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Alternative calcium-sulfate-bearing materials as cement retarders: Part II. FGD gypsum

G. Tzouvalas[1], G. Rantis, S. Tsimas*

Department of Chemical Engineering, Laboratories of Inorganic and Analytical Chemistry, Chemical Engineering School,
National Technical University of Athens, Zografou Campus, 9 Heroon Polytechniou St., GR-157 73, Athens, Greece

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Abstract

The aim of this paper is to investigate the possible displacement of natural gypsum ($CaSO_4{\cdot}2H_2O$) in cement with an alternative setting retarder, such as the industrial by-product derived from flue gas desulfurization process called FGD gypsum. These calcium-sulfate-bearing materials (CSBM), alone or in mixtures, were ground with clinker both in laboratory and industrial scale to examine their influence on the physical and mechanical properties of cement, as well as on the industrial production line of cement. From the present work, it is extracted that the use of mixtures of sulfate-bearing materials with gypsum seems to be advantageous for the actual control of setting time. The addition of FGD gypsum increases setting time without affecting compressive strength profile. During the industrial trial, the formation of hemihydrate form of calcium sulfate dihydrate has a profound regulatory effect on the setting and strength performance of the cement partially replaced with FGD gypsum.

Keywords: Portland cement; Gypsum; FGD gypsum; Setting; Compressive strength

1. Introduction

In the cement industry, natural gypsum ($CaSO_4{\cdot}2H_2O$) is added during grinding of Portland cement to delay the rapid reaction between C_3A ($3CaO{\cdot}Al_2O_3$) and water and to regulate cement setting properties [1,2]. However, its continuous use has led to the reduction of its high-purity stock in some countries. In certain cases, anhydrite ($CaSO_4$) has proven to be particularly reliable for the partial replacement of natural gypsum [3,4]. At the same time, due to environmental concerns, it is essential to examine the possible of by-product gypsum, such as ehydrat-, fluoro-, citro-, titano-, boro-, and FGD gypsum as setting retarders [4,5]. In this case, the effect of the impurities that these materials contain on the properties of cement remains to be studied.

A promising calcium-sulfate-bearing material (CSBM), which can replace mineral gypsum, seems to be desulfogypsum or FGD gypsum, an apparent waste material of the desulfurization process of residual gases with limestone in coal-burning power plants [4–8]. Strong efforts have been made to utilize FGD gypsum from the technical and economic point of view. At the same time, FGD gypsum has gained recognition in the European Union and in the OECD as a product [8]. The chemical reactions that can take place to convert flue gases into gypsum are the following:

$$SO_2 + H_2O \rightarrow H^+ + HSO_3^-$$

$$H^+ + HSO_3^- + 1/2O_2 \rightarrow 2H^+ + SO_4^{-2}$$

$$2H^+ + SO_4^{-2} + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O$$

There are two major methods of producing FGD gypsum: the wet-type scrubbing process, which is the most commonly used (90%), and the dry or semidry scrubbing process. The wet-type scrubbing process contains two alternative aspects: (i) the slurry scrubbing method, which is applied in Greek power plants, where mixture of $CaO/CaCO_3$ with water (slurry) is used, or (ii) the clear solution scrubbing (CSS) process, where either a solution of Na and $CaO/CaCO_3$ is used (dual alkali process, DAP) or a solution at pH 3–4 of sulfate aluminum is used (Dowa process, DP) [9].

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* Corresponding author. Tel.: +30-1-772-3095; fax: +30-1-772-1727.
E-mail addresses: gtzouv@central.ntua.gr (G. Tzouvalas), stangits@central.ntua.gr (S. Tsimas).

[1] Tel.: +30-1-772-2893; fax: +30-1-772-3188.

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2. Experimental

2.1. Laboratory scale trials

Two CSBMs, natural gypsum (as reference material) and FGD gypsum, have been interground in a lab ball mill in different proportions with clinker for an hour. The chemical analysis of these materials, according to ASTM C 471M-95 [10], and the hydrated forms of calcium sulfate, as well as their solubility at 25 °C, are shown in Table 1, while the chemical analysis of the clinker used is shown in Table 2. The percent composition of the laboratory-produced cements and the percentage of SO_3, measured by XRF are shown in Table 3. The specific surface obtained was in the range of 3700–3900 cm^2/g.

