Box-Behnken design optimization of magnesium potassium phosphate cement properties using sodium chloride as retarder

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Abstract: Magnesium potassium phosphate cement (MKPC) pastes based on magnesium oxide (MgO) and potassium dihydrogen phosphate (KDP) was prepared with the addition of sodium chloride (NaCl) as retarder. The experimental results demonstrate that the use of NaCl at concentrations varied from 2 to 6% found to increase the setting time and contribute to the enhancement of final compressive strength. In order to evaluate the influence of this retarder in the total mixture and its interaction between each component, a Box-Behnken design with three variables was established. The influences of MgO/KDP ratio, Water/Binder ratio and the percentage of NaCl were studied. According to the setting time and compressive strength results, an optimum operating condition was introduced. The obtained optimal conditions were examined and analysed by X-ray diffraction (XRD) and scanning Electronic Microscopic (SEM).

Keywords: Magnesium potassium phosphate cement (MKPC), sodium chloride, setting time, compressive strength, Box-Behnken design.

Résumé: Un ciment phosphomagnésien à base d'oxyde de magnésium (MgO) et de phosphate de potassium (KH_2PO_4) a été préparé en ajoutant le chlorure de sodium (NaCl) comme retardateur. Les essais ont montré que l'ajout de NaCl à des concentrations qui varient entre 2 et 6% retarde la prise et améliore la résistance à la compression. Afin d'étudier l'influence de ce retardateur dans le mélange et son interaction avec les autres composants, un plan Box-Behnken avec trois variables a été établi. L'influence du rapport MgO/KDP, le rapport Eau/Liant et le pourcentage de NaCl ont été étudiés. D'après les résultats du temps de prise et de la résistance à la compression, un optimum qui illustre les conditions optimales a été choisi. Le ciment préparé selon ses conditions a été examiné et analysé par diffraction des rayons X (DRX) et Microscopie électronique à balayage (MEB).

Mots clés : Ciment phosphomagnésien, chlorure de sodium, temps de prise, résistance à la compression, Plan Box-Behnken

INTRODUCTION

Cements made from magnesium oxide have been developed for many years. They included magnesia oxychloride cement (MOC), magnesia oxysulphate cement (MOS) and magnesia phosphate cement (MPC) [1]. Among them, MPC has been attracted more attention because of its excellent performance: it sets quickly, has long term strengths, high adhesive properties and better durability. Hence, it is very suitable as rapid repairing materials for the busy transportation infrastructure [2-4].

MPC hardened through acid-base reaction between magnesium oxide and phosphate salt [5]. The traditionally magnesium phosphate materials have been prepared with ammonium dihydrogen phosphate (ADP) as phosphate acid component [6]. However, as the by-product of the reaction, ammonium gas would generate an unpleasant odour, leading to attempts to replace ADP by potassium phosphate cement (KDP) [7]. The reaction product was K-struvite ($MgKPO_4 \cdot 6H_2O$) and the obtained cement is called magnesium potassium phosphate cement (MKPC).

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The acid-base setting reaction of MPC is rapid and exothermic. Therefore, it is important to control the rate of this reaction to obtain hardened MPC with high performance. The rate of the setting reaction is affected by numerous factors mainly reactivity of magnesium oxide [8,9], ratio of composing materials [10-12], type and dosage of retarders [13,14], etc…The nature and dosage of the retarder is among the more influencing factor that affect the hydration rate and hardened properties of the cement. Most common retarders are boric acid, borax and sodium tri-phosphate. Some retarders are less evocated in the literature, among them sodium chloride which has been dealt in previous studies [15,16]. Johnson has proved that sodium chloride can bother the crystallization of struvite and grant retardation to the magnesium phosphate precipitate [14]. Similar observations were showed by Soudée, who suggested that the retardation of the exothermic setting reactions might be due to sodium and chloride ions that obstruct the dissociation of the magnesia. He proved that the addition of sodium chloride improve the setting time and the workability of the cement [15]. In this study, we choose to investigate the effect of sodium chloride as set retarder in the total mixture of MKPC.

Usually the effect of each of these factors has been analysed individually and few researches focused on the interaction between these factors. The design of experiments technique helps to verify whether or not there is a synergistic effect between the variables on the final properties of the cement and to optimize the experimental procedure [17].

