Pergamon

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 34 (2004) 1153–1159

CEMENT AND CONCRETE RESEARCH

Characterization of the Tunisian blast-furnace slag and its application in the formulation of a cement

Basma Samet*, Moncef Chaabouni

Laboratoire de Chimie Industrielle, Ecole Nationale d'Ingénieurs de Sfax, BP W 3038, Sfax, Tunisia

Received 22 July 2003; accepted 1 December 2003

Abstract

The Tunisian blast-furnace slag has been characterized by several physicochemical methods to evaluate its hydraulic reactivity. It has been noted that nearly all the slag is glassy, so its use as a replacement of cement is possible.

This result has been confirmed by different physical tests applied to blended cements as specific surface, normal consistency, setting time, stability to expansion and the minislump.

Finally, a slag cement composition has been formulated and optimized using a mixture design. The optimized formula giving the maximum of compressive strength at 7 and 28 days was 61% clinker, 35% slag, 3% gypsum, and 1% limestone.

Keywords: Cement; Granulated blast-furnace slag; Mixture design; Optimization; Compressive strength

1. Introduction

The blast-furnace slag is a mineral by-product of the iron industry. Its use as a constituent of concrete and cement dates up to more than 100 years [1].

When added to cement, the ground granulated blast-furnace slags (GGBFS) combine with the portlandite (CH) released by cement hydration to give calcium silicate hydrate (C-S-H). This step is activated by alkali salts, which increase the reaction rate.

Although many characteristics of the concrete containing GGBFS are still being discussed, such as creep, shrinkage, resistance to freezing and thawing, the use of the blast-furnace slag in cement and concrete presents many advantages [2]. Indeed, most of the fresh and hardened concrete properties are improved by the addition of GGBFS [3–5]. On the other hand, the use of the slag as a replacement of cement is economical and ecological [6].

The Tunisian slag (from El Fouledh plant) has not been studied as a partial substitute for the Portland cement. Thus, this work is aimed to characterize the local slag by physical and chemical methods, then to formulate cement where the clinker is partially replaced by slag.

The optimization of the slag cement composition is achieved by performing a mixture design.

2. Experimental techniques and methodology

2.1. Raw materials

Cements prepared in this study are composed of four raw materials: clinker, slag, gypsum, and limestone.

Slag: The used slag is a by-product of the "Societe Tunisienne de Siderurgie." It is obtained by quenching the layer floating on the pool of iron in the blast furnace with water. It looks like a coarse sand having a light color and a porous aspect. Its chemical analysis by X-ray fluorescence is presented in Table 1.

Clinker: The clinker is produced at Gabes plant by a dry process. Its chemical and mineralogical compositions are presented in Table 2.

Limestone and gypsum: The former is used as a filler and the latter is added as a set regulator to clinker before its grinding. The chemical analysis of these minerals is presented in Table 3.

* Corresponding author. Tel.: +216-74-276-400; fax: +216-74-274-437.

E-mail address: basma.samet@fss.rnu.tn (B. Samet).

0008-8846/$ – see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2003.12.021

Table 1
Chemical analysis of the slag

Component	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	TiO	MnO	Na_2O	SO_3
Weight percent	29.34	32.82	15.74	1.62	5.12	2.25	0.14	3.23	0.13	1.05

Table 3
Chemical analysis of limestone and gypsum

	CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	SO_3	Total	LOI
Limestone	48.4	5.55	0.63	0.4	0.17	1.88	56.84	40.04
Gypsum	33.51	4.94	0.84	0.51	0.27	24.54	64.62	30.30

2.2. Experimental techniques

Each cement sample is prepared separately by dosing and then grinding together in a rotary ball mill with a capacity of 6 kg its different components (clinker, slag, limestone, and gypsum) to a constant fineness (25% refusal on a 40-μm sieve).

