OPTIMIZATIONOFTHEUSEOF GYPSUM INTHE MANUFACTURING OFPORTLANDCIMENTWITH ADDITIONS (CPJ 35)

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Abstract

The aim of this work was to find the optimum content of gypsum, leading to the manufacture of cement of CPJ35 type with better mechanicalcharacteristics. To achieve this goal, a behavioral study in accordance with standard NF EN 196-1 of august 1995 of the consistency of mortar and normal development of mechanical strength of mortars made with cement sampleswas conductedby making successive increments of gypsum. The results obtained at the end of this phase of experiments have suggested that the time of start making increases with the sulphate content in the cement sets up a threshold value to 2.58%. The optimum sulphation is at 2.015%, value substantially equal to that used in the factory (2%). The cement produced with the optimum value of the sets at the end of the trial period developed 0.031 MPa more than sulphation valuefrom cement produced in Figuil industry.

Keywords: optimum sulphation, gypsum,cement of CPJ35, mechanical strength

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Introduction

Cement is a mineral powder fromthe mixture of clinker, gypsum and additions. It is a hydraulic binder that is when combine with water it forms a plastic paste and progressively becomes hardens even under water [1].Cement isthe main material used by civil engineering in constructions.

The process of cement manufacturing is a complex operation that requires specific selection criteria particularly in the choice of raw materials [2]. Gypsum, calcium sulphatedihydrate ($CaSO_4.2H_2O$) is a raw material that plays an important role in the regulation of the cement by its contribution in sulphate ions $SO_4^{2-}$and on the cement quality. Indeed for certain values of the gypsum content in cement (in excess or by default), the emergence of negative phenomena such as premature stiffening of cement material (flash jack), weak development of mechanical strength of the occurrence of cracks on the multidirectional swelling pressures in the microstructure of material is observed [3].

Lafarge cement plant in Cameroon-Figuil, among other, manufactures artificial Portland cement withadditions of CPJ 35 and operatesthe quarries close to the factory. These quarries have almost all raw materials necessary for the development of cement exceptgypsum. The gypsum used in the preparation of cement in cement factory in Cameroon is imported,hence the need to reduce the quantities used in the manufacture of cement in Cameroon to reduce production costs.

Given the importance of the damage that can cause the gypsum on the quality of the cement and its influence on the production of cement compared to its cost, this study was undertaken to optimize the use of gypsum in the manufacture of Portland cementwith an additions made of CPJ35 at the Cimencam-Lafarge Figuil plant in Cameroon.

Materialsand methods

A behavioral study of the consistency of mortar and normal development of mechanical resistances of mortars made with samples of cement made by successive increments of gypsum during the trial period took place in two phases: In the laboratory and on an industrial scale.

The laboratory study was made within the range of 0 to 5.5% of SO_3 to locate the sulphation area that offers a better development of mechanical resistance, once this area was then established and given the fact that the study was dedicated to an industrial use. Nine tests were made.The formulation of industrial cements is made on the basis of the optimum value of gypsum fixed at the end of the first phase of the experiment on Laboratory cements by successive increment from 0.3% to SO_3.

The investigation on the industrial level using the optimum value as established in the laboratory reference value in which increments were made to formulate seven industrial cement samples: taking into account requirements linked to the manufacture of Portland cement with additions (AJ), seven samples were manufactured with 65% of clinker (CK) as indicated by the Cameroonian standard [3, 4]. The chemical composition of clinker used for cement samples made in the laboratory and on an industrial scale were obtained by X-ray fluorescence spectrometry (AXIOS spectrometer of a P-analytical type).

ResultsandDiscussion

Taking into account the content of SO_3 present in the clinker (see Table 1 and 2), gypsum content used for the different formulations is shown on Tables 3 and 4.

