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Use of a kaolinitic clay as a pozzolanic material for cements: Formulation of blended cement

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Abstract

Local kaolinitic clay (from the region of Tabarka, Tunisia) was tested as a pozzolanic material. Thermal treatments were performed as a means of activation of the minerals. The phase identification, before and after heat treatment, was studied by X-ray diffraction and differential thermal analysis/thermogravimetric analysis (DTA/TGA).

In order to check the effect of three variables (the calcination temperature, the specific surface of the calcined clay and the percentage of incorporation of the heat treated clay in the formula of the blended cement) on the compressive strength of blended cement mortar bars at 7, 28 and 91 days, a Box–Behnken design was set up. It was concluded that the mechanical properties of the blended cements were mainly governed by the percentage of incorporation and the fineness of the calcined clay. It was also demonstrated that increasing the fineness of the calcined clay allowed for increases in the level of cement substitution. Finally, a blended cement composition has been formulated, with optimal results at calcining temperature 700 °C, 30% of calcined clay ground at a Blaine fineness of 7700 cm^2/g.
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Keywords: Clay; Calcination; Cement; Optimisation; Box–Behnken design

1. Introduction

The reasons for partially replacing cement in mortar and concrete with pozzolanic materials are diverse [1]. They include strength enhancement [2,3] and improvement in durability [4]. There are also clear environmental advantages in reducing the quantity of cement used in construction materials. Indeed, cement production is highly energy-intensive process involving significant environmental damage with respect to CO_2 production and raw material acquisition [5]. Among the pozzolanic materials used in the cement industry, blast furnace slag [6] and some activated clays [7] have been successfully tested.

It is possible to obtain pozzolanic materials when clays are thermally heated. Indeed, by heat treatment, the crystal structure of the clay minerals is destroyed and an amorphous or disordered alumino-silicate structure is formed, developing pozzolanic properties [8,9].

The purpose of this investigation is to examine the pozzolanic behaviour of local kaolinitic clay as a function of the calcination temperature, the fineness of the calcined clay and its percentage in the cement in order to optimise a blended cement formula by using Box–Behnken experimental methodology [10].

2. Experimental techniques and methodology

2.1. Raw materials

The blended cements prepared in this study are composed of two raw materials: cement I.42.5 (without secondary constituents and having a minimum compressive strength at 28 days of 42.5 MPa) and calcined clay.

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- *Cement I.42.5*: the cement is produced at Gabès, Tunisia plant by a dry process. It is composed approximately by 95% clinker and 5% gypsum. This cement labelled as "reference" has the chemical and mineralogical compositions presented in Table 1.
- *Clay*: the studied clay is a local one, collected from the region of Tabarka. It is used in hand made pottery. Its chemical composition by X-ray fluorescence is presented in Table 2.

2.2. Experimental techniques

Each blended cement is prepared by grinding separately the calcined clay and cement before their mixing. The calcined clay is ground in a rotary ball mill with a capacity of 6 kg at a dry state. The mixture is then shacked for few minutes in a shaker. The obtained blended cement is then submitted to several tests:

– The normal consistency, the setting times and the stability to expansion are determined according to the European EN 196-3 norm.
– The mechanical properties are assessed on mortar bars $40\times40\times160$ mm in compliance with the EN 196-1 norm.
– The specific surface of the burnt clay is measured by using the Blaine method (EN 196-6).

2.3. Methodology

The purpose of this work is to study the effect of three factors namely calcining temperature (X_1), specific surface of the calcined clay (X_2) and its percentage in the blended cement (X_3) on the compressive strength of the blended cements in order to determine the best experimental conditions allowing the maximization of this response. This has been accomplished by applying response surface methodology (RSM) [11–13]. In order to achieve this purpose, a Box–Behnken design is performed.

For predicting the optimal conditions, a second order polynomial function is fitted to correlate relationship between independent variables and response. For three factors this equation is

$$\hat{y}_i = b_0 + b_1X_{i1} + b_2X_{i2} + b_3X_{i3} + b_{11}X_{i1}^2 + b_{22}X_{i2}^2 + b_{33}Xi_3^2 + b_{12}X_{i1}X_{i2} + b_{13}X_{i1}X_{i3} + b_{23}X_{i2}X_{i3}$$

where X_{ij} is the value of coded variable j at the ith experiment, b_j and b_{ij} are model coefficients, $\hat{y}_i$ is the calculated response value at the ith experiment.

The measured response y_i for the ith experiment is

$$y_i = \hat{y}_i + e_i, \quad (e_i \text{ is the error})$$

To estimate the coefficient values, three levels coded –1, 0, +1 for low, middle and high values respectively are attributed to each of the three retained factors and 15 experiments are carried out according to the Box–Behnken design shown in Table 3.