The different cements are analyzed by X-ray fluorescence (ARL 8400). Their specific surface is measured by Blaine method (EN 196-6). The normal consistency, the setting times, and the stability to expansion are determined according to the European EN 196-3 norm. We remind that the stability to expansion is determined by measuring the expansion of a normal cement paste contained in a Lechatelier apparatus. The measure consists in determining the difference of the distance between two needles fixed to a cylindrical mould containing the sample before and after curing in boiling water during 3 h (EN 196-3 norm).

The rheological behavior is assessed by the minislump test [7]. Finally, the mechanical properties are determined on mortar bars in compliance with the EN 196-1 norm.

2.3. Methodology

The purpose of this work is to study the effect of four component proportions (X_j) on the compressive strengths of the Tunisian slag-based cement to optimize its composition.

Mixture designs are among the most widely used tools for product formulation. They allow modeling the blending surface with some form of mathematical equation so that predictions of the response for any mixture of the ingredients can be made empirically. We choose a second-order mixture model that takes the following canonical form because of the restriction $\Sigma X_j = 1$:

$$Y_i = \hat{Y}_i + e_i = \Sigma b_j X_j + \Sigma b_{jk} X_j X_k + e_i$$

where Y_i is the response value measured at the ith experiment, e_i is the standard deviation, and $\hat{Y}_i$ is the calculated response value at the ith experiment.

To fit the 10-term second-order model, a set of candidate points in the design space is selected using the D-optimal criterion.

In this study, there are restrictions on the component proportions X_j that take the form of lower (L_j) and upper (U_j) constraints as follows:

$$L_j \leq X_j \leq U_j$$

The effect of these upper and lower bound restrictions is to limit the feasible space for the mixture design to a subregion of the original tetrahedron that becomes an irregular convex polyhedron.

A D-optimal design with 43 candidate points has been selected by Nemrod-W software [8], which also generated diagrams of the variance of the predicted responses versus the number of experiments. These plots allow us to choose the number of experiments to be effectively carried out. In this work, only 23 experiments have been retained to be performed.

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

– fit the empirical model
– test the adequacy of the fitted model
– plot the contours of the predicted responses.

3. Results and discussion

3.1. Slag characterization

3.1.1. Granular analysis

The granular distribution of a crude dried sample at 110 °C for 24 h, determined by sieving, is presented in Fig. 1.

It can be noticed that the particle size ranges from 0.1 to 3 mm, which is comparable to a coarse sand.

The apparent density of the slag is $d_{ap} = 0.862$, whereas its real density is $d_r = 2.84$ and its water content is 11.95%. Although the Tunisian slag is amorphous, it presents a high porosity proved by its light color [6] and the deviation between its apparent and real densities. In addition, the slag appears to be spongy by visual examination.

3.1.2. Assessment of the hydraulic reactivity

The hydraulic reactivity of the slag depends on many factors, which are chemical composition, glass content, and

Table 2
Chemical and mineralogical analysis of clinker

	Chemical composition							Bogue composition			
Component	CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	SO_3	others	C3S	C2S	C3A	C4AF
Weight percent	68.67	22.18	3.97	2.66	0.24	0.30	1.98	77.6	5.13	6.03	8.09

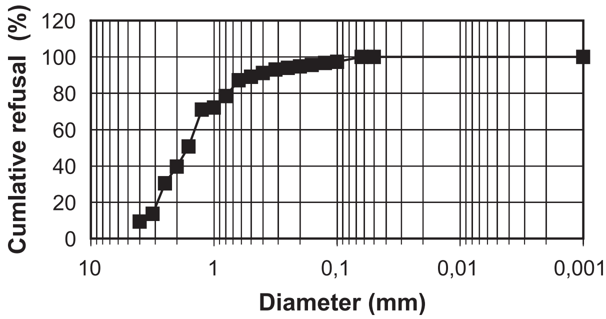

Fig. 1. Granular distribution of the crude slag.

fineness of the ground slag. Due to the complexity of the influencing factors, it is not surprising that earlier, many attempts have been done to relate the hydraulic quality of slag to simplified chemical modules, such as

- F1 = CaO/SiO_2
  if F1 ≤ 1, the slag is said to be acid and its hydraulicity is low
  if F1 ≥ 1, the slag is basic and its hydraulic reactivity is good [6]
- F2 = $CaO + MgO + Al_2O_3/SiO_2$
  this ratio must be higher than 1 [6].
- F3 = $(CaO + CaS + 1/2MgO + Al_2O_3)/(SiO_2 + MnO)$
  The reactivity of slag is good if the ratio F3 is higher than 1.5 [9].

