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SETTING AND HARDENING OF GYPSUM-PORTLAND CEMENT-SILICA FUME BLENDS, PART 1: TEMPERATURE AND SETTING EXPANSION

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ABSTRACT

The present work describes a study of setting and hardening of fresh blends of gypsum binder, Portland cement, and silica fume. Such blends can possess the advantages of gypsum (early hardening, high early strength, enhanced workability) and Portland cement (improved durability in moist conditions), but are free of the deleterious effect of ettringite and thaumasite, which are formed when gypsum and Portland cement interact. In part 1, the temperature and setting expansion dependencies in time are described. The influence of superplasticizer on setting and hardening of gypsum, gypsum-cement, and gypsum-cement-silica fume mixes is analyzed. In part 2, the data of early strength, DTA, XRD, and SEM observations are reported. *© 1998 Elsevier Science Ltd*

Introduction

Gypsum and Portland cement are viable cementitious materials used extensively for production of a wide variety of building components. Gypsum has advantages of early hardening and fine finish, but is limited to internal use because of its sensitivity to water. Portland cement in the hardened state is strong and durable, but unlike gypsum it does not possess early hardening or the finish needed for precast components. Mixing of gypsum and Portland cement is usually unfeasible, because it can result in the formation of ettringite in the blend where gypsum is a minor component, or thaumasite when gypsum is a major one. Both of ettringite and thaumasite cause expansion and lead to deterioration.

In (1), a blend of 75% gypsum binder (calcium sulfate hemihydrate) with a 25% mixture of Portland cement was investigated. An optimum silica fume/Portland cement ratio of 0.25 provided a system with strength levels more than twice as high as those of pure gypsum. The system also exhibited a relatively high wet/dry strength ratio, more than 0.6, after 200 days of water immersion. This improvement was explained in (1) by the reduction in ettringite formation and the development of a microstructure in which gypsum crystals were engulfed by C-S-H. The new data obtained recently (2,3) indicate that silica fume added in optimum amounts prevent the formation of thaumasite, which is much more “dangerous” than ettringite. These results proved the conclusions about possible successful “coexistence” of gypsum and Portland, obtained earlier in the former Soviet Union, even for less active pozzolanic admixtures, such as natural pozzolans (3,4).

The C-S-H is formed, as known, in the result of the pozzolanic reaction between silica fume S, calcium hydroxide CH, and water H:

$$S + 1.7CH + 2.3H = C_{1.7}SH_{4.0} \tag{1}$$

At the same time it is known that by complete hydration of Portland cement the free calcium hydroxide can be formed in amounts up to 30%–40% from the mass of unhydrated clinker. Hence, the theoretical silica fume/Portland cement ratio to obtain stable and water-resistant C-S-H engulfed gypsum crystals can be approximately calculated:

$$\frac{(0.3...0.4)S}{1.7CH} = \frac{(0.3...0.4)SiO_2}{1.7Ca(OH)_2} = 0.14...0.19 \tag{2}$$

This ratio is close to the optimum ratio of 0.25 determined experimentally in (1).

However, it is not enough to find the optimum silica fume/Portland cement ratio in the blend with gypsum; the optimum amount of gypsum in the blend should be stated as well. On one hand, the more gypsum content in the blend, the higher the early strength and the better should be the rest of the properties of the material, bringing the blend nearer to the pure gypsum (low setting time and fine finish as a result of higher setting expansion leading to the forms filling more tightly). In addition, the higher the gypsum content and, consequently, the lower the silicate part of the blend, the less pronounced is the deleterious effect of ettringite and thaumasite. On the other hand, with the increase in the gypsum part of the blend, at some moment the remaining silicate part becomes not enough to create dense durable film engulfing gypsum crystals, which provides their water resistance.

Moreover, the deterioration of gypsum-Portland cement-silica fume materials can depend not only on the presence and the amount of ettringite and thaumasite in the system, but also on the time, the place, and the rate of their crystallization from the solution. It makes the behavior of the hardening gypsum-cement-silica fume (GCSF) system rather complicated.

The object of this study is to reveal specific peculiarities of the setting and hardening of GCSF blends in order to find out the optimum structure possessing both the advantages of gypsum and Portland cement. The behavior of the GCSF blend in fresh state is compared with that of the pure gypsum (G) and the gypsum-Portland cement (GC) blend.

In part 1, the temperature and setting expansion dependencies in time are described. The influence of superplasticizer on setting and hardening of gypsum, gypsum-cement, and gypsum-cement-silica fume mixes is analysed.

In part 2 of the paper, the data of early strength, differential thermal analysis (DTA), x-ray diffraction (XRD), and scanning electron microscopy (SEM) observations will be reported and analysed.

Experimental

The basic GCSF mix studied in the present work was made of a blend of 75% by mass of calcium sulfate hemihydrate, 20% of Portland cement, and 5% of silica fume.

The Portland cement was ASTM type I, having a standard compressive strength of 30 MPa and a specific mass of 3100 kg/m^3 (a product of Nesher Industries, Israel). The calcium sulfate hemihydrate was of the β-type, 93% pure, produced by Gesher Gypsum Works, Israel. The silica fume was of 18.2 m^2/g specific surface area, with 92% SiO_2 content.

