Pergamon

Cement and Concrete Research, Vol. 28, No. 4, pp. 523–531, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(98)00004-0

SETTING AND HARDENING OF GYPSUM-PORTLAND CEMENT-SILICA FUME BLENDS, PART 2: EARLY STRENGTH, DTA, XRD, AND SEM OBSERVATIONS

K. Kovler
Faculty of Civil Engineering, National Building Research Institute,
Technion-Israel Institute of Technology, 32000 Haifa, Israel

(Received July 2, 1997; in final form January 6, 1998)

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 and discussed. *© 1998 Elsevier Science Ltd*

Introduction

It is known that gypsum with an addition of Portland cement and pozzolana has a potential for developing improved durability in water, in spite of the fact that mixing gypsum with Portland cement is unfeasible because it can result in the formation of ettringite and thaumasite, which cause expansion and lead to deterioration (1–4). 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 previous part of this study, the temperature and setting expansion dependencies in time for such a blend were described and discussed (5).

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 (GCSF) fume mixes was analyzed.

It was also found in (5), 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.

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

The object of this study is to reveal specific peculiarities of setting and hardening of GCSF blends, in order to find out the optimum structure possessing both the advantages of gypsum and Portland cement.

Experimental

The GCSF mix studied in the present work was made of a blend of 75% by mass of calcium sulphate 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 sulphate 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.

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 mixes. As it was found in the previous part of the study (5), the superplasticizer is very important factor in the formation of material microstructure. In addition to dispersing silica fume particles, the superplasticizer retards dissolving calcium sulfate hemihydrate during the first minutes after mixing with water, and it results in the setting retardation of the GCSF paste with a desirable degree. Therefore the superplasticizer was incorporated into all the mixes examined in this part of the study, with a constant content of 2% of the blend mass.

The mixes were hand-mixed during 1 min. and cast as cubes 25 × 25 × 25 mm. The specimens were demoulded in 10–12 min. after casting and were examined on compressive strength in early age. Fragments of some of the broken cubes were tested to determine their composition by XRD using CuKα radiation and DTA. Microstructure was characterized by SEM.

Differential Thermal Analysis (DTA)

DTA curves were obtained in a homemade apparatus described in (6), on hardening gypsum-cement (GC) and gypsum-cement-silica fume (GCSF) pastes, at a various times after casting. The specimens were dried by methanol, and the DTA was carried out at a heating rate of 10°C/min, up to a temperature of 250°C. The reference material was anhydrite, anhydrous calcium sulfate.

The DTA diagrams obtained for the GC mixture consisting of 75% calcium sulfate

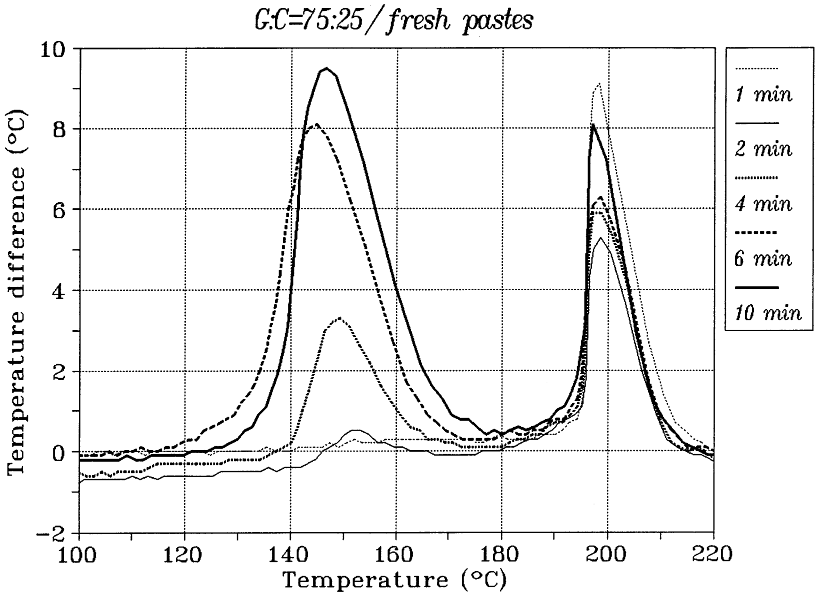

FIG. 1.