The European standard requires that

- F4 = $CaO + MgO/SiO_2 \geq 1$
- F5 = $CaO + MgO + SiO_2 \geq 2/3$ of the slag weight
- The glassy phase must represent at least two-thirds of the slag.

In the case of the Tunisian slag, the values of these ratios are presented in Table 4.

These data do not allow us to predict with assurance the hydraulic reactivity of the Tunisian slag, that is why the sample is analyzed by X-ray diffraction to determine the proportion of the glassy phase in the slag.

3.1.3. X-ray diffraction analysis

The X-ray diffraction analysis of a slag sample is presented in Fig. 2. It shows a dome centered approximately at $2\vartheta = 32°$ corresponding to the diffraction of the glassy mellilite [10] and a very sharp peak due to the presence of quartz. This allows us to conclude that the whole slag is almost glassy and therefore we can expect a good reactivity.

Table 4
Chemical modules of slag

Module	F1	F2	F3	F4	F5
Tunisian slag	0.89	1.52	1.32	1.05	67.28%
Required limit	≥ 1	≥ 1	≥ 1.5	≥ 1	≥ 66.6%
Hydraulic reactivity	acid slag	good	moderate	good	good

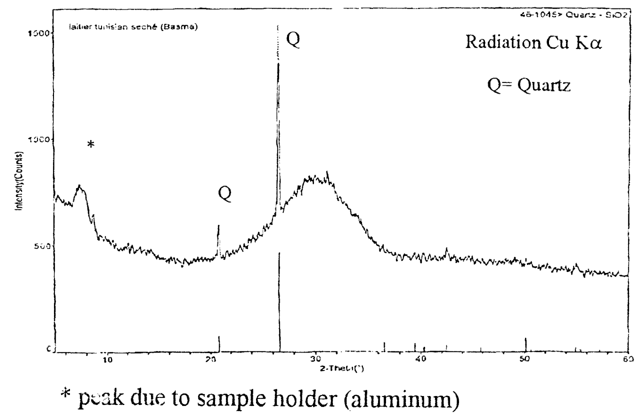

Fig. 2. X-ray diffractogram of slag.

3.2. Preliminary study of some slag cements

To determine the influence of the replacement of a part of the clinker by slag, some mixtures are prepared (Table 5) and studied (Table 6).

Table 5
Composition of some slag cements

Cement	Clinker (%)	Slag (%)	Gypsum (%)	Limestone (%)
A	0.770	0.200	0.030	0.000
B	0.620	0.350	0.030	0.000
C	0.820	0.050	0.030	0.100
D	0.710	0.160	0.030	0.100

Table 6
Characteristics of some slag cements

Cement	Specific surface (cm^2/g)	E/C of normal consistency	Initial setting time	Final setting time	Expansion (mm)	Diameter (mm)[a]
A	3310	0.27	2 h, 20 min	3 h, 25 min	1	112
B	2900	0.275	2 h, 35 min	3 h, 40 min	0.5	122
C	3118	0.255	2 h, 10 min	3 h, 10 min	2	110
D	2860	0.26	2 h, 35 min	3 h, 40 min	1.5	116

[a] Diameter of the grout measured according to minislump test.

