OPTIMIZATION OF SAND WASHING WASTE AS POZZOLANIC MATERIAL

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ABSTRACT

Waste of sand washing collected from the region of Sfax in Tunisia is studied as artificial pozzolan in mortars. The chemical, physical and mineralogical properties of crude and calcined materials are well detailed for understanding its behavior.

The pozzolanic activity of the calcined waste product was tested and its fineness was optimized by using the strength activity index test.

The aim of this study is to investigate and optimize the properties of the blended cement and its paste and mortars in which calcined waste is employed as a pozzolan. In order to check the effect of three variables, (calcination temperature: X1, calcination time: X2 and % of calcined waste in the blended cement: X3) on the compressive strength of blended cement mortar at 28 and 90 days, a Box–Behnken design is set up. The compressive strength is governed especially by the calcination duration and the percentage of the calcined waste in the blended cement. Finally, a blended cement composition has been formulated and optimized. The optimized blended cement contains 30% of calcined waste, heated for 3 hours at a temperature of 650°C.

Keywords: *Waste of sand washing; Blended cement; Waste calcination ; Optimisation; Box–Behnken design.*

1. INTRODUCTION

Pozzolanic materials, like fly ash, slag and calcined clay are known for their improved long term strength and durability when added to cement (Al Rawas 2006 ; Barger 2001 ; Caldarone 1994 ; Chakchouk 2006 ; Coleman 1997 ; Frías 2012 ; Kolani 2012 ; Mensi 1993 ; Pandey 2003 ; Parande 2008 ; Ping 2013; Poon 2006 ; Samet 2004 ; Wild 1996).

Thermal activation of clay minerals, mainly kaolinite, generates highly pozzolanic products namely metakaolinite. Metakaolinite is a thermally activated alumino-silicate material obtained by calcining kaolin (Al Rawas 2006 ; Barger 2001 ; Caldarone 1994 ; Chakchouk 2006 ; Coleman 1997 ; Frías 2012 ; Mensi 1993 ; Paiva 2012 ; Pandey2003 ; Parande 2008 ; Poon 2006 ; Samet 2004 ; Wild 1996) within the temperature range 650–800 °C (Ambroise 1992 ; Poon 2006 ; Saad Morsy 1997 ; Samet 2007) to develop pozzolanic activity. It presents also a micro filler property but increase the water demand of the mixes (Curcio 1998).

Several studies have shown that different clay minerals such as illite, kaolinite, montmorillonite ... could play the role of pozzolan provided they are thermally activated at appropriate temperature (Ambroise 1986; Measson 1978; Mielenz 1950)

The substitution rate of cement by this type of pozzolan varies with different factors and the optimum can be proved by studying separately the effect of many variables, (e.g., calcining temperature, particle shape and size, calcinations time,) (Ambroise 1986; Bich 2005; Salvador 1995).

Treatment and washing silica sand in the region of Sfax (Tunisia) liberates significant based clay secondary product. While the washed sand is used for the preparation (batching and manufacturing) of quality concrete, the amounts of clay produced after washing sand are accumulated and cause a crucial problem of storage for the treatment plant. The use of this clay waste may be considered primarily for the manufacture of a pozzolan in mortars for conception and precast pipelines for sewage network of National Office of Sanitation.

This study is conducted by use of response surface methodology (Box 1978 ; Mathieu 1995 ; Montgomery 1996). For this, a Box–Behnken experimental design is set up to check the effect of three variables: calcination temperature, calcination time and percentage of calcined waste in the cement, on the mechanical properties and to optimize a blended cement formula (Goupy 1999).

2. RAW MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1. Raw materials

The blended cements prepared in this study are composed of the following raw materials:

- Portland cement: a typical commercial type CEM I 42.5 N.
- Calcined waste: obtained by heating waste collected from sand washing station. Its chemical composition is shown in table 1. The thermal treatment of the waste was carried out in a laboratory programmable furnace. The samples are heated from ambient to the desired temperature and held at the selected temperature during a certain time (calcination time). They are then quenched by air to ambient temperature. The calcined samples are stored in dry environment.
- Standard sand: it's an ISO graded sand which complies with the European standard EN-196-1 (EN 196-1, 1995).

