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Alternative calcium sulfate-bearing materials as cement retarders Part I. Anhydrite

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Abstract

The hydration process of cement pastes is of great importance to the physicomechanical properties of the hardened material. Thus, substances that regulate the setting of cement, such as natural anhydrite, have attracted significant scientific interest during the past years. This paper briefly describes the results of utilization of natural anhydrite in cement pastes of CEM-I and CEM-II types. The aim of the study has been to inquire the extent of natural gypsum replacement by natural anhydrite. The result of the hydration process has been expressed by the setting time and the compressive strength development, with respect to the SO_3^{-2} content of each mixture. The experimental data conclude that natural anhydrite can be a very efficient retarder of the setting of cement, with no significant change in the physicomechanical properties of the hardened pastes.

Keywords: Anhydrite; Cement hydration; Setting; Retardation; Calcium sulfate

1. Introduction

The rapid hardening of cement pastes due to the vivid reaction of C_3A with water is usually prevented by adding a substance acting as a retarder of the setting of cement. Cement industry has been using natural gypsum ($CaSO_4$) as a first choice material. Natural gypsum and natural anhydrite coexist in the stocks. These two facts state out how important it is to study if anhydrite can replace gypsum in the utilization of cement. If this proves to be the case, many low-purity (regarding the natural gypsum content) stocks can become exploitable.

The addition of a sulfate-bearing material apart from the setting time also affects the strength growth of the hydrated cement paste and avoids shrinkage. However, if the addition of the abovementioned material exceeds a certain limit, it can lead to a substantial expansion of the concrete [1–3]. This is the main reason why the cement standards define an upper limit to the gypsum content. The required amount of gypsum in a type of cement increases with the amount of C_3A in the clinker and the fineness of the cement. Modification of the sulfate-bearing admixture to the reactivity of the tricalcium aluminate is therefore of significant importance in retarding the setting and improving the strength behaviour of cement [1–3].

Theories on the cement hydration process [1,4,5] suggest that upon contact with water, the $CaSO_4$-bearing materials dissolve into water to give sulfate anions, which react with the C_3A grains forming ettringite, as shown by the chemical Eq. (1):

$$C_3A + 3C\underline{S}H_2 + 26H \rightarrow C_3A.3C\underline{S}.H_{32} \tag{1}$$

The forming ettringite crystals create a thin coating around the anhydrated cement grains, hence preventing the quick reaction of C_3A with water (flash set):

$$C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H \tag{2}$$

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

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and the reduction rate. A subsequent adsorption of sulfate ions results in a further reduction of C_3A hydration [4,5]. The supply of Ca^{2+} and SO_4^{2-} is not only dependent 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, because the particle size distribution and homogeneity of calcium sulfates is improved [1]. In the direction of accomplishing the best setting behavior, the availability of sulfates should be controlled in such a way that sulfates combine exclusively with the hydrating portion of C_3A to give ettringite [6].

Previous investigations have demonstrated that each form of $CaSO_4$ has different solubility [7–9]. This results to different strength of the hardened paste. These authors along with Xiugie and Hui [10] believe that absolute solubility for both gypsum and anhydrite is similar, while the dissolution rate of gypsum is faster than that of anhydrite. There are other authors [11] that have given special attention to the $CaSO_4$/water ratio on the dissolution rate of both types of sulfate-bearing materials.

The dissolution rate of gypsum is relatively stable, while that of anhydrite grows with the increase of solid/water ratio. In a system where solid $CaSO_4$ and $Ca(OH)_2$ coexist, the equilibrium is described by the chemical Eqs. (3) and (4).

$$CaSO_4(s) \Leftrightarrow Ca^{2+} + SO_4^{2+} \tag{3}$$

and

$$Ca(OH)_2(s) \Leftrightarrow Ca^{2+} + 2OH^- \tag{4}$$

At a high $CaSO_4$/water ratio (>0.04), anhydrite dissolves faster than gypsum and results in higher $[SO_4^{2-}]$ concentration, which accelerates C_3A hydration [12]. This, in turn, results in higher $[OH^-]$ concentration. When $Ca(OH)_2$ crystallizes, solid $CaSO_4$ and $Ca(OH)_2$ coexist. Equilibrium (3) and (4) are both reached. The higher solubility of anhydrite results in higher $[Ca^{2+}]$ concentration, which drives $[OH^-]$ down. In a low $[OH^-]$ solution ettringite is formed at a distance from the surface of the solid phase, and the hydration of calcium silicates is accelerated. Thus, a more uniform and denser structure is formed [13,14]. SEM observations have also shown a finer structure in the case of anhydrite cements [15].

