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Prevention of the quality of cement from chemical and mineralogical parameters of the clinker

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ABSTRACT: The quality of cement can be evaluated firstly, by measuring physicochemical parameters of the raw materials, and intermediate products (raw, flour, clinker), which is formed during the manufacturing process, and the cement as a final product. Secondly, by the measurement of physico-mechanical parameters: compressive strengths at early age and long-term, flexion.... etc..

To reduce the number of experiments, orient the use of clinker and predict the quality of cement, we used a mathematical model of multilinear regression to find a correlation between the chemical parameters of clinker and compressive strengths at 2, 7 and 28 days of portland cement without adding CPA.

The results of the statistical and experimental study are highly predictive and reliable.

KEYWORDS: Portland cement, multilinear regression, compressive strengths, clinker.

1 INTRODUCTION

The portland cement clinker is a hydraulic material obtained in the form of nodules after firing at 1450°C of a mixture of limestone clay and rich correction materials of aluminum oxide and iron oxide, followed by quenching up to a temperature equal to 100 ° C. It is composed mainly of four mineralogical phases namely : tricalcium silicate (C_3S) dicalcium silicate (C_2S) tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). The abundance, size, reactivity and distribution of these phases are affected by complex interactions between cooking cooling regime and the nature of the raw material [1]. The nodules of clinker are ground with gypsum only which serves to control setting or with other additions, to obtain a fine powder called respectively portland cement without additions (CPA) or with additions (CPJ).

Cement plants in Morocco produce several types of cement such as: CPJ_{35}, CPJ_{45}, CPJ_{55} and CPA which are differentiated particularly by the type, the percentage of addition, and their compressive strengths at 28 days which are respectively 35, 45 and 55 MPa, according to the standard Moroccan NM 10.1.005 [2]. Therefore, the quality of any type of cement strongly depends on the quality of the clinker. Several earlier work showed the existence of a relationship between the physico-mechanical composition of the cement, chemical and mineralogical composition of the clinker with the use of the univariate modeling [3-5]. These studies have been based on modeling the impact of each clinker factor separately on cement quality while setting the other factors but actually this is not the case, because for all clinker parameters vary simultaneously. The purpose of this is to predict the compressive strengths (RC) of 2, 7 and 28 days of portland cement CPA by determination a correlation between compressive strengths for different ages and mineralogical composition of the clinker, using a multivariate statistical model. In fact, this model has the advantage of putting in evidence the effect of all chemical and mineralogical parameters of the clinker.

The choice of cement CPA is based on the absence of additions in this type of cement in order to avoid interference between the different chemical compositions of cement components. To do this, we had developed 21 types of cement CPA with clinkers of different chemical compositions and with even gypsum. 17 samples were used for modeling and the remaining four samples were used to validate the statistical model applies. Physico-mechanical and chemical analyzes were performed for the thus manufactured cements. The experimental results of compressive strengths were modeled by the method of multiple linear regression.

2 MATERIALS AND METHODS

2.1 MATERIALS

- The clinker is taken from the outlet of the cooler.
- The mixing water : Drinking water
- The Sand and the gypsum are supplied of cement industry “Asment Temara”.

For each matter an average sample was prepared by the quartering method [6] and characterized by X-ray fluorescence Bruker type for determining the chemical composition. For all samples of clinker a chemical analysis of free lime CaO_l was affected in addition to the mineralogical composition C_3S, C_2S, C_3A and C_4AF. The thus produced cements were also characterized by X-ray fluorescence, physico-mechanical tests, refusal 80 microns and by mechanical resistances a 2, 7 and 28 days. All analyzes were performed according to the standard Moroccan NM.10.1.004 [7].

2.2 METHODS

2.2.1 PREPARATION OF CEMENT CPA

The portland cement without additions CPA are prepared from 97% clinker and 3% gypsum. Everything is grounded up to a fineness of 1 ± 0.2 µm in a ball mill. The CPA is ready to physicochemical and mechanical tests according to standard NM 10.1.004.

2.2.2 PREPARATION OF MORTARS

The mortars were prepared with the crushed quartz sand of grain size 0 – 315 µm then the prepared mixed with cement and water in the weight ratios: 3: 1: 0.5 (1350 g of sand, 450 g of the binder and 225 mL of water to fill three specimens of rectangular 4 * 4 * 16 cm), according to the standard methods NM 10.1.004. These components are mechanically kneaded for 10 minutes and were set up by vibration in the test pieces. The latter, after 24 hours of storage at 100% humidity, they were unmolded and were placed in water at 20 °C in a humidity cabinet. They broke after aging of 2, 7 and 28 days, first by bending under constant moment, and the ends thus obtained were then subjected to a simple compression test.