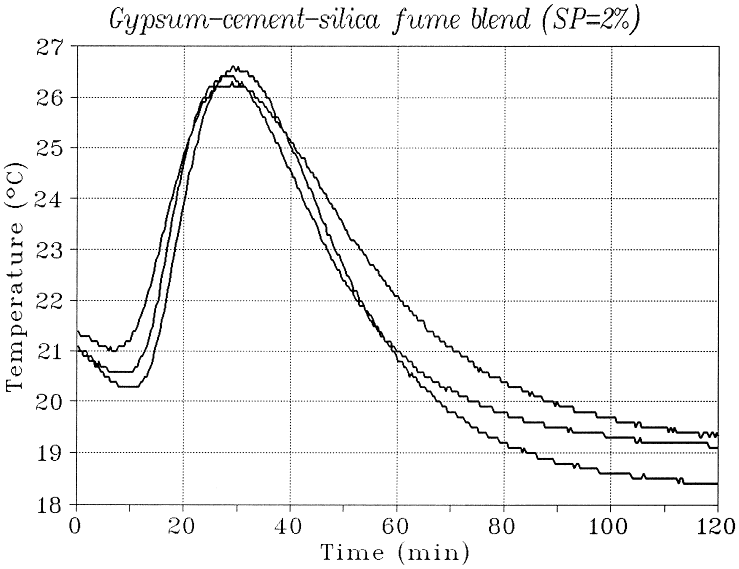

FIG. 1.
Typical examples of the temperature curves for one of the gypsum-cement-silica fume mixes.

In addition, the behavior of pure gypsum and gypsum-Portland cement mixes with various gypsum-cement ratios was studied.

All the mixes were prepared at a water/binder ratio of 0.50. In order to achieve proper dispersion of the silica fume and to improve workability, superplasticizer Rheobild-1000 was incorporated into the part of the mixes.

The mixes were hand-mixed during 1 min. and cast in special form of triangle prism, according to the German standard DIN 13911–6.7.2.

Temperature and setting expansion of the fresh mixes were measured by means of a thermocouple and LVDT, respectively, in a "homemade" apparatus described in (5).

Examples of temperature and setting expansion curves for the GCSF blend with 2% of superplasticizer are shown in Figures 1 and 2, respectively.

Each mix was tested not less than 3 times and then measurement results were averaged. The measurements were continued during 2 h after casting, according to the requirements of German standard DIN 13911–6.7.2. It can be seen that in 2 h both the temperature and the deformation were stabilized. The temperature seems to be more sensitive to the hydration beginning, because it begins to increase somewhat earlier than does the deformation. But the latter indicates precisely the beginning of material setting. This moment was also used for indirect characterization of workability, because, as it was found, the greater the time of setting in the beginning, the better is workability of the paste.

Temperature and Setting Expansion of Pure Gypsum and Gypsum-Portland Cement Blends

In the first stage of the study, the setting and hardening of the pure gypsum and the gypsum-Portland cement blends with different ratios G:C between gypsum binder and

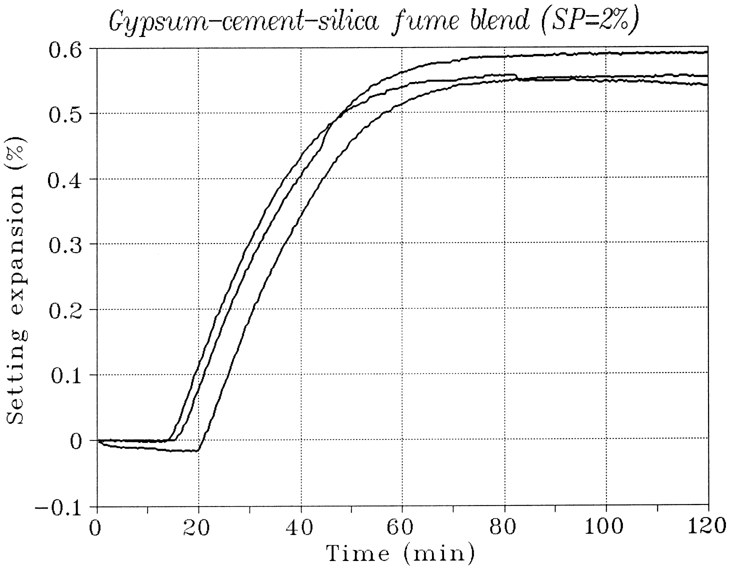

FIG. 2.
Typical examples of the setting expansion curves for one of the gypsum-cement-silica fume mixes.

Portland cement were analyzed. The curves of temperature and setting expansion, obtained in our tests, are shown for such blends, having the gypsum part of 25%, 50%, 75%, and 100% in Figures 3 and 4.

It can be seen that the higher the gypsum content in the blend, the higher both the temperature peak and the maximum setting expansion. These trends coincide with those observed by Alksnis (3), who stated that the blend becomes capable of early hardening when gypsum binder (calcium sulfate hemihydrate) is added to Portland cement in the amount of 25% and more from the mass of the composition. The maximum value of the temperature, indicating the most intensive stage of hydration reaction, is achieved approximately in the same time after casting (13–15 min.), not depending on the gypsum/cement ratio. The beginning of setting determined by means of the setting expansion curves also almost does not depend on G:C (3–7 min.). The reaction of hydration begins practically immediately after mixing with water and proceeds with intensity, approximately proportional to the gypsum content.