DTA diagrams for gypsum-Portland cement mix with 2% of superplasticizer in 1, 2, 4, 6, and 10 min. after casting.

hemihydrate and 25% Portland cement in the very early stages of hardening (up to 10 min. after mixing water was added) are given in Figure 1. Two peaks characteristic of decomposition of gypsum (~150°C) and calcium sulfate hemihydrate (~200°C) are clearly seen. The older the paste, the higher the ratio between the peak of gypsum and that of calcium sulfate hemihydrate. This shows that the amount of gypsum crystals grows in the paste. No signs are seen of the formation of either the high-sulfate form of calcium sulfoaluminate hydrate (ettringite), or of the monosulfate form of calcium sulfoaluminate hydrate (monosulfate), which show usually the peaks at ~125–130°C and at ~190–195°C, respectively. Ettringite was expected to form, because it is known that ettringite is observed in the first stages of Portland cement hydration, when one of the clinker minerals, tricalcium aluminate, reacts with gypsum added in small amounts to the clinker during grinding.

The DTA diagrams of the same fresh paste, but at somewhat later age (15–120 min. after mixing with water), are shown in Figure 2. It can be seen that the general picture did not change. As in the previous case, the two peaks of dihydrate and hemihydrate dominate.

By an assumption that by the age of 2 h all the gypsum binder reacts with water, it is possible to evaluate the degree of hydration from Figures 1 and 2. It follows from the calculation of the ratio between two peaks measured, that ~10% of hemihydrate reacts within the first 2 min., ~50% of gypsum is formed within the first 5 min., and during the following 5 min. the amount of gypsum crystals achieves already ~90%. In other words, the setting starts when about 90% of gypsum is formed in the paste.

Similar results were obtained for the GCSF paste (Fig. 3).

No significant difference was observed between the diagrams of the GC and GCSF pastes also at the age of 1 week (Fig. 4). The cubes were cured in air at a temperature of 20°C and

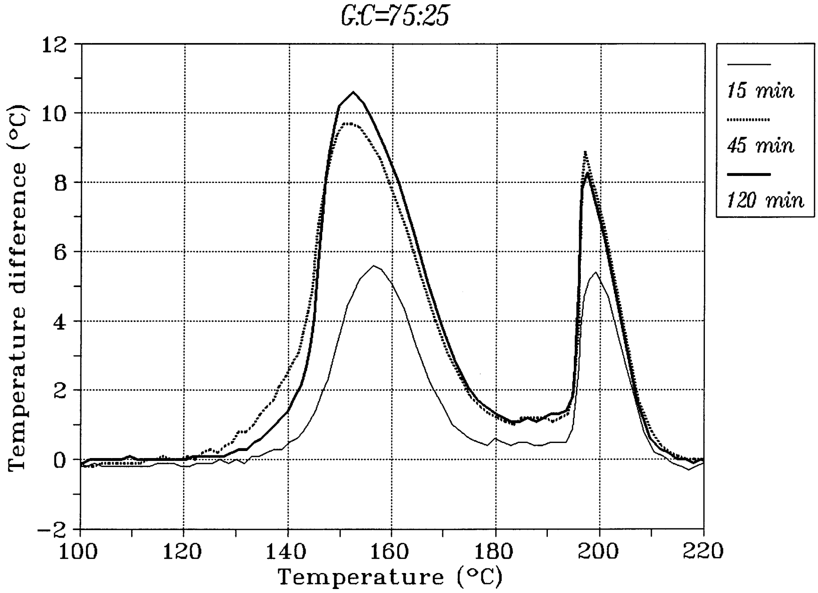

FIG. 2.
DTA diagrams for gypsum-Portland cement mix with 2% of superplasticizer in 15, 45, and 120 min. after casting.

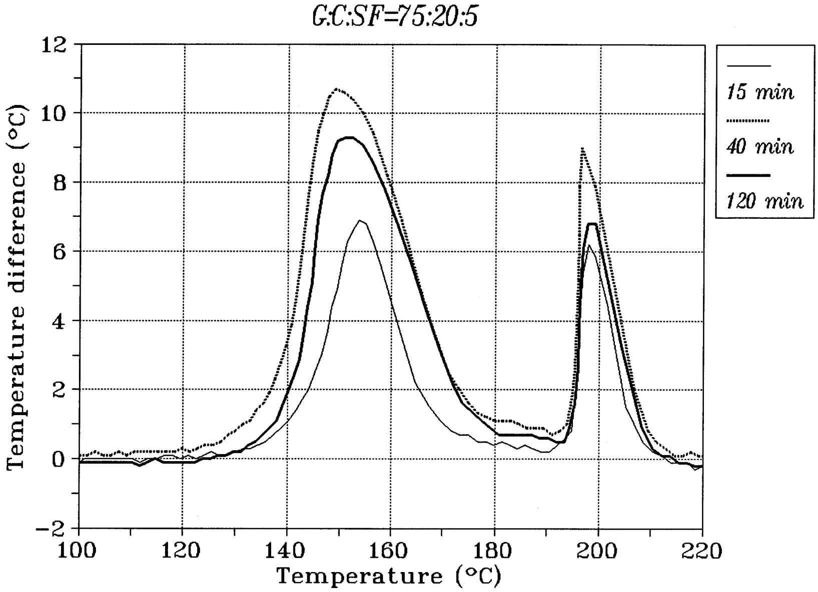

FIG. 3.
DTA diagrams for gypsum-Portland cement-silica fume mix with 2% of superplasticizer in 15, 45, and 120 min. after casting.

