Optimizing the Sulphates Content of Cement Using Multivariable Modelling and Uncertainty Analysis

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This study aims at determining the effect of the cement composition and mortar age on the optimum content of sulphates using maximization of compressive strength as a criterion. Extensive experimentation has been performed to achieve this purpose by utilizing four cement types and measuring the strength at ages ranging from 2 days up to 63 months. Strength is correlated with the ratio of sulphates to clinker content, SO_3/CL and moles SO_3/ moles C_3A. A generalized model correlating SO_3, cement composition and curing time is developed, intensely indicating the necessity of placing the SO_3 target within the optimum region and realizing it as well. The set of four equations involves polynomial and logarithmic equations correlating the variables. A variance analysis based on error propagation technique, proves that SO_3 affects not only average value of strength but also its variability.

Key words:
Cement, sulphates, clinker, strength, optimization, model

Introduction

Two of the main properties characterizing cement quality are the setting time and the compressive strength. Gypsum acts in parallel as a regulator of both characteristics. Thus its impact on cement quality is crucial and dual. Gypsum addition retards the fast exothermic reaction of tricalcium aluminate ($3CaO.Al_2O_3$ or C_3A) by forming ettringite. Generally C_3A reacts with the calcium sulphate phases – bassanite (Cs.0.5H), gypsum (Cs.2H) and anhydrite (Cs) – according to the equation (1).

$$C_3A + 3Cs + 32H = C_3A \cdot 3Cs \cdot 32H \qquad (1)$$

During the concrete production, transfer and placing, the formation of ettringite prevents the false set. However excessive amount of gypsum leads to abnormal and detrimental expansion of concrete and mortar. Hence a maximum limit needs to be defined. European norm EN 197-1:2011 puts such constraints, whose values depend on the cement type. Several cement types are currently permitted to be produced, based on various clinker qualities and a variety of other main components.

The existence of an optimum value of the gypsum content within the cement composition has been already pointed out by several researchers. Lerch[1] found that the optimal sulphates content of Portland cement with respect to mortar strength is closely related with several parameters like hydration heat, length changes of mortar specimens cured in water, alkalis, C_3A content and cement fineness as well. The impact of SO_3 on the hydration of the clinker mineral phases has been investigated by several researchers.[1–7] Soroka et al.[4] concluded that gypsum accelerates the rate of hydration, when its addition is below the optimum SO_3 content, but produces significant retardation when the addition exceeds the optimum.

Hanhan[5] investigated the influence of the SO_3 content of cement on the durability and strength of concrete exposed to sodium sulphate environment, studying cements containing clinker and gypsum. He concluded that there is an optimum SO_3 content for the lowest expansion that is different from that determined from the highest compressive strength. Optimum values also differed for the different cements and from one age to another for the same cement. The results also indicate the dependence of SO_3 content on tricalcium aluminate and alkali content of cements. Jansen et al.[6] analysed the changes detected in the phase composition during the hydration process. They concluded that the cement phases involved in the aluminate reaction (bassanite, gypsum, anhydrite and C_3A) react successively. The importance of both amount and phases of SO_3 that is incorporated in clinker has been investigated by Miller et al.,[8] Taylor[9] and Horkoss et al.[10] Taylor[9] concluded that in concrete made with present-day cements and not subjected to an elevated temperature, no damage through delayed ettringite formation can occur for reasons associated with the SO_3 present in the clinker. Miller et al.[8] proved also that under ambient curing condi-

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tions, the sulphur-containing phases present in present-day commercial clinkers are unlikely to cause any internal sulphate attack that might lead to expansive stress and cracking.

Several also researchers have investigated the impact of the limestone addition to the hydration process and sulphates optimum. [11,12,13] Campiteli and Florindo[11] examined the effects of limestone content and cement fineness on the optimum SO_3 of cement according to ASTM C 563. They found that optimum SO_3 increases with increasing fineness and decreases with increasing limestone content, but neither relationships is linear. Yamashita et al.[12] investigated the influence of limestone powder (LSP) on the optimum SO_3 for Portland cement of different content in Al_2O_3, that was found not negligible. The analysis showed that, a lower than optimal SO_3 content, by increasing SO_3, the cement hydration was promoted mainly into C_3A and the compressive strength increased. At the higher SO_3 content, excess formation of expansive ettringite introduced more pores and compressive strength decreased. By the addition of LSP, the maximum compressive strength was obtained at lower SO_3 content. This effect was significant for cement with high C_3A and C_4AF proportions. Thermodynamic modelling of Lothenbach et al.[13] showed that the stabilisation of monocarbonate in the presence of limestone indirectly stabilised ettringite leading to an increase of the volume of the hydrate phase and a decrease in porosity. The function between gypsum content, porosity and strength of cement mortars has also been examined by Sersale et al. [14] According to this research a content of about 2–3.5% SO_3 promotes a shifting of the pore size distribution to lower values as well as a variation in total porosity. This latter appears to be the main factor governing the influence of SO_3 on the compressive strength. Sideris et al. [15] determined the optimum gypsum content of Portland cement using the hydration criterion of maximum ultimate compressive strength. Tsamatsoulis and Nikolakakos [16] investigated the effect of cement composition and mortar age on the optimum content of sulphates using the maximization of compressive strength as a criterion. Based on extensive experimentation, they derived parabolic and logarithmic formulae to express the above functions. Alexander and Ivanusec [17] studied the long-term effects of cement SO_3 content on the properties of concrete. Strengths were determined, at up to one year, in concretes of high and low water/cement ratio. Strength has been usually independent of, or linearly related to, the SO_3 content of cement. With one-year concrete strength, the dominant factor of cement composition was C_3A. At this age the correlation coefficient of strength with C_3A varied with SO_3. Undersulphated cements displayed a strong negative association between strength and C_3A content, which could account for up to 10 MPa difference in strength.

From the above studies it is derived that SO_3 optimum firstly depends on the cement property under examination. If this objective has been decided, then there are several features affecting the optimum value such as clinker composition and mineral phases, cement composition and fineness, gypsum composition. The compressive strength is usually the main property defining the cement quality and it could be an indicator of the mortar and concrete durability. For this reason the present study focuses on the SO_3 optimization with the objective of maximizing this cement characteristic. For a given clinker quality produced in Halyps cement plant, the main independent parameters analysed are the cement composition and type, the gypsum quality and the age of the mortar. The data presented in an earlier study[16] have been utilized. Mathematical models of the simplest possible form are developed to relate SO_3 with the above variables. The derived equations are generalized as much as possible, aiming at determining the values of SO_3 that can be used as targets in the daily production of the mentioned cement types. The purpose of this generalization is to obtain a multivariable function between the proportions of sulphates and clinker, the curing time and compressive strength describing a large set of data comprising both compositions of cement and time. Moreover, a variance analysis is performed, to determine the effect of SO_3 variance on the variance of strength results.