However, while the maximum temperature depends more or less regularly on the gypsum content, the mechanical properties of the fresh mixes (maximum setting expansion, workability, and rheological characteristics) are strongly influenced by cement content: even a small addition of Portland cement to the gypsum binder results in a drastic decrease of setting expansion (see Fig. 4) and makes workability worse. In other words, there is a significant difference in mechanical behavior of pure gypsum and that of gypsum-cement blends, in which gypsum part dominates.

In order to improve workability of gypsum-cement blends, it was decided to use superplasticizer Rheobild-1000. The influence of the superplasticizer was checked separately for pure gypsum mixes and gypsum-cement blends with the composition of 75:25.

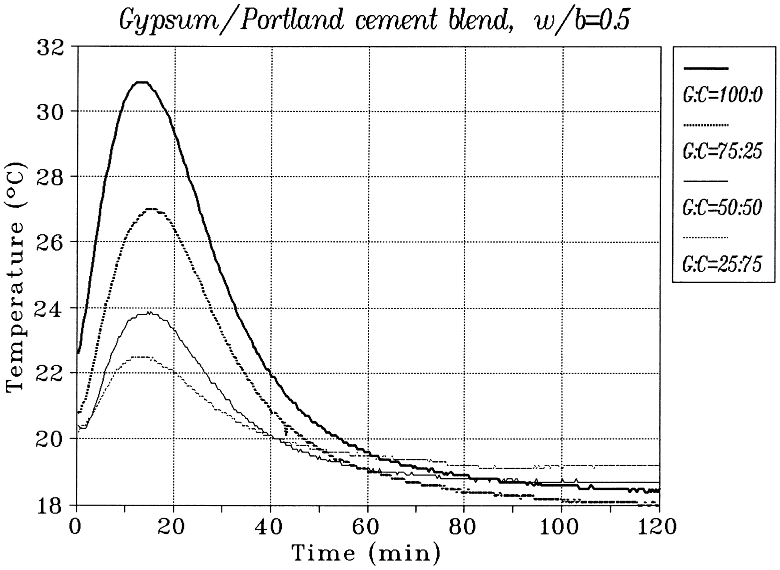

FIG. 3.
Temperature vs. time for fresh gypsum-Portland cement mixes with different ratios gypsum/cement (G: C=100:0, 75:25, 50:50, and 25:75) at constant water/binder ratio of 0.5.

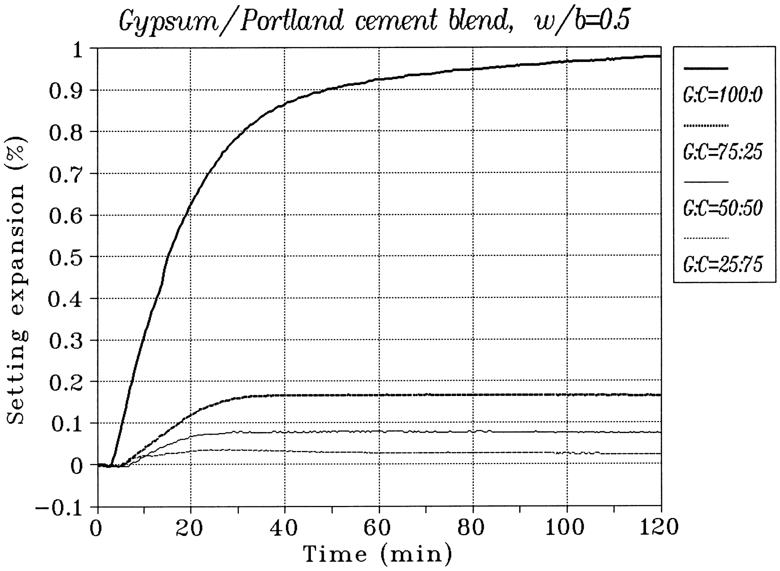

FIG. 4.
Setting expansion vs. time for fresh gypsum-Portland cement mixes with different ratios gypsum/cement (G: C=100:0, 75:25, 50:50, and 25:75) at constant water/binder ratio of 0.5.

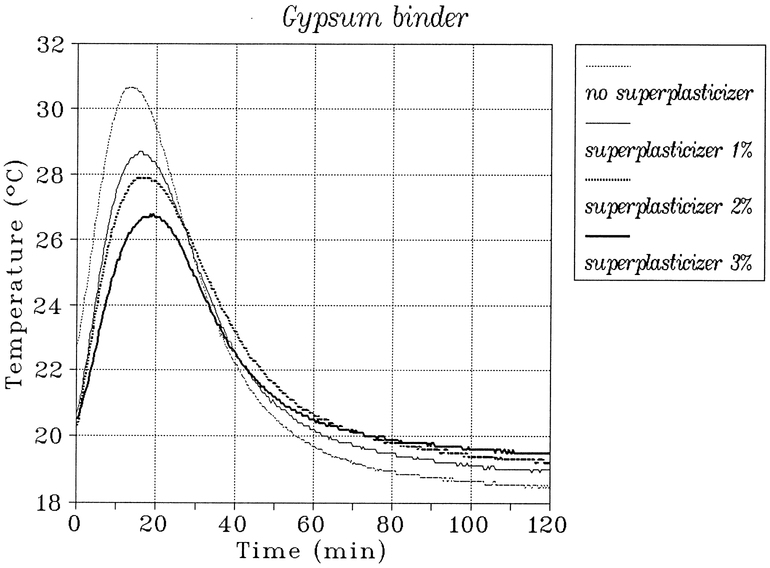

FIG. 5.
Temperature vs. time for pure gypsum mixes.

