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A MATHEMATICAL MODEL FOR THE CONTROL OF CEMENT SETTING USING CALCIUM CHLORIDE AS ACCELERATOR

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ABSTRACT

In this paper a mathematical model for the control of Portland cement setting, using $CaCl_2$ as accelerator, is developed and the importance of chemical-mineralogical and fineness factors is pointed out. It is shown that the ratio C_3A/C_4AF as well as the SO_3 content are the predominant factors affecting the setting, while the fineness parameters, the specific surface and the fraction 3-32μm, also influence the setting time. The effect of fineness parameters is more pronounced upon the final setting.

Introduction

It is well known that $CaCl_2$ greatly affects the hardening of Portland cement pastes. Many researchers have studied the chloro-compounds formed during the hydration of cement in the presence of $CaCl_2$ (1,2,3,4,5) while others studied the influence of $CaCl_2$ on the development of the cement strength and on the rate of hydration (6,7). The accelerating action of $CaCl_2$ is attributed to its effect on the formation, dissolution, migration and crystallisation rate of $Ca(OH)_2$ (7,8).

Although $CaCl_2$ is one of the most widely studied accelerators of cement hydration, little attention has been paid on the correlation between the effect of $CaCl_2$ and the specific characteristics of the cements used, such as the chemical-mineralogical composition and the fineness.

In the present paper a mathematical model for the control of cement setting, using $CaCl_2$ as accelerator, is developed based on three series of data concerning the chemical-mineralogical synthesis of the cement, the parameters of the particle size distribution of the cement and the material distribution in characteristic size fractions.

Experimental

The data used for the development of the setting model are given in Tables 1 and 2, which present the chemical-mineralogical data and the data concerning the fineness of the cements respectively. Chemical grade $CaCl_22H_2O$ (Riedel de Haen) was used. The samples were prepared by adding the appropriate salt solution to Portland cement pastes of standard consistency. The setting time was determined according to the Vicat method. The experimental setting time as well as the % content of $CaCl_2$ of the cements are given in Table 3.

TABLE 1
Chemical and Mineralogical Characteristics
of the Cements Used.

No	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)	Na_2O_{eq} (%)	SO_3 (%)	C_3S/C_2S	C_3A/C_4AF
1	60.5	11.1	7.2	11.9	0.57	2.60	5.45	0.61
2	57.7	14.0	6.0	12.5	0.62	2.50	4.14	0.48
3	53.0	18.5	6.5	12.8	0.59	2.45	2.86	0.51
4	59.3	12.5	6.4	12.4	0.54	2.50	4.73	0.52
5	54.4	16.7	6.8	12.2	0.61	2.70	3.26	0.56
6	56.6	14.9	6.7	12.4	0.60	2.72	3.80	0.54
7	63.0	9.4	6.3	12.2	0.52	2.40	6.70	0.51
8	56.5	15.1	6.9	12.0	0.60	2.60	3.74	0.57
9	54.2	17.0	7.2	11.9	0.59	2.75	3.18	0.61
10	56.2	16.4	7.3	11.1	0.65	2.60	3.42	0.65
11	59.6	12.2	7.0	11.9	0.62	2.60	4.88	0.59
12	62.5	8.8	7.8	11.6	0.54	2.55	7.12	0.67
13	57.0	13.9	6.7	12.8	0.59	2.55	4.10	0.53
14	54.1	16.6	7.1	12.8	0.61	2.40	3.26	0.56
15	59.1	11.9	7.3	12.2	0.54	2.50	4.97	0.60
16	59.8	12.8	6.3	12.2	0.60	2.60	4.65	0.51
17	58.8	13.6	6.9	11.0	0.64	2.66	4.33	0.63
18	49.9	20.8	6.6	13.1	0.65	2.65	2.40	0.50
19	60.0	12.5	6.9	11.3	0.59	2.55	4.78	0.61
20	57.2	15.6	6.9	11.3	0.59	2.60	3.66	0.61
min	49.9	8.8	6.0	11.0	0.52	2.40	2.40	0.48
max	63.0	20.8	7.8	13.1	0.65	2.75	7.12	0.67

Results and discussion

The following series of variables have been tested in order to certify their effect on the cement setting.

a. $CaCl_2$ content.

b. chemical - mineralogical variables: % content of C_3S, C_2S, C_3A, C_4AF, Na_2Oeq, SO_3, fCaO, values of C_3A/C_4AF, C_3S/C_2S.

c. particle size distribution variables: specific surface S_b, position parameter pp of Rosin-Rammler (RR) curve, uniformity factor n of RR curve.

d. size fractions variables : % content in 3-32μm, <3μm, 3-16μm, 16-24μm.