Experimental

Two series of laboratory experiments have been performed: (a) to optimize SO_3 content per cement type and (b) to find the SO_3 optimum at different ages for the same type. All the types utilized conform to EN 197-1:2011. The norm requirements as regards composition and strength limits are shown in Table 1. The Gypsum is not included in the nominal composition: The producer is responsible for adjusting the gypsum content by respecting the maximum SO_3 limit, which for the given cement types is 3.5%. For the first series of experiments the subsequent procedure described further was followed:

(i) All the raw materials have been ground separately in a laboratory mill in order to pass 100% from the 90 microns sieve.

(ii) Convenient quantities were mixed to obtain the designed cement composition.

Table 1 – *Cement types conforming to EN 197-1:2011*

Type	Clinker %	Limestone %	Pozzolans %	Fly ash %	Minor Constituents %	28 days Strength Low Limit Mpa	28 days Strength High Limit Mpa
CEM I 42.5 N	95–100				0–5	42.5	62.5
CEM II A-L 42.5 N	80–94	16–20			0–5	42.5	62.5
CEM II B-M (P-L) 32.5 N	65–79	21–35			0–5	32.5	52.5
CEM IV B (P-W) 32.5 N	45–64		36–55		0–5	32.5	52.5

(iii) Four cement types were obtained: (a) CEM I 42.5 N, (b) CEM II A-L 42.5 N, (c) CEM II B-M(P-L) 32.5 N, (d) CEM IV B (P-W) 32.5 N.

(iv) For each type different percentages of gypsum have been added.

(v) For each type, the same batch of clinker was used. The clinker was analysed with XRF. Physical and chemical characteristics of the clinker as well as the mineral composition according to Bogue formulae are shown in Table 2. The standard equations provided by ASTM C 150 have been utilized to compute the Bogue equations. The chemical analyses of the rest remaining raw materials are presented in Table 3. The loss on ignition (LOI) as 975 °C was

Table 2 – *Clinker physical, chemical and mineral characteristics*

	Blaine $m^2\ kg^{-1}$	R40 %	C_3S %	C_2S %	C_3A %	C_4AF %
Clinker 1	360	16	56.1	19.8	9.2	9.8
Clinker 2	360	18	57.0	18.3	8.7	9.7
Clinker 3	340	22	57.5	17.7	8.3	9.6

	LOI %	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	SO_3 %	K_2O %	Na_2O %	Ins. Res. %
Clinker 1	0.20	21.66	5.53	3.22	66.08	1.81	1.08	0.61	0.00	0.35
Clinker 2	0.30	21.35	5.31	3.20	65.54	2.05	1.38	0.81	0.06	0.30
Clinker 3	0.51	21.27	5.14	3.14	65.48	2.05	1.47	0.90	0.03	0.30

Table 3 – *Chemical analyses of the raw materials*

	LOI at 975 °C %	LOI at 215 °C %	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	SO_3 %	K_2O %	Na_2O %
Mineral gypsum	21.73	18.08	0.52	0.05	0.05	34.23	1.18	43.81	0.04	0.00
Chemical gypsum	22.57	17.55	0.85	0.22	0.14	35.85	0.14	41.27	0.04	0.00
Pozzolans	7.00		71.40	12.15	0.99	1.03	0.47	0.00	3.97	2.98
Fly ash	0.96		47.15	16.97	9.23	17.63	2.77	3.14	1.82	0.33
Limestone	43.28		0.34	0.13	0.13	54.80	1.27	0.00	0.04	0.00

	$CaCO_3$ %	$MgCO_3$ %	Total Gypsum Cs · 2H, Cs · 0.5H, Cs %	Cs · 2H %	Cs.0.5H %	Cs %
Mineral gypsum	5.3	2.5	91.6	84.0	0.0	7.6
Chemical gypsum	11.1	0.3	87.4	82.3	0.0	5.1

measured according to EN 196-2 while LOI at 215 °C was determined according to ASTM C 471M.

(vi) Two kinds of gypsum were utilized: Mineral and chemical gypsum from desulphurization (FGD). For both materials and based on the mass balance of the oxides and LOI at 975 °C and 215 °C, the percentages of $CaCO_3$, $MgCO_3$, gypsum dihydrate (Cs.2H), hemihydrate (Cs.0.5H) and anhydrite (Cs) were calculated. The results are shown in Table 3.

From Table 2 it can be observed that the three clinker batches do not differ from one another considerably with regard to the measured characteristics. Both kinds of gypsum can be characterized by high purity and of elevated Cs.2H content. The cement types and the compositions are presented in Table 4. For CEM I, the sum of %Gypsum and %Clinker was kept apparently constant. For the rest other cement types %Gypsum was changed with simultaneous change of the following components: In CEM II B-M 32.5 and CEM II A-L 42.5, change of gypsum with limestone while in CEM IV B 32.5 gypsum was increased and pozzolans decreased. For each cement composition the SO_3 and 28 days strength values are also shown. It is observed that an SO_3 value exists in each composition, where a

Table 4 – *Cement compositions and strength results*

Clinker %	Gypsum %	SO_3 %	SO_3/Cl %	Str_28 Mpa
		CEM I 42.5(1)		
100	0	1.08	1.08	49.0
99	1	1.50	1.51	49.6
98	2	1.90	1.94	51.9
97	3	2.28	2.35	50.8
96	4	2.72	2.83	51.7
95	5	3.18	3.35	54.0
94	6	3.56	3.79	52.2
93	7	3.91	4.21	52.0
		CEM II A-L 42.5(1)		
80	0	0.75	0.94	38.7
80	2	1.44	1.80	46.4
80	3	2.01	2.51	46.7
80	4	2.42	3.02	48.6
80	5	2.96	3.70	49.2
80	6	3.39	4.24	48.4
80	7	3.94	4.93	48.0
		CEM II B-M (P-L) 32.5(1)		
65	0	0.76	1.17	31.7
65	1	1.18	1.81	36.4
65	2	1.78	2.73	36.9
65	3	2.13	3.27	38.1
65	4	2.58	3.97	36.5
65	5	3.05	4.69	35.3
65	6	3.51	5.40	35.8
65	7	3.94	6.06	33.9