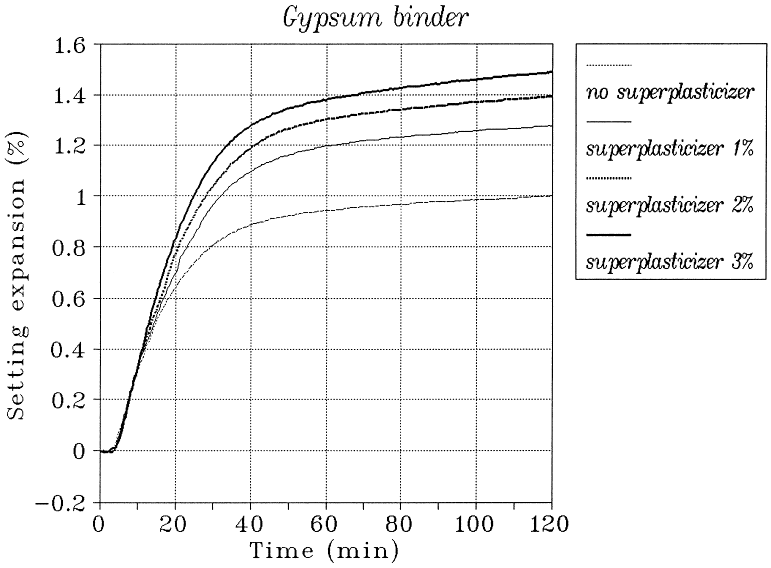

FIG. 6.
Setting expansion vs. time for pure gypsum mixes.

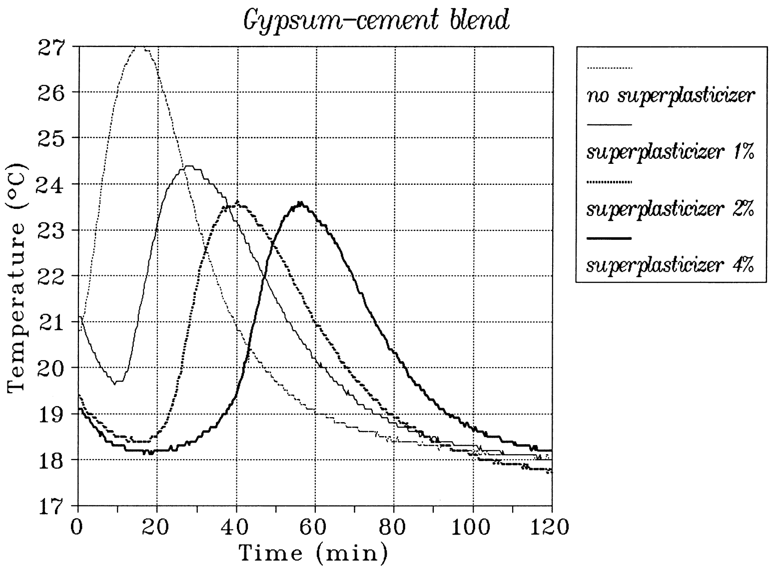

FIG. 7.
Temperature vs. time for gypsum-Portland cement mixes.

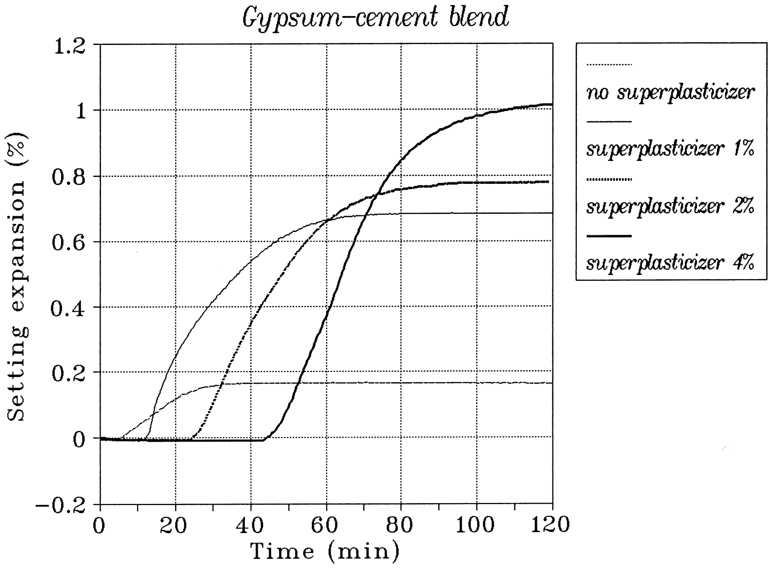

FIG. 8.
Setting expansion vs. time for gypsum-Portland cement mixes.