Table 1: Chemical composition of the studied crude waste

Oxide	$\%SiO_2$	$\%Al_2O_3$	$\%Fe_2O_3$	$\%CaO$	$\%MgO$	$\%K_2O$	$\%SO_3$
Crude waste(%wt)	45.93	13.49	5.31	12.45	2.11	1.46	1.11

2.2. Sample preparation

All sample preparations were processed in a similar manner according to European Standard EN 196-1 (EN 196-1, 1995). Potable water was first introduced in the mechanical mixer. The dry mix solids (cement and calcined waste) were then added to the water solution and mixed for 30 s at low speed; sand was added and mixed for 30 s. Then, the mixing proceeds in a sequence of three steps: 30 s mix at high speed, 90 s in rest and 60 s mix at high speed. The mortars were cast into 4*4*16 cm molds for 24 h and cured with plastic sheet.
The specimens were demolded after 24 h and left in the moist curing room until compressive strength measurement.

2.3. Experimental techniques

Chemical composition of samples was determined by X-ray fluorescence (ARL 8400, software XRF 386). X-ray diffraction (XRD) was carried out to determine the mineralogical composition of the crude and calcined sample. X-ray diffractometer used in this investigation was a Brucker D8. The generator settings were 45 kV and 40 mA and the wavelength (λ) was 1.5418 Å (CuK). The scanning rate was 1° (2θ/min) from 5 to 60°. The crystalline phases were identified from the powder diffraction files (PDF) of the International Center for Diffraction Data (ICDD).
Thermal behavior of the waste was carried out by differential thermal analysis coupled with thermogravimetry (DTA/TG) by using SETARAM apparatus. The heating rate is 10°C/min and the reference material is alumina.
The compressive strength was determined by MATEST CYBER-PLUS EVOLUTION 50KN machine and the average value of three specimens is reported.

2.4. Methodology

The purpose of this work is to study the effect of three factors, namely calcination temperature of the waste (X1), its calcination time (X2) and its percentage in the blended cement (X3) 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) (Box 1978 ; Mathieu 1995 ; Mathieu ; Montgomery 1996). In order to achieve this purpose, 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:

$$\hat{Y}i = b_0 + b_1 X_{i1} + b_2 X_{i2} + b_3 X_{i3} + b_{11} X_{i1}^2 + b_{22} X_{i22} + b_{33} X_{i32} + b_{12} X_{i1}X_{i2} + b_{13}X_{i1}X_{i3} + b_{23}X_{i2}X_{i3}$$

Where

- X_{ij} is the value of the coded variable j at the i^{th} experiment
- b_j and b_{ij} are the model coefficients
- $\hat{Y}i$ is the calculated response value at the i^{th} experiment
- The measured response y_i for the i^{th} experiment is $y_i = \hat{Y}i + e_i$. (ei 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 19 experiments are carried out according to the Box–Behnken design shown in Table 2.

Table 2: Box–Behnken design for three variables

N°Exp	X1	X2	X3
1	-1.0000	-1.0000	0.0000
2	1.0000	-1.0000	0.0000
3	-1.0000	1.0000	0.0000
4	1.0000	1.0000	0.0000
5	-1.0000	0.0000	-1.0000
6	1.0000	0.0000	-1.0000
7	-1.0000	0.0000	1.0000
8	1.0000	0.0000	1.0000
9	0.0000	-1.0000	-1.0000
10	0.0000	1.0000	-1.0000
11	0.0000	-1.0000	1.0000
12	0.0000	1.0000	1.0000
13	0.0000	0.0000	0.0000
14	0.0000	0.0000	0.0000
15	0.0000	0.0000	0.0000
16	-0.4082	-0.2357	-0.1667
17	0.4082	-0.2357	-0.1667
18	0.0000	0.4714	-0.1667
19	0.0000	0.0000	0.5000

The graphical representation of the distribution of the experimental points is given in Figure 1. They correspond to 12 experiments at the middle of the edges of the experimental domain, 3 experiments at the centre and 4 point test. The experiments repeated at the centre of the domain (13–15 in Table2) permit to calculate an independent estimation of the pure experimental error variance.