Table 7
Experimental domain

X_j	L_j (lower constraint)	U_j (upper constraint)
X_1: % Clinker	60	92
X_2: % Slag	5	35
X_3: % Gypsum	3	7.5
X_4: % Limestone	0	10

Table 8
Mixture design and the measured responses

Experiment no.	Clinker (K)	Slag (S)	Gypsum (G)	Limestone (C)	y_1 (MPa)	y_2 (MPa)
1	0.9200	0.0500	0.0300	0.0000	42.8	27.5
2	0.8750	0.0500	0.0750	0.0000	44.0	30.3
3	0.8200	0.0500	0.0300	0.1000	44.7	33.5
4	0.7750	0.0500	0.0750	0.1000	44.0	30.3
5	0.6200	0.3500	0.0300	0.0000	43.4	24.7
6	0.6000	0.3500	0.0500	0.0000	38.4	24.0
7	0.6000	0.3250	0.0750	0.0000	38.0	22.0
8	0.6000	0.2700	0.0300	0.1000	39.5	27.6
9	0.6000	0.2250	0.0750	0.1000	36.0	22.2
10	0.8975	0.0500	0.0525	0.0000	44.5	28.7
11	0.8700	0.0500	0.0300	0.0500	45.0	33.2
12	0.7700	0.2000	0.0300	0.0000	45.0	28.9
13	0.8250	0.0500	0.0750	0.0500	43.7	32.6
14	0.7375	0.1875	0.0750	0.0000	40.6	25.9
15	0.7975	0.0500	0.0525	0.1000	41.2	32.0
16	0.7100	0.1600	0.0300	0.1000	44.4	33.6
17	0.6100	0.3500	0.0300	0.0100	47.1	29.7
18	0.6000	0.2750	0.0750	0.0500	37.8	22.2
19	0.6000	0.3100	0.0300	0.0600	38.9	27.2
20	0.6000	0.2475	0.0525	0.1000	36.2	23.5
21	0.8475	0.0500	0.0525	0.0500	40.3	32.0
22	0.7230	0.2250	0.0520	0.0000	41.5	26.5
23	0.7010	0.2070	0.0500	0.0420	37.5	26.5
24	0.7010	0.2070	0.0500	0.0420	39.4	26.5
25	0.7010	0.2070	0.0500	0.0420	37.8	26.5
26	0.7010	0.2070	0.0500	0.0420	40.0	27.5

Table 9
Analysis of variance of the response y_1

Source of variation	Sum of squares	Degree of freedom	Mean square	Ratio	Significance
Regression	205.8439	9	22.8715	8.7974	***
Residuals	41.5970	16	2.5998		
Validity	(37.1695)	(13)	2.8592	1.9373	31.9%
Error	(4.4275)	(3)	1.4758		
Total	247.4409	25			

*** Significant at 99.99%.

3.2.1. Specific surface

All the cements are ground at a constant 40 μm refusal: 25 ± 2%. The Blaine fineness range from 2860 to 3310 cm^2/g. Globally, we note that the specific surface decreases when the slag proportion increases (Table 6). This proves that the slag is harder to grind than the clinker.

3.2.2. Normal consistency

The W/C ratio has been varied between 0.255 and 0.275. We note that the water demand increases with the slag replacement proportion in the cement (Table 6). This phenomenon was observed by several authors [11]. It seems that the high porosity of the slag is responsible for the increase of water demand.

3.2.3. Setting time

Table 6 clearly shows that the slag addition is responsible for a retarding effect on the setting time, which remains in conformity with the European norms.

This behavior can be easily explained as follows: It is known that the addition of slag to cement generally increases the setting time. This retarding effect is more pronounced in the absence of activators (alkali or calcium ions). In our case, the moderate retarding effect is related to a low level of alkali (0.24%) made good by a high concentration in calcium (68.67%) in the clinker (Table 2).

3.2.4. Stability to expansion

The addition of slag is apparently very effective in retarding expansion and this effectiveness is especially clear with a slag content >30% (Table 6). This can be explained by the fact that increasing the slag content reduces the C/S ratio. Several studies show that a C-S-H of a low C/S blend appears less crystalline than in Portland cement. This phenomenon leads to a high dense structure that is very effective in retarding expansion. This behavior is pronounced by the fact that the slag cement is lower in portlandite than the Portland cement.

3.2.5. Rheological behavior

The rheological behavior has been studied using the minislump test [7]. Replacing part of clinker content by slag has increased the plasticity of cement grout samples.