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

	Gypsum	Anhydrite
Combined water (%)	19.30	1.81
SO_3 (%)	43.41	51.31
SiO_2 (%)	0.65	2.77
CO_2 (%)	2.51	3.44
CaO (%)	32.40	37.63
R_2O_3[a] (%)	0.03	0.05
MgO (%)	0.92	2.14
$CaSO_4{\cdot}2H_2O$ (%)	90.97	8.74
$CaSO_4$ (%)	1.87	80.31
Solubility (g/100 g H_2O)	0.260	0.198

[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: $Fe_2O_3 + Al_2O_3$.

Kumar and Kameswara Rao [16] has also studied the hydration of cement based on the solubility of the cement components and states that the presence of a strong anion, such as SO_4^{2-} in the solution, reduces the solubility of less strong anions, such as silicates and aluminates, but tends to accelerate the solubility of calcium anions, thus effecting the setting time.

Anhydrite cements have also been produced from by-products rich in calcium sulfate, such as phosphogypsum. The impurities, such as phosphates, fluorides, organic matter and alkalies, prevent phosphogypsum from direct use in building materials, due to their bad effect on setting time and strength. Researches carried out by Singh and Garg [15] have shown that impurities can be made inactive by heating of phosphogypsum. At elevated temperatures, phosphogypsum is transformed to anhydrite and the impurities are covered by insoluble calcium pyrosulphate, making them inactive. Cement produced this way develops similar strength and is also less energy intensive than Portland cement. The strength development of these cements is once again related to the fine and sharp-edged structure of the hydration products. Singh and Garg [15], using the results from DTA, also report that with the hydration progress, anhydrite is inverted, to some extent, to gypsum.

It is appropriate however to use anhydrite for cement, with a low aluminate content, and for slag cements. The slower dissolution of anhydrite may have adverse effects on the setting of cements with a high alkali or aluminate content [17].

2. Experimental

Two calcium sulfate-bearing materials (CSBMs), gypsum (as reference material), and natural anhydrite were used as setting retarders. The chemical analysis of these materi-

Table 3
CSBM % addition and % SO_3 of CEM-I cement mixtures with either gypsum or anhydrite as CSBM

Sample	% Addition	% SO_3	Sample	% Addition	% SO_3
CG1	4.0	2.37	CA1	3.5	2.33
CG2	4.5	2.58	CA2	4.0	2.64
CG3	5.0	2.93	CA3	4.5	2.77
CG4	5.5	3.12	CA4	5.0	3.24
CG5	6.5	3.54	CA5	5.5	3.42
CG6	7.0	3.93	CA6	6.5	3.83
CG7	7.5	4.31	CA7	7.0	4.55

Table 4
Admixing ratios for CEM-I cement mixtures, % SO_3 and specific surface of laboratory-produced cements with mixture of gypsum and anhydrite

	CGA1	CGA2	CGA3	CGA4	CGA5	CGA6	CGA7
% Clinker	94.5	94.23	94.04	93.94	93.83	93.73	93.5
% Mixture, gypsum–anhydrite	5.5	5.77	5.96	6.06	6.17	6.27	6.5
% SO_3	3.42	3.42	3.36	3.46	3.45	3.44	3.54
Specific surface—Blaine (cm^2/g)	3900	3710	3720	3610	3610	3670	3850

als, according to ASTM C 471M-95 [18], the hydrated forms of calcium sulfate, as well as their solubility at 25 °C, are shown in Table 1. The clinker used was chemically characterized by XRF as shown in Table 2.

Clinker was interground in a laboratory ball mill with suitable quantities of gypsum (G) and anhydrite (A) to produce CEM-I type of cement, here referred to as CG (with gypsum) and CA (with anhydrite), respectively. The percent addition of each material in mixtures with clinker 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 determined optimum SO_3 content of cements with either gypsum or anhydrite, cement mixtures using blends of gypsum and anhydrite were also prepared (CGA). The mixtures of CSBMs expressed as gypsum/anhydrite were as follows: 0:100, 40:60, 50:50, 60:40, 70:30, and 100:0, as shown in Table 4. The specific surface obtained was in the range of 3600–3900 cm^2/g.