Clinker %	Gypsum %	SO_3 %	SO_3/Cl %	Str_28 Mpa
		CEM IV B (P-W) 32.5(1)		
62	0	1.36	2.20	42.7
62	1	1.78	2.87	43.8
62	2	2.20	3.55	44.9
62	3	2.57	4.15	46.6
62	4	3.13	5.04	46.1
62	5	3.44	5.55	44.1
62	6	3.82	6.16	42.2
62	7	4.14	6.67	43.1
		CEM I 42.5(2)		
100	0	1.38	1.38	46.5
99	1	1.78	1.80	48.8
98	2	2.16	2.20	49.8
97	3	2.66	2.75	51.1
96	4	2.99	3.11	51
95	5	3.51	3.71	50.2
94	6	3.90	4.16	49.7
93	7	4.33	4.67	47.6
		CEM I 42.5(3)		
100	0	1.47	1.47	44.9
99	1	1.84	1.85	45.9
98	2	2.34	2.39	46.1
97	3	2.74	2.82	47.6
96	4	3.22	3.35	50.8
95	5	3.66	3.85	51.5
94	6	4.21	4.48	51.5
93	7	4.49	4.82	50

(1) Clinker No 1, mineral gypsum
(2) Clinker No 2, mineral gypsum
(3) Clinker No 3, FGD gypsum

Table 5 – *Clinker, gypsum and cement characteristics*

	C_3S %	C_2S %	C_3A %	C_4AF %
Clinker	53.3	21.0	8.9	9.3
Cement	Blaine $m^2\ kg^{-1}$	R40 %	SO_3 %	Clinker %
(A)	318	14	1.47	79.5
(B)	324	13	3.64	79.5

	LOI at 975 °C %	LOI at 215 °C %	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	SO_3 %	K_2O %	Na_2O %
	20.80	17.26	0.51	0.03	0.04	34.53	1.18	42.28	0.04	0.00

	$CaCO_3$ %	$MgCO_3$ %	Total Gypsum Cs · 2H, Cs · 0.5H, Cs %	Cs · 2H %	Cs · 0.5H %	Cs %
Gypsum	5.1	2.5	91.8	84.1	0.0	7.7

maximum strength is achieved. This value is not the same for all the cement types but is strongly related to the clinker content.

The second series of experiments was designed as follows: During an industrial scale grinding of CEM II A-L 42.5N, initially the gypsum was decreased to 0.5% with a parallel increase of the limestone content. Sampling was performed after the cement mill reached a steady state (sample (A)). Then the gypsum content was increased to 7% while limestone was reduced accordingly. A second sample, named sample (B), was taken after the mill was stable. The characteristics of the clinker and of the two samples are indicated in Table 5. The same table also shows the chemical analysis of the mineral gypsum used, as well as its content in Cs · 2H, Cs · 0.5H and Cs. As it can be seen, the gypsum composition is very similar to the one used in the first series of tests. The temperature at the mill outlet is kept continuously less than 100° C, therefore, transformation of Cs · 2H to Cs · 0.5H is not expected during grinding. Using the extreme cement samples (A) and (B), additional ones were also prepared and chemical analyses were performed. The full series of samples is presented in Table 6. The benefit of this method of sample preparation is that the cement is industrially produced. With these five samples, mortars were prepared and the compressive strength was measured at various ages ranging from 2 days up to 63 months.

Table 6 – *Samples of variable SO_3 content*

Sample	Composition	SO_3
1	100% (A)	1.47
2	75% (A) + 25% (B)	2.02
3	50% (A) + 50% (B)	2.50
4	25% (A) + 75% (B)	3.04
5	100% (B)	3.64

Correlation of strength with the sulphates content

Optimum gypsum for different cement types

The measurable quantity with which the percentage of gypsum is regulated is the $\%SO_3$ content of cement. Sulphates become mainly from gypsum but also from fly ash and clinker, especially when pet coke is used as fuel. Thus, the function between strength measured at 7 and 28 days – Str7 and Str28 respectively – and the mass ratio $\%SO_3$/Clinker – SO_3/CL – is studied. These functions for each tested cement composition are given in Figures 1 and 2. A second order equation is fitted for each age and cement type studied. Clear SO_3 optimum points appear for each cement type. For all cement types, except CEM IV, the maximum strength seems to appear in a narrow area of SO_3/CL.

To analyse in more detail this initial observation, the following dimensionless strength at 7 and 28 days are considered:

