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Use of inorganic setting retarders in cement industry

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Abstract

The majority of cement plants in Greece mainly use natural gypsum to prevent rapid cement setting. The partial or total replacement of gypsum by materials, which contain calcium sulfate, has been instigated by two facts. Firstly, the increasing availability of low-cost by-products containing calcium sulfate and secondly, the prospect that, in the near future, the quarries will mine rock that is a mixture of gypsum and anhydrite. The aim of this paper is to discuss results from laboratory and industrial scale trials where calcium sulfate bearing materials (CSBM) such as natural gypsum, anhydrite and FGD gypsum have been used in various proportions in the cement production. The operational parameters and conditions of the cement mill during the industrial trials and the profile of the calcium sulfate hydrated forms in the produced cement are examined. The addition of FGD gypsum increases setting time without affecting compressive strength profile. The degree of dehydration of the dihydrated calcium sulfate regulates setting and strength performance of the cement partially replaced with either anhydrite or FGD gypsum.

Keywords: Portland cement; Gypsum; Anhydrite; FGD gypsum; Setting; Strength

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1. Introduction

The most common cement setting retarder used in industry is natural gypsum, which is primarily a dihydrated product of calcium sulfate ($CaSO_4 \cdot 2H_2O$). The need for gypsum in cement increases with increasing amount of C_3A and alkalies in the clinker and the fineness of the cement [1–3]. Gypsum also promotes cement strength at an optimum content value [4].

Gypsum quarries are steadfastly moving into mining rock that is a mixture of gypsum and anhydrite. Partial replacement of the gypsum with anhydrite is possible for the majority of types of clinker. Hence, anhydrite is used in cements with a low aluminate content and in slag cements. The slower dissolution of anhydrite may have adverse effects on the setting of cements with a high alkali or aluminate content [1,5].

An increasingly available low-cost by-product, containing calcium sulfate, is FGD gypsum. This calcium sulfate bearing material is the product of the de-sulfurization process of residual gases with limestone in coal burning power plants [5,6]. Phosphogypsum is another industrial by-product from the phosphoric acid and fertilizer industry. It consists mainly of $CaSO_4 \cdot 2H_2O$ and contains some impurities such as P_2O_5, and F^-. The impurities present in phosphogypsum retard the hydration of cement to a large extent; therefore its use is restricted in the production of high aluminate cements [6–8].

The variable solubility of the calcium sulfate bearing materials induces a range of available sulfate concentration during cement hydration. Immediately after mixing cement with water, the sulfates react with tricalcium aluminates forming ettringite. It is assumed that ettringite forms initially on the reacting C_3A surface, a more-or-less impermeable coating that impedes diffusion of the ions needed to form the hydrates that cause setting [1,9,10]. Retardation has also been attributed to an underlying layer of hydrous alumina or AFm phase [1]. According to another theory C_3A dissolves incongruently in the liquid phase, leaving an alumina-rich layer on the surface with adsorbed Ca^{2+}, thus lowering the number of active dissolution sites and the reduction rate. A subsequent adsorption of sulfate ions results in a further reduction of C_3A hydration [9,10]. The supply of

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Ca^{2+} and SO_4^{2-} is not only depended on their concentration, but also on their physical and chemical nature. Thus, more ions are supplied when gypsum is interground rather than blended with clinker, since the particle size distribution and homogeneity of calcium sulfates is improved. As far as the chemical nature is concerned, hemihydrate or γ-$CaSO_4$ supplies ions more quickly than does gypsum [1,11].

The partial replacement of natural gypsum with CSBMs not only affects the setting time but also influences grindability, compressive strength and volume stability [1,2,9]. During industrial production of cement, hydrated calcium sulfates undergo partial dehydration at 110–130 °C in the cement mill forming hemihydrate ($CaSO_4 \cdot 0.5H_2O$) and in some cases total dehydration, at 170–190 °C, forming soluble anhydrite (γ-$CaSO_4$) [3]. This could cause cement false set. Thus, water is sprayed in the interior of the mill to maintain temperature below 120 °C, to minimize gypsum dehydration. On the other hand excess of water in the mill along with storage conditions could cause reduction of cement compressive strength. The conditions in the mill, which affect the dehydration of dihydrated calcium sulfate, were monitored through the construction of mill thermal balances. The relative humidity in the mill was controlled by the quantity of sprayed water. The latter varied by using clinker of different temperatures (109–250 °C). Finally, the temperature profile of the mill and the dew point of the process were estimated in relation to the setting retarder composition materials.