Table 1: Chemical composition of clinker used in the laboratory

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	CaO	Mn_2O_3
Content %	20,65	4,47	3,2	65,36	2,68	0,74	0,44	0,58	0,52	0,17	2,40	0,05

Table 2: Chemical composition of the clinker used on an industrial scale

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	CaO	Mn_2O_3
Content %	19,32	4,42	3,8	65,61	3,48	0,68	0,62	0,55	0,62	0,18	3,02	0,07

Table 3: Formulations of cements manufactured in laboratory

Sample	% CK	% GY	% AJ	m_{CK} (g)	m_{GY} (g)	m_{AJ} (g)	m_T (g)
Test 1	65	0	35	3250	0	1750	5000

Test 2	65	2,5	32,5	3250	125	1625	5000
Test 3	65	3	32	3250	150	1600	5000
Test 4	65	3,5	31,5	3250	175	1575	5000
Test 5	65	4	31	3250	200	1550	5000
Test 6	65	4,5	30,5	3250	225	1525	5000
Test 7	65	5	30	3250	250	1500	5000
Test 8	65	5,5	29,5	3250	275	1475	5000
Test 9	65	6	29	3250	300	1450	5000

AJ = Portland cement with additions, CK = clinker, GY = gypsum

Table 4: Formulation of cements manufactured on an industrial scale

Sample	% CK	% GY	% AJ	m_{CK} (g)	m_{GY} (g)	m_{AJ} (g)	m_T (g)
Cem 1	65	3,350	31,65	15600	804	7596	24000
Cem 2	65	4,077	30,923	15600	978,48	7421,52	24000
Cem 3	65	2,621	32,379	15600	629,04	7770,96	24000
Cem 4	65	4,806	30,194	15600	1153,44	7246,56	24000
Cem 5	65	1,893	33,107	15600	454,32	7945,68	24000
Cem 6	65	5,533	29,467	15600	1327,92	7072,08	24000
Cem 7	65	1,168	33,832	15600	208,32	8192,68	24000

AJ = Portland cement with additions, CK = clinker, GY = gypsum

The tests determination of compressive strengths for 2, 7 and 28 days of age , the time of initial setting , the sharpness of grinding, the sulfate content and insoluble residues on cement was conducted in accordance to thestandard of NF EN 196-1 August 1995 on the quality control of the cementmanufacturing. The results for each of these formulations produced are shown on

Tables 5 and 6.

Table 5: Results of Chemical and physico-mechanical analysis for laboratory ciments

Sample	$\%SO_3$	%	R_C 2Days (MPa)	R_C7Days (MPa)	R_C 28_{Days}	T $_{initialsetting}$(min)	Mixingwater(%)

		RI			(MPa)		
Test 1	0,74	3,33	12,50	19,50	26,80	58	29
Test 2	1,05	1,29	13,20	21,20	29,50	135	28,4
Test 3	1,67	1,05	14,00	22,00	28,10	160	28
Test 4	1,74	1,33	15,20	24,80	32,10	165	28,2
Test 5	1,98	1,04	16,10	25,50	32,30	172	28
Test 6	2,06	1,65	15,50	23,50	34,50	174	28,2
Test 7	2,19	1,08	15,80	24,50	33,00	172	28,2
Test 8	2,30	1,33	13,80	24,50	30,50	173	28
Test 9	2,44	1,18	14,30	23,50	31,50	174	28,2

IS = insoluble residues; RC = resistance to compression; SSB = Blaine specific surface area

Table 6: Results of chemical and physico- mechanical analysis on industrial cements

Sample	$\%SO_3$	%RI	R_C 2Days (Mpa)	R_C 7Days (Mpa)	R_C 28Days (MPa)	T initial setting (min)	Mixing water (%)	SSB (cm^2/g)
Cem 1	2,58	2,04	13,80	27,70	32,9	240	30	4002
Cem 2	2,69	6,17	13,50	28,50	32,5	238	30	4026
Cem 3	2,09	2,26	13,70	29,60	34,8	220	30	4036
Cem 4	3,17	3,33	12,20	26,20	31,9	131	30	4015
Cem 5	1,87	1,95	14,20	30,00	35,3	206	30	4083
Cem 6	3,6	5,98	11,50	23,90	31,7	237	30,2	4052
Cem 7	1,52	6,93	10,10	24,40	31,4	204	30,4	4142