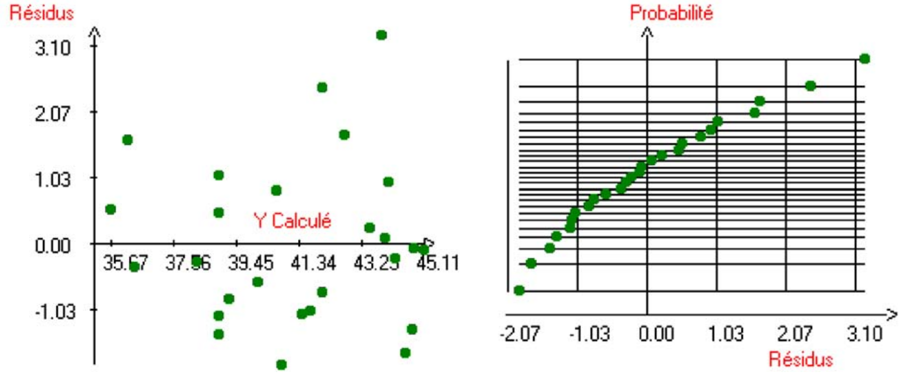

Fig. 3. Graphic study of the residues.

Table 10
Validation of the model

Test point	$\hat{Y}$ calculated (MPa)	Y measured (MPa)
Test 1	40.7	39.7 ± 1.6
Test 2	37.9	39.1 ± 1.6

This phenomenon has been explained by the fact that replacing a certain fraction of clinker by slag, which is less reactive, reduces the amount of ettringite developed during the early hydration and results in higher plasticity of the cement.

3.3. Optimization of cement slag formulation

This work is especially aimed to the formulation of a slag cement product. The quality of the prepared cements is assessed by the compressive strengths at 7 and 28 days noted, which are R_{c_7} and $R_{c_{28}}$, respectively.

To limit the number of experiments and to lead rapidly to the optimal formula, we apply the mixture design methodology [12] to four components, namely, clinker, slag; gypsum, and limestone.

An experimental domain without any constraint is a regular tetrahedron, in which the vertices represent the pure components. It is evident that the domain must be reduced because it is not logical to explore the characteristics of the pure components.

The explored experimental domain expressed in terms of mixture proportions X_j is shown in Table 7:

To satisfy the D-optimal criterion, the software Nemrod-W [8] selected 43 candidate points of the mixture space. These points are extreme vertices, midpoints of the edges, centroids of the faces, and some points from the interior of the experimental domain. The 23 experimental points (selected based on the diagram of the variation of the predicted variance versus the number of experiments) and the corresponding responses are shown in Table 8.

Table 11
Analysis of variance of the response y_2

Source of variation	Sum of squares	Degree of freedom	Mean square	Ratio	Significance
Regression	297.2101	9	33.0233	21.8549	***
Residuals	24.1764	16	1.5110		
Validity	(23.4264)	(13)	1.8020	7.2081	6.6%
Error	(0.7500)	(3)	0.2500		
Total	321.3865	25			

*** Significant at 99.99%.

Point 18 is the center of the domain. The last three experiments represent its replication for the experimental error evaluation.

Two responses, y_1 and y_2, are measured:

$-y_1$: compressive strength at 28 days in MPa
$-y_2$: compressive strength at 7 days in MPa.

3.3.1. Study of the response y_1: compressive resistance at 28 days

Fitted to 23 response values in Table 6, the second-order model for the response y_1 is presented by the following equation:

$$\begin{aligned} y_1 = {} & 53.916x_1 + 57.173x_2 + 4195.777x_3 + 293.698x_4 \\ & + 21.188x_1x_2 - 4606.555x_1x_3 - 5093.472x_2x_3 \\ & - 246.249x_1x_4 - 461.571x_2x_4 - 4977.869x_3x_4 \end{aligned}$$

The analysis of variance for this model is shown in Table 9.