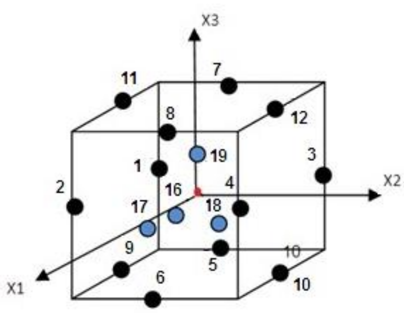

Figure1. Distribution of the experimental points in a three variable Box– Behnken design

NemrodW software (Mathieu 1995) 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:

- 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. Material characterization

3.1.1. Physico-chemical characterization

The X-ray fluorescence was conducted to determine the chemical composition of the crude sample which is reported in table 1. For the waste we notice that's an alumino-silicate material containing a high amount of SiO_2. In addition, this waste is rich in CaO with some Fe_2O_3.

The results of X- ray diffraction (figure 2) indicate that this material contains a fraction of clay mineral based on kaolinite and illite. X ray diffraction patterns reveal also the presence of associated minerals (quartz and calcite) in a high quantity indicating that the clay is not pure. Dolomite and muscovite are also present in the studied waste.

The diffractogram of heat treated specimen for 3 hours at 750°C is also presented in Figure 2. It contains only illite, calcite, quartz and traces of muscovite whose structures have not been altered by calcination.
The heating treatment causes the disappearance of the crystalline structure of kaolinite and the appearance of an amorphous phase, potentially reactive with $Ca(OH)_2$ of cement.

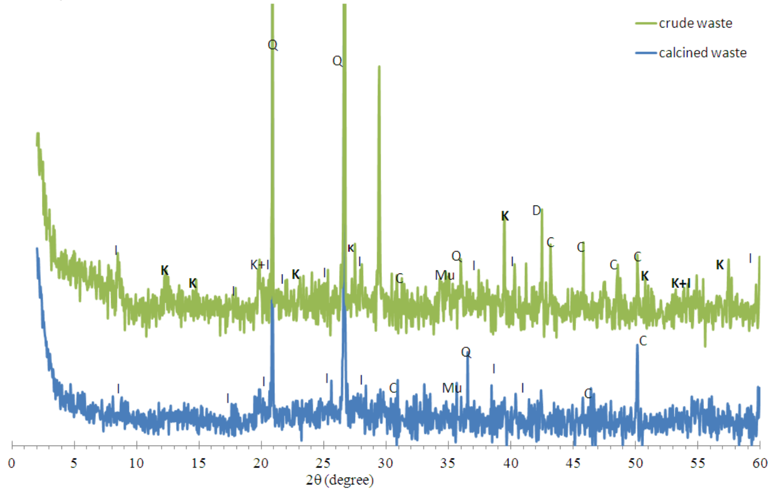

Figure 2: X-ray diffractogram of the waste product before and after calcination
k: kaolinite, I: Illite, Q: quartz, C:calcite, D: dolomite, Mu: Muscovite

3.1.2. Thermal characterization

DTA and TGA were carried out on the waste sample using a heating rate of 10°C/min. These techniques were merely used as complementary methods with respect to the other techniques. The interpretation (Brindley 1959; Mackenzie 1970 ; Taylo 1969) of the DTA-TGA curves of the crude samples leads to the following results (Fig. 3):