IS = insoluble residues; RC = resistance to compression; SSB = Blaine specific surface area

From the results of chemical and physico- mechanical analysis,the curves for the variation of the initial setting time and mechanical resistance developed by thecementations'material according to the content SO_3wasplotted using Excel program.The curves obtain are shown onFigures 1, 2, 3 and 4.

Curves for cement samples made in the laboratory

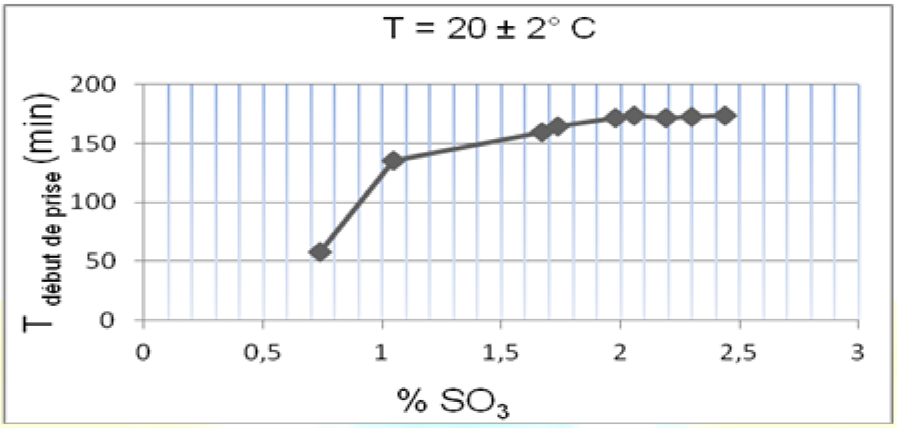

Figure 1: Variation of the start time as a function in taking the sulphate content of the cement sample from the laboratory.

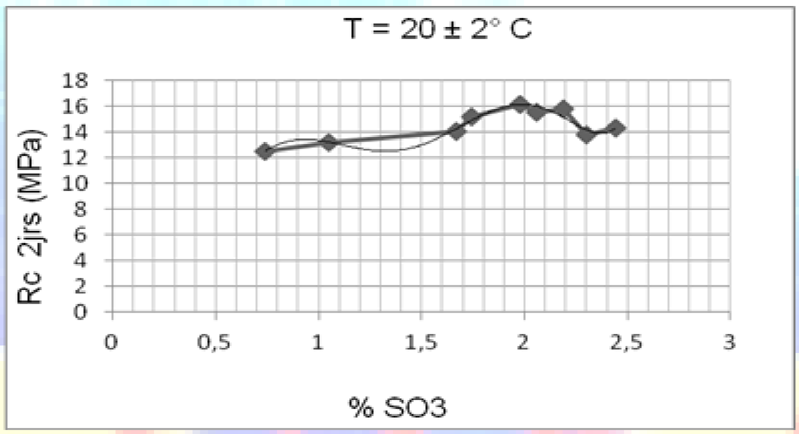

Figure 2: Changes in mechanical strengths in 2 days of treatment as a function of the sulphate content of the cement sample from the laboratory.