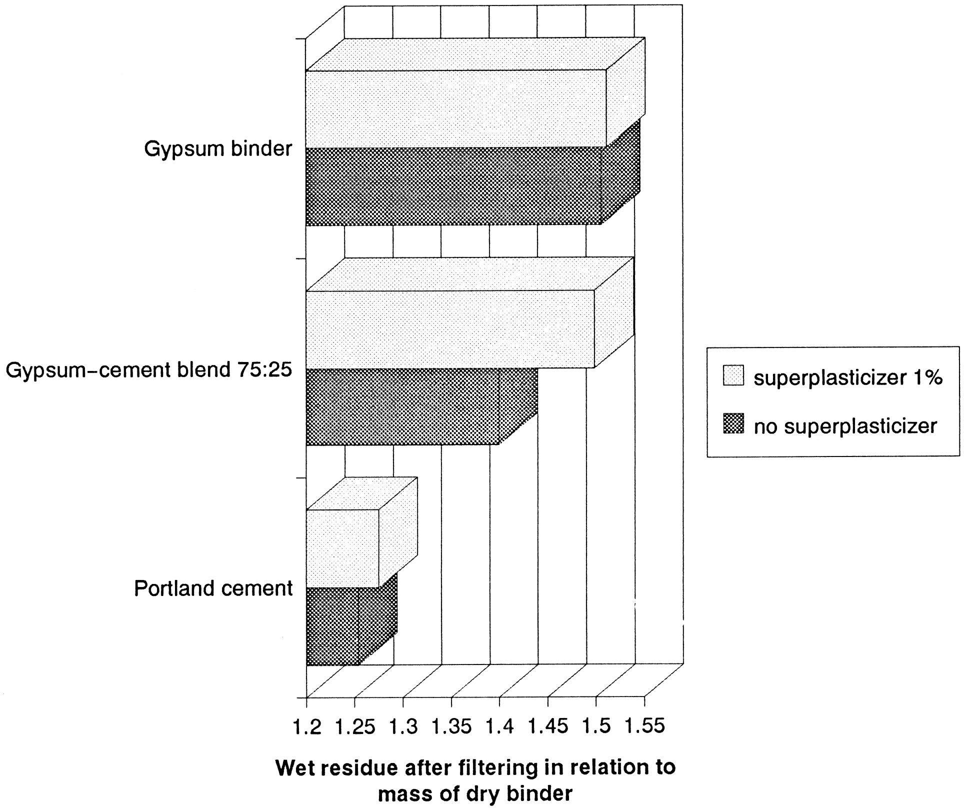

FIG. 9.
Wet residue after vacuum filtering in relation to mass of dry binder for water suspensions of pure gypsum binder, gypsum-Portland cement blend 75:25, and Portland cement alone.

Effect of the Superplasticizer on the Temperature and Setting Expansion of the Fresh Gypsum-Cement Mixes

Pure Gypsum

The development of temperature and setting expansion for pure gypsum binder mixed with water and superplasticizer is shown in Figures 5 and 6. It can be seen that the addition of the superplasticizer can influence both of these parameters to a very limited extent: the temperature insignificantly decreases and the setting expansion deformation increases. It should be noted that the superplasticizer used does not practically delay the setting beginning and the time of achieving maximum temperature of hydration reaction. The initial rate of setting expansion is also not affected.

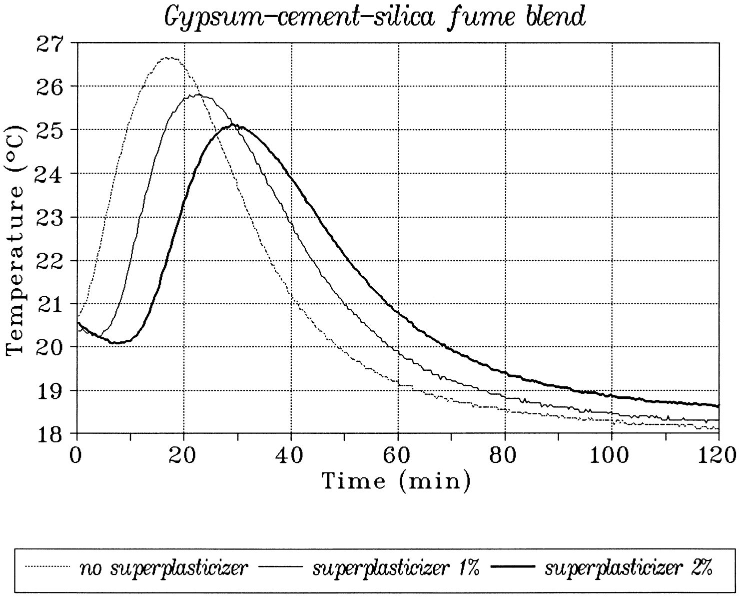

FIG. 10.
Temperature vs. time for GCSF mixes.