2. Experimental

2.1. Laboratory production

Three calcium sulfate-bearing materials (CSBM), gypsum (as reference material), anhydrite and FGD gypsum were used as setting retarders. The chemical analysis of these materials, according to ASTM C 471M-95 [12], the hydrated forms of calcium sulfate as well as their solubility at 25 °C are shown in Table 1.

Clinker was interground with suitable mixtures of (i) gypsum and anhydrite (CGA), (ii) gypsum and FGD gypsum (CGF), in order to produce cement type I (CEM I). The addition of the mixtures of the three CSBM was in the range of 5.8–6.7%, while clinker's admixing ratios laid from 94.2% to 93.3% respectively. This was aiming at achieving the same SO_3 value (~3.5%) for all cements, which has been shown to be the optimum percentage [13]. In Table 2 the ratios of clinker and mixtures of calcium sulfate-bearing materials expressed as gypsum/material [20/80 (0), 40/60 (1), 50/50 (2), 60/40 (3), 70/30 (4), 100/0 (5)] are summarized. In the same table the XRF measured values of SO_3, and the specific surface after an hour of intergrinding are included.

2.2. Industrial production

The influence of gypsum's dehydration and the presence of hemihydrate and anhydrite to the compressive strength and setting time of cement was investigated in cement samples (CEM I) that were produced on an industrial scale. Clinker with a temperature ranging from 110 to 250 °C was interground in an industrial ball mill with mixtures of CSBM [100% gypsum (CG), 100% anhydrite (CA), 75% gypsum/25% FGD (CGF)] and filler (limestone). It is understandable though that these ratios are nominal since gypsum and anhydrite were not 100% pure in their composition. Lower content of added CSBM than in the laboratory-produced cements was due to handling and operational procedures. However it is expected that the addition will have an effect on the cement properties. The temperature at the exit of the mill was always maintained below 118 °C by spraying the necessary quantities of water in the middle and/or at the inlet of the mill. The conditions of the mill were evaluated through the construction of thermal balances. The clinker temperature, the SO_3 content of cements, the admixing ratios of gypsum

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

	Gypsum	Anhydrite	FGD Gypsum
Combined water, %	19.30	1.81	18.05
SO_3, %	43.41	51.31	42.19
SiO_2, %	0.65	27.70	0.30
CO_2, %	2.51	3.44	1.58
CaO, %	32.40	27.63	33.40
R_2O_3,[a] %	0.03	0.05	0.10
MgO, %	0.92	2.14	0.10
$CaSO_4 \cdot 2H_2O$	90.97	8.74	87.96
$CaSO_4$	1.87	80.31	2.17
Solubility (g/100 g H_2O)	0.260	0.198	0.273

[a] R_2O_3: $Fe_2O_3 + Al_2O_3$.

Table 2
Admixing ratios for cement mixtures, % SO_3 and specific surface of laboratory produced cements

	CGA0	CGA1	CGA2	CGA3	CGA4	CG5
% Clinker	94.23	94.04	93.94	93.83	93.73	93.5
% mixture gypsum-anhydrite	5.77	5.96	6.06	6.17	6.27	6.5
% SO_3	3.42	3.36	3.46	3.45	3.44	3.54
Specific surface-Blaine (cm^2/g)	3710	3720	3610	3610	3470	3850
	CGF0	CGF1	CGF2	CGF3	CGF4	CGF5
% Clinker	93.22	93.26	93.28	93.30	93.32	93.5
% mixture gypsum–FGD gypsum	6.78	6.74	6.72	6.70	6.68	6.5
% SO_3	3.54	3.55	3.58	3.55	3.49	3.54
Specific surface-Blaine (cm^2/g)	3780	3760	3830	3590	3600	3850

Table 3
Clinker temperature, % SO_3 of industrially produced cements and admixing ratios of dihydrate and anhydrite to CSBM

	CG1	CG2	CA1	CA2	CGF1	CGF2	CGF3
Clinker temperature (°C)	250	192	250	109	250	189	133
% SO_3	2.63	2.67	2.88	2.42	2.78	2.92	2.95
% dihydrate	3.70	3.70	2.80	2.12	4.73	4.54	4.71
% anhydrite	0.64	0.64	1.02	1.25	0.36	0.43	0.35
Blaine (cm^2/g)	3515	3540	3400	3380	3605	3670	3540
H_2O (kg/h)	5894	4146	5724	1182	6252	3966	2142
Dew point (°C)	73	66	74	39	76	65	53

(dihydrate) and anhydrite to the CSBM, the water sprayed and the dew point for each grinding trial are shown in Table 3.