The study extended further to CEM-II-type cement mixtures. A pozzolanic material, fly ash (F; 3.8% SO_3, 1.1% Na_2O, 0.7% K_2O, 31% CaO, 28% SiO_2) from a power plant was used to produce CEM-II-A and -B types (80% and 65% clinker). This specific fly ash was produced in the power plant (Ptolemaida region) and is a pozzolanic material widely used by the Hellenic cement industry. All these compositions are summarized in Tables 5 and 6. The specific surface obtained was in the range of 5000 cm^2/g.

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

The comparative study of the laboratory CEM-I-type cement based on the percent 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

Table 5
Admixing ratios of CSBM and F in CEM-II-A cement mixtures (80% clinker) and % SO_3 of cement

	CGF1	CGF2	CGF3	CAF1	CAF2	CAF3
% CSBM	4	5	6	4	5	6
% F (fly ash)	16	15	14	16	15	14
% SO_3	2.87	3.31	3.67	2.99	3.46	3.84

Table 6
Admixing ratios of CSBM and F in CEM-II-B cement mixtures (65% clinker) and % SO_3 of cement

	CGF1	CGF2	CGF3	CAF1	CAF2	CAF3
% CSBM	4	5	6	4	5	6
% F (fly ash)	31	30	29	31	30	29
% SO_3	3.00	3.35	3.67	3.16	3.51	3.80

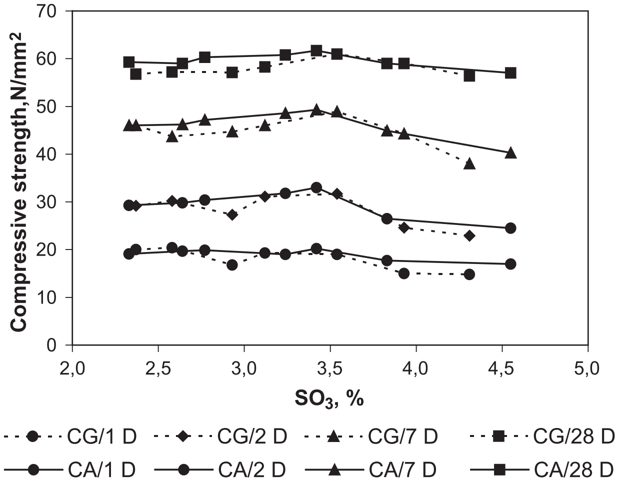

Fig. 1. Comparison of compressive strengths of CG and CA cements vs. % SO_3.

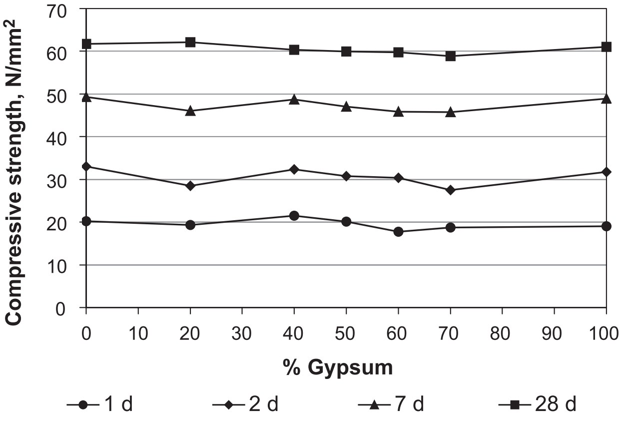

Fig. 2. Compressive strengths of CGA cements vs. the ratio of gypsum in the mixture of CSBM.