Based on the derived optimum SO_3 content of cements with either gypsum or FGD gypsum, cement mixtures using blends of gypsum and FGD gypsum (CGF) were also prepared [4]. The ratios of the mixtures of CSBM expressed as natural gypsum to FGD gypsum ratio were 0:100 (CGF1), 20:80 (CGF2), 40:60 (CGF3), 50:50 (CGF4), 60:40 (CGF5), 70:30(CGF6), and 100:0 (CGF7). In Table 4, the ratios of clinker and mixtures of CSBMs, as well as the measured values of SO_3 by XRF and the specific surface of the produced cements, are summarized.

To expand the whole project to pozzolanic cements (CEM II-A), clinker (80%) was also interground with each of these CSBM [gypsum (G), FGD gypsum (F)] and fly ash [P (3.8% SO_3, 1.1% Na_2O, 0.7% K_2O, 31% CaO, 28% SiO_2)]. All these compositions are summarized in Table 5. Specific surface values were at 4100 cm^2/g.

2.2. Industrial scale trials

Table 1
Chemical analysis, hydrated forms determination, and solubility of calcium sulfate bearings used in laboratory-produced cements

	Gypsum	FGD gypsum
Combined water (%)	19.30	18.05
SO_3 (%)	43.41	42.19
SiO_2 (%)	0.65	0.30
CO_2 (%)	2.51	1.58
CaO (%)	32.40	33.40
R_2O_3[a] (%)	0.03	0.10
MgO (%)	0.92	0.10
$CaSO_4·2H_2O$ (%)	90.97	87.96
$CaSO_4$ (%)	1.87	2.17
Solubility (g/100 g H_2O)	0.260	0.273

[a] R_2O_3: $Fe_2O_3 + Al_2O_3$.

Table 2
Chemical analysis of clinker

%	SO_3	SiO_2	CaO	R_2O_3[a]	MgO	Na_2O	K_2O	C_3S	C_2S	C_3A	C_4AF
Clinker	0.71	22.0	66.2	8.5	1.92	0.14	0.6	63.9	14.9	6.7	11.2

[a] R_2O_3: $Fe_2O_3 + Al_2O_3$.

During the industrial production of cement, in the cement mill, gypsum undergoes partial dehydration at 110–130 °C to form hemihydrate ($CaSO_4·0.5H_2O$) and, in some cases, undergoes total dehydration, at 170–190 °C, to form soluble anhydrite (γ-$CaSO_4$) [11,12,13]. To apply the laboratory findings in industrial trial, the clinker, at various temperatures (130–250 °C), was fed into a ball mill (95 t/h) with mixtures of CSBM [100% gypsum (CG), 75% gypsum/25% FGD (CGF)] and filler (limestone) to produce cement (CEM I). Although, it is understandable that these ratios are nominal, inasmuch as natural gypsum was not 100% pure in its composition. The temperature at the exit of the mill was maintained below 118 °C by spraying the necessary quantity of water at the inlet and/or the middle of the mill. The quantity of sprayed water and the mill dew point for each trial were calculated through the construction of mill heat balances. The industrial scale trials took place at Kamari Plant (Elefsis, Greece) of Titan Cement. All these, in addition to clinker temperature, SO_3 values obtained for cements, and the admixing ratios of gypsum (ehydrate) and anhydrite to the CSBM, are shown in Table 6. The specific surface obtained was in the range of 3500–3650 cm^2/g. The degree of gypsum dehydration may be calculated as follows [14]:

$$\%\,\text{Dehydration} = 100 \times \frac{\%\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}\cdot\dfrac{\text{MWCaSO}_4\cdot 0.5\text{H}_2\text{O}}{\text{MWCaSO}_4\cdot 2\text{H}_2\text{O}}}{\%\text{CaSO}_4\cdot 2\text{H}_2\text{O} + \%\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}\cdot\dfrac{\text{MWCaSO}_4\cdot 0.5\text{H}_2\text{O}}{\text{MWCaSO}_4\cdot 2\text{H}_2\text{O}}}$$

The content of ehydrate, hemihydrate, and anhydrite in cement was determined by differential thermal analysis (Netzsch STA 409-DSC/TG). In Table 7, the results from the calcium sulfate hydrates (ehydrate, hemihydrate, and anhydrite) determination in the produced cements and the degree of gypsum's dehydration are summarized.