Gypsum-Portland Cement Blends

The temperature and setting expansion curves for the gypsum-Portland cement (75:25) blends are presented in Figures 7 and 8. It can be seen that, in contrast to the pure gypsum, the addition of the superplasticizer very strongly influences both of the parameters measured. It was found visually that even a small amount of the superplasticizer significantly improved workability of the mixes. Maximum temperatures are somewhat decreased. However, the main results were in the delay of setting and in the drastic (by 4–5 times) growth of the maximum setting expansion deformation, which practically achieved that of pure gypsum mix without superplasticizer. The hydration reaction in the blend without superplasticizer begins immediately after mixing with water. Each additional percent of the superplasticizer delayed the hydration by ≈15 minutes; this can be identified by the "moving" of the temperature curves to the right side of the graph (see Fig. 7). This leads to the conclusion that the superplasticizer acts mainly on the cement part of the blend, but in such a way that its action is indirectly reflected on the crystallization of calcium sulfate dihydrate; from the mechanical point of view the superplasticizer releases internal stresses in the microstructure formed and provides better (more free) conditions for the development of the framework made of gypsum crystals. This is clearly indicated by the delay at the beginning of the setting and by the drastic growth both in the setting expansion rate and in the maximum expansion deformation.

Thus, in spite of the fact that the superplasticizer does not influence the time of crystallization of gypsum crystals alone, in the blend with a relatively small amount of Portland cement it resulted in pronounced delay of setting. Taking into account that the precipitation of gypsum crystals from an over-saturated solution is preceded by the stage of dissolving of

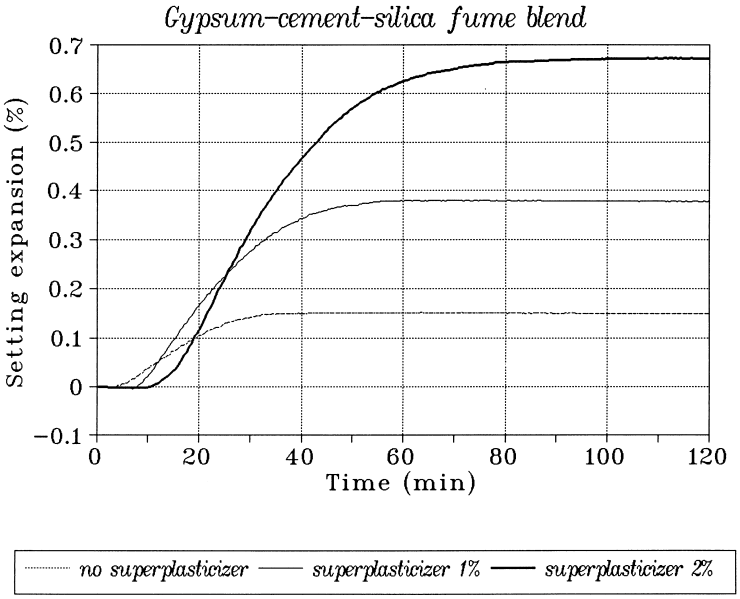

FIG. 11.
Setting expansion vs. time for GCSF mixes.

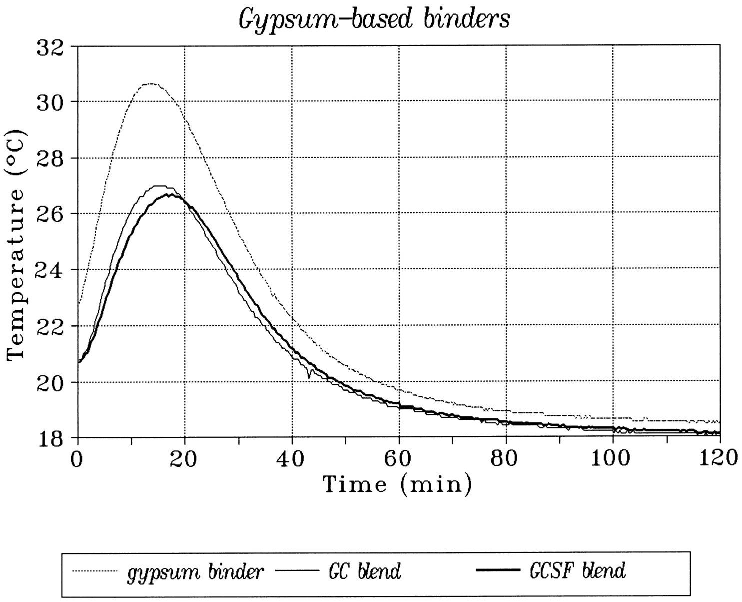

FIG. 12.
Temperature curves for different gypsum-based mixes, no superplasticizer.

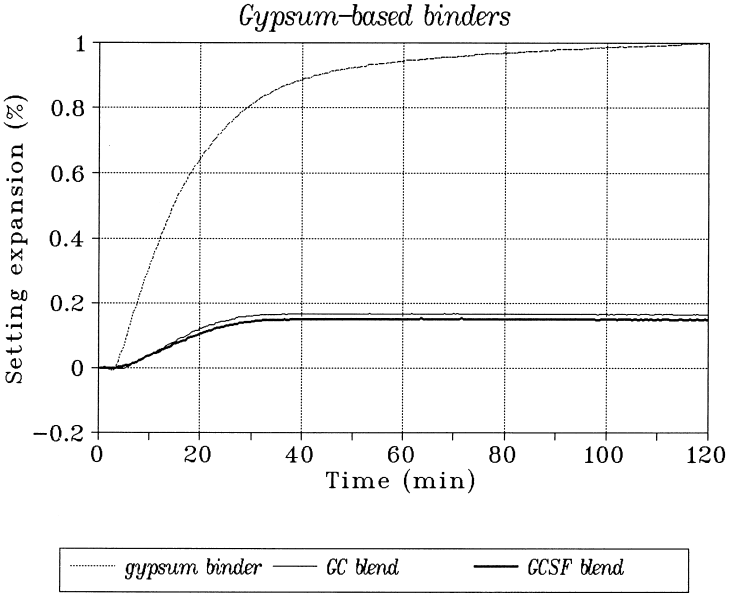

FIG. 13.
Setting expansion curves for different gypsum-based mixes, no superplasticizer.