The regression sum of squares is statistically significant at 99.99%. The evaluation of the experimental error and the

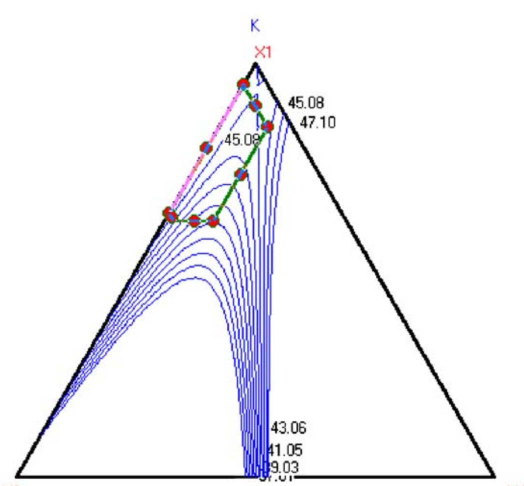

Fig. 4. Isoresponse curves of y_1 for $G = 0.0300$.

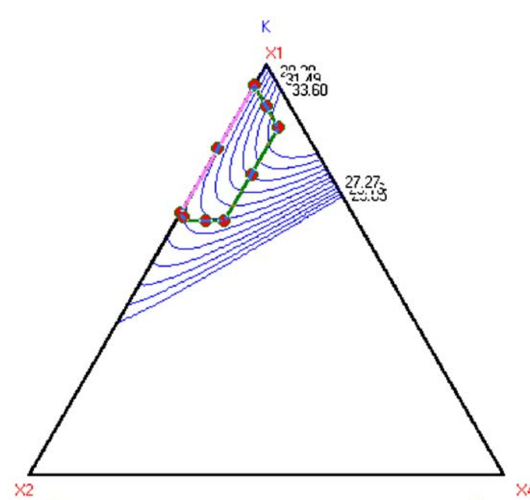

Fig. 5. Isoresponse curves of y_2 for $G = 0.0300$.

determination of the residual sum of squares allow us to validate the adequacy of the fitted model.

Fig. 3 presents a plot of the residuals versus the predicted responses and a normal probability plot of the residuals. These plots are satisfactory.

To confirm the adequacy of the model, we compare the calculated and the measured responses of two test points (Table 10). The standard deviation of the response y_1, evaluated by the replication of the center, is $\sigma_{y_1} = 1.612$.

Globally, all the prepared cements develop high compressive strengths at 28 days (Table 6). These values are higher than the limit required by the European norms ($R_{c_{28}} \geq 32.5$ MPa).

Fig. 4 represents the isoresponse curves of $R_{c_{28}}$. It shows that when the percentages of limestone are relatively high (5–10%), the $R_{c_{28}}$ decrease with increasing the amounts of slag. In addition, we note that the resistance is improved when the clinker proportion increases. However, high levels of $R_{c_{28}}$ can also be obtained by replacing a high proportion of clinker by slag and slightly reducing the amount of limestone in the blended cement. This procedure can lead to an $R_{c_{28}}$ value of 47 MPa. The corresponding composition is 61% clinker, 35% slag, 3% gypsum, and 1% limestone. This procedure is interesting since it allows obtaining a cheaper product (rich in slag).

3.3.2. Study of the response y_2: compressive strength at 7 days

The calculation steps are the same as those of the response y_1. The corresponding mathematical model is

$$\begin{aligned} y_2 = {} & 29.948x_1 + 27.493x_2 + 1705.815x_3 - 267.799x_4 \\ & + 25.972x_1x_2 - 1790.694x_1x_3 - 2354.005x_2x_3 \\ & + 455.957x_1x_4 + 211.193x_2x_4 - 2550.118x_3x_4 \end{aligned}$$

The analysis of variance of the response y_2 is shown in Table 11.

For the second response, the proposed model is valid and the regression is excellent (Fig. 5). The standard deviation of the response y_2 is $\sigma_{y_2} = 1.229$; consequently, the model is made valid (Table 12).