$$RelStr7 = \frac{Str7}{MaxStr7} \tag{1}$$

$$RelStr28 = \frac{Str28}{MaxStr28} \tag{2}$$

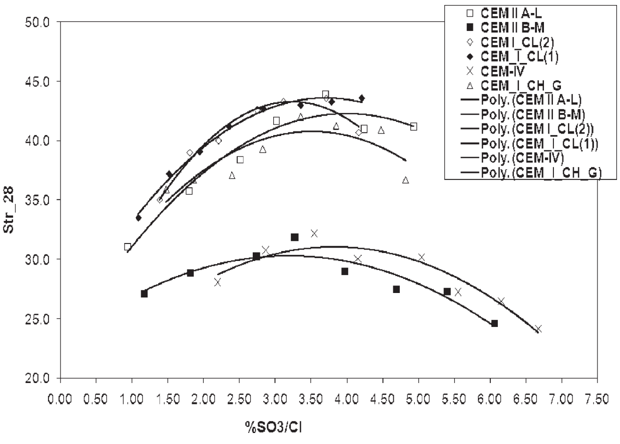

Fig. 1 – *Function between Str7 and %SO_3/Cl*

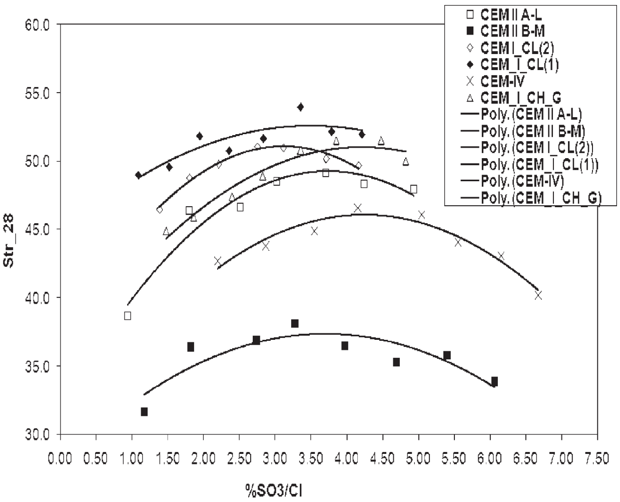

Fig. 2 – *Function between Str28 and %SO_3/Cl*

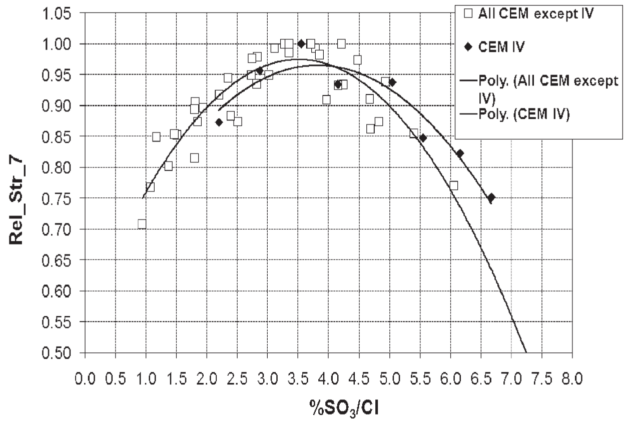

Fig. 3 – *Relative 7 days strength as function of %SO_3/Cl*

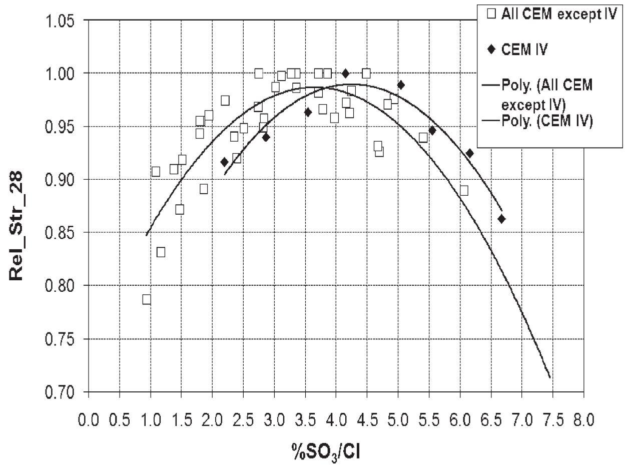

Fig. 4 – *Relative 28 days strength as function of %SO_3/Cl*

Where *strX* = the compressive strength for a certain SO_3/CL at age *X*, *MaxStrX* = the maximum strength of the given cement type at age *X*, *RelStrX* = the relative strength for a value of SO_3/CL at age *X* and *X* = 7 or 28 days. The results of relative strength at 7 and 28 days as a function of the ratio SO_3/CL are shown in Figures 3 and 4. Parabolic equations describe satisfactorily the actual functions for both 7 and 28 days strength given by the general formula (3). Two second-order equations have been computed for all the CEM type except CEM IV and two more equations specifically for CEM IV. The position of *SO3/CL* where the maximum relative strength occurs is provided by equation (4). The coefficients of the four equations, the respecting regression coefficients, R and the *SO3/CL* position of the maximum strength are demonstrated in Table 7.

$$RelStr\,X = C_2 \cdot \left(\frac{SO_3}{CL}\right)^2 + C_1 \cdot \left(\frac{SO_3}{CL}\right) + C_0 \quad (3)$$

$$\frac{SO_3}{CL_{Opt}} = -\frac{C_1}{2C_2} \quad (4)$$

Table 7 – *Coefficients and parameters of equations (3), (4)*

	All CEM types except CEM IV		CEM IV	
	RelStr7	RelStr28	RelStr7	RelStr28
C_2	–0.034	–0.019	–0.028	–0.020
C_1	0.24	0.14	0.21	0.17
C_0	0.56	0.73	0.56	0.63
R	0.90	0.84	0.95	0.96
$(SO_3/CL)_{opt}$	3.5	3.7	3.8	4.3

From Figures 3, 4 and results of Table 7 the subsequent conclusions can be drawn:

(i) Parabolic equations correlate sufficiently the experimental results with acceptable regression coefficients.

(ii) The optimum SO_3/CL ratio for CEM IV is higher than that of all the other cement types, due to the high percentage of fly ash in this cement type, as fly ash contains ~3% SO_3. It is concluded that not all SO_3 of the fly ash act like the gypsum sulphates.

(iii) For CEM I, CEM II A-L and CEM II B-M the function between compressive strength and SO_3/CL is described from one single equation. Consequently the significant issue as concerns SO_3 control, is not only the gypsum content, but the ratio between gypsum and clinker, for a given clinker quality.

(iv) The optimum SO_3/CL for the 28 days strength is located in a position higher than that of 7 days strength.

A function between clinker C_3A and SO_3 optimum is already mentioned in the literature.[1,5,6] To investigate this relation the function between strength at 7 and 28 days and the ratio of moles SO_3/ moles C_3A is plotted in Figures 5, 6 in a similar way with that of Figures 3, 4. The C_3A contained in the cement is considered. Four parabolic equations expressing the functions shown in Figures 5, 6 have been derived, described by the general formula (5).

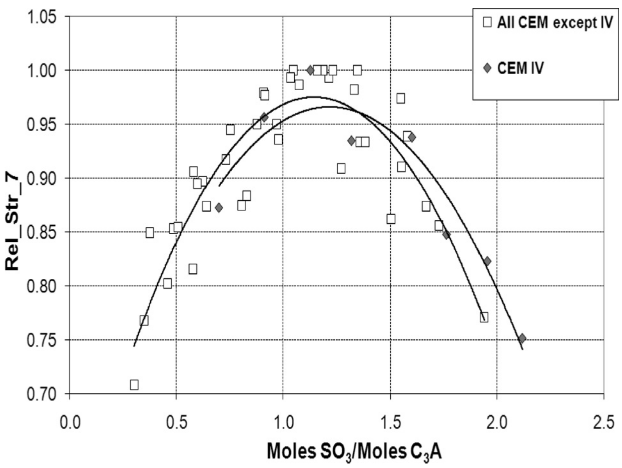

Fig. 5 – *Relative 7 days strength as function of Moles SO_3/Moles C_3A*

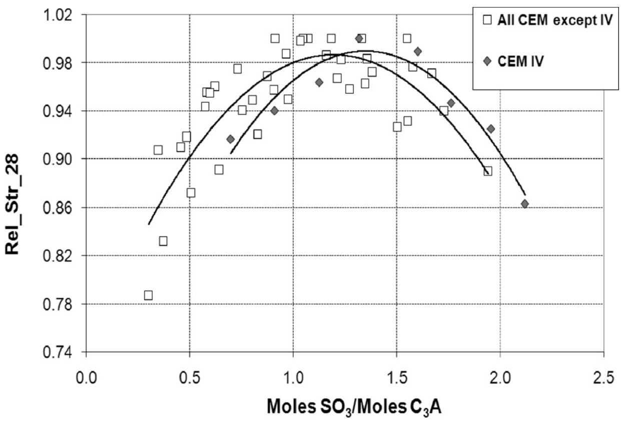

Fig. 6 – *Relative 28 days strength as function of Moles SO_3/Moles C_3A*

$$RelStr\,X = C_2 \cdot \left(\frac{MSO_3}{MC_3A}\right)^2 + C_1 \cdot \left(\frac{MSO_3}{MC_3A}\right) + C_0 \quad (5)$$