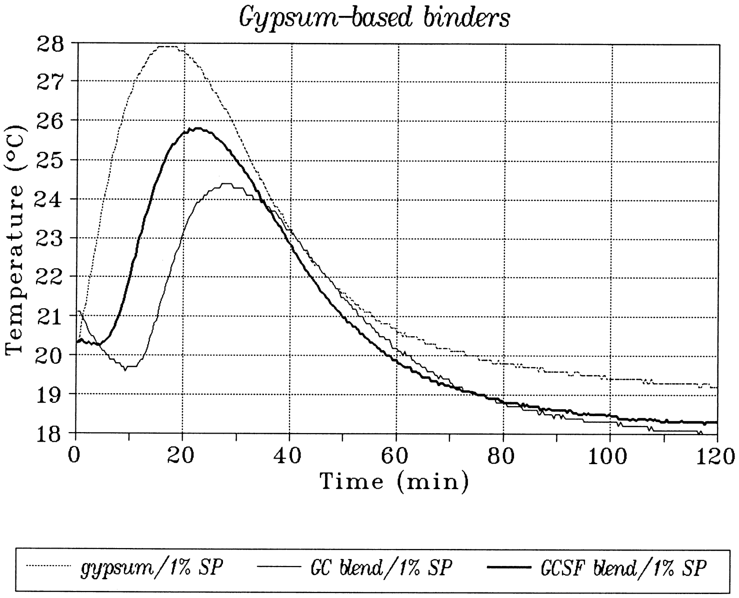

FIG. 14.
Temperature curves for different gypsum-based mixes at 1% of super-plasticizer Rheobild-1000.

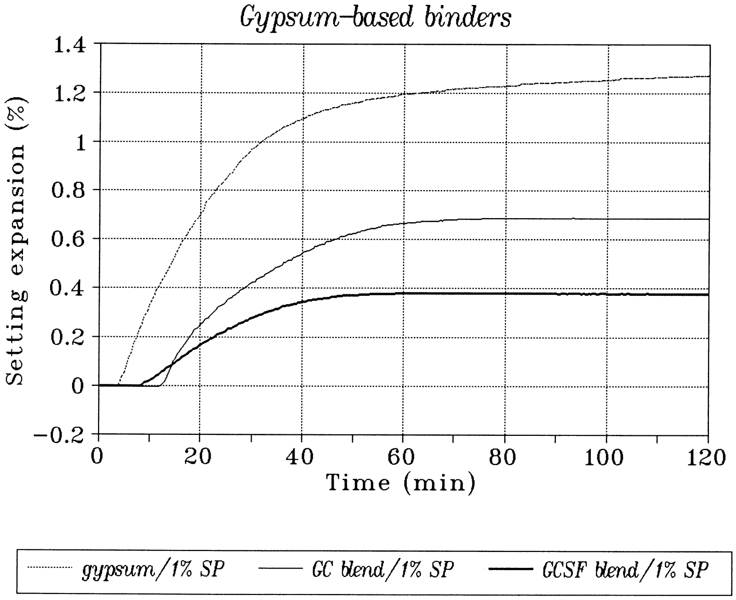

FIG. 15.
Setting expansion curves for different gypsum-based mixes at 1% of super-plasticizer Rheobild-1000.

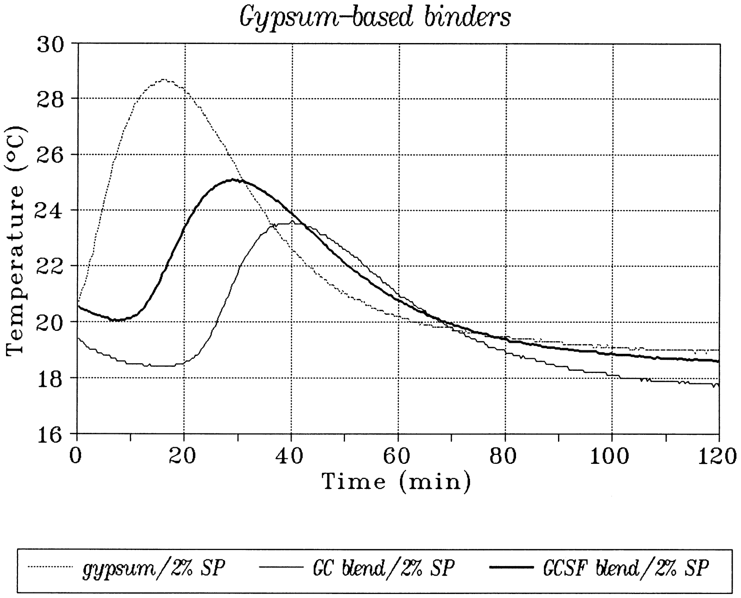

FIG. 16.
Temperature curves for different gypsum-based mixed at 2% of super-plasticizer Rheobild-1000.