At the same time, physicomechanical properties, such as setting time and compressive strength of the produced cement, were determined based on EN norms.

Table 3
% SO_3 of cement mixtures[a] with different materials versus their percent addition

Sample	% Addition	% SO_3
CG1	4.0	2.37
CG2	4.5	2.58
CG3	5.0	2.93
CG4	5.5	3.12
CG5	6.5	3.54
CG6	7.0	3.93
CG7	7.5	4.31
CF1	4.0	2.46
CF2	4.5	2.69
CF3	5.5	3.12
CF4	6.5	3.47
CF5	7.0	4.06
CF6	7.5	4.36

[a] CG: clinker–gypsum, CF: clinker–FGD gypsum.

Table 4
Admixing ratios for cement mixtures, % SO_3, and specific surface of cements

	CGF1	CGF2	CGF3	CGF4	CGF5	CGF6	CGF7
% Clinker	93.5	93.22	93.26	93.28	93.30	93.32	93.5
% Mixture gypsum–FGD gypsum	6.5	6.78	6.74	6.72	6.70	6.68	6.5
% SO_3	3.47	3.54	3.55	3.58	3.55	3.49	3.54
Specific surface—Blaine (cm^2/g)	3850	3780	3760	3830	3590	3600	3850

The comparative study of the laboratory CEM-I-type cement based on the percentage of soluble SO_3 was carried out by mixing 1 g of cement and 30 ml of water for an hour. After filtration (white ribbon filter), the filtrate was heated, and 10–15 ml of $BaCl_2$ (10% w/w) was added. $BaSO_4$ precipitated, and its mass was determined through filtration (blue ribbon filter) and the burning of the filter at 950 °C. Soluble SO_3 was then determined by multiplying the coefficient .343 with the quantity of $BaSO_4$.

3. Results and discussion

3.1. Laboratory production

The compressive strengths for 1, 2, 7, and 28 days, according to EN 196.2, for FGD gypsum are compared with gypsum in Fig. 1. From this figure, it is derived that the optimum percentage of SO_3 relating to the compressive strength is 3.5% for cements with gypsum and FGD gypsum. It is also shown that the results of compressive strength of cements with FGD and natural gypsum are in the same order. This is clearer for SO_3 percentages around the optimum addition of 3.5%.

The 28-day compressive strength results (EN 196.1) for cements with mixtures of sulfate-bearing materials (CEM I) are shown in Fig. 2. We must point out that no significant differences, except for the 20:80 mixture, are observed concerning the compressive strength of mixtures. The compressive strengths of CGF cements showed the same values for all examined ratios. It is also evident from Fig. 3 that in the admixture gypsum/FGD gypsum, ehydrates of both origins exhibit a similar behavior in cement strength performance. Optimum compressive strength is accomplished when the ratio between ehydrate content of gypsum and of FGD gypsum ranges from 0.7 to 1.6.

As it is extracted from Fig. 4, cements with FGD gypsum showed relatively higher setting times. In Fig. 5, the initial setting times of all mixtures versus the percent content of gypsum in the cement sample are plotted. It is evident that the addition of FGD gypsum leads to slightly higher setting times. It is also extracted that FGD is a very good controller of setting, as it can give, in mixtures with gypsum, a large range of setting time (115–170 min). The FGD gypsum is a better retarder than gypsum, although they both contain the same chemical compound (i.e. $CaSO_4 \cdot 2H_2O$).

Table 5
Admixing ratios of CSBM and P in cement mixtures (CEM II-A) and % SO_3 of cements

	CGP1	CGP2	CGP3	CFP1	CFP2	CFP3
% CSBM	4	5	6	4	5	6
% P	16	15	14	16	15	14
% SO_3	2.85	3.25	3.65	2.99	3.42	3.84

The aforementioned remarks are confirmed from Fig. 6, where the setting time increases as more ehydrate of FGD gypsum replaces ehydrate of gypsum in the admixture. The difference in reactivity of the two CSBMs is attributed to the difference in the morphology and the crystal lattice of the ehydrate. Gypsum is found in the shape of compressed sheets as a result of geological effects caused by heat and pressure changes. The theoretical crystalline system of gypsum is monoclinic. FGD gypsum is crystallized in rounded hexagons, which are an indication that soluble anhydrite of hexagonal crystal lattice is formed. Moreover, FGD gypsum's higher solubility can be a fact (Table 1), which prolongs the setting process. It must be also pointed out that FGD gypsum contains a small percentage of $CaSO_3 \cdot 0.5H_2O$, which may retard the setting further.