Once dihydrate and hemihydrate in cement have been formed, the degree of gypsum dehydration is calculated by the equation:

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

In the same time physico-mechanical properties, such as setting time and compressive strength of the produced cement were determined based on EN-norms.

The content of dihydrate, hemihydrate and anhydrite in cement was determined by differential thermal analysis (Netzsch STA 409 – DSC/TG). In Table 4 the results from the calcium sulfates hydrates (dihydrate, hemihydrate, anhydrite) determination in the produced cements and the degree of gypsum's dehydration are summarized.

3. Results and discussion

3.1. Laboratory production

In Fig. 1 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. The FGD gypsum is a better retarder than gypsum, although they both contain the same chemical compound, i.e. $CaSO_4 \cdot 2H_2O$. In Fig. 2, the setting time increases as more dihydrate of FGD gypsum replaces dihydrate 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 dihydrate. Gypsum is found

Table 4
Percentage of calcium sulfate hydrates (dihydrate, hemihydrate, anhydrite) and % degree of dehydration in industrially produced cements

	T clinker (°C)	Dihydrate (%)	Hemihydrate (%)	Anhydrite (%)	% Dehydration
CG1	250	1.70	1.69	0.64	54.13
CG2	192	1.17	2.13	0.64	68.31
CA1	250	1.17	1.38	1.03	58.48
CA2	109	2.68	0.01	1.24	0.44
CGF1	250	2.04	1.95	0.34	53.14
CGF2	188.5	0.94	3.02	0.43	79.19
CGF3	133	1.84	2.40	0.35	60.70

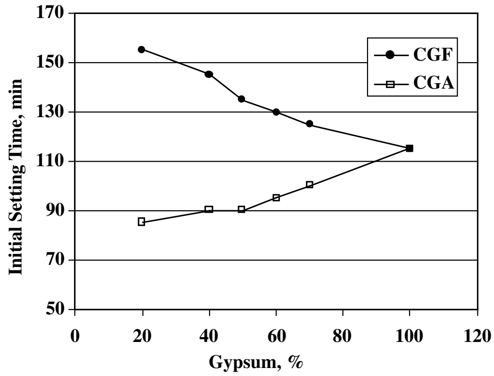

Fig. 1. Setting time for CGA and CGF cements vs gypsum content.

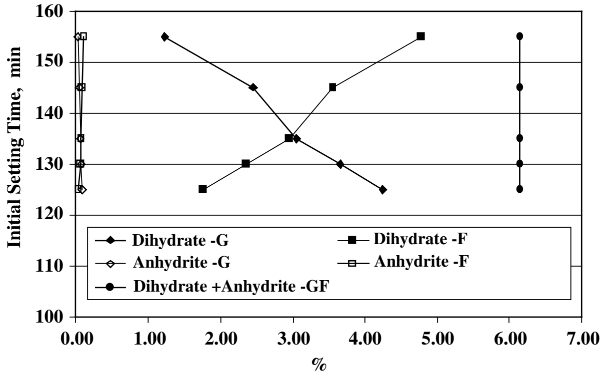

Fig. 2. Cement with admixtures of gypsum and FGD gypsum: initial setting time vs dihydrate and anhydrite content of a different origin.

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. 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, furthermore. As illustrated in Fig. 3, the differences in reactivity are also reflected in the respective dehydration profile (dynamic step 1 °C/min, isothermal step 30 min). In gypsum, water is slowly removed, starting at temperatures below 90 °C; whereas in FGD gypsum, water is rapidly lost forming a sharper peak, starting at temperatures above 95 °C.

On the other hand, the addition of anhydrite accelerates the setting of laboratory-produced cement. The faster setting of anhydrite is caused by the increasing amount of $CaSO_4$ in the admixture (Fig. 4). As anhydrite content increases by 1%, the initial setting time decreases by 5 min. The anhydrite, which is crystallized in the orthorhombic system, has the lowest solubility among the studied CSBMs, and this could affect the cement setting properties, the most.