The graphical representation of the distribution of the experimental points is given in Fig. 1. They correspond to 12 experiments at the middle of the edges of the experimental domain and 3 experiments at the centre. The experiments repeated at the centre of the domain (13–15 in Table 3) permit to calculate an independent estimation of the pure experimental error variance.

Experiment were carried in duplicate and mean values are given. NemrodW software [14] was used for the regression analysis of the experimental data obtained.

Following the program of experimentation, the data are used in the response surface methodology to

Table 3
Box–Behnken design for three variables

Experiment no.	X_1	X_2	X_3
1	−1	−1	0
2	+1	−1	0
3	−1	+1	0
4	+1	+1	0
5	−1	0	−1
6	−1	0	+1
7	+1	0	−1
8	+1	0	+1
9	0	−1	−1
10	0	+1	−1
11	0	−1	+1
12	0	+1	+1
13	0	0	0
14	0	0	0
15	0	0	0

Table 1
Chemical and mineralogical composition of cement

	Chemical composition								Bogue composition			
Component	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	K_2O	CaO_{free}	LOI	C_3S	C_2S	C_3A	C_4AF
Weight %	65.3	21.1	4.7	2.8	2.3	0.5	0.8	0.9	59.3	15.8	7.76	8.59

Table 2
Chemical composition of the clay

Component	CaO	SiO_2	Al_2O_3	SO_3	K_2O	MgO	Fe_2O_3	Total
Weight %	0.0	58.3	28.7	0.1	1.5	0.3	2.8	84.13

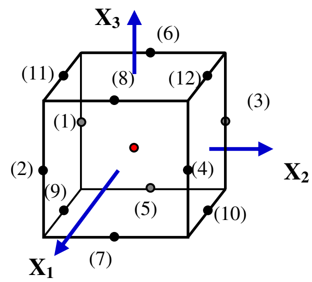

Fig. 1. Distribution of the experimental points in a three variable Box–Behnken design.

– fit the empirical model,
– test the adequacy of the fitted model,
– plot the contours of the predicted responses,
– determine the optimal conditions.

3. Results and discussion

3.1. Characterisation and conditioning of the clay

3.1.1. Clay characterisation

3.1.1.1. X-ray diffraction analysis. The X-ray diffractogram of the clay sample is presented in Fig. 2.

It shows that the clay collected from the region of Tabarka is composed of kaolinite combined with quartz and some anatase (TiO_2). We notice that the peaks relative to quartz (which is well crystallised) seem more intense than those of kaolinite, while the X-ray fluorescence shows that the fraction of the clay mineral ($\%Al_2O_3 = 28.7\%$, corresponding approximately to 72% of kaolinite) is more abundant than quartz (≈25%).

3.1.1.2. Differential thermal analysis and thermogravimetry. The thermogram of the studied clay is presented in Fig. 3.

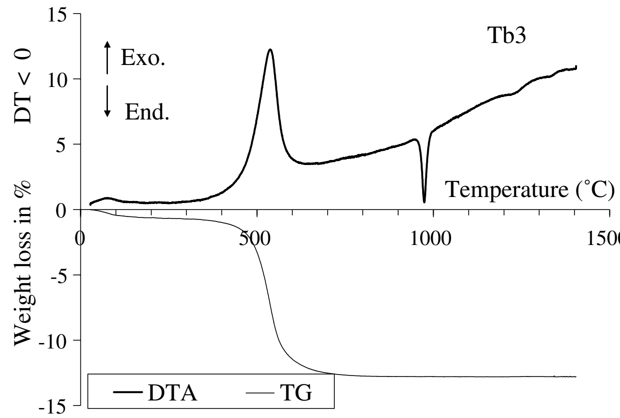

Fig. 3. Thermogram of the clay.

The thermogram examination shows three phenomena. The first one is endothermic between 27.5 °C and 160 °C with a weight loss of 1% due to water loss. The second one, also endothermic between 428 and 620 °C is associated to the dehydroxylation of the clay. It includes the endothermic peak corresponding to the transition $SiO_2\alpha \rightarrow SiO_2\beta$: the thermal analysis of the heat treated clay at 800 °C shows clearly this phenomenon. The weight loss corresponding to dehydroxylation is about 9%. The third one which is exothermic (937–1018 °C) is relative to the re-organisation of the structure. This last phenomenon is not accompanied by any weight loss.