The selection of the variables that contribute to the estimation of the cement setting time is based on stepwise regression analysis. In figure 1 the variables that are inserted in the mathematical model by this statistical procedure are illustrated.

TABLE 2
Fineness Characteristics of the Cements Used

No	S_b (cm^2/g)	n	pp (μm)	<3μm (%)	3-32μm (%)	3-16μm (%)	16-24μm (%)
1	4220	0.99	16.1	16.7	70.4	41.9	16.3
2	3940	1.02	16.3	16.5	70.2	40.2	17.7
3	3820	0.97	17.8	16.0	70.9	38.6	18.8
4	3940	1.01	15.2	17.5	70.9	42.4	16.8
5	3900	0.99	18.2	15.7	68.4	37.9	17.3
6	3870	1.03	16.1	15.5	72.8	43.2	17.9
7	4100	1.05	16.0	15.7	70.5	39.9	19.4
8	3910	1.00	15.6	17.5	70.0	41.2	16.6
9	3750	1.00	16.0	17.1	70.7	39.7	17.8
10	3230	0.92	23.6	14.0	60.2	32.8	13.0
11	4000	0.97	17.4	16.2	71.3	40.2	18.4
12	4050	1.01	16.4	16.6	70.4	39.0	18.3
13	3980	1.02	16.4	15.6	71.9	41.8	18.0
14	3900	0.99	16.2	17.0	72.0	41.0	16.8
15	4000	1.03	17.5	14.6	71.7	37.9	19.8
16	3500	0.93	22.5	14.1	62.7	33.7	15.8
17	3320	0.94	23.2	13.6	62.1	32.8	16.1
18	3720	0.99	17.6	15.5	69.3	39.6	17.3
19	3260	0.97	22.7	13.0	60.5	32.7	15.5
20	3540	0.97	19.5	14.9	66.7	38.1	16.6
min	3230	0.92	15.2	13.0	60.2	32.7	13.0
max	4220	1.05	23.6	17.5	72.8	43.2	19.8

Variables	initial setting time	final setting time
$CaCl_2$ (%)	[shaded]	[shaded]
C_3A/C_4AF	[shaded]	[shaded]
SO_3 (%)	[shaded]	[shaded]
S_b (cm^2/g)	[shaded]	[shaded]
pp (μm)		[shaded]
3-32 μm (%)	[shaded]	[shaded]
3-16 μm (%)		[shaded]

FIG. 1
Selected variables by stepwise regression analysis for the estimation of cement setting time (shading=selection)

The stepwise regression analysis of the data presented in Tables 1, 2 and 3 leads to the relation 1.

TABLE 3
Measured Initial and Final Setting Time of the Cements Used

	Initial setting tine (min)				Final setting time (min)			
No	0% $CaCl_2$	0.5% $CaCl_2$	1.0% $CaCl_2$	1.5% $CaCl_2$	0% $CaCl_2$	0.5% $CaCl_2$	1.0% $CaCl_2$	1.5% $CaCl_2$
1	75	55	45	35	120	100	80	60
2	140	130	85	85	190	170	120	120
3	115	95	85	55	160	130	110	80
4	130	90	80	65	160	120	110	90
5	115	100	85	60	170	140	120	100
6	135	125	90	55	170	170	130	90
7	100	75	45	35	130	120	80	60
8	120	85	80	60	170	120	110	110
9	150	130	90	55	200	180	130	80
10	120	80	65	40	160	105	90	60
11	175	120	90	60	220	160	130	90
12	105	80	55	45	150	110	90	70
13	105	80	70	50	150	130	100	70
14	110	90	70	40	150	120	100	70
15	130	110	75	65	190	150	120	90
16	130	90	75	45	170	130	100	70
17	90	75	50	45	140	100	70	60
18	120	130	95	70	190	170	130	90
19	120	110	100	60	160	150	130	90
20	115	95	60	50	160	120	100	80

$$\begin{vmatrix} t_i \\ t_f \end{vmatrix} = \begin{vmatrix} -43.321 & -95.169 & 51.627 & -0.028 & 0.000 & 2.120 & 0.000 \\ -54.213 & -115.138 & 116.062 & -0.057 & -3.877 & 7.204 & -7.235 \end{vmatrix} \cdot \begin{vmatrix} CaCl_2\ (\%) \\ C3A/C4AF \\ SO_3\ (\%) \\ S_b\ (cm^2/g) \\ pp(\mu m) \\ 3\text{-}32\mu m\ (\%) \\ 3\text{-}16\mu m\ (\%) \end{vmatrix} \quad (1)$$

where t_i, t_f are the initial and final setting time (min) respectively.