The 28-day compressive strength results (EN 196-1) for cements with mixtures of sulfate-bearing materials (CEM I) are shown in Fig. 5. The compressive strength performance of the tested mixtures presented no significant differences except the mixture 1 (gypsum/CSBM: 20/80) where the addition of anhydrite increases the

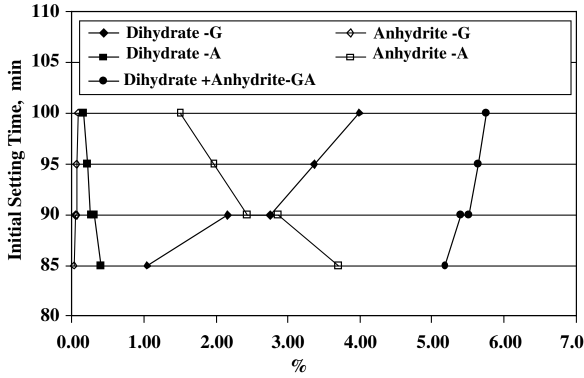

Fig. 4. Cement with admixtures of gypsum and anhydrite: initial setting time vs dihydrate and anhydrite content of a different origin.

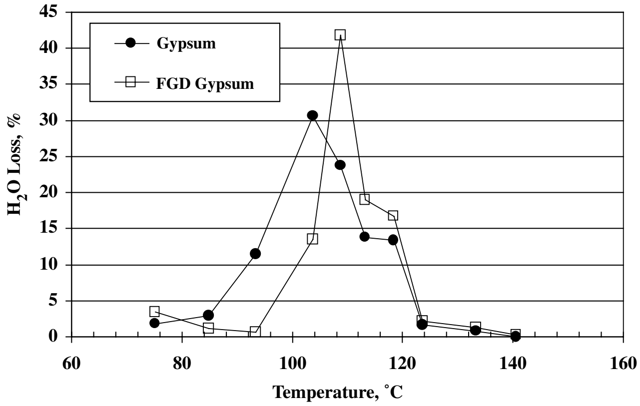

Fig. 3. Gypsum and FGD gypsum dehydration profile.

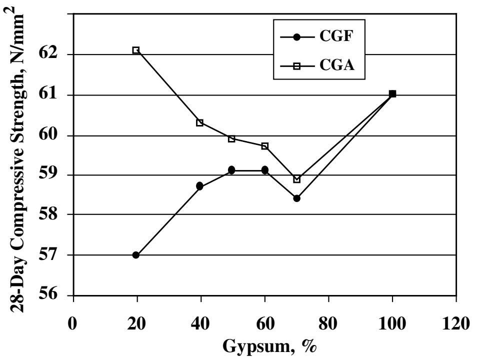

Fig. 5. Twenty eight-day compressive strength for CGA and CGF cements.

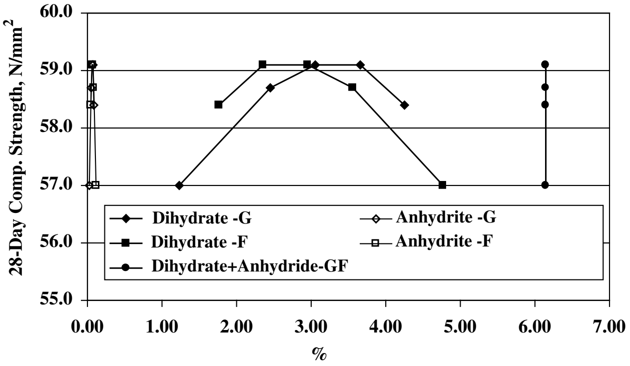

Fig. 6. Cement with admixtures of gypsum and FGD gypsum: 28-day compressive strength vs dihydrate and anhydrite content of a different origin.

compressive strength, while the same addition of FGD gypsum reduces the compressive strength. However, in the admixture gypsum/FGD gypsum, dihydrate of both origins exhibits a similar behavior in cement strength performance as it is shown in Fig. 6. Optimum compressive strength is accomplished when the ratio between dihydrate content of gypsum and of FGD gypsum ranges from 0.7 to 1.6. Moreover in the admixture gypsum/anhydrite, as anhydrite increases by 2% the cement 28-day compressive strength increases by 3 N/mm^2 (Fig. 7).

The product of gypsum dehydration in the cement mill is primarily hemihydrate calcium sulfate. In order to investigate hemihydrate's effect on the properties of cement, clinker was interground with different proportions of chemically pure hemihydrate ($CaSO_4 \cdot 0.5H_2O$), pure dihydrate ($CaSO_4 \cdot 0.5H_2O$) and mixtures of them. In Table 5 the different synthesis of the laboratory-produced cements are summarized. Overall, the hemihydrate decreases the cement setting time and increases the strength, as depicted in Figs. 8 and 9.