3.1.2. Clay calcination

First, we remind [15] that the optimal calcination temperature to obtain pozzolanic material must be situated between the end of dehydroxylation and the beginning of recrystallization.

Results obtained from the thermal analysis of the crude clay allow us to retain a calcination temperature interval between 600 and 800 °C. The heat treatment duration was fixed to five hours.

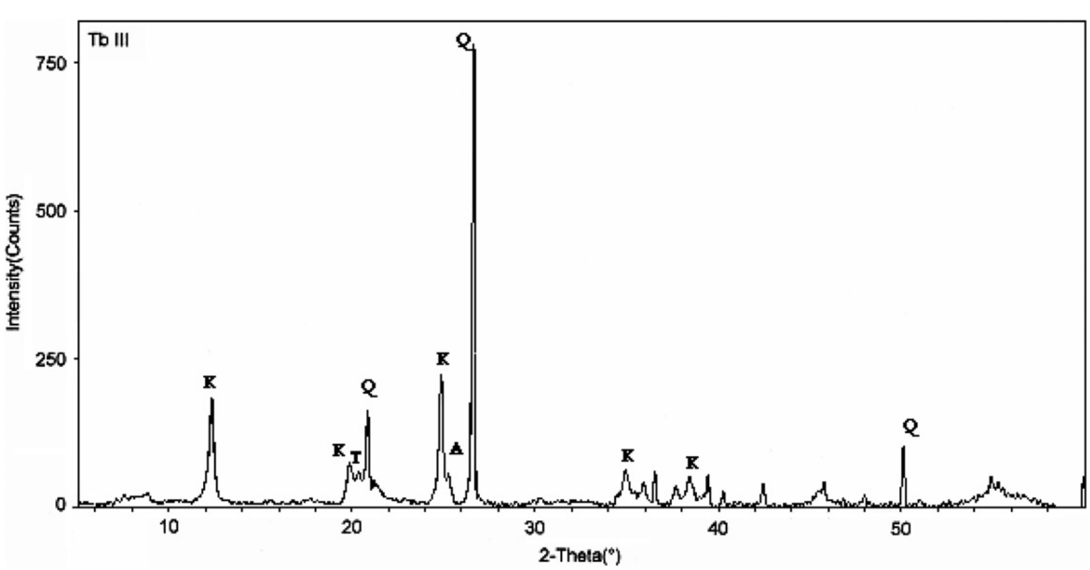

Fig. 2. X-ray diffractogram of the clay. k: kaolinite, Q: quartz, T: titanium oxide, A: anatase.

In order to examine the structure of the clays after calcination, the heat treated samples are analysed by X-ray diffraction. The diffractograms of the crude sample and calcined ones at 600, 700 and 800 °C are presented in Fig. 4. These three temperatures correspond to the levels of this factor prescribed by the Box–Behnken design.

We notice that the diffractograms of the calcined clay at 600, 700 and 800 °C are similar. The heat treatment leads to:

– the disappearance of the peaks relative to kaolinite,
– the appearance of a dome (between $2\theta = 20$ and 30°) indicating the formation of an X-ray amorphous phase,
– the emergence of a small peak attributed to illite ($2\theta = 9.5°$ corresponding to $d = 10$ Å [16]. This peak is too small to be detected in the crude clay. It is to be noticed that the illitic structure persistence after calcinations at 800 °C has also been pointed out by He et al. [17].

These results clearly show that during calcination, the kaolinite is transformed into an amorphous phase, potentially reactive with $Ca(OH)_2$ of cement.

3.2. Optimisation of blended cement formula

This work is especially aimed to the formulation of blended cement using the calcined clay from Tabarka region. The quality of the prepared cements will be checked by the measure of the compressive strengths at 7, 28 and 91 days noted y_1, y_2 and y_3 respectively.

The explored experimental domain and the levels attributed to each variable are shown in Table 4.

Table 5 represents the experimental design together with the measured responses. All experiments are performed in duplicate and the average of the observations is used.

3.2.1. Mathematical models

The observed responses are used to compute with Nemrod software the model coefficients using the least square method [13,18,19]. This allows us to write the resulting estimated models:

$$y_1 = 32.400 + 0.712X_1 + 3.512X_2 - 3.150X_3 + 0.581X_1^2 + 0.941X_2^2 + 0.006X_3^2 + 0.578X_1X_2 + 1.963X_1X_3 + 1.602X_2X_3 \quad (1)$$

Table 4
Variables and experimental domain

Variables	Levels		
	−1	0	+1
x_1: Calcination temperature (°C)	600	700	800
x_2: Specific surface of the calcined clay (cm²/g)	4300	6000	7700
x_3: % Calcined clay in the blended cement	10	20	30