$$\frac{MSO_3}{MC_3A_{Opt}} = -\frac{C_1}{2C_2} \quad (6)$$

Where MSO_3/MC_3A = the molecular ratio of sulphates to tricalcium aluminate. The position of MSO_3/MC_3A where the maximum relative strength occurs is provided by equation (6). The coefficients of the four equations, the regression coefficients and the $(MSO_3/MC_3A)_{Opt}$ are shown in Table 8. For all the CEM types except CEM IV, the optimum ratio is found between 1.1 and 1.2. The optimum of 28 days strength is located in a higher position than that of 7 days. The corresponding optimum molecular ratio for the CEM IV is higher, indicating that not all SO_3 of the fly ash behave like gypsum sulphates.

Table 8 – *Coefficients and parameters of equations (5), (6)*

	All CEM types except CEM IV		CEM IV	
	RelStr7	RelStr28	RelStr7	RelStr28
C_2	–0.32	–0.176	–0.27	–0.20
C_1	0.74	0.42	0.67	0.54
C_0	0.55	0.74	0.56	0.63
R	0.90	0.83	0.95	0.96
$(MSO_3/MC_3A)_{opt}$	1.14	1.19	1.22	1.35

Optimum gypsum for different ages of the mortars

Using the five samples shown in Table 6, standard mortars were prepared and the compressive strength was measured at 2, 3, 7, 14, 28 days as well at 3, 6, 14, 30 and 63 months. The results are shown in Figure 7. The parabolic equations fitting

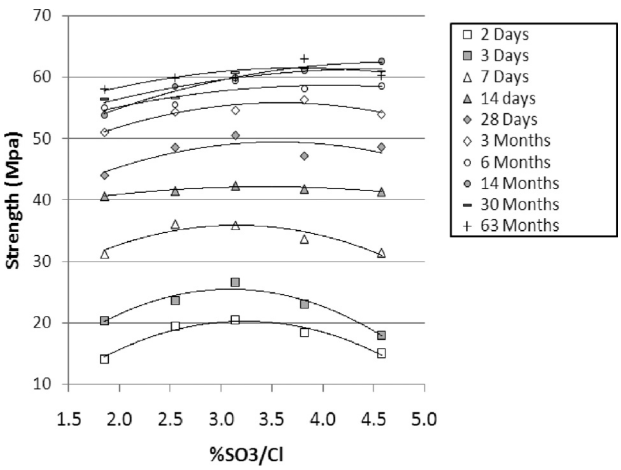

Fig. 7 – *Strength as function of $\%SO_3$/Cl and age*

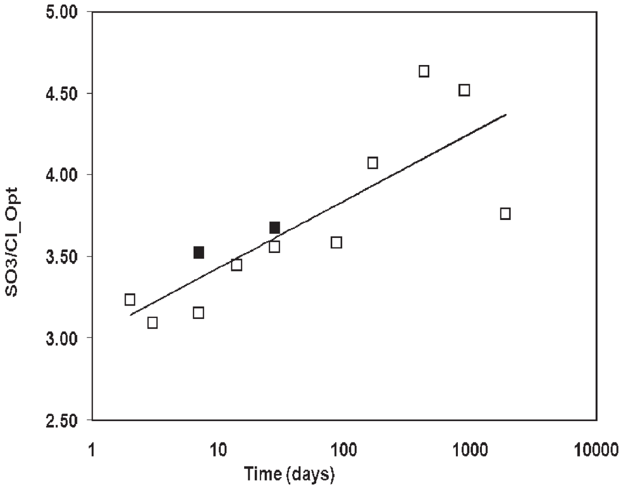

Fig. 8 – *Optimum SO_3/Cl as function of curing time*

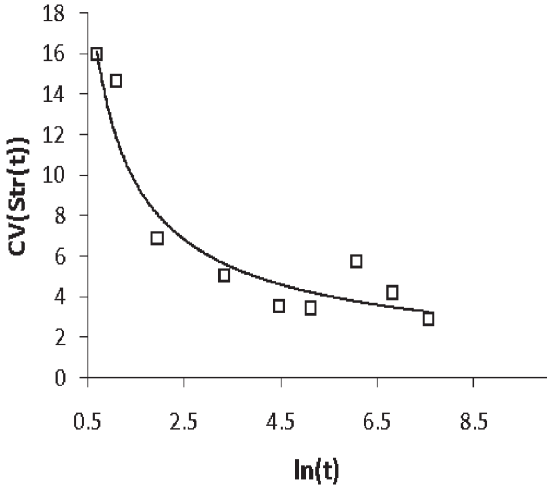

Fig. 9 – *CV of strength as function of curing time*

the experimental data for each age are also demonstrated. An increase in the optimum SO_3/CL as the age augments was observed, as shown in Figure 7. To evaluate if such function can be derived, the position of the optimum SO_3/CL as a function of the curing time is shown in Figure 8. In the same figure the optimums found by equations (3) and (4) are also added (the two black points). An adequate correlation exists between optimum sulphates and time, expressed by equation (7). The regression coefficient of this equation is equal to 0.815.

$$\frac{SO_3}{CL_{opt}} = 0.18 \cdot \ln(t) + 3.02 \tag{7}$$

The time, t, in the above equation is expressed in days. Variable t, takes discrete values t_i belonging to the vector (2, 3, 7, 28, 87, 168, 431, 903, 1908). Function (7) is very useful and practical for the process quality control: For the given clinker quality and for three cement types, involving limestone and pozzolans as main components, the SO_3 target can be decided based on the clinker content and the preferable age where the strength has to be maximized. From Figure 7 it seems that the cement strength is more sensitive to SO_3 changes in earlier ages than in the older ones. The above was investigated as follows: For each age t expressed in days, the coefficient of variation was considered, calculated from formula (8). Then, this variable was plotted as a function of the logarithm of age, $ln(t)$. The results are presented in Figure 9.

$$CV(str(t)) = \frac{Std.Dev.(Str(t))}{Average(Str(t))} \cdot 100 \tag{8}$$

A strong relation between the two parameters is found described by the power law equation (9). The respecting regression coefficient is 0.93.

$$CV(Str(t)) = 12.61 \cdot [\ln(t)]^{-0.67} \tag{9}$$

Figure 9 and equation (9) suggest the high importance of SO_3 optimum in early and typical 28 days strength. For older age, the impact of SO_3 drops but remains always significant.