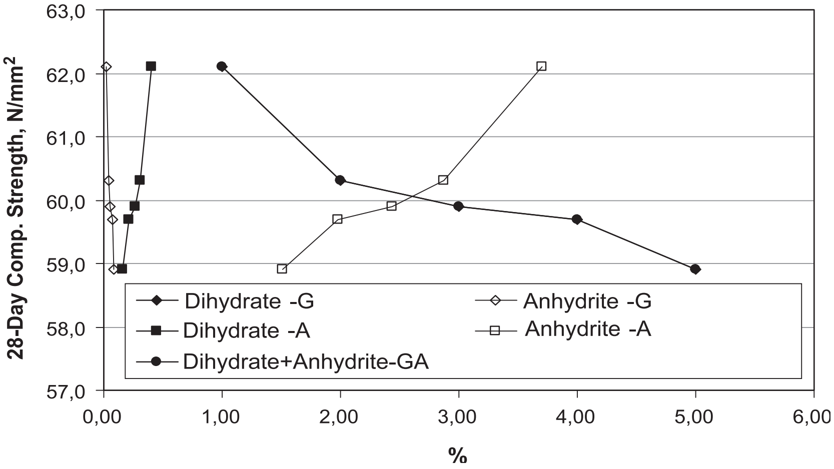

Fig. 3. Cement with admixtures of gypsum and anhydrite: 28-day compressive strength vs. dihydrate and anhydrite content of a different origin.

(blue ribbon filter) and the burning of the filter at 950 °C. Soluble SO_3 was then determined by multiplying the coefficient 0.343 ($MW\ SO_3/MW\ BaSO_4$) with the quantity of $BaSO_4$.

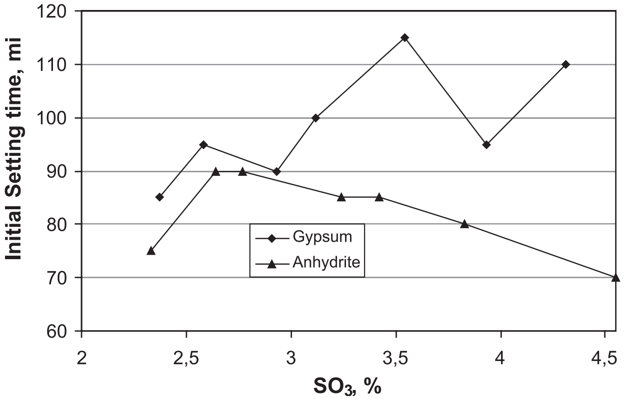

Fig. 4. Setting times of CG and CA cements.

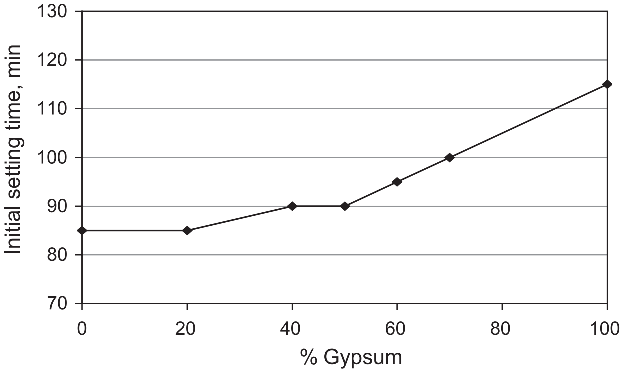

Fig. 5. Setting times of CGA cements vs. the ratio of gypsum in the mixture of CSBM.

Finally, the rate of hydration reactions was followed by nonevaporable water (NEW) measurements. The NEW content represents the hydration products that undergo dehydration between 75 and 950 °C. Cement pastes were prepared with either types of cement (CEM-I and CEM-II) at a W/C ratio of 0.5. Their hydration process was interrupted at 5, 15, 30, 60, 120 min and 6, 12, and 24 h by submerging the hydrating paste in acetone for 10 min and washing with diethyethylether. After treatment of the samples in vacuum, to evaporate the remaining organic solvents, the NEW content was measured by the difference in weight at 75 °C for 24 h and 950 °C for 1 h.

3. Results and discussion

The addition of anhydrite in CEM-I-type cement mixtures increases the compressive strength in all ages, especially near the optimum percentage of SO_3, which is for both gypsum and anhydrite, around 3.5% (Fig. 1).

The compressive strength of CGA cements showed almost similar performance at the examined ratios, as it is

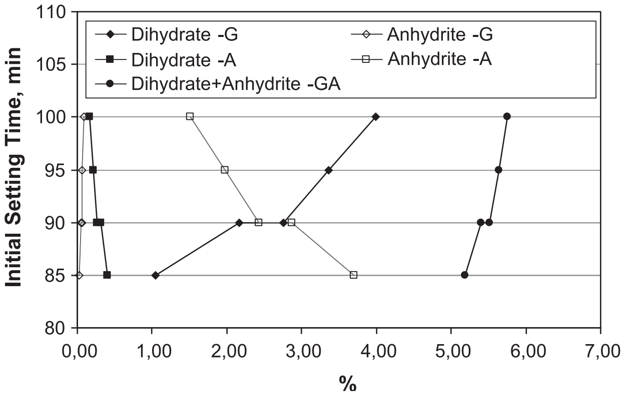

Fig. 6. Cement with admixtures of gypsum and anhydrite: initial setting time vs. dihydrate and anhydrite content of a different origin.