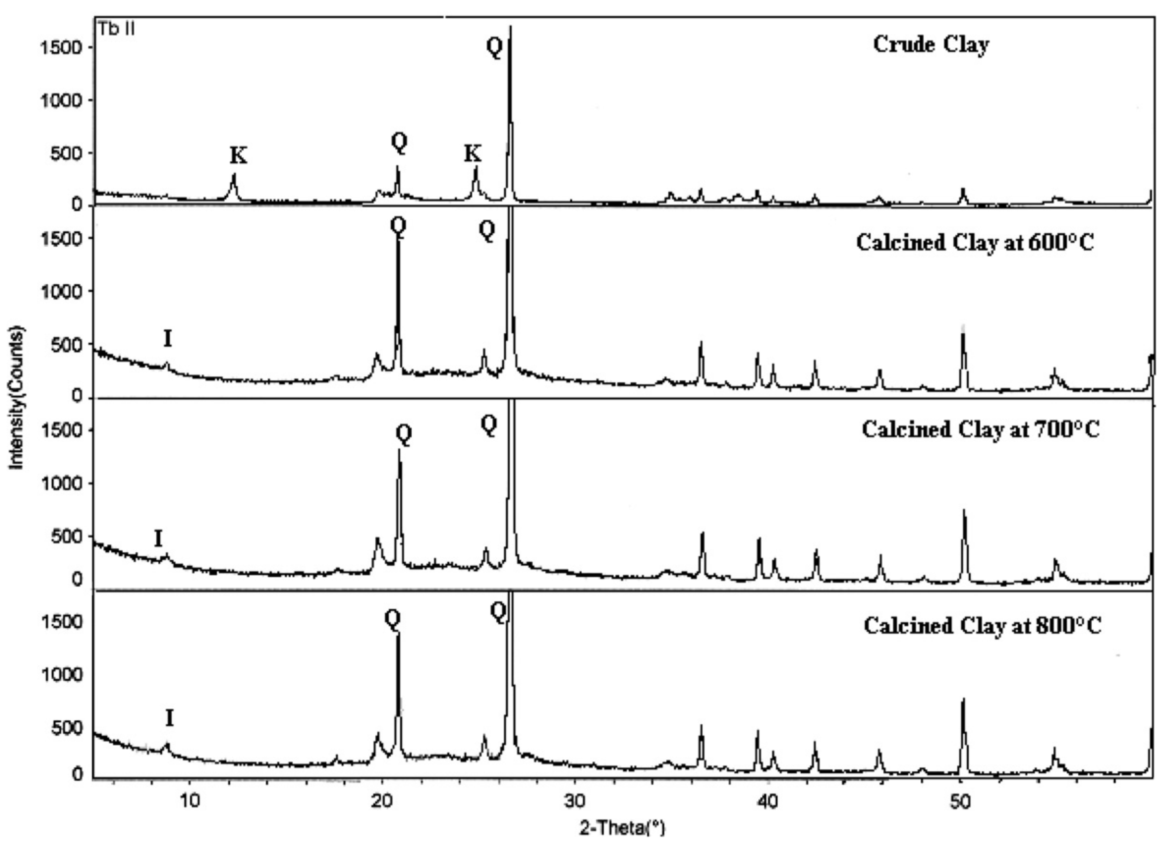

Fig. 4. Diffractograms of the crude clay and calcined samples treated at 600, 700 and 800 °C. I: illite, k: kaolinite, Q: quartz.

Table 5
Box–Behnken design and the measured responses

Experiment no.	Calcination temperature (°C)	Specific surface (cm^2/g)	% Calcined clay	y_1 (MPa)	y_2 (MPa)	y_3 (MPa)
1	600	4300	20	30.7	39.4	44.0
2	800	4300	20	30.8	44.1	45.5
3	600	7700	20	35.9	48.7	52.9
4	800	7700	20	38.3	53.1	57.4
5	600	6000	10	37.5	49.9	55.8
6	800	6000	10	35.2	50.7	53.1
7	600	6000	30	26.9	37.3	41.4
8	800	6000	30	32.4	49.9	51.2
9	700	4300	10	34.1	49.4	56.4
10	700	7700	10	38.6	54.1	57.4
11	700	4300	30	24.9	37.1	42.1
12	700	7700	30	35.9	53.1	55.0
13	700	6000	20	32.4	46.9	52.4
14	700	6000	20	32.8	46.6	53.7
15	700	6000	20	32.1	46.2	53.0

$$y_2 = 46.550 + 2.801X_1 + 4.881X_2 - 3.335X_3 - 0.866X_1^2 + 0.634X_2^2 + 1.256X_3^2 - 0.093X_1X_2 + 2.940X_1X_3 + 2.830X_2X_3 \quad (2)$$

$$y_3 = 53.07 + 1.619X_1 + 4.352X_2 - 4.121X_3 - 2.788X_1^2 - 0.381X_2^2 + 0.062X_3^2 - 0.748X_1X_2 + 3.140X_1X_3 + 2.988X_2X_3 \quad (3)$$