The initial setting time and 28-day compressive strength for the CEM-II-A-type cements are presented in Figs. 7 Figs. 8. The setting time results showed that the FGD gypsum increases the setting time of the cement comparing

Table 6
Clinker temperature, admixing ratios of dihydrate and anhydrite to CSBM, water sprayed, and mill dew point

	CG1	CG2	CGF1	CGF2	CGF3
Clinker temperature (°C)	250	192	250	189	133
% Dihydrate	3.70	3.70	4.73	4.54	4.71
% Anhydrite	0.64	0.64	0.36	0.43	0.35
H_2O (kg/h)	5894	4146	6252	3966	2142
Dew point (°C)	73	66	76	65	53

Table 7
% SO_3, calcium sulfate hydrates (dihydrate, hemihydrate, anhydrite), and % degree of dehydration in industrially produced cements

	T clinker (°C)	% SO_3	Dihydrate (%)	Hemihydrate (%)	Anhydrite (%)	% Dehydration
CG1	250	2.63	1.70	1.69	0.64	54.13
CG2	192	2.67	1.17	2.13	0.64	68.31
CGF1	250	2.78	2.04	1.95	0.34	53.14
CGF2	189	2.92	0.94	3.02	0.43	79.19
CGF3	133	2.95	1.84	2.40	0.35	60.70

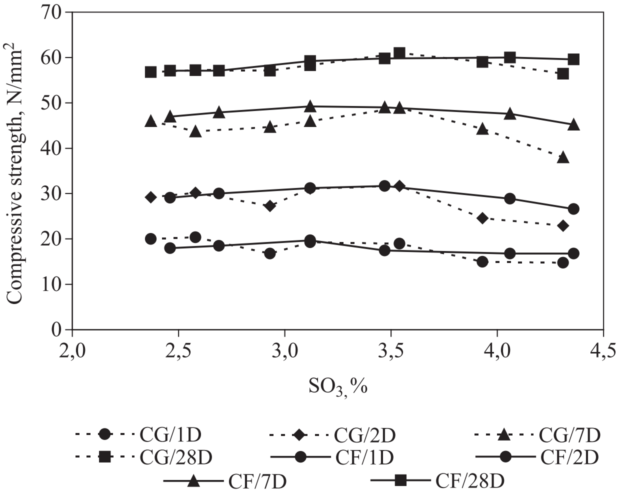

Fig. 1. Comparison of compressive strengths of CG and CF cements versus % SO_3.

to natural gypsum. FGD gypsum can replace natural gypsum without any negative effect on the compressive strength of the cement. The optimum addition of CSBM to cement (CEM II) is about 4–5% (Fig. 8).

Finally, the ratio of soluble SO_3 to the setting time for the laboratory cements is plotted in Fig. 9. The more FGD gypsum added in the mixture of FGD gypsum/natural gypsum, the more soluble SO_3 in cement becomes available, and consequently, the higher the obtained setting times become. This must be attributed to the fact that FGD gypsum is more soluble than natural gypsum (Table 1).

The results of the tests on the laboratory-produced cements with various admixtures were encouraging as far as the setting and strength performance was concerned. Consequently,

- initial setting time increases with FGD gypsum, and
- cement strength does not deteriorate with the addition of FGD.

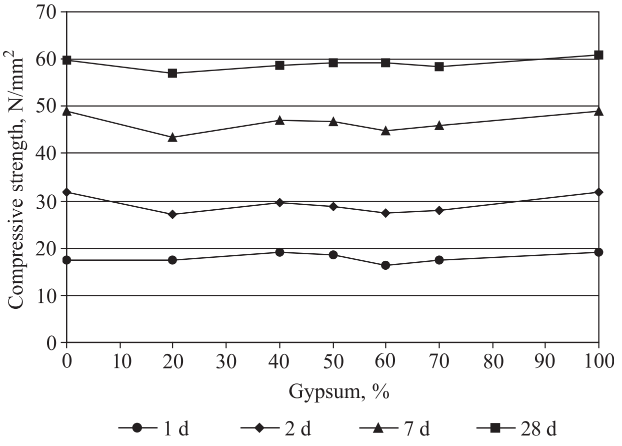

Fig. 2. Compressive strengths of CGF cements versus the ratio of gypsum in the mixture of CSBM.