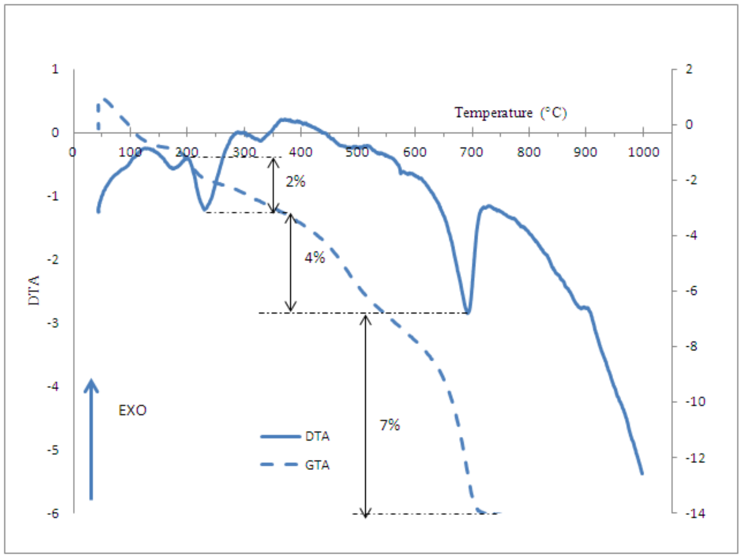

Figure 3: Thermogram DTA/GTA of the waste

- A small endothermic peak between 120 and 180°C accompanied by 1% weight loss. This transformation is due to the removal of adsorbed and interlayer water from the clay mineral.
- An endothermic phenomenon between 240 and 320°C accompanied by a weight loss of 2% attributable to muscovite or decomposition of the organic material
- An endothermic phenomenon between 520 and 540°C which correspond to the loss of hydroxyl groups from the clay mineral structure (clay dehydroxylation) which correspond to a weight loss of 4% due to the removal of combined water of kaolinite. This value has been exploited to estimate the kaolinite content to 28%.
- An endothermic phenomenon between 600 and 700°C with a weight loss of 7% is attributed to carbonate dissociation.
- An exothermic peak around 930°C without any weight loss is relative to structural reorganization of métakaolin (Jouenne 1984).

We remind that the pozzolanic activity is obtained when the clay is heated at a temperature between the end of dehydroxylation and the beginning of recrystallization (Al Rawas 1998).

3.2. Preliminary tests

Preliminary tests are carried out in order to select the fineness of the calcined waste that induces a pozzolanic behavior. For this, different blended cements containing 80% Portland cement and 20% ground calcined waste, with different finenesses, are prepared and checked for their compressive strengths on mortar bars at 28 days. The compressive strength of each batch is an average of three tests. The maximum standard deviation of all the tests was 10%. Results are compared to those of a control mortar (100% Portland cement). The pozzolanic activity is evaluated using the strength activity index (SAI) defined as (ASTM C 311 – 02):

$$\text{Strength Activity Index (SAI)} = (A/B)^* \, 100$$

Where Aand B are the average compressive strength of blended and control cement mortar bars respectively. The strength activity indexes of control mortars and mortars containing pozzolan are shown in Figure 4.

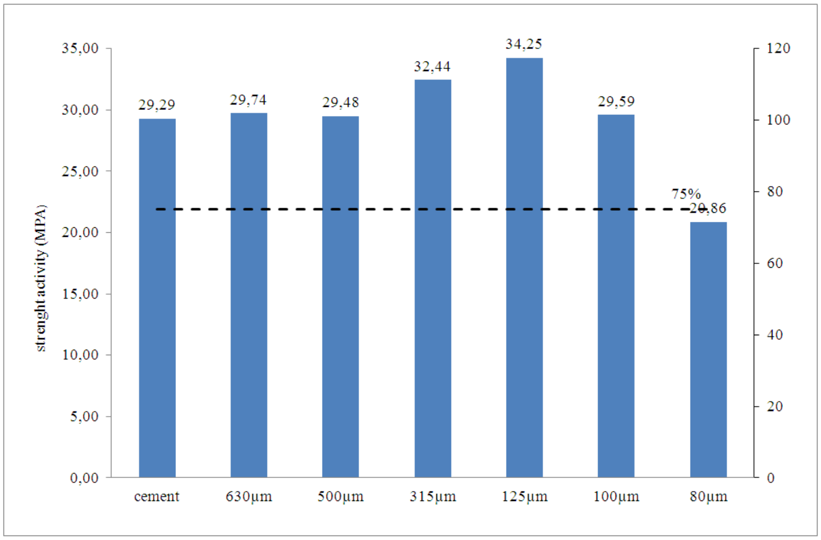

Figure 4: Evolution of compressive strength and strength activity index versus and fineness of calcined waste