The relation (1) results to:

$$t_i = -43.320(\%\ CaCl_2) - 95.169(C_3A/C_4AF) + 51.627(\%\ SO_3) - 0.028S_b + 2.120(\%\ 3\text{-}32\mu m) \quad (2)$$

$$t_f = -54.213(\%\ CaCl_2) - 115.138(C_3A/C_4AF) + 116.062(\%\ SO_3) - 0.057S_b - 3.877pp + 7.204(\%\ 3\text{-}32\mu m) - 7.235(\%\ 3\text{-}16\mu m) \quad (3)$$

In order to investigate the fitting of the multiple regression models 2 and 3 to the set of data, the statistic multiple coefficient of determination R^2 (R square) is determined. The R^2 is 0.9814 and 0.9905 for the models 2 and 3 correspondingly. That means that the

98.1% to 99.1% of the sum of squares of deviations of the measured setting time values about their mean is attributable to the least-squares prediction equations therefore the model fits the data best.

The F-test statistics are 729 and 979 for the models 2 and 3 correspondingly which greatly exceed the tabled values 2.36 and 2.16. That means that at least one of the parameters of the independent variables does not equal zero for a confidence interval of 95%.

The adequateness of the obtained mathematical models has been examined by Student's t-test and all calculated values of t-test are less than tabulated at a=0.05. Therefore an exact functional dependence can be established between the studied variables and the cement setting time. The average residuals between measured and computed setting time are 12.6% and 8.4% for the models 2 and 3 correspondingly or more specifically 10min for both models.

In Figure 2 the effect of $CaCl_2$ content on the cement setting is given (cement No 4) while in Figure 3 the values of initial and final setting time vs. computed values are presented. As it is seen the simulation of the setting development is very satisfactory.

From the relations 2 and 3 it is obvious that the ratio C_3A/C_4AF as well as the SO_3 content of the cement are the significant factors for the setting time. More specifically the increase of ratio C_3A/C_4AF leads to lower setting time while the increase of SO_3 content leads to higher setting time.

The cement setting time is also affected by the values of S_b and % content in the particle fraction 3-32μm. The increase of S_b and % content in 3-32μm leads to lower and higher setting time respectively.