Generalized equation between strength, SO_3 and time

The data demonstrated in Figure 7 provide the challenging opportunity to investigate the possibility of deriving of a generalized function between compressive strength, content of SO_3 and curing time. To that end, a stepwise procedure was implemented. The multivariable modelling is initialized with the parabolic equations between strength and SO_3/CL. At time t, expressed in days, this function is given by equation (10).

$$Str(t) = A_2(t) \cdot \left(\frac{\%SO_3}{Cl}\right)^2 + A_1(t) \cdot \left(\frac{\%SO_3}{Cl}\right) + A_0(t) \tag{10}$$

Parameters A_0, A_1, A_2 are functions of time. Especially, due to equation (7), variables A_1, A_2 are connected with the formula (11).

$$-\frac{A_1(t)}{2 \cdot A_2(t)} = L_1 \cdot \ln(t) + L_0 \tag{11}$$

The values of A_2 (t) and A_0 (t) are computed with a nonlinear regression technique. Parameters A_1 (t) result from A_2 (t), taking into account equation (7) coefficients. Thus, L_0, L_1 are initialized with L_0 = 3.02, L_1= 0.18. The values of $A_0(t)$, $A_2(t)$ are plotted as a function of $ln(t)$ in Figures 10 and 11, respectively, from where strong correlations are observed between these two coefficients and time. Two models, containing a minimum degree of independent parameters and having high regression coefficients are chosen to describe these correlations, given by equations (12), (13).

$$A_2(t) = M_1 \cdot \ln(\ln(t)) + M_0 \quad (12)$$

$$A_0(t) = N_3 \cdot (\ln(t))^3 + N_2 \cdot (\ln(t))^2 + N_1 \cdot \ln(t) + N_0 \quad (13)$$

The initial values of M_1, M_0 and N_3, N_2, N_1, N_0 are presented in Figures 10, 11 respectively. In these regressions, the values of L_0 and L_1 shown in equation (7) were used. The stepwise process to calculate the final parameters of the multivariable model proceeds as follows:

(i) The system of equations (10) – (13) is considered.

(ii) The time invariant parameters L_k, M_k with k=0, 1 and N_k with k=0, 1, 2, 3 are initialized with the values of equation (7) and Figures (10), (11). Therefore the number of freedom of the model, *df*, equals 8.

(iii) The system of equations is solved for each discrete time t_i, i=1 to N and SO_3/CL_j, j=1 to M and the calculated strength $Str_{Calc,\ i,j}$ is computed. The actual strength values are named $Str_{Act,i,j}$ and N=9, M=5.

(iv) The residual error of the model is computed by formula (14)

$$s_{res}^2 = \sum_{i=1}^{N}\sum_{j=1}^{M} \frac{(Str_{Act,i,j} - Str_{Calc,i,j})^2}{N \cdot M - df} \quad (14)$$

(v) Using the Newton-Rahson non-linear regression method the optimum model parameters are determined minimizing the residual error. After the calculation of the optimal values the model regression coefficient is also computed.

The model parameters, residual error and regression coefficient are presented in Table 9. The parity plot of actual and calculated strength is depicted in Figure 12, where it can be observed that the model results match experimental data well. The generalized multivariable model between strength, SO_3 and time is applied for the following ranges of input data: $SO_3/CL \in (1.5, 4.8)$ with a step 0.3 and time, t ∈ (2, 3, 7, 28, 60, 90, 180, 500, 1000, 2000) expressed in days. The results are shown in Figure 13 from where the high importance of SO_3 optimization in early and typical strength is verified. The generalized model is applied for ages from 2 to 2000 days and for different SO_3/CL ratios. To evaluate the distance from the maximum strength for each age, the difference Strength(t)-Strength(t)$_{Max}$ is plotted. The corresponding functions are depicted in Figure 14. A SO_3/CL=3.1 corresponds to the optimum sulphates for 2 days strength. This gypsum content provides a 28 days strength 0.3 MPa less than the maximum

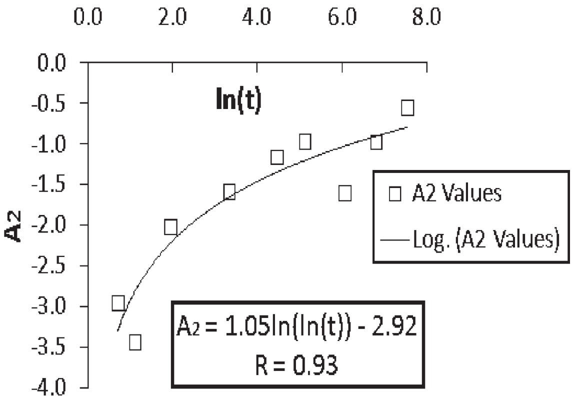

Fig. 10 – *Coefficient A_2 as function of ln(t)*

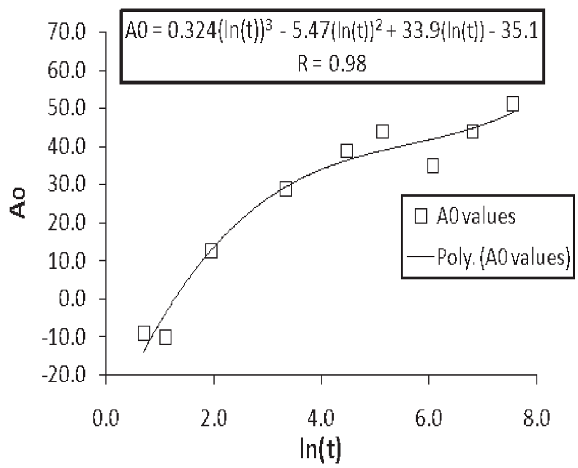

Fig. 11 – *Coefficient A_0 as function of ln(t)*

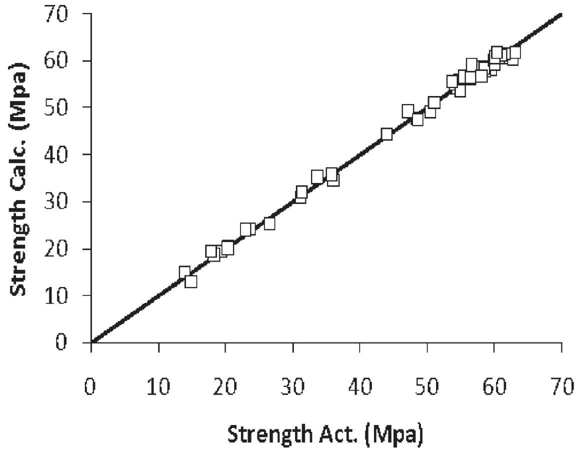

Fig. 12 – *Parity plot of actual and calculated strength*

Table 9 – *Generalized model parameters*

L_0	3.00	M_0	–3.05	N_0	–29.3
L_1	0.159	M_1	1.05	N_1	25.8
				N_2	–3.08
				N_3	0.130
s_{res}=1.21 Mpa					
R=0.997					