The quality of fit of the polynomial model equation was expressed by the square multiple correlation coefficient R^2

$$R^2 = \frac{\sum (\hat{y}_i - \bar{y})^2}{\sum (y_i - \bar{y})^2}$$

$\bar{y}$ is the mean of responses.

The correlation coefficients of the three responses are presented in Table 6.

The calculated values of this coefficient for the three responses, presented in Table 6, indicate a high degree of correlation between the experimental and the predicted values. Indeed, only 1–2% of the total variations are not explained by the regression.

The analysis of variance (ANOVA) for these models carried out using NemrodW, are shown in Tables 7–9. These tables show how the total calculated sum of squares are distributed among the different sources of variations [18,19]. As it can be seen, the three regression sums of squares are statistically significant.

The evaluations of the residual sum of squares with 5 degrees of freedom and the experimental error (calculated with 2 degrees of freedom from the repeated experiments at the centre of the domain) allow us to validate the adequacy of the three fitted models.

Table 6
Correlation coefficients of the regressions

Response	y_1	y_2	y_3
R^2	0.993	0.992	0.983

Table 7
Analysis of variance of the response y_1

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F ratio	Significance
Regression	213.4263	9	23.7140	76.4352	***
Residuals	1.5513	5	0.3103		
Validity	1.3063	3	0.4354	3.5544	22.7%
Error	0.2450	2	0.1225		
Total	214.9776	14			

*** Significant at 99.9%.

Table 8
Analysis of variance of the response y_2

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F ratio	Significance
Regression	419.6521	9	46.6280	66.0112	***
Residuals	3.5318	5	0.7064		
Validity	3.2118	3	1.0706	6.6913	13.4%
Error	0.3200	2	0.1600		
Total	423.1840	14			

*** Significant at 99.9%.

Table 9
Analysis of variance of the response y_3

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F ratio	Significance
Regression	413.6625	9	45.9625	33.7439	**
Residuals	6.8105	5	1.3621		
Validity	5.9764	3	1.9921	4.7769	17.8%
Error	0.8341	2	0.4170		
Total	420.4730	14			

** Significant at 99%.

The plots of the residuals versus the predicted responses and normal plot probability of the residuals of the responses show a random distribution. This confirms the adequacy of the models. Fig. 5 shows the normal plot probability for response y_1.

We can then conclude that each second order model is adequate and can be used as prediction equation.

3.2.2. Model exploitation

The purpose of the following paragraph is to find out the best experimental conditions, which lead to maximize the compressive strength.

The second order model with square terms describes a variety of shaped response surfaces. The stationary point of the response surface can be a maximum, a minimum or a saddle point (minimax). It is rather difficult to comprehend how the surface is shaped by mere inspection of the algebraic expression of the model. But the nature of stationary point is conveniently determined by using different mathematical tools. In this study, isocontour plots are used to find the optimal conditions.

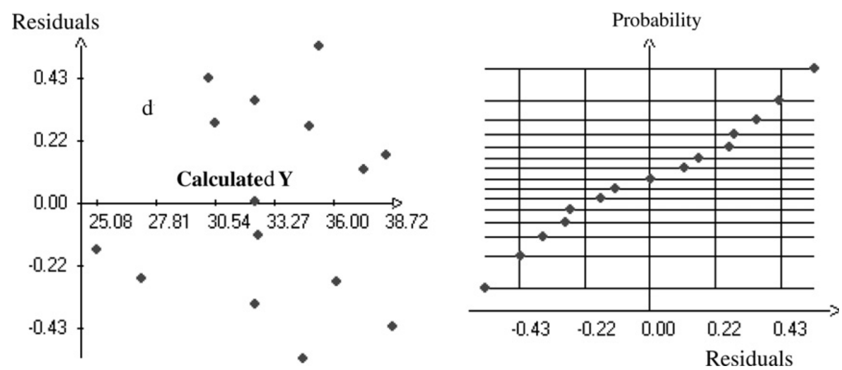

Fig. 5. Graphic study of the residues of the response y_1.