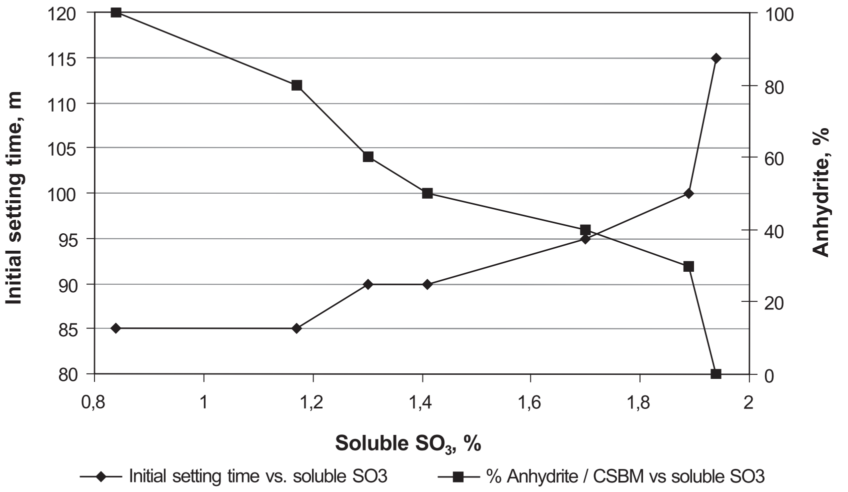

Fig. 7. Initial setting times of CGA cements (CEM-I) vs. the ratio of soluble SO_3 of cement.

shown from Fig. 2. Moreover, Fig. 3 shows that in the admixture gypsum/anhydrite, as anhydrite increases by 2%, the cement's 28-day compressive strength increases by 3 N/mm^2.

Cements with anhydrite set faster than those with gypsum (Fig. 4), and both present an optimum but at different % SO_3 content. In Fig. 5, it is evident that the addition of anhydrite accelerates the setting of cement. The faster setting of anhydrite is caused by the increasing amount of $CaSO_4$ in the admixture (Fig. 6). As anhydrite content increases by 1%, the initial setting time decreases by 5 min.

Next, the ratios of soluble SO_3 vs. the setting time for the CGA cements are plotted in Fig. 7. The more anhydrite is added in the mixture of anhydrite/natural gypsum, the less soluble SO_3 in cement is available for ettringite formation, and consequently, the lower setting times are obtained. This must be attributed to the fact that anhydrite is less soluble than natural gypsum (Table 1) and can be an explanation for the faster setting of anhydrite.

The use of anhydrite in cement type CEM-II has similar behavior to the time of initial setting with the previous case of CEM-I-type mixtures (Fig. 8).

The compressive strength of CEM-II cement mixtures shows that anhydrite increases the 28-day strength for all different compositions. There is an optimum of anhydrite, around 5%, which gives the highest strength, while gypsum's optimum addition is about 4% (Fig. 9). This could be explained if we consider that gypsum is more soluble than anhydrite; hence, when cement is mixed with water, 4% of gypsum can give about the same percentage of soluble SO_3^{2-} as 5% of anhydrite.

Fig. 10 clearly shows that between the two CEM-I mixtures, the one containing anhydrite gives higher NEW at all times. This leads to the conclusion that cements with anhydrite hydrate faster than the ones with gypsum, and thus, more C-S-H is produced for anhydrite cements. That is why anhydrite increases the compressive strength com-

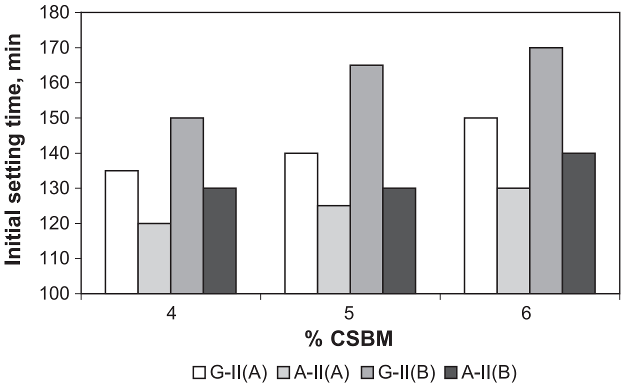

Fig. 8. Setting time of CG and CA (CEM-II) with 80% (A) and 65% (B) clinker vs. % CSBM.