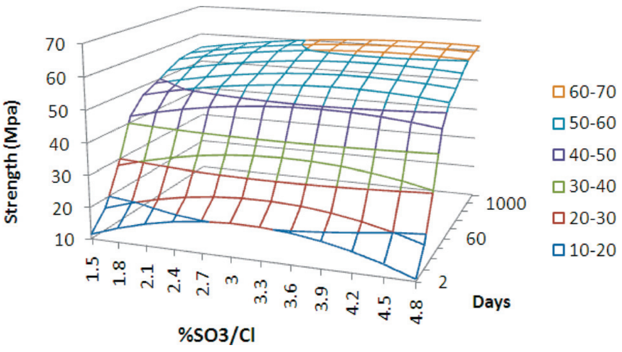

Fig. 13 – *Compressive strength as function of %SO_3/Cl and time*

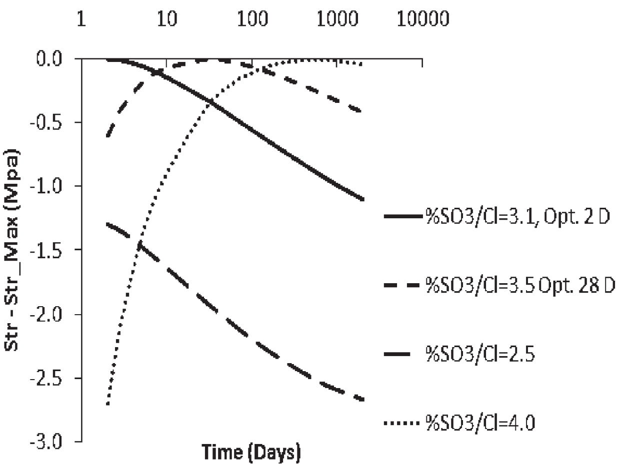

Fig. 14 – *Difference strength – strength$_{Max}$ as function of %SO_3/Cl and time*

one, a difference which cannot be considered significant. In case the optimum gypsum for 28 days strength has been chosen, corresponding to SO_3/CL=3.5, then 2 days strength is 0.6 MPa less than the maximum one. This difference is serious in some cases, especially if the producer aims to maximize the early cement strength. A selection SO_3/CL = 2.5, a value far from the optimum region, leads to strength significantly lower than maximum for any age. The differences become: –1.3 MPa at 2 days, –1.9 MPa at 28 days, – 2.3 MPa at 180 days and –2.6 MPa at 1000 days. On the contrary if a high value of SO_3/CL = 4.0 is chosen corresponding to maximum strength at 180 days, the impact of this selection on early strength is detrimental. All the above results have critical economical effects and indicate the high importance of gypsum regulation in the optimum region depending on the clinker quality and cement type. The above analysis is a good tool for avoiding mistakes concerning the decision about the sulphates target, based only to raw materials cost: There are cases where the gypsum is more expensive than other raw materials, so the producer decides an SO_3 target lower than optimum. Then, as the strength is lowered, the clinker is increaed to reach the strength target, leading to a cost higher than that if SO_3 is located in the optimum area. On the contrary, if the producer compares the gypsum cost with that of clinker, he could increase gypsum by decreasing clinker. If SO_3/CL is higher than the optimum value, then a drop in strength is observed. The producer will probably increase clinker by decreasing other raw materials less expensive than gypsum, with a parallel increase of the cost, as in the previous case.

Variance analysis and error propagation

The position of optimum SO_3 affects the compressive strength values as indicated from equations (4), (6) and (10) – (13). Due to these models, the variance of sulphates it is expected to have an impact on the strength variance as well. To prove the above, an analytical model of the entered variables is developed.

If a variable y is connected with the independent variables x_1, x_2, …x_n via a formula $y = f(x_1, x_2, ...x_n)$, then the variance of y can be determined from the respecting variances of x_i by applying equation (15):

$$\sigma_y^2 = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i} \right)^2 \cdot \sigma_i^2 \tag{15}$$

As independent parameters, the following three are considered: SO_3 content, clinker fraction, CL=%Cl/100 and laboratory reproducibility in strength measurement, σ_R. The variance of the 28 days strength as a function of these three parameters based on equation (11) for all CEM types except CEM IV, is expressed by equation (16):

$$\sigma_{str}^2 = MaxStr28^2 \cdot \left[\left(2B_2 \cdot \frac{SO_3}{CL^2} + B_1 \frac{1}{CL} \right)^2 \cdot \sigma_{SO_3}^2 + \right. \\ \left. + \left(2B_2 \cdot \frac{SO_3^2}{CL^3} + B_1 \frac{SO_3}{CL^2} \right)^2 \cdot \sigma_{CL}^2 \right] + \sigma_R^2 \tag{16}$$

This analytical model is utilized for two cement types, CEM II B-M (P-L) 32.5 and CEM A-L 42.5, using the following parameters:

CEM B-M (P-L) 32.5: *MaxStr28*=38.1 MPa, *CL*=0.65, SO_3 from 1.8% to 3% with a step 0.1%.

CEM A-L 42.5: *MaxStr28*=49.2 MPa, *CL*=0.82, SO_3 from 2.4% to 3.6% with a step 0.1%.