Taking into account ASTM norm (C618-02) (ASTM C 618 – 02) which recommends a minimum strength activity index of 75% for a pozzolanic material, it appears that:

- Compared to reference mortar (containing pure cement), the compressive strength of mortars made with blended cement (80% Portland cement, 20% ground calcined waste) is improved except the specimens containing calcined waste ground at a fineness of 80µm
- The pozzolanic activity is improved by increasing the grinding fineness but it seems that with the finenesses 100 and 80µm, some agglomeration occurs, which reduces the contact surface between the water and the waste during the mixing. Consequently the strengths of the corresponding mortars decrease. The highest compressive strength is developed with wastes ground at 125µm. Thus, for the rest of this study, the waste will be ground at 125µm.

3.3. Optimization of blended cement formula

This work is especially aimed to the formulation of blended cement by adding calcined waste. The quality of the prepared cements is assessed by the measure of the compressive strength responses at 28, and 90 days noted y1, and y2 respectively.
The explored experimental domain and the levels attributed to each variable are shown in Table 3.

Table 3: variables and experimental domain

Variables	Level		
	-1	0	+1
X1: calcination temperature (°C)	600	700	800
X2: calcinations time(h)	3	4	5
X3: percentage of calcined clay in the blended cement (%)	10	20	30

3.3.1. Matematical models

The observed responses (table 4) are used to compute with Nemrod software the model coefficients using the least square method (Carlson 1992 ; Mathieu 1996; Montgomery 1991). This allows us to write the resulting estimated models

$$Y_1 = 36.996 - 1.711X_1 + 0.583X_2 - 3.095X_3 - 5.383X_1^2 + 1.310X_2^2 - 0.734X_3^2 - 1.212X_1X_2 - 1.506X_1X_3 - 0.553X_2X_3$$

$Y_2 = 39.361 - 1.484X_1 - 0.824X_2 - 2.044X_3 - 3.265X_1^2 - 0.273X_2^2 - 0.525X_3^2 + 1.469X_1X_2 - 3.425X_1X_3 - 3.266\ X_2X_3$

Table 4: Box–Behnken design and the measured responses

N°Exp	Temperature (°C)	Calcination time (hour)	% substitution (%)	Y1(MPa)	Y2(MPa)
1	600	3.0	20.00	33.9	39.9
2	800	3.0	20.00	30.0	35.1
3	600	5.0	20.00	38.1	33.6
4	800	5.0	20.00	29.5	34.7
5	600	4.0	10.00	32.1	38.6
6	800	4.0	10.00	34.2	41.5
7	600	4.0	30.00	30.6	36.4
8	800	4.0	30.00	26.7	25.6
9	700	3.0	10.00	40.8	34.7
10	700	5.0	10.00	42.0	41.5
11	700	3.0	30.00	34.1	42.2
12	700	5.0	30.00	33.2	35.8
13	700	4.0	20.00	38.2	38.2
14	700	4.0	20.00	35.1	38.9
15	700	4.0	20.00	35.8	39.7
16	659	3.8	18.33	35.9	40.5
17	741	3.8	18.33	36.8	38.9
18	700	4.5	18.33	39.7	39.6
19	700	4.0	25.00	35.3	38.5

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

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

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

The calculated values of this coefficient for the two responses, presented in Table 5, indicate a good degree of correlation between the experimental and the predicted values. The analysis of variance (ANOVA) for these models carried out using NemrodW, are shown in Tables 6–7. These tables show how the total calculated sum of squares are distributed among the different sources of variations (Carlson 1992 ; Mathieu 1996)
As it can be seen, the regression sums of squares are statistically significant. The evaluations of the residual sum of squares with 9 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 both fitted models.