2.2.3 MATHEMATICAL MODEL OF THE MULTILINEAR REGRESSION:

Multiple linear regression analysis is an extension of simple linear regression analysis, used to assess the association between two or more independent variables and a single continuous dependent variable. The multiple linear regression equation is as follows:

$$y_i = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \cdots + \beta_p x_p + \varepsilon_i \quad (1)$$

Where:

- y_i is the predicted or expected value of the dependent variable
- x_1 through x_p are p distinct independent or predictor variables
- β_0 is the value of *y* when all of the independent variables (x_1 through x_p) are equal to zero, and
- β1 through β_p are the estimated regression coefficients. Each regression coefficient represents the change in y relative to a one unit change in the respective independent variable. In the multiple regression situation, β_1, for example, is the change in y relative to a one unit change in x_1, holding all other independent variables constant (i.e., when the remaining independent variables are held at the same value or are fixed). Again, statistical tests can be performed to assess whether each regression coefficient is significantly different from zero.

In our case: y_i is the compressive strength at 2, 7 and 28days x_{ij} is C_3S, C_2S, C_3A and C_4AF

The coefficient of determination R^2 was measured according to the following formula:

R² = variability explained by the regression (SCE)/ / total variability (SCT) = SCE / SCT

$$\mathbf{SCE} = \sum_{\mathbf{i}}(\hat{y}_{\mathbf{i}} - \bar{y})^{\mathbf{2}} \qquad \mathbf{SCE} = \sum_{\mathbf{i}}(\mathbf{y}_{\mathbf{i}} - \bar{y})^{\mathbf{2}} \quad \mathbf{(2)}$$

The coefficient of multiple determination measures the proportion of the variance of the dependent variable y explained by a set of k explanatory variables x, which was calculated according to the following equation [8]:

$$\mathbf{R^2_{mult}} = \sum_{\mathbf{j=1}}^{\mathbf{k}} \mathbf{a'_j r_{yx_j}} \quad (3)$$

Where:

a'_j: regression coefficient centered-reduced of the j^{eme} predictor

r_{yxj}: simple linear correlation coefficient between y and x_j

The results of R^2 and R^2_{mult} were evaluated by Fisher's test [9] which consists to check:

$$\mathbf{F} = \frac{\mathbf{S_1^2}}{\mathbf{S_2^2}} = \frac{\frac{\mathbf{SCE_1}}{\mathbf{DDL_1}}}{\frac{\mathbf{SCE_2}}{\mathbf{DDL_2}}} \sim \mathbf{F(DDL_1, DDL_2)} \quad (4)$$

With DDL_1 et DDL_2 : degrees of freedoms

3 RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF MATERIALS

The mineralogical and chemical composition of samples of the clinker and the gypsum are presented in tables 1 and 2. Table 3 shows the chemical composition of cement CPA developed and table 4 describes the results of cements compressive strengths at different ages.

Table 1. Mineralogical composition of clinker (%)

clinker	MgO	C_3S	C_2S	C_3A	C_4AF	CaO_l
1	1,75	56,85	18,18	8,67	8,48	1,62
2	2,60	57,33	17,01	7,19	10,85	0,67
3	2,24	53,52	19,43	7,21	10,58	2,18
4	1,98	55,00	18,31	7,27	10,28	2,41
5	1,46	50,42	23,40	8,33	10,67	1,06
6	2,66	62,01	10,07	7,15	9,25	2,10
7	1,50	65,02	9,18	3,64	15,34	0,82
8	2,75	58,22	16,88	7,29	10,29	0,71
9	1,07	54,14	19,76	8,99	9,95	1,28
10	1,07	55,73	16,92	9,23	10,29	0,88
11	7,47	57,35	14,38	3,62	12,17	0,51
12	2,73	60,44	11,02	11,12	9,07	0,60
13	7,28	55,33	15,05	3,99	11,99	0,65
14	3,86	57,35	15,64	5,74	9,65	0,96
15	1,55	48,40	23,95	8,35	10,19	2,07
16	2,58	63,46	8,20	7,51	9,37	2,32
17	1,37	57,62	15,10	9,44	9,86	0,88

