_3) were selected as the independent variables. The PC replaced by other ingredients was by mass and defined as a weight percentage of the total binder mass. The variable levels were selected to vary from 0 to 60%

Table 1 Chemical and physical characteristics of the binder materials

Binder	Chemical composition (%)											Physical characteristic
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	P_2O_5	SrO	d_{50} (μm)
GPC	20	4.6	3.1	63.41	1.6	0.19	0.37	2.6	0.3	0.1	0.1	17
LS	5.5	0.8	0.7	50.8	0.8	0.11	0.19	0.1	0.1	< 0.1	< 0.1	22.2
MK	71.18	25.99	0.42	0.31	0.15	0.11	0.04	0.08	1.38	0.06	0.01	18.3
GYP	3.9	1	0.4	30.8	0.3	0.15	0.16	41.5	0.1	< 0.1	0.4	25.4

GPC, general-purpose cement; GYP, gypsum; MK, metakaolin; LS, limestone

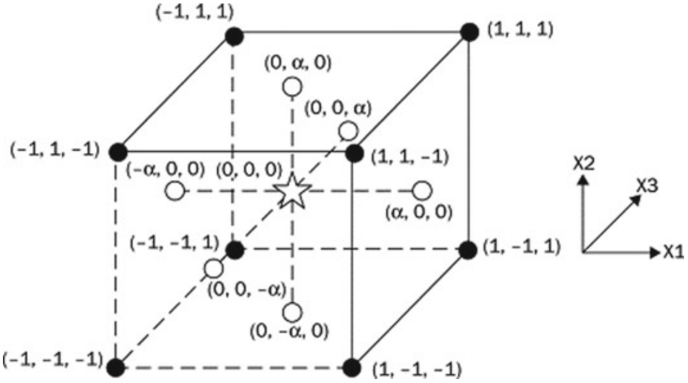

Fig. 1 Schematic illustration of central composite rotational design

for MK, 0% to 30% for LS and 0% to 5% for GYP. The effect of each independent variable was assessed at five levels with a code value of –alpha, –1, 0, 1, + alpha (factorial, axial and central points). The spatial schematic illustration of CCRD is shown in Fig. 1. Three replicates are considered at the central point, resulting in 17 experimental runs. The mix proportions are shown in in Table 2.

The compressive strength of the mortar sample at 28 days (Y_1), CO_2 emissions (Y_2), and materials cost (Y_3) were taken as the response variables. The 28-day compressive strength was recorded experimentally, while the environmental responses, such as CO_2 emissions and materials cost, were evaluated based on per kg of mortar sample. The relevant information on CO_2 emission and the material cost was collected from previous publications or estimations of local materials' market prices. All data used are shown in Table 3. The cost of mortar casting procedures and the emission from mortar service life were not taken into account.

The Design-Expert 12.0.3.0 (Sat-Ease Inc., Minneapolis, MN, USA) software was used to develop the mathematical design and ANOVA of the experiments. The quadratic polynomial model was used to predict the optimal conditions, where Y is the response value, β is the regression coefficient, ε is the random error, X_i and X_j are the independent variables, and k is the number of variables.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j>1}^{k} \beta_{ij} X_i X_j + \varepsilon \tag{1}$$

Table 2 Central composite design matrix and LC3 mortar mix proportions

Run no	Coded values			Level of variables (%)			Mixture proportion (kg/m3)						
	x1	x2	x3	MK	LS	GYP	MK	LS	GYP	GPC	Sand	Water	SP
1	−1	−1	−1	12.16	6.08	1.01	7.23	3.61	0.60	48.00	163.44	28.78	0.23
2	1	−1	−1	47.85	6.08	1.01	28.44	3.61	0.60	26.79	163.44	28.78	0.40
3	−1	1	−1	12.16	23.92	1.01	7.23	14.22	0.60	37.39	163.44	28.78	0.26
4	1	1	−1	47.85	23.92	1.01	28.44	14.22	0.60	16.18	163.44	28.78	0.37
5	−1	−1	1	12.16	6.08	3.99	7.23	3.61	2.37	46.23	163.44	28.78	0.27
6	1	−1	1	47.85	6.08	3.99	28.44	3.61	2.37	25.02	163.44	28.78	0.46
7	−1	1	1	12.16	23.92	3.99	7.23	14.22	2.37	35.62	163.44	28.78	0.28
8	1	1	1	47.85	23.92	3.99	28.44	14.22	2.37	14.41	163.44	28.78	0.61
9	−1.68	0	0	0.00	15.00	2.50	0.00	8.92	1.49	49.04	163.44	28.78	0.20
10	1.68	0	0	60.00	15.00	2.50	35.67	8.92	1.49	13.38	163.44	28.78	0.57
11	0	−1.68	0	30.00	0.00	2.50	17.83	0.00	1.49	40.13	163.44	28.78	0.34
12	0	1.68	0	30.00	30.00	2.50	17.83	17.83	1.49	22.29	163.44	28.78	0.28
13	0	0	−1.68	30.00	15.00	0.00	17.83	8.92	0.00	32.69	163.44	28.78	0.33
14	0	0	1.68	30.00	15.00	5.00	17.83	8.92	2.97	29.72	163.44	28.78	0.36
15	0	0	0	30.00	15.00	2.50	17.83	8.92	1.49	31.21	163.44	28.78	0.37
16	0	0	0	30.00	15.00	2.50	17.83	8.92	1.49	31.21	163.44	28.78	0.36
17	0	0	0	30.00	15.00	2.50	17.83	8.92	1.49	31.21	163.44	28.78	0.39