In contrast with $R_{c_{28}}$, R_{c_7} is improved when the amount of limestone is increased and slag is decreased. These facts can be explained as follows:

–At 7 days, the fine particles of limestone logged in the pores of the hydrated pastes, improved the mortar compacity, and consequently, the compressive strength.

–The slag particles do not contribute to strength development until 7 days of hydration especially because the blended cement was ground to a fineness of an ordinary Portland cement and the mortar was cured at an ordinary temperature. In fact, several authors indicate that the blended cement must be ground at a fineness of 3000–4000 cm^2/g [13] and cured at relatively high temperature [4,5] to improve the hydraulicity and the strength development.

Table 12
Validation of the model

Test point	$\hat{Y}$ calculated (MPa)	Y measured (MPa)
Test 1	28.4	27.7 ± 1.2
Test 2	27.5	27.2 ± 1.2

Taking into account that the compressive strength at 28 days is the best criterion to assess the cement quality, we have relied on this property to determine the optimum formulation. This response has been maximum ($R_{c_{28}} = 47$ MPa) for the experiment E_{20} (K = 61%, S = 35%, G = 3%, and C = 1%). As expected, its resistance after 7 days hydration is not the best ($R_{c_7} = 29.7$ MPa), but this value is in good agreement with the European standard ($R_{c_7} \geq 16$ MPa).

4. Conclusion

This study has been devoted to the characterization of a Tunisian blast-furnace slag and its use as an additive for cements.

The replacement of a part of clinker by slag has led to the following results:

- an acceptable extension of the setting time, an improvement of the rheological behavior, and a very good stability to expansion
- an improvement of the compressive strength at 28 days, but with a slight decrease at 7 days

The optimal composition, found by the mixture design, is 61% clinker, 35% slag, 3% gypsum, and 1% limestone and the corresponding $R_{c_{28}}$ and R_{c_7} are 47 and 29.7 MPa, respectively.

References

[1] M. Moranville-Regourd, Cements made from blast-furnace slag, Lea's Chemistry of Cement and Concrete Ed. P.C; 1998, pp. 633–674.
[2] ECOTRADE s.p.A, Etude sur le laitier de haut-fourneau de Ecotrade', Report No. rpm 96/13, 194/E, July 29, 1996.
[3] K. Sakai, H. Watanabe, M. Suzuki, K. Hamazaki, Properties of granulated blast-furnace slag cement concrete, ACI Spec. Publ. SP-132 (1993) 1367–1383.
[4] F.S. Fultron, The properties of Portland cement containing milled granulated blast-furnace slag, Portland Cem. Inst. Memogr. (1984) 4–66.
[5] F.J. Hogan, J.W. Muesel, The evaluation for durability and strength development of ground granulated blast-furnace slag, Cem. Concr. Aggreg. 3 (1) (1981) 40–52.
[6] P.C. Nkinamubanzi, P.C. Aïtcin, L'utilisation du laitier dans la fabrication du ciment et du béton, Cim. Bétons Plâtres Chaux 843/2 (2000) 116–125.
[7] D.L. Kantro, Influence of water reducing admixtures on properties of cement paste. A miniature slump test, Cem. Concr. Aggreg. 2 (1980) 95.

[8] D. Mathieu, J. Nony, R. Phan-Tan-Luu, Nemrod-W Software, LPRAI, Marseille, 1999.
[9] F. Keil, Slag cements, Proc. 3rd Int. Congr. Chem. Cem. London (1952) 549–550.
[10] E. Douglas, A. Elola, V.M. Malhotra, Characterization of ground blast-furnace slags and fly ashes and their hydration in Portland cement blends, Cem. Concr. Aggreg. 12 (2) (1990) 38–46.
[11] K. Sato, E. Kenoshi, K. Fukaya, Properties of very fine blast furnace slag prepared by classification, 8th Int. Congr. Chem. Cem. Rio De Janeiro 4 (Theme 3) (1986) 239–244.
[12] J. Goupy, Plan des mélanges', Ed. Dunod, 2001.
[13] M. Venuat, La pratique des ciments et des bétons, Ed. Moniteur, 1997, pp. 229–239.