Table 5: Correlation coefficients of the regressions

Responses	Y1	Y2
R^2	0.883	0.771

Table 6: Analysis of variance of response Y1

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F ratio	Significance
Regression	256.9641	9	28.5516	7.5802	0.294 **
Residuals	33.8992	9	3.7666		
Total	290.8633	18			

** Significant at 99%

Table 7: Analysis of variance of response Y2

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F ratio	Significance
Regression	206.3778	9	22.9309	3.3715	4.23 *
Residuals	61.2118	9	6.8013		
Total	267.5896	18			

* Significant at 95%

To confirm the adequacy of the models, we compare the calculated and the measured responses of four test points (Table 8). The standard deviations of the responses y_1 and y_2, evaluated by the replication of four runs carried out at the centre of the domain, are $\sigma_{y1} = 1.6$ and $\sigma_{y2} = 0.6$ MPa respectively.
Results of these tests allow us to validate the two models

3.3.2. Model exploitation

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. 5, 6 and 7 represent the response surfaces and isoresponse curves of Y1. First, we notice that the pozzolanic reactivity of the calcined waste is relatively low because it was not ground to a high fineness. Curcio et al. (Curcio 1998) proved that coarse metakaolin gives relatively low strength at early ages, but better compressive strength at 90 days due to the low pozzolanic activity.

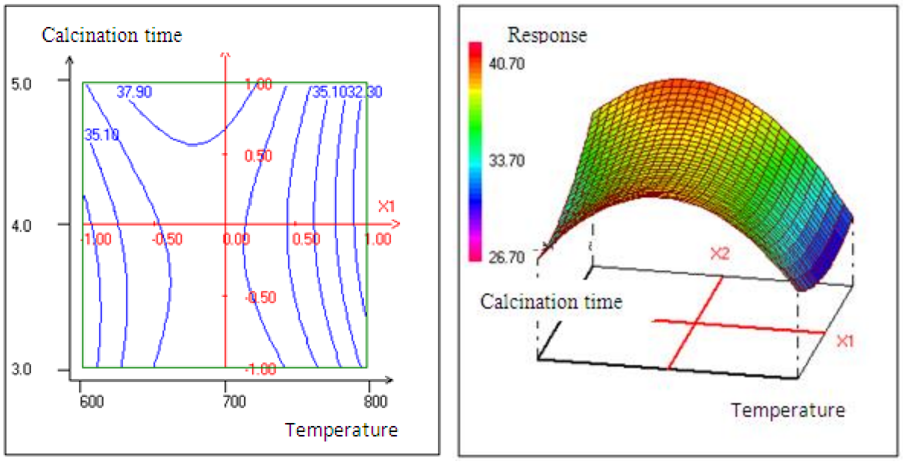

Figure 5: Isocontours and response surfaces of the response Y1 in the plan Temperature, duration of calcination
% of calcined clay in the mortar =20%

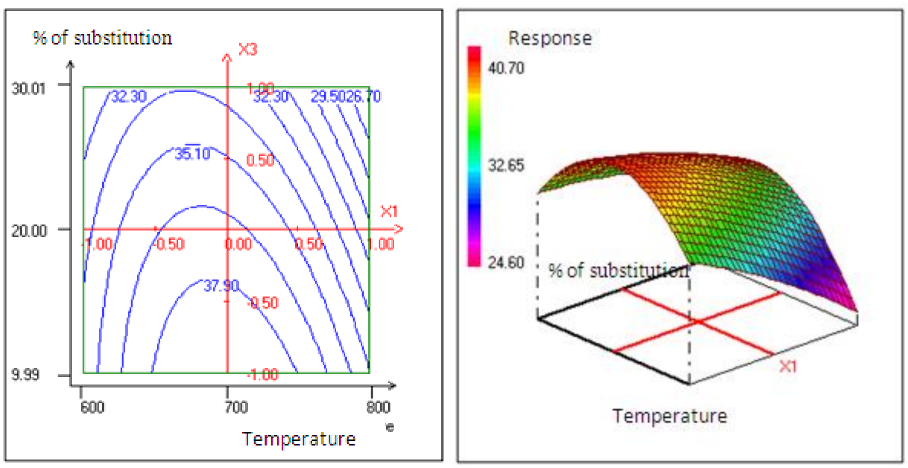

Figure 6: Isocontours and response surfaces of the response Y1 in the plan Temperature, % of calcined clay in the mortar
Duration of calcination, =4 hours.