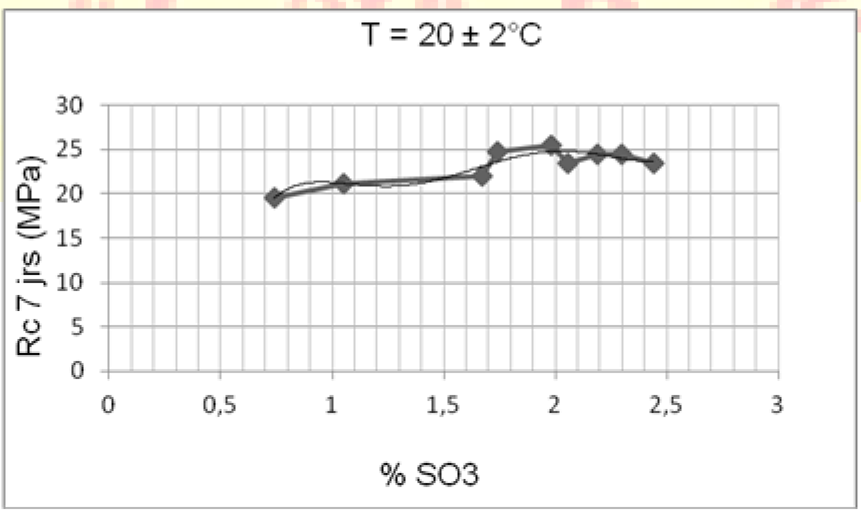

Figure 3:Changes within 7 days of mechanical resistance based cure of the sulphate content of the cement sample from the laboratory.

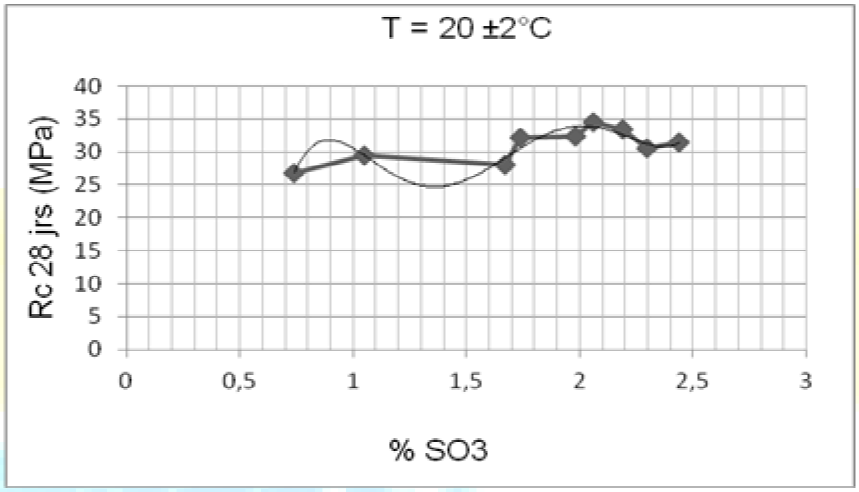

Figure 4: Variation of the mechanical strength at 28 days of treatment as a function of the sulphate content of the cement sample from the laboratory.

Figure 1 shows the effect of an increase insulphate concentration on the time of initial setting of the cement samples produced in the laboratory. It is noted that the initial setting time increases dramatically with the content of sulphates present in the cement. Meanwhile, as from 1.98% of SO_3 a significant increase in the starting time that seems to be constantis observed. Figures 2, 3 and 4 on the other hand represent the effects of the variation of the sulphate content in the cement on the development of mechanical strength of the material. The general observationdone here is a gain resistors with increasing sulphatecontentisrecorded.This gain is significant between 0.74% and 1.98% for the two cements and seven days of treatment. However beyond 1.98%, the mechanical strengths atthese different times fall with increasing sulphate content. For samplesof 28 days of treatment, resistors gainobserved between 0.74% and 2.06% and the drop is recorded beyond 2.06%. Itisalsonoted that the influence of the sulphate content in cement is mostly felt on those of young age (2 to 7 days). This is apparent given the fact that the curve RC = f (% SO_3) becomes less steep with increasing curing time.