3.2.2.1. Isocontour plot analysis. The relationship between the responses and the experimental variables can be illustrated graphically by plotting the response values versus the levels of variables taken two at the time. The topography of these response surfaces also can be illustrated by isoresponse contour lines which represent lines of constant response represented on two variables plan. Such plots are helpful in studying the effect of the variation of the factors in the studied domain and consequently, in determining the optimal experimental conditions.

Figs. 6a–6c represents the response surfaces and isoresponse curves of y_1. It shows that the compressive strength at 7 days increases with the specific surface of the calcined clay (X_2) but decreases with increasing the percentage of calcined clay (X_3) in the blended cement (Fig. 6a). It can also be seen that the calcining temperature (X_1) has no sensible effect on y_1 (Figs. 6b and 6c). For this reason, in the following paragraphs, only the isocontours plots at 700 °C are discussed for the responses y_2 and y_3.

Response surfaces and isoresponse curves, obtained for y_2 and y_3 are respectively shown in Figs. 7 and 8.

From examining these figures, we note that the compressive strengths measured at, 28 and 91 days are improved essentially when the amount of calcined clay decreases and the specific surface of the burnt clay increases. Furthermore, by increasing the fineness of the calcined clay, it is possible to raise the level of replacement of cement by calcined clay. Indeed, if we compare the behaviour of the composition corresponding to the highest compressive strength (point A) to that of B which has approximately the same R_c but containing more calcined clay, we can state that cement B is economically more interesting than cement A. This choice is also supported by the fact that the calcined clay is easier to grind than clinker.

We can also notice, as pointed out by Wild et al. [20], that the specific surface influences the compressive strength at 7 and 28 days more than that of 91 days.

On the other hand, we have observed that increasing the percentage of calcined clay leads to lowering in the compressive strength because the studied clay contains a high fraction of quartz which acts as diluent. Indeed, Kostuch et al. [21] demonstrated that the feed clay (kaolin) should

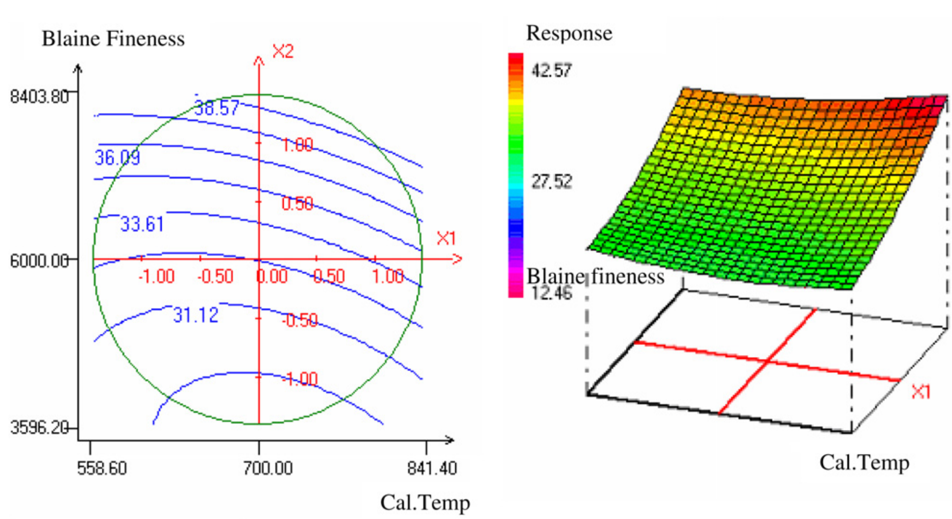

Fig. 6a. Isocontours and response surfaces of the response y_1 in the plan:Cal. temp., Blaine fineness. % Cal. clay = 20.00%.