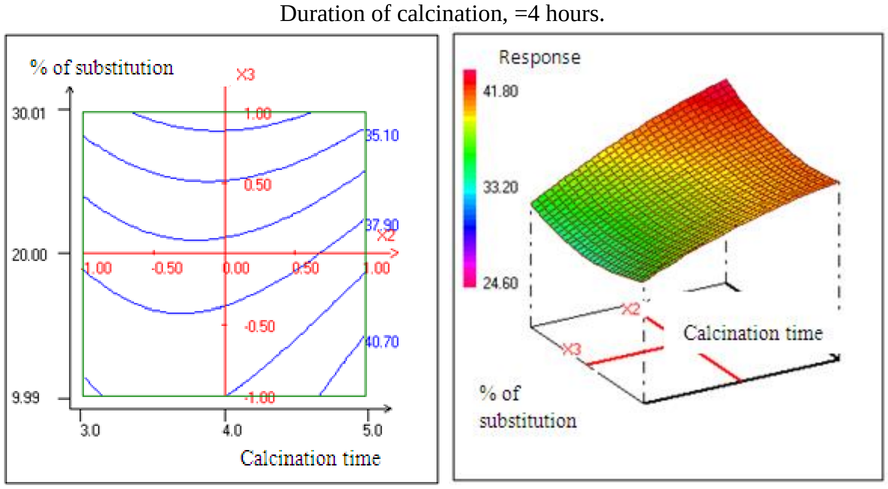

Figure 7: Isocontours and response surfaces of the response Y1 in the plan duration of calcination, % of calcined clay in the mortar, Temperature = 700°C.

Figs 5, 6 and 7 also show that the compressive strength at 28 days increases slightly with increasing calcinations time (X2), but decreases with increasing the percentage of calcined clay (X3) in the blended cement (Fig. 7). It can also be seen that the optimum of calcining temperature (X1) is slightly below the center point (≈680°C).

For the compressive strength at 90 days, the isoresponse curves (figs. 8-10) show that this response increase by increasing the calcination temperature until 680°C, by reducing the calcination time and the percentage of calcined waste in the blended cement. The Rc90 is maximum (40,6MPa) for a calcination temperature of 650°C, a calcination time of 3 hours and a percentage substitution about 20% (point M in fig.8).

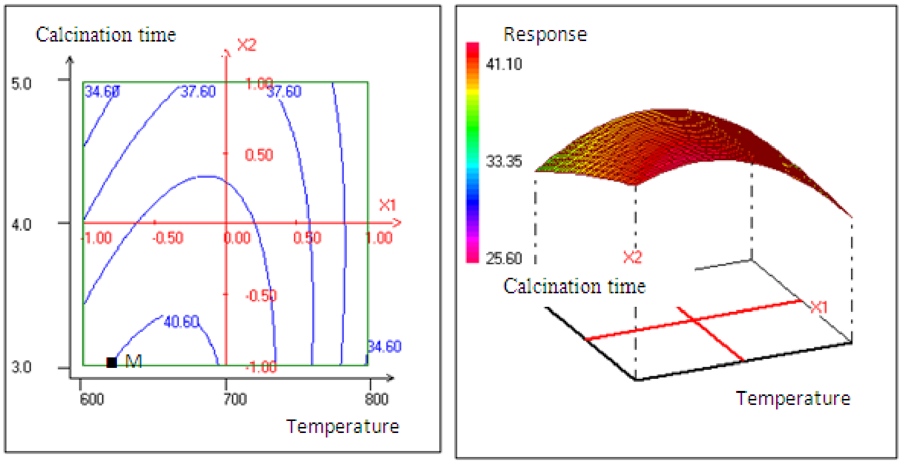

Figure 8: Isocontours and response surfaces of the response y2 in the plan Temperature, duration of calcination % of calcined clay in the mortar =20%.