With regard to the above-mentioned observations, the main goal of the present paper is to study the interaction between the sodium chloride and the other reactants in order to found the optimum formulation that gives appropriate setting time and higher compressive strength. Therefore, a Box-Behnken experimental design [18 -19] was set up to check the effect of three variables: percentage of sodium chloride in the cement, MgO/KDP ratio and Water/binder (W/b) ratio on the strength and the setting of the MKPC paste and to optimize a blended cement formula.

EXPERIMENTAL PROCEDURES

1. Materials and cement formulation

MKPC pastes were prepared by mixing powder which included magnesia (magnesium oxide) (MgO >98% -Loba chemie), KDP (KH_2PO_4 >99% - SIGMA-ALDRICH) and sodium chloride ($NaCl$ >99% SIGMA-ALDRICH) with de-ionized water. Magnesia was calcined at 1100°C for 2h to reduce its reactivity. Aggregates were not used in this research to prevent additional disruption from the impurities of aggregate. The mixtures were stirred for 60 seconds to obtain homogenous pastes and then cast into in cylindrical plastic moulds (20 mm diameter × 40 mm length). All specimens were demoulded within 24 hours after casting and cured in laboratory air (25 ± 2°C).

2. Analysis method

MKPC pastes were characterized in term of their setting time and mechanical properties. The setting time was measured using manual Vicat apparatus following the standard EN 196-3 [20]. The compressive strength of the hardened MKPC specimen was measured by a mechanical tester according to NF EN 196-1 [21] using a LLOYD EZ50 universal testing machine**.** A set of 3 samples was tested for each specimen at a crosshead speed of 1 mm/min

The crystalline phases of the MKPC pastes at the ages of 28 days were identified by X-Ray powder diffractometer X'per PRO PANalatycal (Philips) with CuKα radiation ($\lambda_{K\alpha}$ =1.54 Å). The microstructure of the cement was characterized by scanning electron microscopy (SEM) FEI Quanta 200.

3. Design of experiment

The purpose of this work is to study the effect of three factors, namely MgO/KDP ratio (X_1), W/b ratio (X_2) and NaCl percentage (X_3) on the two responses: setting time (Y_1) and compressive strength after 28 days (Y_2) in order to determine the best experimental conditions allowing the maximization of responses.

Response surface methodology using Box Behnken Design is seemed necessary to achieve this goal. The variation of the setting time (Y_1) and compressive strength (Y_2) and versus the three retained variables X_1, X_2 and X_3 was studied using a polynomial second degree model given by the following equation:

$$Y= b_0 + b_1X_1 +b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{23}X_2X_3 + b_{13}X_1X_3 \quad (1)$$

Where:

Y: the measured response variables

b_0 is a constant

b_1, b_2 and b_3: linear coefficients
b_{11}, b_{22} and b_{33}: quadratic coefficients
b_{12}, b_{13} and b_{23}: interactive coefficients

A total of 15 experiments, including three replicates at the centre point, were necessary to estimate the 10 coefficients of the model using multiple linear regression analysis.

Statistical analysis was performed using the software STATISTICA (version 7.0) for the experimental design and regression analysis of the experimental data. The effect of each variable and their interactions on the setting time and the compressive strength were studied. The significance of the regression coefficients was tested by a *t*-test. A probability (*P*) for a given factor less than 0.05 was considered as significant. The validity of the polynomial model equation was checked by analysis of variance (ANOVA) and by the correlation coefficient R^2. The statistical significance was checked by the *F*-test.

RESULTS AND DISCUSSIONS

1. Preliminary tests

Preliminary tests were carried out in order to select the field of NaCl dosage that delay the setting time and improve the mechanical properties at the same time. Therefore, MKPC pastes were prepared by the addition of different amounts of NaCl; 2%, 4%, 6% and 8%; MgO/KDP and W/b ratios were maintained at 1 and 0.25, respectively. Moreover, a control specimen was prepared with de-ionised water (NaCl free) for the sake of comparison.

Fig. 1 displays the effect of NaCl dosage on the setting of MKPC pastes. Compared to the control sample which has a setting time of 2 min, NaCl has extended gradually the setting time to reach a value of 27 min with 8% NaCl. Moreover, the addition of NaCl dosage above 4% has more effectiveness in the retarding mechanism.

Fig. 2 shows the effect of NaCl dosage on the compressive strength of the MKPC pastes at different curing days. There is a progressive increase in the compressive strength as the NaCl dosage increases. However, the addition of high dosage of NaCl (8%) results in noticeable strength reduction until 13.7 MPa at 28 days. Thus, NaCl dosage will be selected to be varied from 2 to 6% for the rest of this study.