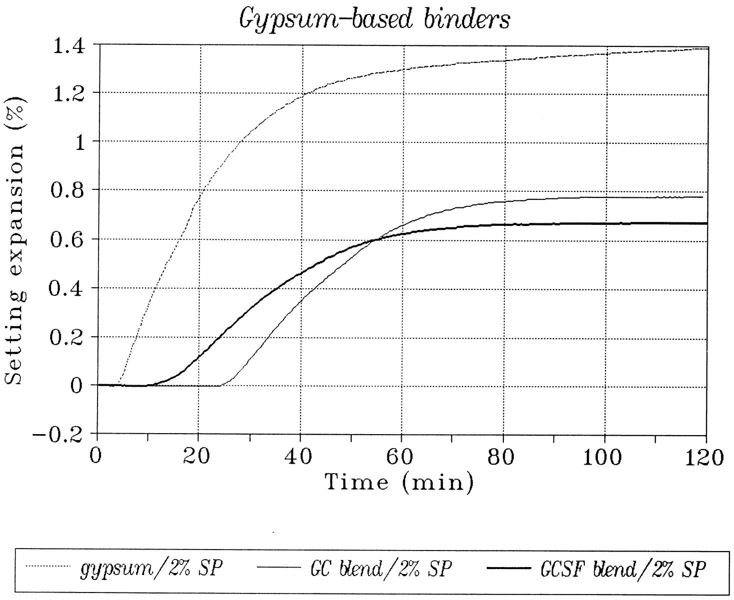

FIG. 17.

Setting expansion curves for different gypsum-based mixes at 2% of super-plasticizer Rheobild-1000.

calcium sulfate hemihydrate crystals, it can be assumed that an addition of superplasticizer temporarily prevents calcium sulfate hemihydrate from dissolving.

In order to check this assumption, the following simple test was carried out. The water suspensions of pure gypsum binder, Portland cement, and a gypsum-cement blend (of the composition 75:25) were prepared separately at the water/solid ratio of 5:1. After continuous mixing for 3 min., the suspensions were filtered under vacuum for 1.5 min. and the wet residues were weighed. Then the test was repeated with an addition of 1% superplasticizer. The results are shown in Figure 9. It can be seen that the superplasticizer added to pure gypsum binder as well as to Portland cement alone practically does not change solubility of these systems. However, added to the gypsum-cement blend it does significantly decrease immediate solubility.

Temperature and Setting Expansion of Gypsum-Cement-Silica Fume Blends

The temperature and setting expansion curves for the gypsum-cement-silica fume blend (composition of 75:20:5) are presented in Figures 10 and 11. They show the trends similar to those of gypsum-cement system.

Figures 12 and 13 show that there is no difference in the behaviour of fresh gypsum-cement and gypsum-cement-silica fume mixes without superplasticizer. That is why all that was said in the previous section about gypsum-cement mix can be applied to the GCSF blend to the same extent.

However, the equal amounts of the superplasticizer here influence setting time, temperature, and setting expansion less than in gypsum-cement blends. This can be clearly seen from

Figures 14-17, in which the time dependencies of temperature and setting expansion are assembled separately for the mixes with 1% (Figs. 14 and 15) and 2% of superplasticizer (Figs. 16 and 17).

The explanation of the less effective action of the superplasticizer in GCSF blends is simple. The substitution of 5% of the cement part of the binder by silica fume having much higher specific surface results in the increasing adsorption of superplasticizer on the solid particles. Consequently, the most active part of the superplasticizer, which remained in the liquid phase, decreases.

Conclusions

In (1), a blend of 75% gypsum binder, 20% Portland cement, and 5% silica fume was recommended for obtaining gypsum-based materials with improved resistance in humid environment. In the present paper, the properties of the fresh pastes made of this blend were studied.

It was shown that while the maximum temperature depended regularly on the gypsum content, the mechanical properties of the fresh pastes (maximum setting expansion, workability, and rheological characteristics) were strongly influenced by cement content. Even a small addition of Portland cement to the gypsum binder resulted in a drastic decrease of setting expansion and made workability worse. In order to improve workability of gypsum-cement blends, it is desirable to use superplasticizer. The influence of superplasticizer on setting and hardening of gypsum, gypsum-cement, and gypsum-cement-silica fume (GCSF) mixes was analyzed.

It was also found that the superplasticizer used (Rheobild-1000) influenced temperature and setting expansion of pure gypsum paste to a limited extent, but added to gypsum-Portland cement paste it resulted in the decrease of the initial solubility of hemihydrate, in the delay of setting, and in the drastic growth (by 4–5 times) of the maximum setting expansion. It was concluded that the superplasticizer acts on the cement part of the blend, but in such a way that it is indirectly reflected in the crystallization of calcium sulfate dihydrate, releasing internal stresses in the microstructure formed and providing better (more free) conditions for the development of the framework made of gypsum crystals.

The experimental results obtained in the present study should be checked in the other tests by means of the various physical and chemical methods (DTA, XRD, SEM, and strength in early age). The appropriate results will be reported and analyzed in the part 2 of the paper.

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