For both CEM types a coefficient of variation of σ_R equal to 2% is supposed. Thus σ_R=0.76 MPa for CEM B-M 32.5 and σ_R=0.98 MPa for CEM II A-L 42.5. For both CEM types σ_{CL}=0.02 is assumed

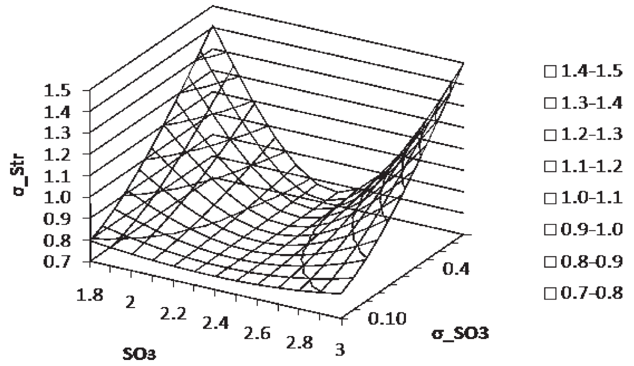

Fig. 15 – *Strength 28 days standard deviation as function of %SO_3 content and standard deviation for CEM II B-M (P-L) 32.5*

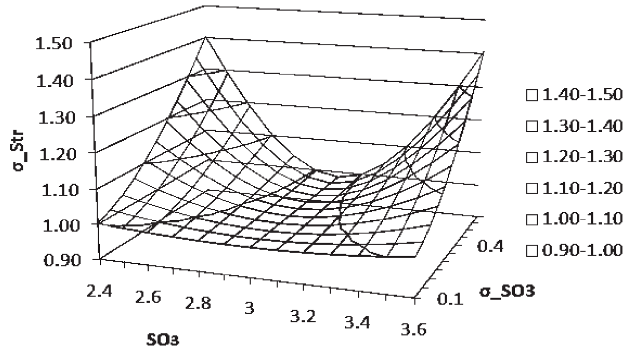

Fig. 16 – *Strength 28 days standard deviation as function of %SO_3 content and standard deviation for CEM II A-L 42.5*

and σ_{SO3} is ranging from 0.1% to 0.6% with a step of 0.05%. Coefficients B_1, B_2 are taken from Table 7. The analytical model is applied to these data and the function between σ_{str}, σ_{SO3} and SO_3 is shown in Figures 15, 16 for the two cement types mentioned. The following remarks can be made from these Figures: If the SO_3 target is placed at the optimum value and this target is realized, then independently of the SO_3 standard deviation, strength deviation remains low. On the contrary, as the SO_3 value differs from the optimum value, then an increase of the SO_3 variance, leads to a significant increase of the strength variability. When the SO_3 standard deviation is extremely high, then any difference from the optimum SO_3 is going along with a sharp deterioration of strength deviation.

Conclusions

Based on experimental design, test execution, statistical modelling and processing, the optimization of the sulphate content of cement was attempted. The analysis involves four cement types produced according to the norm EN 197-1. Compressive strength was correlated with the ratio between sulphates and clinker content – SO_3/CL. Concerning 7 and 28 days compressive strength, for three cement types not containing fly ash as main compound, a common region of the optimum SO_3/CL is determined. For the cements having fly ash as main compound, optimum sulphates are found in a distinguishable region from the previous differing 0.6% of SO_3/CL in the 28 days strength. Consequently for the cements containing high percentages of fly ash, separate control of the optimal gypsum dosage is required. Strength is also correlated with the ratio % moles SO_3/ moles C_3A. For all CEM types except CEM IV, the optimum ratio was found between 1.1 and 1.2. The corresponding optimum molecular ratio for the CEM IV is higher, indicating that not all SO_3 of the fly ash behave like gypsum sulphates.

Extensive long term laboratory tests have been performed to investigate the impact of the mortar curing time on the optimum sulphate content. For ages from 2 days till to 63 months, a generalized model is constructed between strength, sulphates and logarithm of time presenting a regression coefficient higher than 0.995. It is concluded that an increase in mortar age causes a respective increase of the sulphates optimum. This conclusion is very important when the age in which the strength maximization is desirable is to be decided. The generalized correlation proves the high significance of realizing an SO_3 target located in the optimum region corresponding to early or typical strength and the critical economical effect of such decisions and actions.

In parallel by utilizing the error propagation methodology, a variance analysis is performed between strength and SO_3 variance. This treatment indicates that if a significant difference of SO_3 value from the optimum one exists, then an increase of the SO_3 variance, leads to a noticeable growth of the strength variability. Therefore the selection of an optimal SO_3 target, based on the analysis presented, can lead to an optimal Clinker/Cement ratio, in order to achieve a certain strength target with a parallel minimal strength variability. The above can be characterized as a contribution to the improvement of both cement plant operation and product quality.

The crucial role of gypsum on the cement quality, proved for a wide range of cement products with concrete correlations, renders imperative stricter controls and regulation of sulphate content, during the production operation. Modern control techniques could be used in achieving this aim.

Nomenclature

A_0, A_1, A_2 – Coefficients of equation (10)
B_1, B_2 – Coefficients of equation (16)
Blaine – Cement specific surface, m^2 Kg^{-1}
C_0, C_1, C_2 – Coefficients of equations (3) and (5)
C_2S – Dicalcium silicate, %
C_3A – Tricalcium aluminate, %
C_3S – Tricalcium silicate, %
$C_3A \cdot 3Cs \cdot 32H$ – ettringite
C_4AF – Tetracalcium ferroaluminate, %
CL – Clinker fraction
CV – Coefficient of variation
$Cs \cdot 2H$ – Dihydrate gypsum, %
$Cs \cdot 0.5H$ – Hemihydrate gypsum, bassanite, %
Cs – Anhydrite, $CaSO_4$, %
df – degrees of freedom in equation (14)
LOI – Loss on ignition, %
L_0, L_1 – Coefficients of equation (11)
M – Maximum number of cement compositions in equation (14)
MaxStr7 – Maximum strength at 7 days, MPa
MaxStr28 – Maximum strength at 28 days, MPa
MSO_3/MC_3A – Molecular ratio between SO_3 and C_3A
M_0, M_1 – Coefficients of equation (12)
N – Maximum number of time intervals in equation (14)
N_0, N_1, N_2, N_3 – Coefficients of equation (13)
R – Regression coefficient
R40 – Residue on sieve of 40 microns, %
RelStr7 – Dimensionless strength at 7 days
RelStr28 – Dimensionless strength at 28 days
RelStrX – Dimensionless strength at X days, X=7, 28
SO_3 – Sulphates, %
SO_3/CL – Mass ratio between SO_3 and clinker content, %
Str_{Act} – Actual strength in equation (14), MPa
Str_{Calc} – Strength calculated from the model in equation (14), MPa
Str7 – Compressive strength at 7 days, MPa
Str28 – Compressive strength at 28 days, MPa
Str(t) – Strength at time t, MPa
s_{res} – Residual error in equation (14), MPa
t – Time, days
x_i – Independent variables in equation (15)
y – Dependent variable in equation (15)

Greek symbols

σ_i^2 – Variance of the variable x_i in equation (15)
σ_{CL}^2 – Variance of the variable CL
σ_R – Laboratory reproducibility in 28 days strength, MPa
σ_{SO3}^2 – Variance of the SO_3, $(\%)^2$
σ_{str}^2 – Variance of the strength, MPa^2
σ_y^2 – Variance of the variable y in equation (15)

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