2. Box-Benkhen design experiments for maximum compressive strength and setting time.

2.1. The identification of significant factors

According to previous researches [22-25], the field of MgO/ KDP ratio was selected from 1 to 5 and W/b ratio was ranged from 0.2 to 0.35. While, NaCl dosage was selected, according to this study, to be varied from 2 to 6%. The operating conditions were given in table I.

The quality of the prepared cements was assessed by measuring the setting time (Y_1) and the compressive strength responses at 28 days (Y_2). The data obtained from the Box Benhken design were fitted to second order polynomial equation.

The significance of the coefficients of the model was determined by analysis of variance (ANOVA). Table II illustrates only significant coefficients and corresponding p-values which are inferior to 0.05, indicating the considerable effect

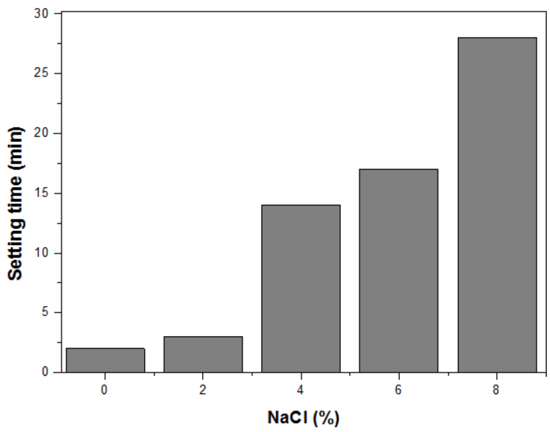

Figure.1 Setting time of MKPC pastes as function of sodium chloride dosage.

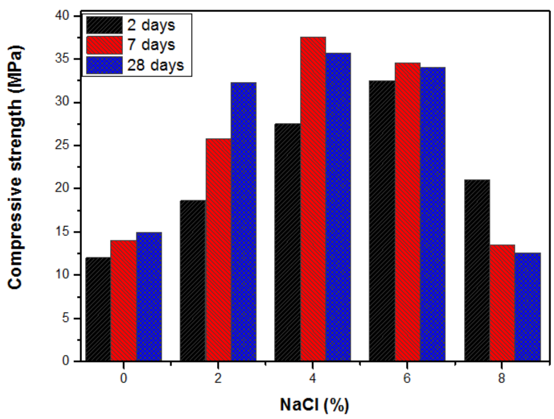

Figure.2 Compressive strength of MKPCs as function of sodium chloride dosage.

Table I : Coded levels, condition runs and measured responses used in experimental design for response surface methodology

Experiments [a]	Independent Variables			Experimental Responses	
	MgO/KDP X_1	NaCl (%) X_2	W/b X_3	Setting time (min) Y_1	Compressive strength (MPa) Y_2
1	1(-1)	2(-1)	0.275(0)	3.50	32.76
2	5(+1)	2(-1)	0.275(0)	1.50	27.08
3	1(-1)	6(+1)	0.275(0)	28.00	24.87
4	5(+1)	6(+1)	0.275(0)	15.00	21.07
5	1(-1)	4(0)	0.2(-1)	19.50	38.00
6	5(+1)	4(0)	0.2(-1)	16.00	42.92
7	1(-1)	4(0)	0.35(+1)	22.50	21.86
8	5(+1)	4(0)	0.35(+1)	17.00	27.07
9	3(0)	2(-1)	0.2(-1)	1.00	35.42
10	3(0)	6(+1)	0.2(-1)	18.50	14.70
11	3(0)	2(-1)	0.35(+1)	4.00	20.97
12	3(0)	6(+1)	0.35(+1)	22.00	12.87
13	3(0)	4(0)	0.275(0)	15.00	38.08
14	3(0)	4(0)	0.275(0)	16.00	35.75
15	3(0)	4(0)	0.275(0)	15.50	37.22

[a] Standard order

Table II: Regression Coefficients of the predicted second-order polynomials models for the setting time and the compressive strength.