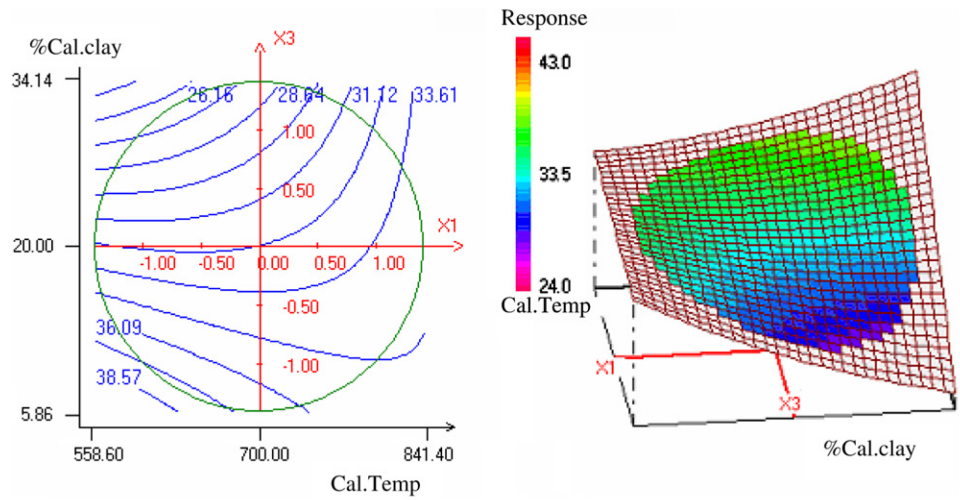

Fig. 6b. Isocontours and response surfaces of the response y_1 in the plan:Cal. temp., % Cal. clay. Blaine fineness = 6000 cm^2/g.

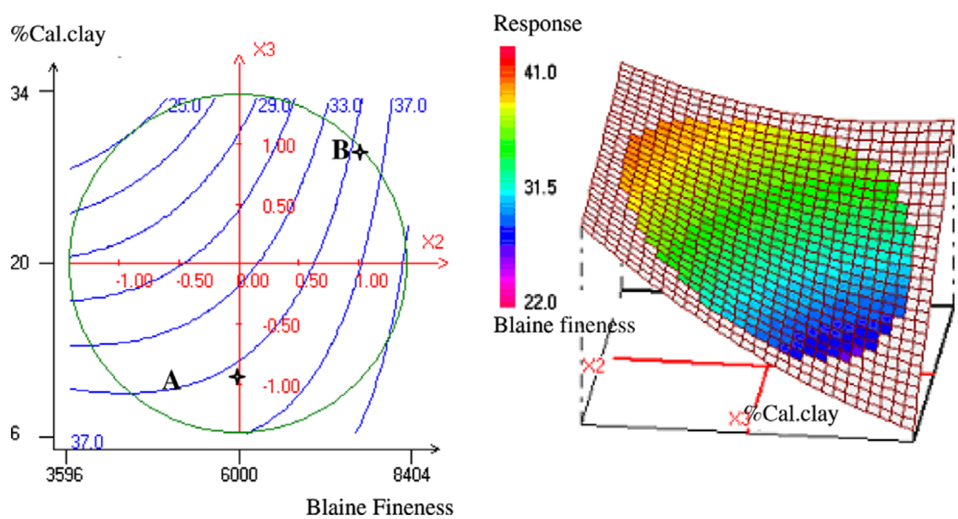

Fig. 6c. Isocontours and response surfaces of the response y_1 in the plan:Blaine fineness., % Cal. clay. Cal. temp = 700.00 °C.

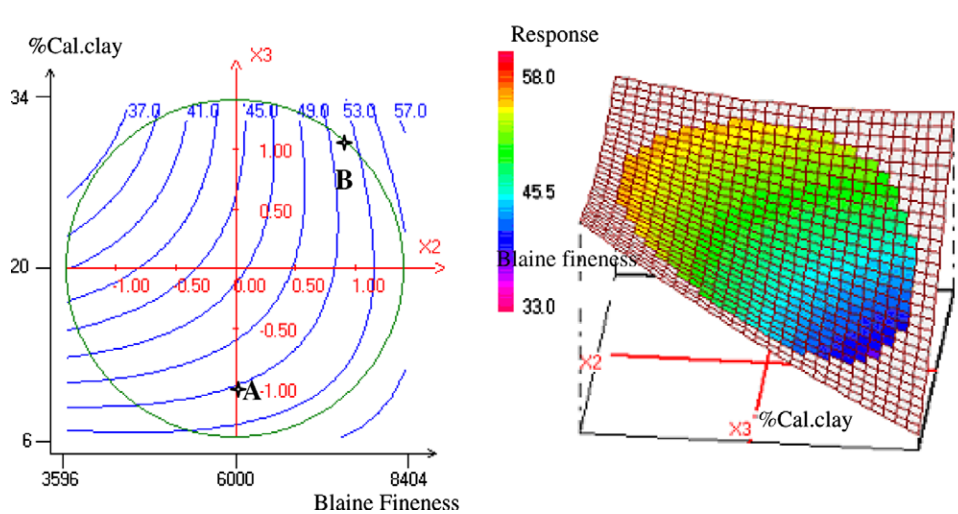

Fig. 7. Isocontours and response surfaces of the response y_2 in the plan:Blaine fineness., % Cal. clay. Cal. temp = 700.00 °C.