Table 2. Chemical composition of gypsum (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	MgO	K_2O	TiO_2	MnO	P_2O_5	SrO	Gypsum Purity
1,95	0,29	0,30	34,82	40,36	0,73	0,07	0,02	0,02	0,00	0,177	86,77

Table 3. Chemical composition of CPA cement developed (%)

CPA	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	MgO	K_2O	TiO_2	MnO	P_2O_5	SrO	CaO_l
1	20,89	5	2,7	64,22	2,77	1,7	0,81	0,36	0,07	0,23	0,067	1,62
2	20,2	4,84	3,76	63,38	2,8	2,56	0,78	0,4	0,08	0,22	0,06	0,672
3	20,19	4,77	3,6	64,03	2,88	2,22	0,82	0,35	0,08	0,22	0,066	2,18
4	20,25	4,74	3,44	64,39	3,08	1,9	0,82	0,36	0,07	0,22	0,063	2,41
5	20,55	5,12	3,63	64,64	2,8	1,37	0,82	0,36	0,08	0,26	0,066	1,064
6	19,1	4,5	3,04	62,87	2,33	2,57	1,24	0,31	0,038	0,076	0,046	2,02
7	19,6	4,33	5,04	63,05	1,30	1,46	1,091	0,23	0,11	0,093	0,018	0,78
8	20,4	4,66	3,38	62,39	0,60	2,65	0,17	0,42	0,045	0,067	0,816	0,67
9	20,2	5,28	3,27	63,28	1,41	1,04	0,28	0,33	0,12	0,13	0,3	1,23
10	19,94	5,42	3,38	62,94	2,00	1,03	0,84	0,26	0,027	0,046	0,019	0,83
11	19,38	3,76	4	58,55	0,38	7,24	1,32	0,25	0,14	0,094	0,036	0,5
12	19,12	5,85	2,98	62,62	1,57	2,61	1,03	0,31	0,067	0,069	0,09	0,56
13	19,16	3,87	3,94	58,38	1,34	7,06	0,22	0,4	0,18	0,78	0,7	0,56
14	19,89	4	3,17	60,88	1,85	3,72	1,33	0,2	0,076	0,16	0,32	0,9
15	20,19	5,09	3,35	62,57	1,75	1,51	0,8	0,38	0,074	0,27	0,054	2,02
16	18,96	4,55	3,08	63,02	2,13	2,52	1,27	0,3	0,045	0,086	0,038	2,24
17	19,85	5,43	3,24	62,85	1,67	1,31	1,15	0,22	0,076	0,076	0,019	0,84

Table 4. Compressive strength of CPA cement developed at different ages

Time / CPA	Compressive strength at different ages (days)		
	2	7	28
1	16,55	27,6	41,20
2	21,85	28,3	49,55
3	17,8	20,3	41,2
4	16,65	27,15	39,60
5	16,75	27,00	40,20
6	32,8	48,5	59,2
7	26,4	42	55,9
8	22,1	37,9	53,4
9	22,5	39,5	57,6
10	23,9	41,3	56,1
11	18,6	32,3	42,1
12	28,9	42,6	53,7
13	15,6	28,4	51,4
14	26,4	41,2	53,7
15	20,8	33,8	49,3
16	29,6	46,5	56,7
17	31,8	46,5	56,8

3.2 DEVELOPMENT OF MATHEMATICAL MODELS

The technique of multiple linear regression of data from 17 clinkers and cements CPA corresponding (Table 1 and 4) was performed using the statistical software treatment "MINITAB 15." The development of this regression from the terms tested was made by the method of step-down (search meaningful terms after discarding those whose contribution to the model is not significant). The rejection threshold was set at 5% and the model was retained to a maximum coefficient of determination after validation of the Fisher test.

The results of this treatment showed that the mathematical models which validating a model corresponding to a correlation between compressive mineralogical parameters of the clinker are:

- **2 days :**

$$Y_{2jrs} = 283,18 - 3,95MgO - 2,55C_3S - 3,2C_2S - 2,36C_3A - 2,81C_4AF - 4,20CaO_l \quad (5)$$

- **7 days :**

$$Y_{7jrs} = 449,94 - 6,18\ MgO - 4,08C_3S - 4,72C_2S - 4,22C_3A - 4,56C_4AF - 6,77CaO_l \quad (6)$$

- **28 days :**

$$Y_{28jrs} = 369,46 - 4,95MgO - 3,19C_3S - 3,51C_2S - 3,4C_3A - 3,2C_4AF - 5,65CaO_l \quad (7)$$

As for all analyzes of linear model, before looking at the results, we must check that the validation of the model assumptions are satisfied. For this, we use statistical tests that are the subject of the next section.