Setting time model					**Compressive strength model**				
	Regression coefficients [a]	Standard error	F-value	p -Value		Regression coefficients [a]	Standard error	F-value	p -Value
$\mathbf{a_0}$	14.04167	0.144338	97.2835	<0.00001	$\mathbf{a_0}$	26.6325	0.340127	78.3017	<0.00001
$\mathbf{a_1}$	-3	0.353553	-16.9706	0.003454	$\mathbf{a_2}$	-5.34	0.833137	-12.8190	0.00603
$\mathbf{a_2}$	9.1875	0.353553	51.9723	0.000370	$\mathbf{a_3}$	-6.03375	0.833137	-14.4844	0.004733
$\mathbf{a_3}$	1.3125	0.353553	7.4246	0.017661	$\mathbf{a_{22}}$	5.51104	0.613172	-17.9755	0.003081
$\mathbf{a_{11}}$	-0.9687	0.260208	-7.446	0.017563	$\mathbf{a_{33}}$	2.50229	0.613172	-8.1618	0.01468
$\mathbf{a_{22}}$	2.7187	0.260208	20.8967	0.002282	$\mathbf{a_{23}}$	3.155	1.178233	5.3555	0.033143
$\mathbf{a_{33}}$	-0.6562	0.260208	-5.044	0.037129					
$\mathbf{a_{12}}$	-2.75	0.5	-11	0.008163					

[a] Only terms with $p < 0.05$ were included

Table III: Analysis of variance (ANOVA) of the second order polynomial models for the setting time and the compressive strength after 28 days.

Setting time						Compressive strength					
Source of variation	SS	DF	MS	F-value	p -Value	Source of variation	SS	DF	MS	F-value	p -Value
(R^2=0.983)						**(R^2=0.906)**					
Regression	920.7019	7	131.52	53.74	<0.0001	Regression	1107.586	5	221.5172	23.6426	<0.0001
Residuals	17.1311	7	2.4473			Residuals	84.325	9	9.3694		
lack of fit	7.12	5	1.425	5.7	0.15596	lack of fit	108.452	7	15.4931	11.603	0.084674
Pure error	0.5	2	0.25			Pure error	2,776	2	1.3882		
Total	937.833	14				Total	1191.911	14			

DF: degree of freedom; SS: sum of squares; MS: mean square.
R^2: correlation coefficient
ST: setting time
CS: Compressive strength

of these coefficients on respective variable. As it can be seen, all the linear and the quadratic coefficients were significant on the setting time (Y_1), only an interaction term (a_{12}) between the two factors MgO/ KDP ratio and NaCl percentage. For the second response (Y_2), the significant factors are: NaCl percentage (a_2), W/b (a_3), two quadratic terms (a_{22} and a_{33}) and an interaction (a_{23}) between the factors two and three.

2.2. Response surface analysis of setting time

Taking into account only significant factors, the obtained model that shows the relationship between the setting time and the controllable variables can be written according to the following equation:

$$Y_1 = 14.04167 - 3X_1 + 9.1875X_2 + 1.3125X_3 - 0.9687X_1^2 + 2.7187X_2^2 - 0.6562X_3^2 - 2.75X_1X_2 \quad (2)$$

The model adequacy was confirmed by the analysis of variance (ANOVA) by F-Test. As shown in table III, the F value of regression coefficient is superior to the tabulated Value ($F_{regression}$ = 53.74 > $F_{tabulated}$ (7, 7, 0.05) = 3. 8) which indicated that the variables of the model have a significant effect on the setting time response at 95% confidence. Also, the ratio of the mean square of lack-of-fit and pure error are inferior to the tabulated Value ($F_{lack\text{-}of\text{-}fit}$ = 5.7 < $F_{tabulated}$ (5, 2, 0.05) = 19.3) which means that the lack-of-fit statistic was not significant (p > 0.05), hence the model is valid. The correlation coefficient R^2 was calculated to be 0.983. This value ensured a satisfactory adjustment of the model to the experimental data and indicated that the model could explain 98.3% of the variability in the response.

Two and three dimensional response surfaces were plotted for the results of the setting time as presented in Fig. 3 which shows the interaction between the two factors: MgO/KDP ratio and NaCl dosage. The retarding of the setting time is higher when NaCl percentage is increased. The increase of the setting time takes place up to maximum addition with the maximum of NaCl and the minimum of MgO/KDP ratio. A setting time greater than 20 min is assumed as a good workability. This behaviour is achieved with an addition of NaCl higher than 4% and MgO/KDP ratio less than 3 when W/b ratio was kept at the centre level.