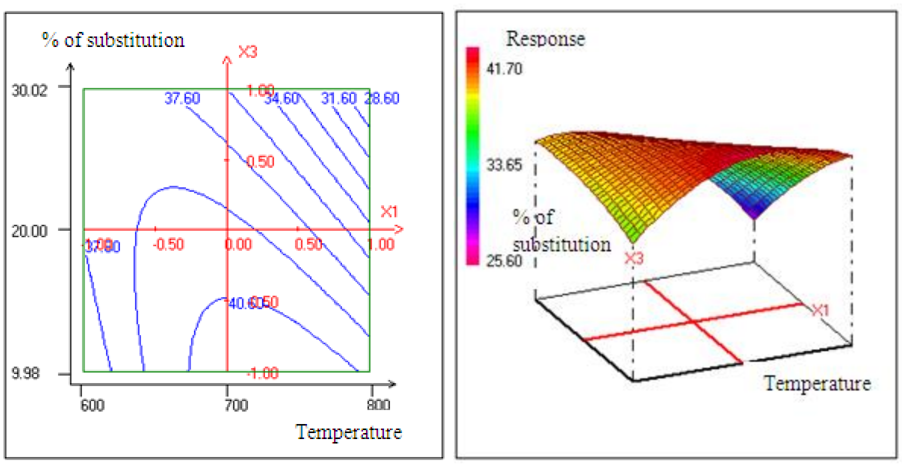

Figure 9: Isocontours and response surfaces of the response y2 in the plan Temperature, % of Calcined clay in the mortar, duration of calcination =4 hours.

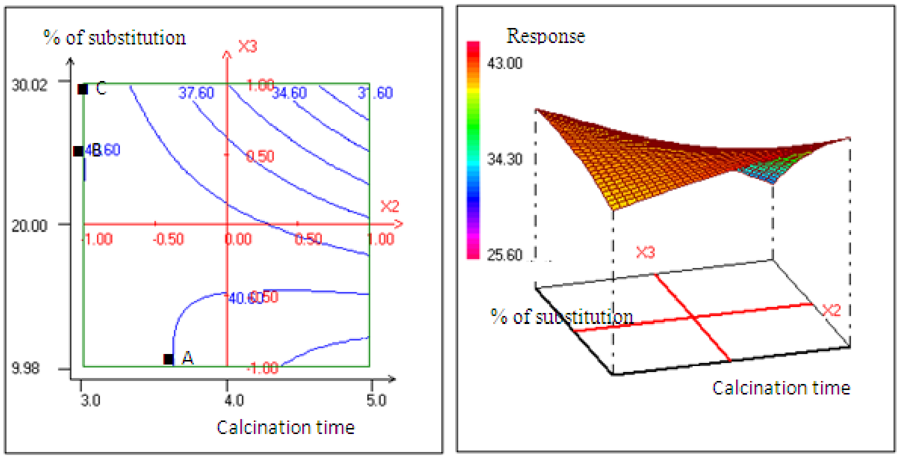

Figure10: Isocontours and response surfaces of the response y1 in the plan calcination duration, % of Calcined clay in the mortar, Temperature = 700°C

Furthermore, at the same calcination temperature, at 700°C (fig. 10), it is possible to raise the level of replacement of cement by calcined clay. This can be demonstrated by the comparison of the behavior of the two blends A (containing 10% of calcined waste, y_2= 40.6 MPa) and B (containing 27% of calcined clay y_2= 40.6 MPa). Cement B, which contains more calcined clay as cement replacement, is economically more interesting than cement A for the same compressive strength.

In addition, a slightly lower compressive strength (≈40MPa) can be obtained with cement C which contains 30% of calcined waste.

4. CONCLUSIONS

Waste of sand washing from the region of Sfax region is a high industrial discharge. Its valorization interests many research. In this study, it is tested as a pozzolanic material. After its physicochemical characterization, the waste was used as a pouzzolan in order to formulate blended cement. The optimization of the latter has been achieved by setting up a Box–Behnken design with three factors namely: calcination temperature, calcination time 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 fineness of the calcined waste and the optimum fineness is 125µm. For finer particles, agglomeration leads to the decrease of the pozzolanic activity.
- At 90days, the compressive strengths are improved essentially when the amount of calcined clay in the blended cement increases and the calcinations time decreases.
- the optimum formulae can contain up to 30% of calcined waste treated at 650°C for 3 hours

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