3.3 ADJUSTMENT MODELS

One of the objectives of modeling is to predict the value of the compressive strength with knowledge the chemical and mineralogical composition of the clinker. But if the fit is bad, the good prediction model can't be expected.

Table 5. Parameters for validating mathematical models

Time / Parameters	Mathematical model of the compressive strength at different ages (days)		
	2	7	28
R^2_{mult}	0,93	0,95	0,92
R^2	0,86	0,90	0,85
Standard error	2,6	3,4	3,4

From the results of table 5, we find that:

- The variability explained by the model of 2, 7 and 28 days is respectively 93%, 95% and 92%, showing that the quality of the fit and the variance of the compressive strength explained by the models are good.
- The variation of the predicted value relative to the measured value is the order of 2.6 for the model of 2 days and 3.4 for the model of 7 and 28 days.

3.4 SIGNIFICANCE TEST OF THE REGRESSION FROM THE FISHER TEST F:

Fisher test shows that, the connection between C_3S, C_2S, C_3A, C_4AF, CaO_l, MgO and compressive strength is significant, by suggesting the following assumptions:

- Assumptions :

H_0: $b_1 = b_2 = b_3=b_4=b_5 = b_6 = 0$ Y isn't dependent on variables X_i.

Where: **b_i =** coefficient of factor i which can be C_3S, C_2S, C_3A, C_4AF, CaO_l or MgO.

H_1: At least one coefficient is non-zero Y depends at least on one variable X_i

- **Decision Rule:**

At risk 5%, H_0 is rejected if: $F \geq F_{0,95.(6.10)}$

Where: $F_{0,95.(6.10)}$ is a fractile of the fisher law at 10 and 6 degrees of freedom, determined from the following table of Fischer:

Table 6. Test Fischer's data

	Degree of freedom	*Sum of squares*	*Mean squares*	*F*	*F*0.95,(6,10)*
Mathematical model of the compressive strength at 2 days					
Regression	6	434,475	72,412	10,280	3,22
Residues	10	70,440	7,044		
Total	16	504,915			
Mathematical model of the compressive strength at 7 days					
Regression	6	1024,321	170,720	14,864	3,22
Residues	10	114,854	11,485		
Total	16	1139,175			
Mathematical model of the compressive strength at 28 days					
Regression	6	650,29	108,382	9,433	3,22
Residues	10	114,90	11,490		
Total	16	765,19			

The flaying of the results of the test Fischer's analysis unveiled that the observed F is greater than the $F_{0,95.(6.10)}$ for the three models (Table 6). So we reject the null hypothesis H_0, what means that we accept the alternative hypothesis H_1 that at least one of the six variables of the clinker, helps to explain the compressive strength at 2, 7 and 28 days. This allowed us to conclude that there is a linear relationship between chemical parameters of the clinker and the compressive strength at different ages.

3.5 The effect test of factors:

For each parameter, Table 7 gives the observed statistic and the critical probability associated to hypothesis tests:

$\mathbf{H_0}$ {parameter is null} $\mathbf{H_1}$ {parameter is non-null}

This test checks whether the effect of factors is significant or not by analyzing its critical probabilities.

Table 7. Testing the effect of clinker factors on compressive strength of the CPA cements

	Mathematical model of the compressive strength at different ages (days)					
	2		***7***		***28***	
Settings clinker	**Coefficients**	**probability**	**Coefficients**	**probability**	**Coefficients**	**probability**
Constant	283,182	$1,924.10^{-05}$	449,945	$2,77.10^{-06}$	369,465	$1,60.10.^{-05}$
MgO (X_1)	-3,948	0,0004	-6,179	$8,53.10^{-05}$	-4,953	0,0005
C_3S (X_2)	-2,554	$3,17.10^{-05}$	-4,076	$4,52.10^{-06}$	-3,187	3,86.10-05
C_2S (X_3)	-3,197	$2,72.10^{-05}$	-4,723	$7,66.10^{-06}$	-3,509	9,62.10-05
C_3A (X_4)	-2,364	0,0218	-4,222	0,0035	-3,401	0,0121
C_4AF (X_5)	-2,810	0,0124	-4,556	0,0031	-3,205	0,0217
CaO_l (X_6)	-4,203	0,0135	-6,769	0,0036	-5,650	0,0104