The excel program was used to establish the optimum sulphation on different resistance curve. The polynomial regression curves relating to each of them with the characteristics (mathematical expression and correlation coefficient) were given below:

Hydrated cements at 2 days of treatment

y = 20,04x6 - 168,8x5 554,6x4 + - + 735,7x2 896,2x3 - 279,4x 47.46 $R^2 = 0.916$

Hydrated Cements at 7 days of treatment

y = 18,93x5 - 157,2x4 499,9x3 + - + 757,8x2 548,3x - 130.9 $R^2 = 0.833$

HydratedCementsat 28 days of treatment

y = 75,72x5 -628,5x4 2004x3 + - + 2201x 3049x2 - 572.7 $R^2 = 0.851$

Following the mathematical analysis of each of these curves, the optimum sulphationvalues for each onewasestablishedtobe 2.08%, 2.04 % and 2.02 %ofSO_3respectively. The values below or aboveare values which the material develops low resistances.Following the test donneon cement manufacturing in the laboratory and given the fact that this sulphate content in cement significantly influences the development of mechanical strengths at the younger age of material [4],the results obtained between two and seven days of age wasdevelopedtoobtainthe average value of the optimal sulphate content that is 2.06 % of SO_3 corresponding to 5.029 % of gypsum which is the value that meets all the deadlines for laboratory samples.

Curves for cement samples manufactured on an industrial scale

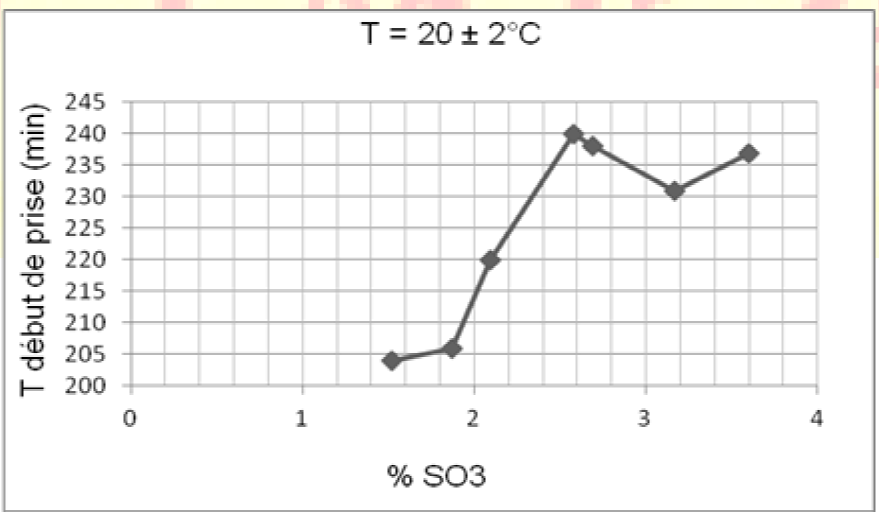

Figure 5: Variation of the initial setting time based on the sulfate content for samples of industrial ciments.

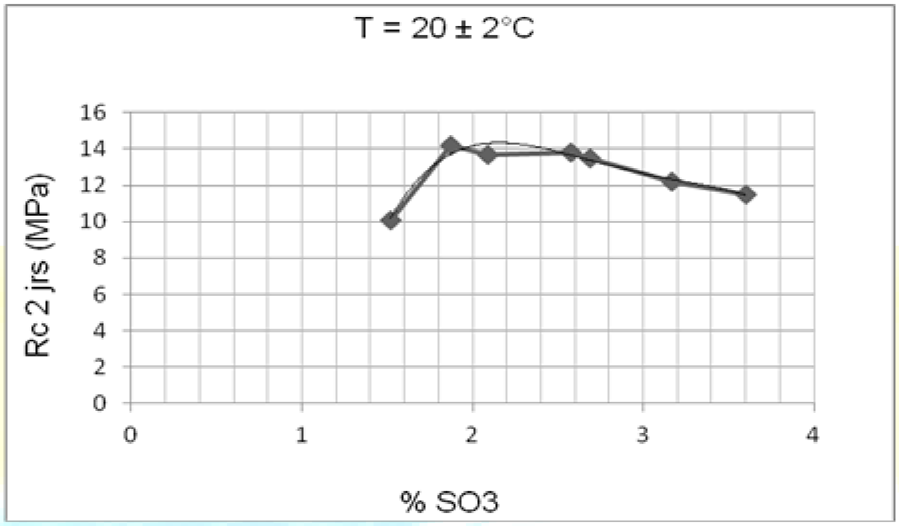

Figure 6: Variation of the mechanical resistance for 2 days of treatment as a function of the sulphate content for samples of industrial cements.