GPC, general-purpose cement; GYP, gypsum; MK, metakaolin; LS, limestone; SP, superplasticizer

Table 3 Relevant data on emission and cost for LC3 mortar manufacture

Response	Binder materials						
	MK	LS	GYP	GPC	Sand	Water	SP
CO_2 emission, kg CO_2/kg mortar	0.25	0.026	0.14	0.79	0.002	0.007	2.96
Materials cost AUD/kg mortar	0.306	0.001	1.320[a]	0.550[a]	0.5	0.003[a]	16.667[a]

[a] Average price from local suppliers

GPC, general-purpose cement; GYP, gypsum; MK, metakaolin; LS, limestone; SP, superplasticizer

3 Mathematical Modelling and Statistical Analysis

3.1 ANOVA and Adequacy Checking

The ANOVA for the surface response model revealed the model's accuracy and reliability. Specifically, the p-value and F-value at a 95% confidence level were computed to verify the model and the model's terms significant degree for each response. A $p\text{-value} < 0.05$ and a larger F-value indicated the model terms have a significant influence, while $p\text{-values} \geq 0.05$ are considered insignificant. In addition, the lack of fit test measured the degree of fitting between the predicted model and input variables. If the p-value for lack of fit is > 0.05 (non-significant), it implies that: (1) the generated model fits the experimental data well, and (2) the independent variables have considerable effects on the response. When the p-value is < 0.05, seriously insufficient fitting is recorded, indicating the model was not well fitted to the input data. The ANOVA results for Y_1 to Y_3 are shown in Table 4. The response for the model showed a $p\text{-value} < 0.05$ indicating a good fit; however, the response for the lack of fit had a $p\text{-value} > 0.05$, indicating an insignificant lack of fit.

The regression coefficients (β_0, β_i, β_{ii}&β_{ij}) were estimated by ANOVA, and the regression models for each response as functions of %MK, %LS and %GYP are summarised in Table 5. The coefficient of determination (R^2) was obtained to ascertain the accuracy of the predicted function. For all responses, the R^2 values were >95%, which indicated a high degree of correlation to the experimental data.

3.2 Interaction Effects on Response

The three-dimensional response surface plots (see Fig. 2) were shown to evaluate the influence of interactions of different variables on the corresponding response value. The plot presented the interaction of two variables considering that the third variable was fixed on the central point in the CCRD design. The significance of the variables interaction is denoted by the surface steepness and the variable interaction p-value [6]. Therefore, the variable interaction with the smallest p-value was considered to study the influence of two independent variables on the responses. Based on the

Table 4 Analysis of variables of the test results

Response	28-day compressive strength		CO_2 emission		Materials cost	
Source	F-value	p-value	F-value	p-value	F-value	p-value
Model	19.47	0.0004	3726.21	< 0.0001	26.62	0.0001
Interactions						
X_1	34.24	0.0006	21,471.1	< 0.0001	18.74	0.0034
X_2	77.75	<0.0001	11,880.6	< 0.0001	183	<0.0001
X_3	0.043	0.8414	175.77	< 0.0001	29.81	0.0009
X_1X_2	5.8	0.0468	0.5253	0.4921	0.474	0.5131
X_1X_3	4.41	0.0738	3.43	0.1063	3.34	0.1102
X_2X_3	0.08	0.7861	1.67	0.2367	1.62	0.2431
X_1^2	51.12	0.0002	0.2767	0.6151	0.227	0.6483
X_2^2	10.59	0.014	1.73	0.2303	1.71	0.2321
X_3^2	8.75	0.0212	0.2367	0.6415	0.235	0.6427
Lack of fit	2.14	0.3479	14.73	0.0648	14.6	0.0653

Table 5 Regression models for each response

Response	Predicted regression function	R^2 (%)	R^2– predicted (%)
28-day compressive strength	$Y_1 = 37.664 + 0.272x_1 - 0.0732x_2 + 2.181x_3 + 0.00896x_1x_2 + 0.0468x_1x_3 - 0.0126x_2x_3 - 0.0112x_1^2 - 0.0204x_2^2 - 0.667x_3^2$	96.16	73.50
CO_2 emission	$Y_2 = 0.192 - 0.00127x_1 - 0.00179x_2 - 0.00182x_3 + 8.757\text{E-}07x_1x_2 + 0.000013x_1x_3 - 0.00019x_2x_3 + 2.677\text{E-}07x_1^2 - 2.675\text{E-}06x_2^2 - 0.000036x_3^2$	99.95	99.52
Materials cost	$Y_3 = 0.472 - 0.000546x_1 - 0.00122x_2 + 0.000246x_3 + 4.74\text{E-}06x_1x_2 + 0.000075x_1x_3 + 0.000105x_2x_3 + 1.38\text{E-}06x_1^2 - 0.000015x_2^2 - 0.000202x_3^2$	97.16	77.51