The analysis of results of table 7 reveals that:

The hypothesis $H_0 = a_{CaOl}$ *= a_{MgO}= a_{C3S}= a_{C2S}= a_{C3A} = a_{C4AF} = 0} is rejected. So the critical probability of all the factors is less than 0,05. This has shown that the six parameters forming the equations of 2, 7 and 28 days, were significantly non-null, what means that these variables provide a significant and sufficient amount of information to the three models (5, 6 and 7). As these six variables are linearly related to the compressive strength and therefore they will be optimized. The results obtained must be validated experimentally to justify the reliability of the model applied.

3.6 Experimental validation test of the three mathematical models

This test consists in measuring the deviation between the calculated value of the compression strength, from mathematical equations established and experimentally measured value. This gap must be less than or equal to the standard error calculated for each model.

Table 8. Validation of the mathematical model established for the compressive strength of CPA cement

	mathematical model established for the compressive strength of CPA cement (days)											
	2				7				28			
	$Y_{2jrs} = 283{,}18 - 3{,}95X_1 - 2{,}55X_2 - 3{,}20X_3 - 2{,}36X_4 - 2{,}81X_5 - 4{,}20X_6$				$Y_{7jrs} = 449{,}94 - 6{,}18X_1 - 4{,}08X_2 - 4{,}72X_3 - 4{,}22X_4 - 4{,}56X_5 - 6{,}77X_6$				$Y_{28jrs} = 369{,}46 - 4{,}95X_1 - 3{,}187X_2 - 3{,}51X_3 - 3{,}40X_4 - 3{,}20X_5 - 5{,}65X_6$			
CaO_l	1,01	0,67	0,84	1,96	1,01	0,67	0,84	1,96	1,01	0,67	0,84	1,96
MgO	1,54	1,28	1,34	1,37	1,54	1,28	1,34	1,37	1,54	1,28	1,34	1,37
C_3S	57,09	55,50	59,47	55,44	57,09	55,50	59,47	55,44	57,09	55,50	59,47	55,44
C_2S	16,76	19,17	14,59	17,32	16,76	19,17	14,59	17,32	16,76	19,17	14,59	17,3
C_3A	7,17	8,07	7,78	7,80	7,17	8,07	7,78	7,80	7,17	8,07	7,78	7,80
C_4AF	11,80	10,94	11,13	10,95	11,80	10,94	11,13	10,95	11,80	10,94	11,13	10,9
RC measured	25,2	24,9	27,2	23,8	37,4	35,9	38,9	36,0	52,0	51,7	53,0	49,8
RC calculated	23,34	22,44	26,15	21,89	37,73	36,86	41,15	37,65	53,17	52,68	55,22	52,5
deviation calculated e_c*	1,86	2,46	1,05	1,91	0,3	1,0	2,2	1,6	1,2	1,0	2,2	2,7
Error model e_m*	2,7				3 ,4				3,4			
Remarque	$e_c < e_m$											

e_c =\| Y mesured – Y calculated from the mathematical model \|

e_m : calculated by the software MINITAB 15

The results in table 8 show that the variability explained by the models 1, 2 and 3 is good, seen that the results of calculated deviations are always less than 2.7, 3.4 respectively for the models of 2, 7 and 28 days. So, the three models are experimentally reliable and predictive.

4 Conclusion

The mathematical models developed to prevent the compressive strength of CPA cement at 2, 7 and 28 days, have the following characteristics:

- The R^2_{mult} established models for different ages vary between 0.92 and 0.95 (nearly 1), indicating that the models are able to properly present data distribution.
- The critical probability of each factor of the mineralogical composition of the clinker (CaO_l, C_3A, C_3S, C_2S, C_4AF and MgO) is less than 0.05 that is to say that these factors have significant influences to a level risk of 5%.
- The explanatory variables provide a significant amount of information to all three models, according to the Fisher test
- The practical test model validation is positive.

In conclusion, the established models are statistically and experimentally validated and predictive, ie the compressive strength at different ages could be theoretically expected from the mineralogical and chemical composition of the clinker without resorting to experiments and whatever the chemical and mineralogical composition of clinker. This will allow the manufacturer of industrial cement to gain time for the quality prediction of cement as well as economic and environmental gain.

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