The results of the tests on the laboratory-produced cements with various admixtures showed that there are two groups of CSBMs that have conflicting or limiting effects on the setting and strength performance. Consequently,

- initial setting time increases with gypsum and primarily with FGD gypsum, and
- cement strength increases with hemihydrate and anhydrite.

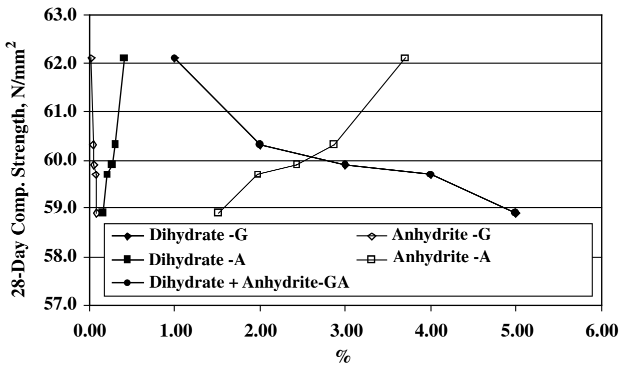

Fig. 7. Cement with admixtures of gypsum and anhydrite: 28-day compressive strength vs dihydrate and anhydrite content of a different origin.

Table 5
Admixing ratios of laboratory produced cements with chemically pure dihydrate and hemihydrate of calcium sulfate

% $CaSO_4 \cdot 2H_2O$	% $CaSO_4 \cdot 0.5H_2O$	% clinker
1	4.075	94.9
2	3.075	94.9
3	2.075	94.9
4	1.075	94.9
5	0.075	94.9

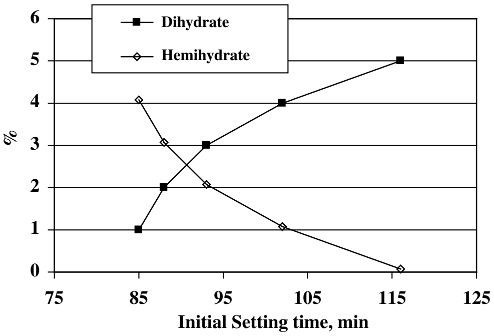

Fig. 8. Cement with admixtures of dihydrate and hemihydrate: initial setting time vs dihydrate and hemihydrate content.

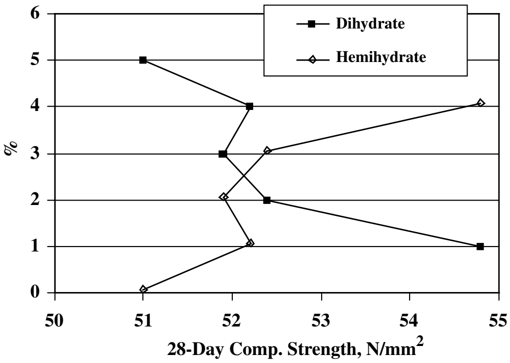

Fig. 9. Cement with admixtures of dihydrate and hemihydrate: 28-day compressive strength vs dihydrate and hemihydrate content.

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

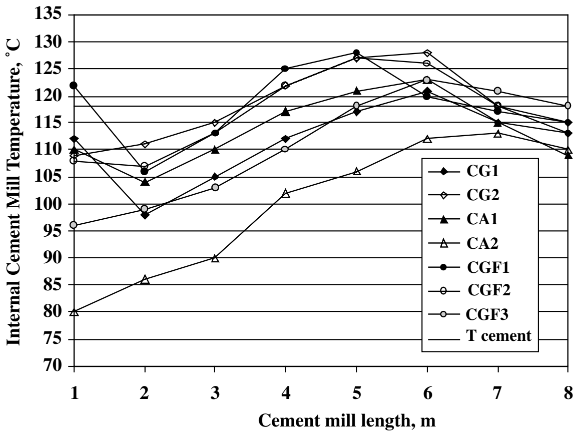

Fig. 10. Cement with various admixtures of gypsum, FGD gypsum and anhydrite produced in industrial scale: internal cement mill temperature vs cement mill length.

behavior of each CSBM in the cement setting was confirmed from the industrial samples. The increasing content of anhydrite in the cement had an accelerating effect on setting (Fig. 11). The effect was more pronounced in the case where the clinker temperature was 250 °C. In this case, a large amount of water was sprayed in the mill to avoid complete gypsum dehydration and as a result, mill dew point increased and dehydration was restrained to comparable levels (Fig. 12). The cement samples with the highest three setting times contained FGD gypsum. Therefore, it was obvious that the addition of FGD gypsum increased the setting time.