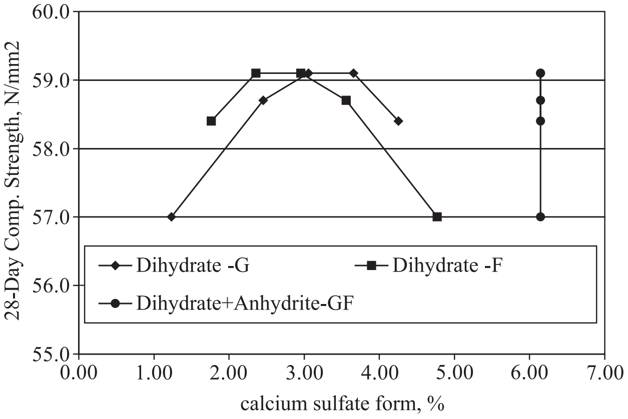

Fig. 3. Cement with admixtures of gypsum and FGD gypsum: 28-day compressive strength versus dihydrate and anhydrite content of a different origin.

3.2. Industrial production

In Fig. 10, the profile of the internal mill temperature for each trial is plotted. Temperatures did not exceed 130 °C, and gypsum dehydration was limited to the formation of hemihydrate and not γ-$CaSO_4$. The behavior of each

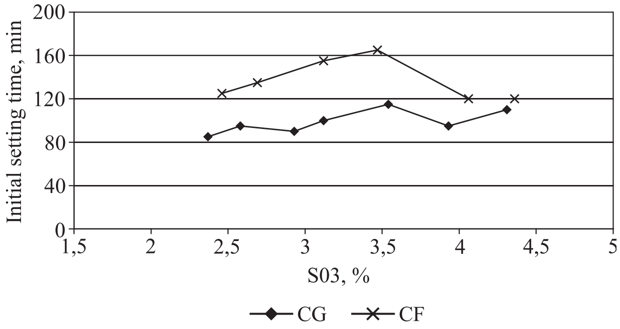

Fig. 4. Setting times of CG and CF cements.

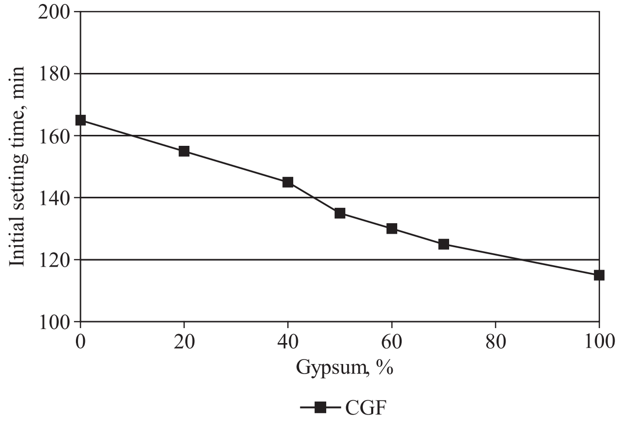

Fig. 5. Setting times of CGF cements versus the ratio of gypsum in the mixture of CSBM.

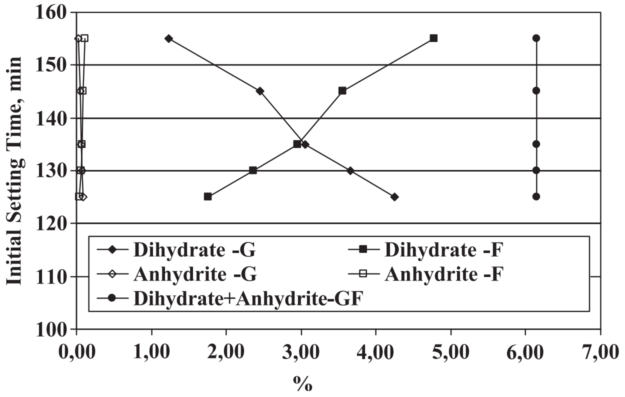

Fig. 6. Cement with admixtures of gypsum and FGD gypsum: initial setting time versus dihydrate and anhydrite content of a different origin.