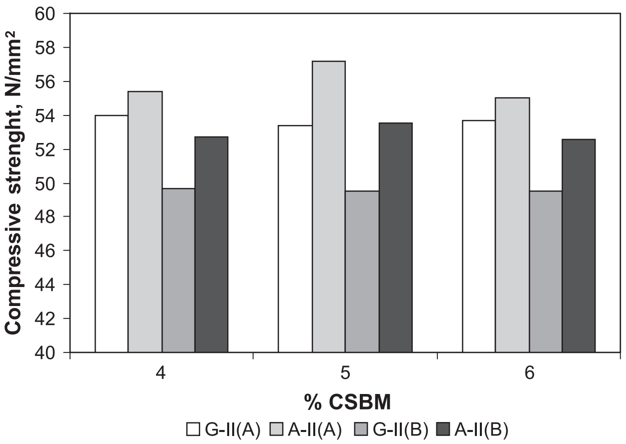

Fig. 9. Compressive strength of CG and CA (CEM-II) with 80% (A) and 65% (B) clinker vs. % CSBM.

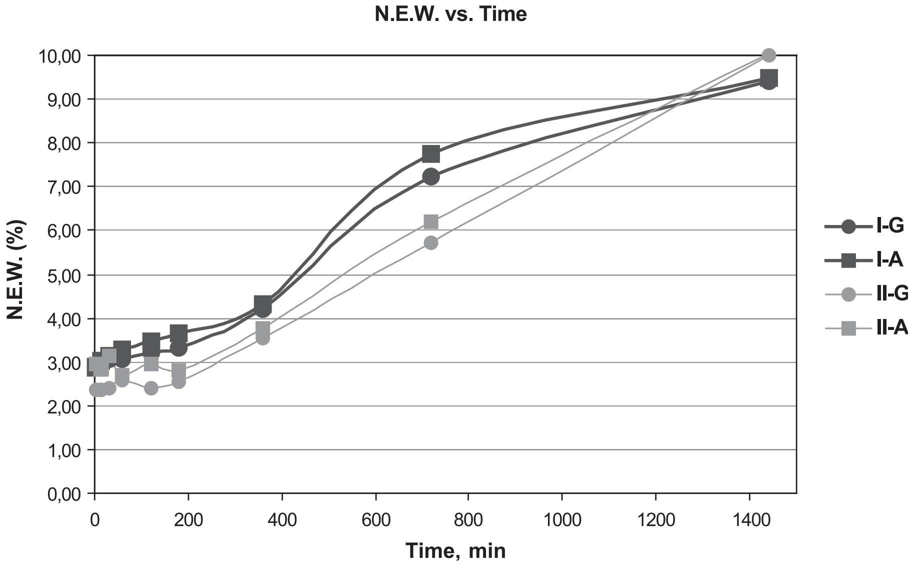

Fig. 10. NEW content of CG and CA (CEM-I and CEM-II) vs. time.

pared with gypsum. This proves to be the case in CEM-II mixtures as well.

4. Conclusions

The study of laboratory-produced cements with a diversified setting retarder composition showed that natural anhydrite is an alternative to gypsum based on the setting and strength results. Anhydrite shows at least similar to gypsum behavior in compressive strength development, especially in the range of the optimum SO_3 addition (about to 3.5%). This was confirmed by the determination of NEW where anhydrite cements showed the higher values for all examined times. Anhydrite also seems to accelerate the hydration reactions and reduces the setting time. A possible explanation is that the addition of anhydrite in the mixture of CSBM reduces the available soluble SO_3, which retard C_3A hydration.

The use of mixtures of gypsum and anhydrite seems to be advantageous for the precise control of setting time because with the proper ratio of gypsum to anhydrite, we can achieve a desired setting time between 85 and 115 min. This fact makes mining stocks where natural gypsum and anhydrite coexist more exploitable for the cement industry.

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