Contrary to laboratory produced cement results, the increase in anhydrite content in industrially produced cement, lead to decreasing compressive strength as it was derived from Fig. 13. The relative compressive strength values to the specific surface (Blaine measurements) show a reduction in strength of 2.5 N/mm^2 by an increase of 0.8% in $CaSO_4$ content indicated that the activity of anhydrite in strength performance was outweighed by other cement components.

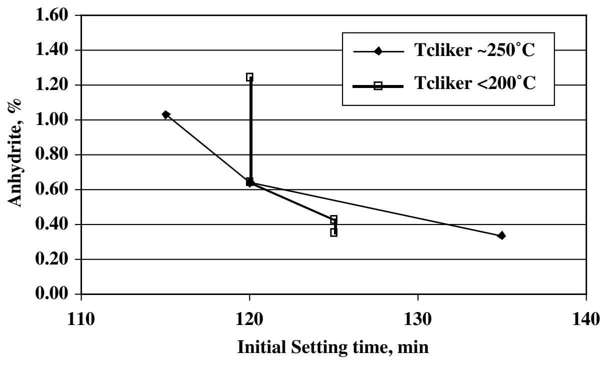

Fig. 11. Cement with various admixtures of gypsum, FGD gypsum and anhydrite produced in industrial scale: anhydrite content vs initial setting time.

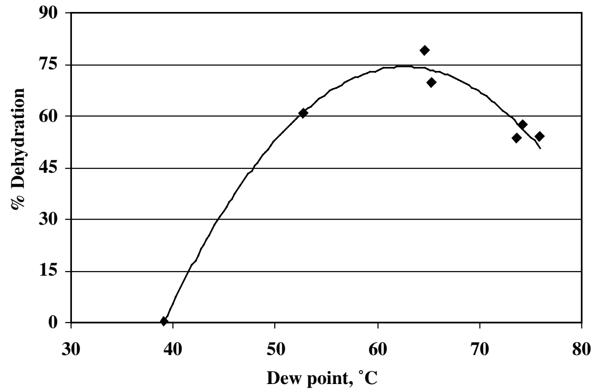

Fig. 12. Cement with various admixtures of gypsum, FGD gypsum and anhydrite produced in industrial scale: gypsum dehydration vs cement mill Dew point.

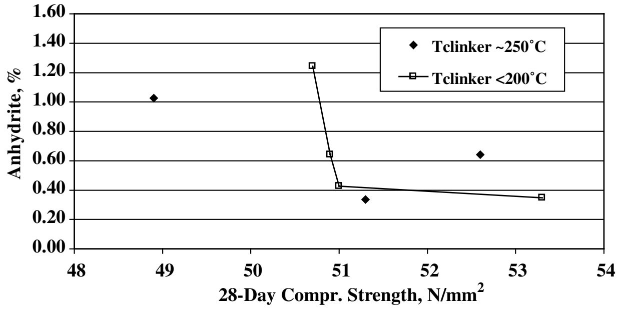

Fig. 13. Cement with various admixtures of gypsum, FGD gypsum and anhydrite produced in industrial scale: anhydrite content vs 28-day compressive strength.

If linear regression analysis is applied on the data that include hydrate forms of calcium sulfate, clinker, SO_3 content, and specific surface (Blaine), the results can be explained by the derived weighing factors for each cement component. In cement setting the presence of hemihydrate and anhydrite has a shortening effect. On the other hand, the forms of calcium sulfate have a little positive effect on the differentiation of the 28-day compressive strength, as their factors are small. Still, hemihydrate is considerably more significant than the rest of the $CaSO_4$ forms, since higher compressive strengths were achieved in samples with a high hemihydrate content. For this set of data, the coefficient factor (R^2) is excellent. In this case clinker's temperature was between 130 and 190 °C (Table 3) and the dehydration exhibited a maximum value for dew point in the range of 55–65 °C.

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 and strength results. However, the high moisture content of FGD gypsum (~10%) could cause handling and feeding problems when it is used in large percentages. Only minimal partial replacement of gypsum by natural anhydrite could prevent cement quality setbacks. Gypsum dehydration and formation of hemihydrate occurs 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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