CSBM in the cement setting was confirmed from the industrial samples. The cement samples with the three highest setting times contained FGD gypsum. Therefore, it was obvious that the addition of FGD gypsum increased the setting time.

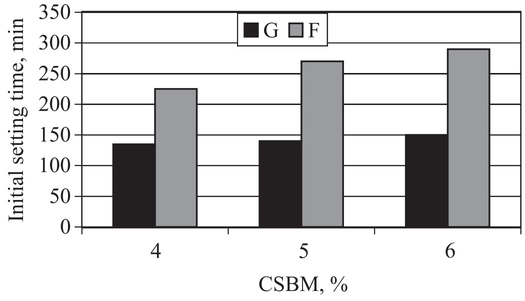

Fig. 7. Setting time of CEM II-A cements with natural gypsum and FGD gypsum.

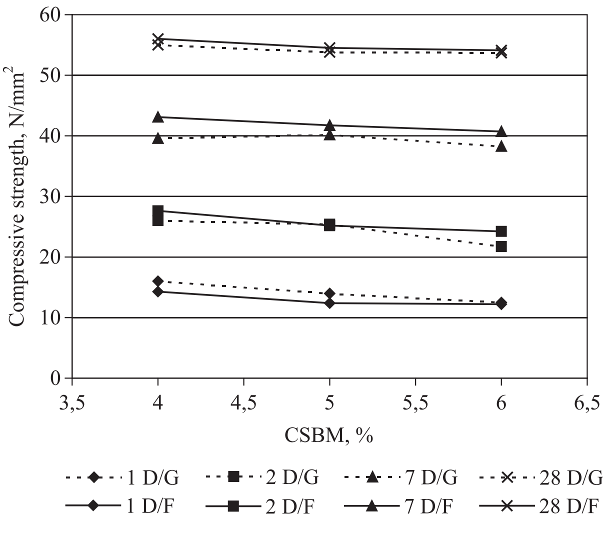

Fig. 8. Compressive strengths (1, 2, 7, and 28 days) of CEM II-A cements with natural gypsum and FGD gypsum.

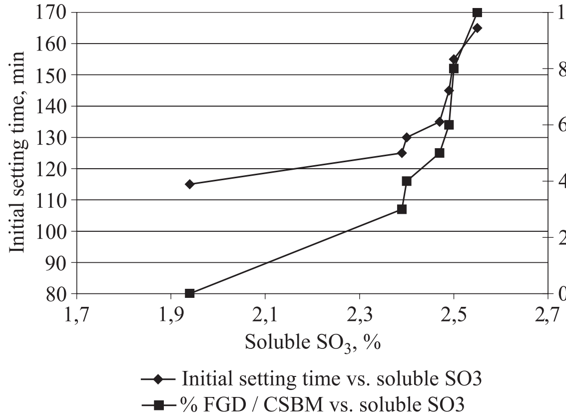

Fig. 9. Setting time of CGF cements (CEM I) versus the ratio of soluble SO_3 of cement.

In cement setting, the presence of hemihydrate and anhydrite has a shortening effect (Fig. 11). On the other hand, the forms of calcium sulfate have a little positive effect on the differentiation of the 28-day compressive

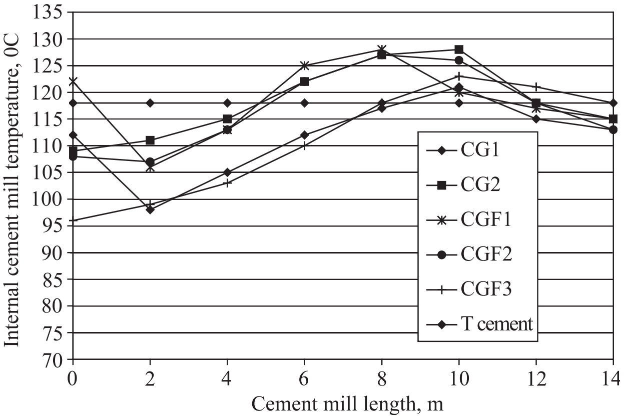

Fig. 10. Cement with various admixtures of gypsum and FGD gypsum produced in industrial scale: internal cement mill temperature versus cement mill length.