2.3. Response surface analysis of the compressive strength after 28 days

Analysis of variance demonstrates the relationship between the compressive strength after 28 days and significant MKPC preparation parameters with a satisfactory regression coefficient (R^2=0.906). Eq. (3) shows the mathe-

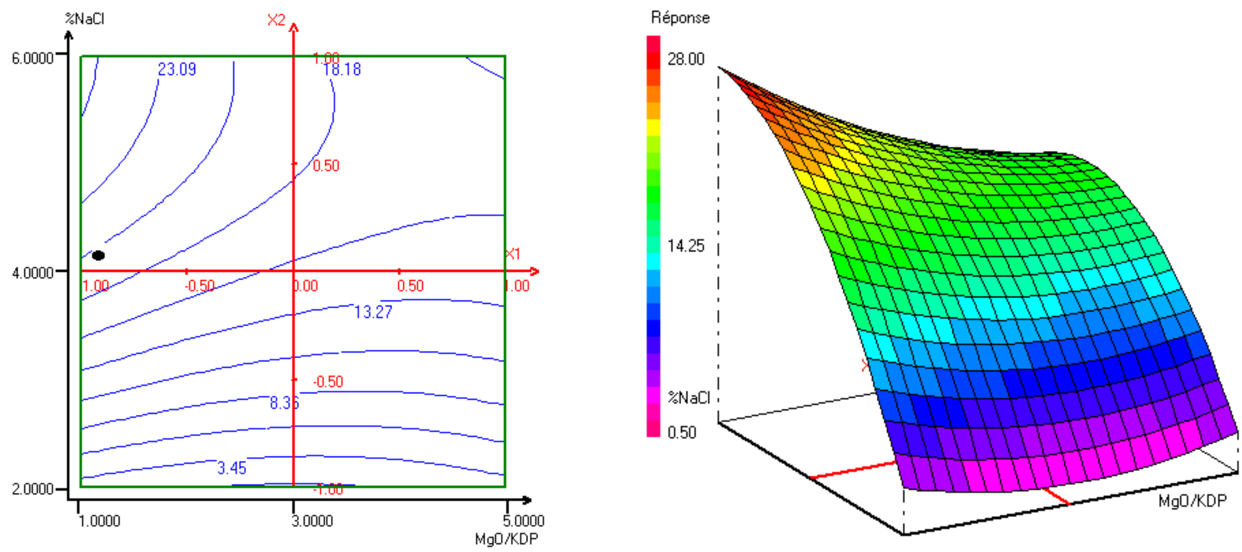

Figure.3 Isocontours (2D, left) and response surface plots (3D, right) showing the interaction between MgO/KDP ratio and NaCl percentage on the setting time. (W/b=0.275)

matical model that describes the relationship between the significant independent variables and response of the compressive strength.

$$Y_2= 26.6325- 5.34\ X_2- 6.03375\ X_3+5.51104\ X_2^2 + 2.5022\ X_3^2 + 3.155\ X_2X_3 \qquad (3)$$

According to Fisher's *F*-test, the F value of regression coefficients is superior to the tabulated value ($F_{regression}$ = 23.6426 > $F_{tabulated}$ (5, 9, 0.05) =3.48) and the p-value corresponding was smaller than 0.0001, which indicated that the variables are independent. On the other hand, the ratio of the mean square of lack-of-fit and pure error are inferior to the tabulated value ($F_{lack\text{-}of\text{-}fit}$ = 11.603 < $F_{tabulated}$ (7, 2, 0.05) = 19.35) indicating that the lack-of-fit statistic was not significant (p>0.05), hence, the model is valid.

Fig. 4 presents the two and three dimensional responses surface of the significant interaction between W/b ratio and NaCl percentage. At a fixed MgO/KDP = 1 which gives the higher setting time,