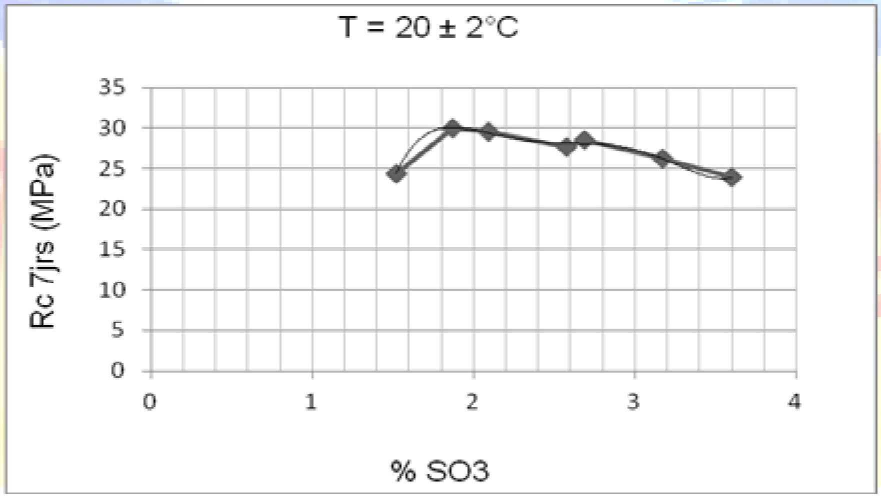

Figure 7: Change within 7 days of mechanical resistance based on treatment of the sulfate content for cement industrial ciment.

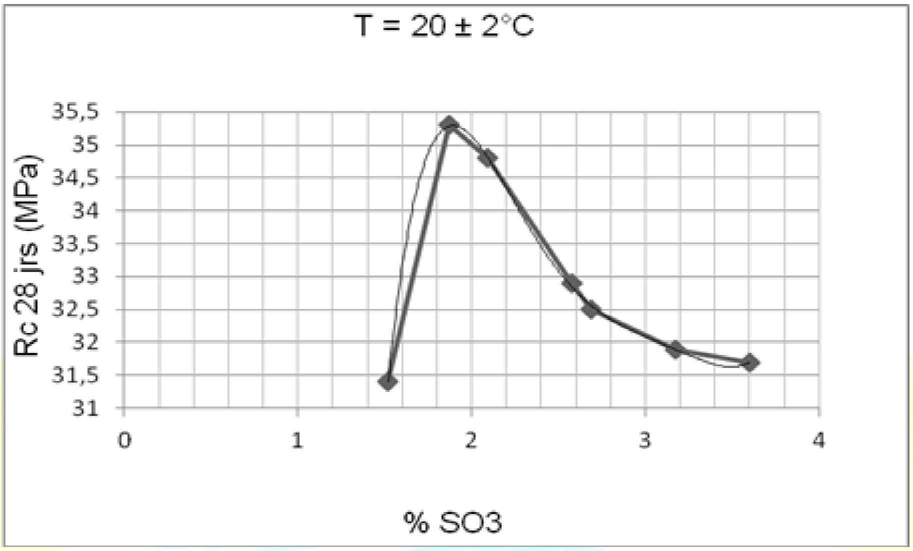

Figure 8: Variation of the mechanical strength at 28 days of treatment according to the sulphate content for samples of industrial ciments.