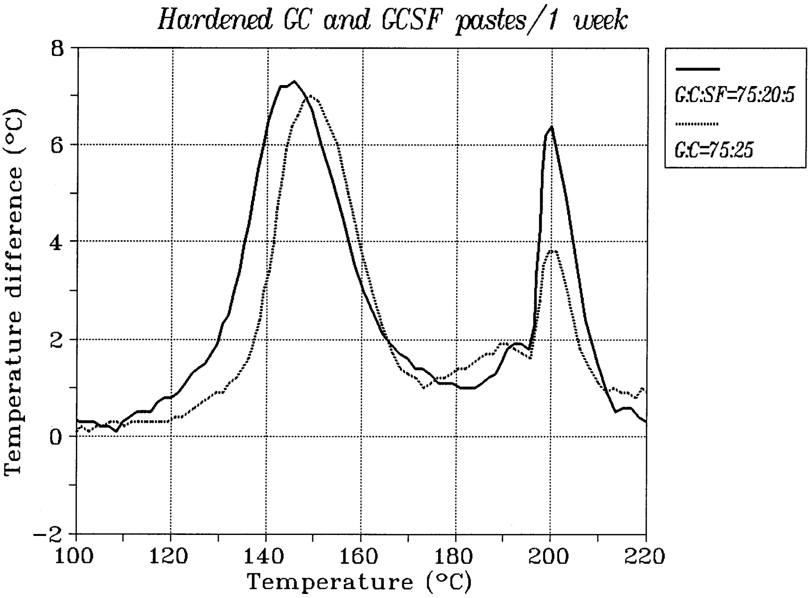

FIG. 4.
DTA diagrams for gypsum-Portland cement and gypsum-Portland cement-silica fume mixes with 2% of superplasticizer in 1 week after casting.

relative humidity of 65%. The only difference in comparison with the DTA curves obtained at younger age is very small peak at ~190°C, which could indicate monosulfate.

X-ray Diffraction (XRD)

The XRD patterns of both GC and GCSF pastes at very young ages (up to 2 h), tested both in dry and wet states, do not show any peaks except those characteristic of gypsum (7.56, 4.27, 3.79, 3.05 Å) and calcium sulfate hemihydrate (6.01, 3.46, 3.00 Å). However, already by 2 h after mixing the blend with water the XRD peaks for hemihydrate disappear (Fig. 5).

The XRD data confirm the conclusion obtained earlier that the formation of gypsum does control the beginning of hardening process of gypsum-Portland cement blends in which gypsum is a major component. They also did not show any signs of the formation of ettringite or other hydrates.

Compressive Strength in Early Age

The compressive strength was tested for both GC and GCSF pastes cast as 25-mm cubes. The development of compressive strength in time after casting is shown in Figure 6. It can be seen that the strength increases similarly for both gypsum-cement and GCSF mixes. In other words, the presence of 5% silica fume in the blend does not influence the mechanical strength in early age, because a pozzolanic reaction between silica fume, calcium hydroxide and water requires much longer curing.

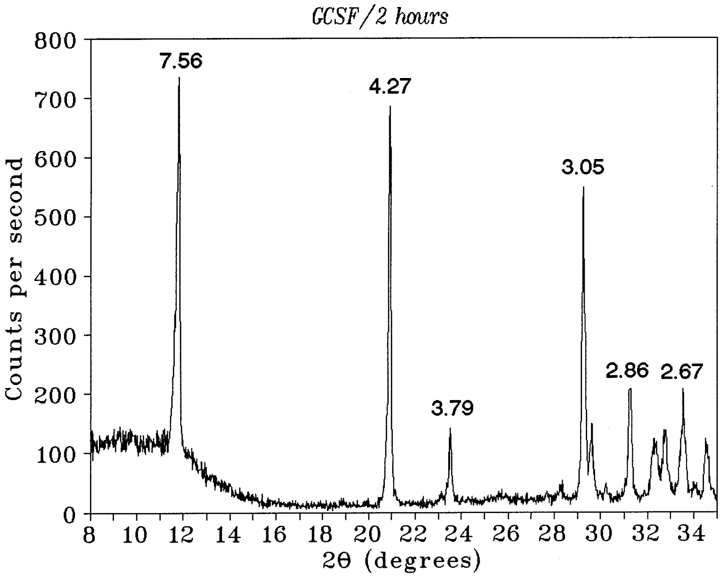

FIG. 5.
XRD diagram for gypsum-Portland cement-silica fume mix with 2% of superplasticizer, 120 min. after casting.