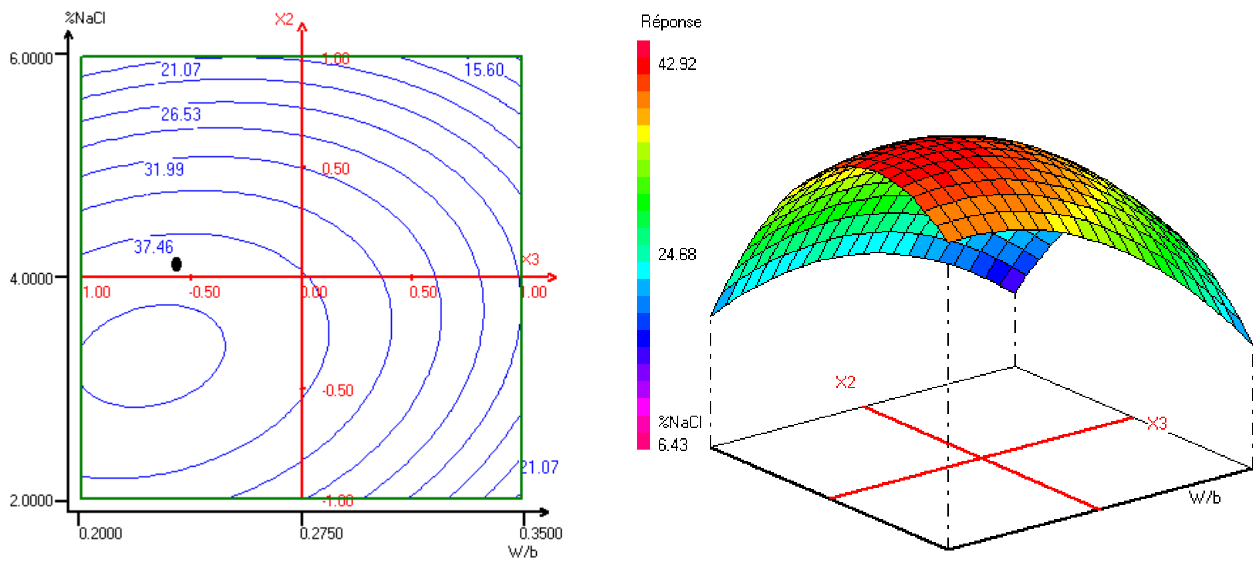

Figure.4 Isocontours (2D, left) and response surface plots (3D, right) showing the interaction between W/b ratio and NaCl percentage on the compressive strength. (MgO/KDP= 1)

the maximization of two responses is reached when NaCl is in the medium level (0) and W/b ration in its lowest level (-1).

2.4. Optimization of MKPC formulation

The basic objective of optimization is to find a compromise in factors values in order to reach higher values in responses. In our study, the maximum compressive strength at 28 days and a setting time higher than 20 min were the two responses that should be respected to achieve this optimization. Thus, the contour plots shown in fig. 3 and 4 were used to determine the operating conditions allowing a compromise between the two responses. The optimum point was marked in the area which corresponds to following conditions: W/b= 0.233; NaCl percentage = 4% and MgO/KDP=1. Under these conditions, the responses Y_1 and Y_2 were respectively, 20.5 min and 39.36 MPa. These conditions were experimentally validated and the obtained sample has a setting time of 22 min and a compressive strength of 38.03 MPa.

2.5. Optimum characterization

The crystalline phases of the MKPC pastes with 4% NaCl (under the optimum conditions) and without NaCl (Control specimen) after curing for 28 days are shown in Fig. 5. It can be seen that the two specimens are primarily composed of two hydration products $MgKPO_4.6H_2O$ and unreacted MgO. For the specimen with 4% NaCl, two new phases appeared: KCl and $NaMgPO_4$. It may that the formation of these phases is responsible of the retarding effect of sodium chloride. In fact, occurrence of Na^+ and Cl^- released from sodium chloride will consume K^+ to form KCl and Mg^{2+}, PO_4^{3-} to form $NaMgPO_4$. Therefore, the decrease in the concentration of K^+, Mg^{2+}, PO_4^{3-} will cause a

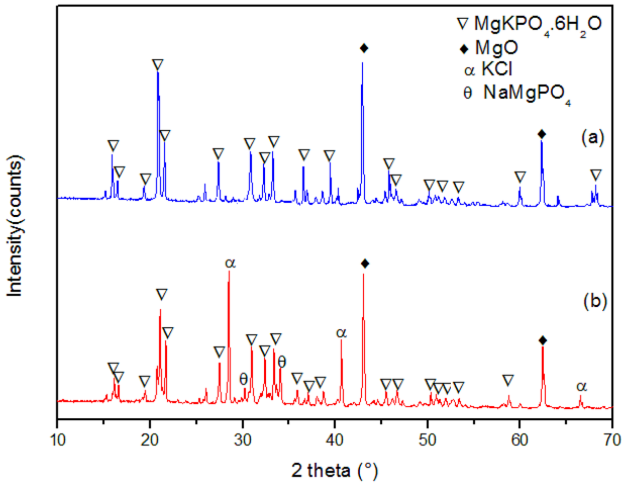

Figure.5 X-ray diffractograms of MKPC pastes
a) without the addition of NaCl
b) Under the optimum conditions (with 4%NaCl).