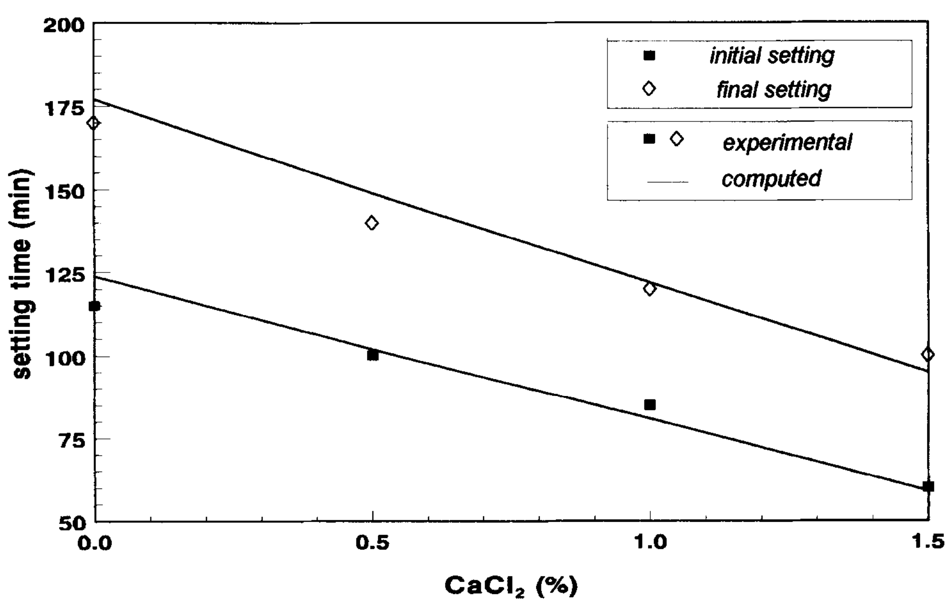

FIG. 2.
Effect of $CaCl_2$ on the cement setting

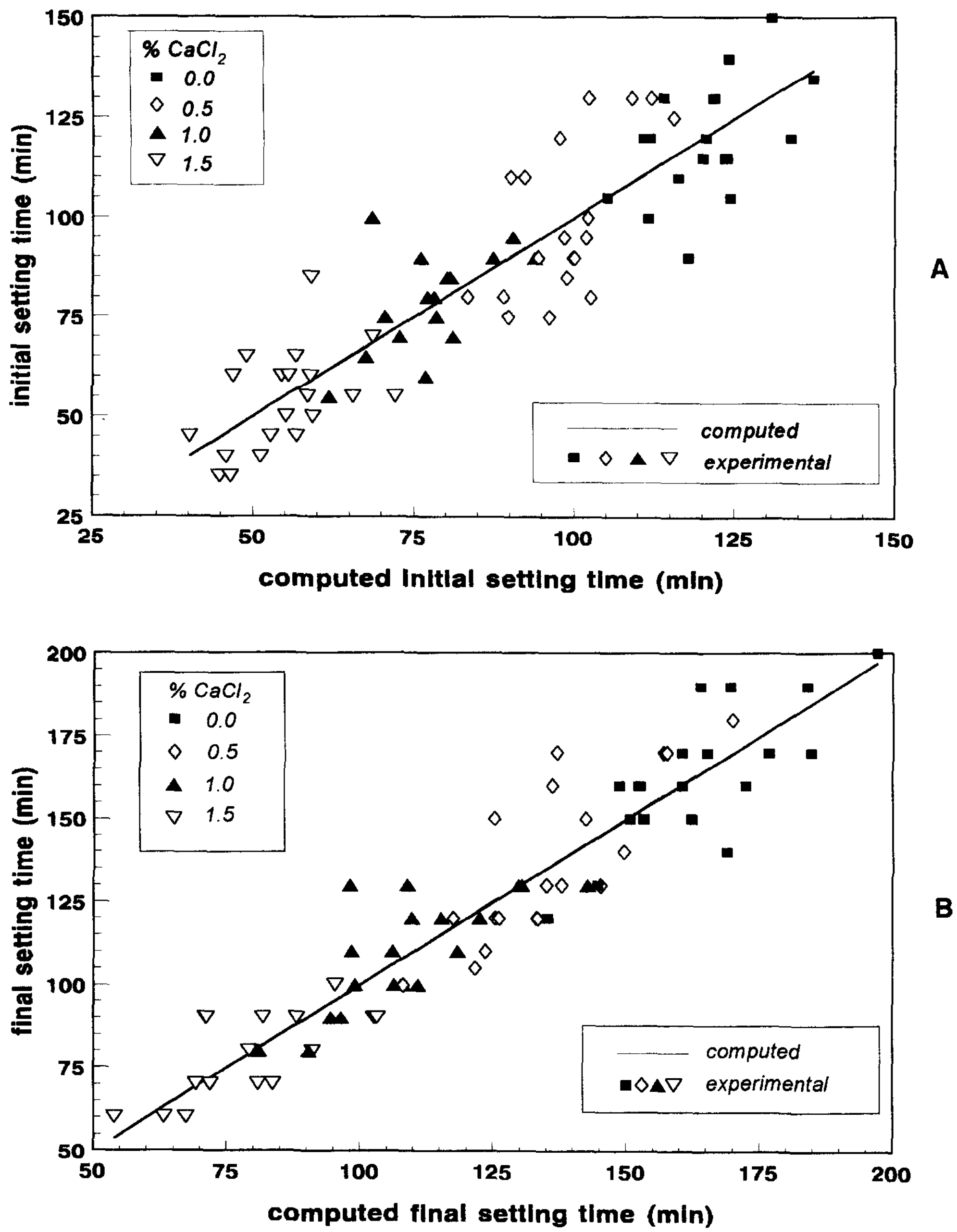

FIG. 3.
Initial (A) and final (B) setting time vs. computed cement setting time

The final setting is more affected, compared to the initial setting, by the fineness parameters. Specifically the final setting time is additionally affected by the position parameter (pp) of Rosin-Rammler curve as well as by the fraction 16-24μm. This is expected since greater grains of cement are involved during the development of the hydration process.

It must be noticed that it is not possible to extract conclusions concerning the individual contribution of the fineness parameters on the setting time since these variables are strongly correlated.

The relations 2 and 3 permit the estimation of the amount of $CaCl_2$ that must be added in a cement in order to achieve the desired initial and final setting time. For example, it is possible to attain t_i=60-80min and t_f=90-110min by adding 0.83%-1.13% of $CaCl_2$ in a cement having C_3A/C_4AF=0.60, SO_3=2.6%, S_b=3700cm^2/g, pp=19.5μm, 3-32μm=66.5% and 3-16μm=38%.

Conclusions

The following conclusions can be drawn from the present study:

- A mathematical model for the estimation of the cement setting time, in the presence of $CaCl_2$,is developed based on stepwise regression analysis.
- The proposed model computes the cement setting time with a satisfactory accuracy.
- The setting time is affected mainly by the ratio C_3A/C_4AF and the % SO_3 content.
- The specific surface and the fraction 3-32μm influence the setting time.
- The final setting is more affected, compared to the initial setting, by the fineness parameters.

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