ANOVA results shown in Table 4, the selected variable interaction is X_1X_2, X_1X_3 and X_1X_3 for 28-day compressive strength (Y_1), CO_2 emissions (Y_2) and materials cost (Y_3).

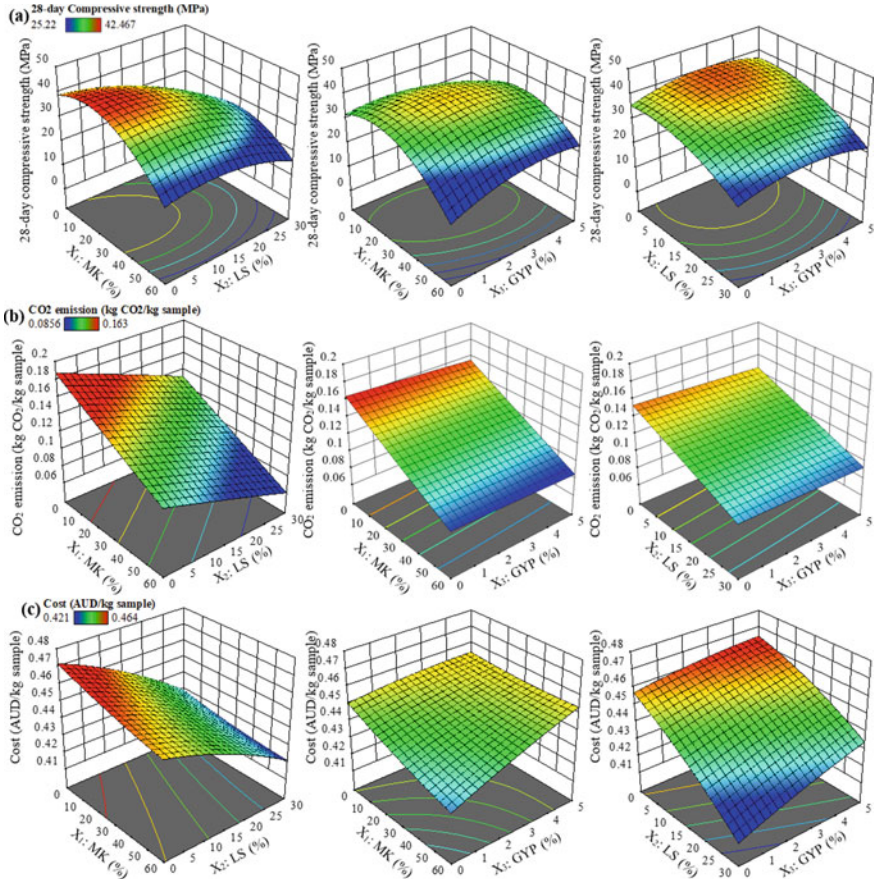

Fig. 2 Three-dimensional response surface plots. **a** 28-day compressive strength, **b** CO_2 emissions, **c** materials cost. GYP, gypsum; MK, metakaolin; LS, limestone

3.3 Response Surface Optimization Analysis

A multi-objective optimization scheme was conducted to determine an optimum formulation of %MK, %LS and %GYP, which satisfied the desired strength specifications while simultaneously minimizing the CO_2 emission and materials cost. The desirability function approach (range from 0 to 1) was used for this purpose. A desirability value of 1 represents the ideal case, while 0 indicates the responses are outside their acceptable limits. The optimal design was verified by the experimental result and shown in Table 6. An overall desirability of 0.72 indicated a reliable result.

Table 6 Optimization results and predicted desirability

Optimum design	Response	Goal	Predicted value	Experimental value	Desirability
%MK = 34.16	28-day compressive strength, MPa	Maximize	34.35	35.63	0.72[a]
%LS = 20.6	CO_2 emission, kg CO_2/kg sample	Minimize	0.109	0.110	
%GYP = 1.94	Materials cost, AUD/kg sample	Minimize	0.436	0.437	

[a] Predicted overall desirability. GYP, gypsum; MK, metakaolin; LS, limestone

4 Conclusion

This study examined the effects of formulation on strength performance, CO_2 emission, and production cost of LC3 cement. The following conclusions were drawn based on the experimental results.

- ANOVA showed satisfactory fit and accuracy of the developed quadratic models.
- The optimization results confirmed that the optimal percentages of MK, LS and GYP were 34.16%, 20.6% and 1.94%, respectively.

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