Figure 5 shows the effect of increase of the sulphate concentration on the time of initial setting of the cement samples manufactured on an industrial scale. It is noted that the initial setting time increases with the sulfate content present in the cement to a threshold value set at 2.58% from which there has been a fall time of initial setting.

Figures 6, 7 and 8 show the effects of the variation of the sulphate content in the cement on the development of mechanical strength of the material. Here, a rapid gain resistors at1.87%isobserved and a significant drop in resistance beyond this contentisalsoobserved. In summary, the findings made are the same as those observed on the samples of cement made in the laboratory (resistors gain with the increase of the sulphate content in the material up to a certain content and significant influence on the development sulfates mechanical strength of the material at the young age).

As seen previously,the excel program was used to establish the optimum sulphation on different resistance curve. The polynomial regression curves relating to each of them with the characteristics (mathematical expression and correlation coefficient) were given below:

Hydrated cementsat 2 days of treatments

$$y = - + 1{,}757x4\ 20{,}82x3 - 91{,}58x2\ 174{,}9x + - 107.9 \quad R^2 = 0.950$$

Hydrated cements at 7 days of treatment

$$y = 9{,}977x5 - 132{,}7x4 + 694{,}9x3 - 1789x2 + 2264x - 1096 \quad R^2 = 0.988$$

Hydrated cements at 28 days of treatment

$$Y = 3{,}135x5 - 44{,}44x4\ 249{,}1x3 + - + 688{,}4x2\ 932{,}6x - 458.8 \quad R^2 = 0.999$$

Following the mathematical analysis of each of these curves,the optimum sulphationvalues for each one wasestablishedto be 2.15%, 1.88 % and 1.87 %of SO_3respectively.The values below or beyond are values which the material develops low resistances . Given that the content of this sulfates in cement significantly influences the development of mechanical strength of the material at the young age [4], the value of the optimum sulphation meeting all deadlines is the average value of the optimum set to 2 and 7 days of treatment or a grade of 2.015 % SO_3 , corresponding to 4.891 % of gypsum. Takingintoaccount that the results obtained are dedicated to industrial use, onlythe optimization results obtained during testing on an industrial scalewillberetainedthatis2.015 % to SO_3corresponding to 4.891 % of gypsum.

Tothe observations done on Figures 1 and 5, it can be deduced that the sulphate ions present in the solution during the cement hydration phenomenon retards celitehydration (C_3A).It is responsible for the rapid stiffening of the cement paste by forming an ettringitelayer around it [5] where there will be an increase inthe initial start time.

However, the excessive content observed during experiment was 2.58%, the oversaturation of SO_4^{2-} ions can cause premature stiffening of the cement paste result in their precipitation as gypsum crystals in the microstructure of the cement paste [6]. In Figure 1, this phenomenon is not howeverobserved. For the manufacturer itisnotnecessaryto exceed a grade of 2.58% ofSO_3 in the 35 CPJ to notbe confronted to this phenomenon. As regards to the developing of the mechanical strength of the cementations' material according to the sulphate content, it is simply because the hydration of C_3A is slowed down by the formation of ettringite layer around it which promotes the complete hydration of the C_3S responsible for the development of mechanical strength of the material [6]. The drop in resistance observed in certain contents is due to the fact that the cement paste was subjected to false sulfate taken phenomenon due to the oversaturation of theSO_4^{2-} ions solution [2]. The zigzag shape of the curves RC = f (SO_3) are related to the fact that the grinding finenessparticles and the content of insoluble residues of the different samples varies constantly. These factors changes good development of the resistance of material when the first is low or when the second is high [2]. As for the establishedsulphation optimum value,a comparative study of the characteristics of the CPJ 35 cement type produced with the optimum amounts to the end of the trial period with those of a CPJ 35 recorded in product quality index

(P.Q.I) of theFiguilfactorywasmade.