decrease in K-struvite precipitation which results in a lower early hydration rate of MKPC and a rise in the setting time [26]. It may also that the presence of sodium and chloride ions will change the ionic strength of the solution containing magnesium, ammonium and phosphate ions. Consequently, solubility products of magnesia and potassium phosphate were also changed. Otherwise, sodium and chloride ions caused deceleration of passing to the solution of the magnesia and a decrease in his wetting which result in deficiency in the hydration of the pastes [15]. In fact, high exothermicity of the reaction caused by the dissociation of the magnesia accelerates the kinetics and the set of the cement. However, slow setting leads to better strength development [8],

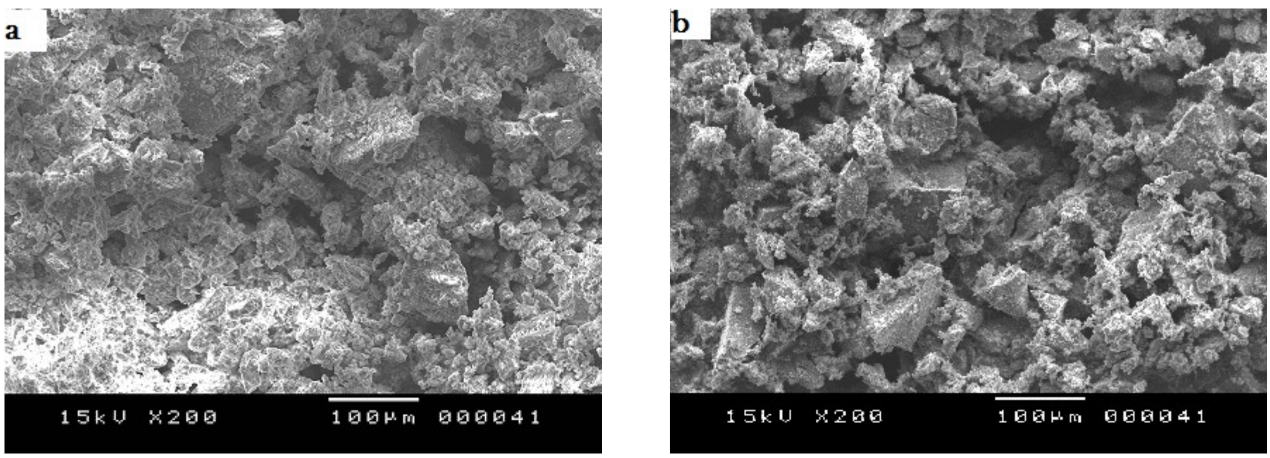

Figure.6 SEM photos of the MKPC pastes a) control specimen b) With the addition of 4% NaCl

which may explain the improvement in the compressive strength.

In order to provide information on the effects of the sodium chloride on microstructure, the optimum and the control specimens were examined using SEM. As shown in Fig. 6, the control specimen is mainly formed with MKP hydration product and formed homogeneous surface. The addition of sodium chloride decreases the proportion of hydration product and an heterogeneous surface was formed with the two new phases KCl and $NaMgPO_4$. The two specimens microstructure reveal a very porous structure due to the fast setting process.

CONCLUSION

The addition of sodium chloride at concentrations varied from 2 to 6% found to increase the setting time and contribute to the enhancement of final compressive strength.

The statistical method for the Box-Behnken was employed in order to model and optimize the chosen responses (Setting time and compressive strength). According to the three factors fields, two valid models were established. Based on these models, the addition of 4% sodium chloride under the established conditions (MgO/KDP =1 and W/b = 0.233) showed a MKPC paste with high compressive strength (39.36 MPa) and an adequate setting time (20.5 min). These results were experimentally validated and the obtained sample has a setting time of 22 min and a compressive strength of 38.03 MPa.

According to SEM and XRD analysis of the optimum specimen, the retarding effect of sodium chloride may be explained by the change in the ionic strength of the mixture and therefore the solubility product of MgO and KDP. When the solubility product of the reactants decreased, the rate of precipitation of K-struvite also decreased and, therefore there is formation of new phases (KCl and $NaMgPO_4$).

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