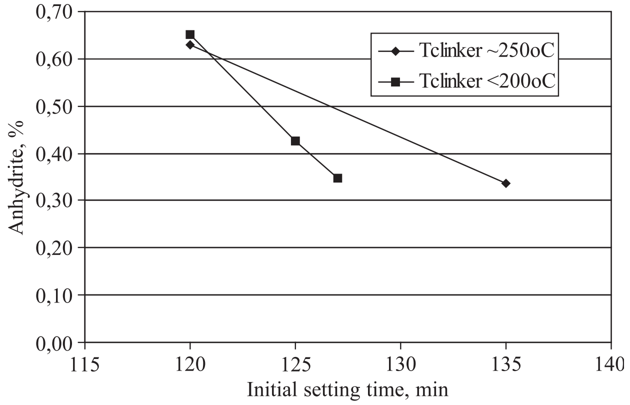

Fig. 11. Cement with various admixtures of gypsum and FGD gypsum produced in industrial scale: anhydrite content versus initial setting time.

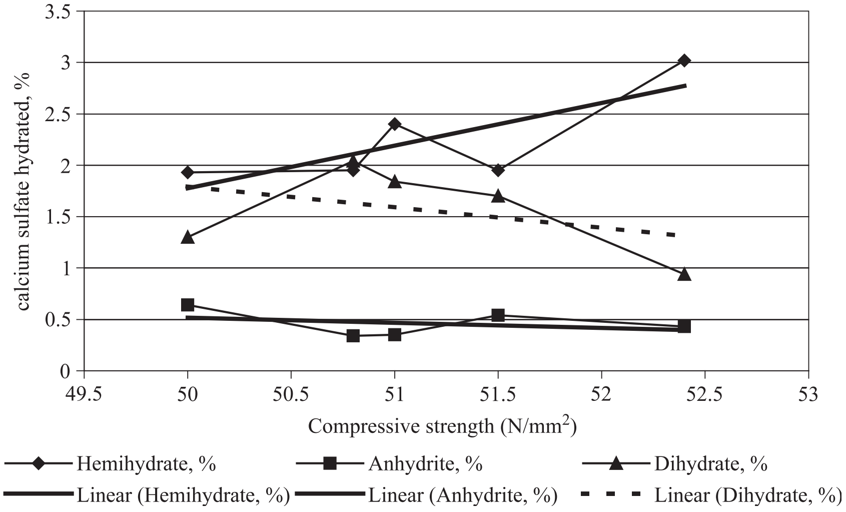

Fig. 12. 28-day compressive strength of cements produced in industrial scale versus the ratio of dihydrate, hemihydrate, and anhydrite in cement.

strength. Still, hemihydrate is considerably more significant than the rest of the $CaSO_4$ forms, inasmuch as higher compressive strengths were achieved in samples with high hemihydrate content (Fig. 12). In this case, clinker's temperature was between 130–190 °C (Table 7), and the dehydration exhibited a maximum value for dew point in the range of 55–65 °C (Table 6).

4. Conclusions

The study of laboratory- and industrial-produced cements with a diversified setting retarder composition showed that FGD gypsum is a suitable alternative to gypsum based on the setting results. FGD gypsum showed about 1-h delay in its initial setting time compared with natural gypsum. This must be attributed to the different solubility of each CSBM and consequently to the different quantities of soluble SO_3 that exist in cement after its mixture with water and react with C_3A retarding its hydration. FGD gypsum showed similar behavior to that of gypsum in compressive strength development, especially in the range of the optimum SO_3 addition (about to 3.5%).

However, according to industrial scale estimations, the high moisture content of FGD gypsum (approximately 10%) could cause handling and feeding problems when it is used in large percentages. The use of mixtures of sulfate-bearing materials with gypsum seems to be advantageous for the precise control of setting time.

Gypsum dehydration and formation of hemihydrate occur in industrial cement mill, which has a diverse effect on setting and compressive strength depending on the composition of the setting retarder. The extent of dihydrate conversion to hemihydrate depends on the temperature of the clinker and the relative humidity within the mill. By controlling these two parameters through the quantity of sprayed water in the mill, optimum degree of dehydration is observed at a dew point about 55–65 °C.

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