P.Q.I of the Figuilfactory defines values that guarantee the quality of manufactured cement. The values that are recorded there include among others are:

- The mechanical strength,
- The grindingfineness,
- The initial timesetting,
- Sulphate content and other constituents.

Table 7 summarizesthe P.Q.Iof the Figuilfactory relative tothiswork.

Table 7: Storage of theproductqualityindex P.Q.Iof Figuil plant for a cement of class CEM II (CPJ35)

Characteristics	**%SO_3**	**R_C 2 days (MPa)**	**R_C 28days (MPa)**	**T initial setting time (min)**	**% mixing water**
Value	1,80 - 2,15	14 - 18	30 - 38	150 - 224	27 – 32

Considering the fact that the optimizationtests carried outin thisresearch work intended for industrial application andtakingintoaccountthatduringtheindustrialtestsallmanufactures' conditions with production conditions (grindingtemperature, particle size of the cement powder, ventilation ...) wererespected [1],the optimization results on samples of industrial cements was foundto be2.015 % of sulfates corresponding to 4.891 % pure gypsum to 41.2 %.

Table 8 below summarizes the characteristics obtained by simulation (from Figures 5, 6 and 8) for cement containing 2.015 % sulfate.

Table 8: Characteristic values on samples of cement made during the trial period

Characteristics	**%SO_3**	**R_C 2 days (MPa)**	**R_C 28days (MPa)**	**$T_{initial\ setting\ time}$(min)**	**% mixing water**
Value	2,015	14,1	34,8	~ 220	~ 30

Comparison of Tables 7 and 8 reveals the fact that quality values indices of cement was2.015% sulfate are in accordance with those specified by the P.Q.I plant. It isclearlyappearedthat the cement made with the sulfate content is perfectly marketable in terms of product quality.

Considering calculations made by simulation, it has been established that industrial production of cement clinker containing 65% and 2.015% SO_3 developed a mechanical strength of more than 0,031 MPa at the same cement clinker content and containing 2% SO_3 two days age.

At the end of the polynomial regression analysis of the curves corresponding to the variation in the mechanical strength and the time of initial setting according to its sulphate content material, it is found that the optimum gypsum established at the end of the trial period corresponds to a content of 2.015% SO_3.

Conclusion

For the gypsumoptimization results ofPortland cement with additions obtained at the end of the trial period through the study of polynomial regression curves on resistance variation curves compression at different time (2,7 and 28 days) and the setting time according to the sulphate content of cement, the following conclusionscanbemade:

- The intake sulfates in cement significantly influences the development of mechanical strengths at an early age of the material. However, it takes a minimum of sulphate content for it to develop at an acceptable level of mechanical strength at 28 days of age.
- The contribution of sulphates (gypsum) significantly improved development of mechanical resistance of the material provided that it is equal to 2.015%.
- Outside the interval [1.87% - 2.19%] of SO_3 in the cement, the developing of mechanical resistance of the material is seriously disrupted and a reduction of a few mega-pascal on the mechanical strength of the materialisrecorded.
- The mechanical strengths of the material decline with increase in the content of insoluble residues arising from the presence of the uncombined silica during clinkerisationoperation.

- The initial setting time increases with the sulfate content in cement to a certain value due to the formation of the microcrystals of ettringite. In fact, this curing time is significantly reduced when sulphate ions are oversaturated in the pore solution which causes the phenomenon of false sulphate plug.

- The optimization result obtained at the end of the trial period (2.015% SO_3) used to enter the factory production service to the fact that the chemical composition of clinker used did not significantly changed given the fact that the sulphate content recorded in the P.Q.I which sensibly to the same as that established at the end of the trial period (sulphate target set at the Figuilfactory: 2%). However, the slight difference between the two cases saves in percentage of clinker and gypsum purity equal tofew mega-pascal that permitthe reduction of the clinker content used. Then thiscontentwasmovedfrom 65% to 64.86% of the clinker.

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