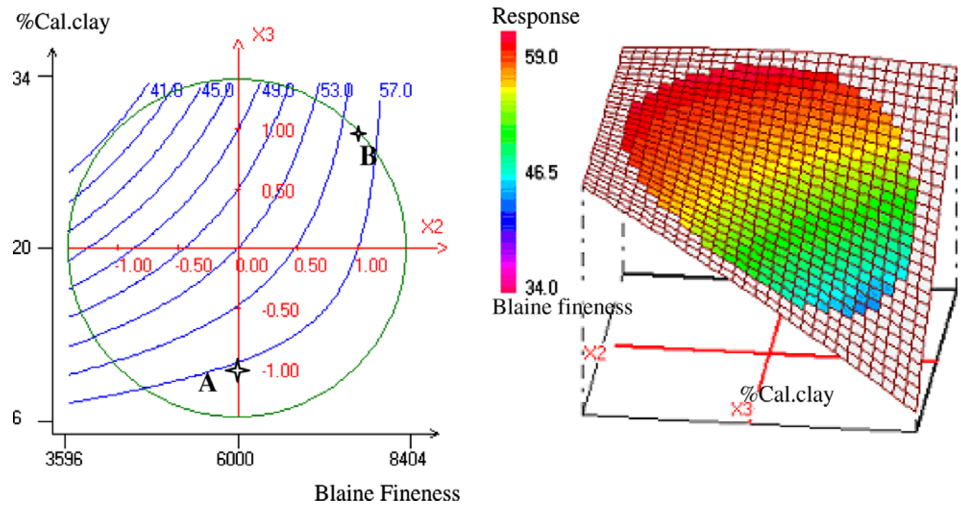

Fig. 8. Isocontours and response surfaces of the response y_3 in the plan:Blaine fineness., % cal. Clay. Cal. temp = 700.00 °C.

be either naturally pure or refined by standard mineral processing techniques, otherwise the impurities would act as diluent. To improve the compressive strength, especially those at early age, we intend to separate by physicochemical methods the clay from the silicious fraction.

3.2.2.2. Result confirmation. Optimal conditions ($X_1 = 0$, $X_2 = +1$, $X_3 = +1$) were verified experimentally and compared with the calculated data from the model. The measured responses, the predicted values and the standard deviation of the three responses are presented in Table 10.

The verification revealed a high degree of accuracy of the model of more than 99%, which is an evidence for the model validation under the investigated conditions.

To evaluate the influence of replacement of part of cement by calcined clay on its classical properties, the water demand for normal consistency, the setting time and the stability to expansion are measured for the optimal composition and compared to those of the reference cement (without any additions). The obtained results are presented in Table 11.

The comparison between the properties of the optimal blended cement and the reference cement shows that:

– The W/C ratio for normal consistency increases from 27% to 31% by adding the calcining clay. This phenomenon was pointed out by several authors [22]. It seems that the porosity and the fineness of the calcined clay are responsible for the increase of water demand.
– The calcined clay addition is responsible for an accelerating effect on the setting time, which remains in spite of everything in conformity with the European norms. This behaviour, observed by several authors [23], has been explained by the increasing of the rate of hydrolysis of clinker silicates and of the calcined clay aluminates [24].
– The blended cement shows a very low expansion. Similar results have been explained by the increase in calcium-silicate hydrate (C–S–H) content and changes to the C/S ratio of the C–S–H gel, as well as reduction in porosity of the microstructure and permeability [25].

Table 10
Predicted and measured responses at the optimum

	y_1 (MPa)	y_2 (MPa)	y_3 (MPa)
Predicted response	35.9	53.1	55.0
Measured response	36.2	53.7	54.5
Standard deviation	0.6	0.8	1.2

Table 11
Characteristics of the blended cements

Experiment	E/C of normal consistency (%)	Initial setting time (min)	Final setting time (min)	Expansion (mm)
Optimum	31	90	165	0.5
Reference	27	120	195	0.5

4. Conclusion

A local kaolinitic clay has been thermally activated and used as a pozzolan in a blended cement. The formulation of the latter has been achieved by setting up a Box–Behnken design with three factors namely: calcining temperature, specific surface of the calcined clay and the percentage of cement replacement. This study leads to the main following results:

- the mechanical properties of the blended cements are governed by the percentage of cement replacement and the fineness of the calcined clay,
- by increasing the fineness of the calcined clay, it is possible to increase the level of replacement of cement,
- the compressive strength decreases with increasing the percentage of calcined clay because the latter contains a high fraction of non-clay minerals which act as diluent,
- the optimum formulae can contain up to 30% of calcined clay provided that the specific surface of the clay is about 7700 cm^2/g.

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