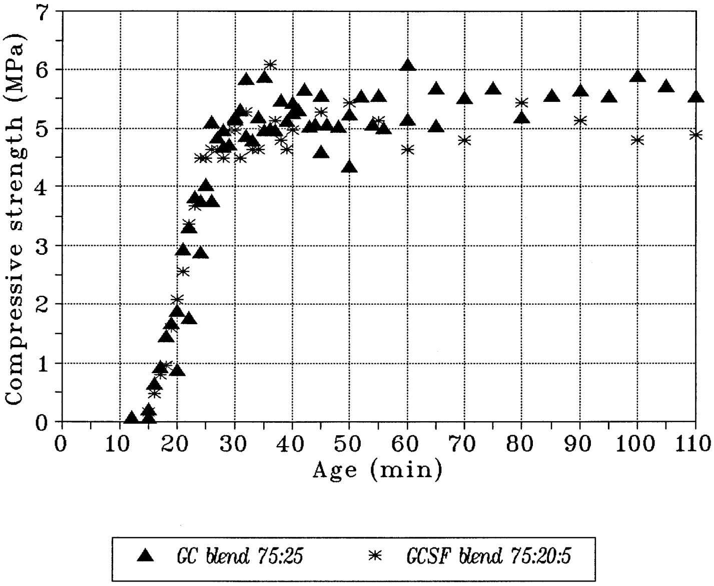

FIG. 6.
Cube compressive strength vs. time after casting for gypsum-Portland cement (GC) and gypsum-Portland cement-silica fume (GCSF) pastes.

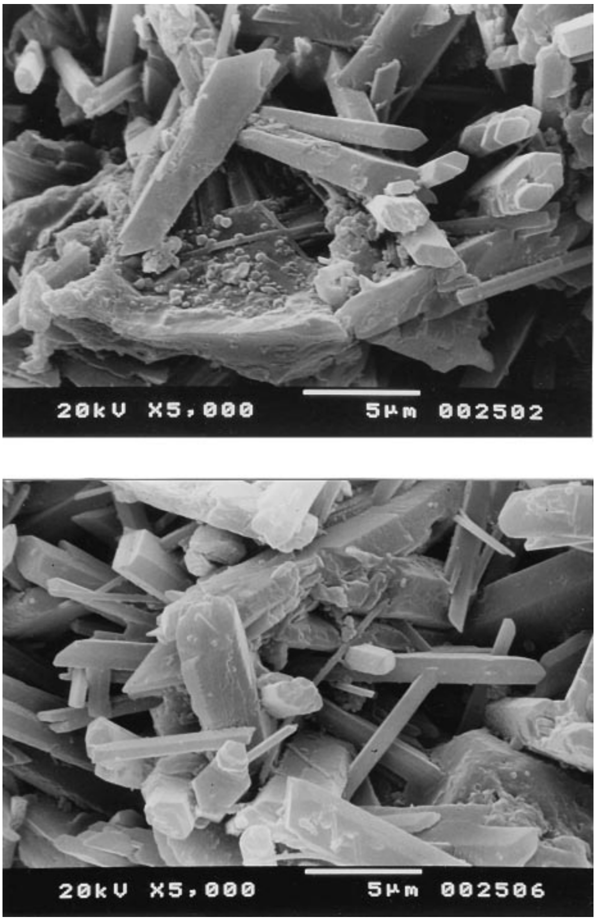

FIG. 7.
Micrographs of the microstructure of gypsum-Portland cement paste at early age (4 h).

The growth of the strength was observed already at 15–20 min. after casting. The fast strength growth was ended already in 26–28 min. after casting, when the strength achieves the maximum value, which practically does not change during four h of continuous testing. Slow strength growth at later ages can be caused, as shown in (1), by drying of the material and/or by hydration of the silicate part of the blend. However, the structure of gypsum-cement materials formed at the very beginning of the hardening is strong enough to make the early demoulding possible. It has to be emphasized that the strengthening of the materials studied here is very similar to that of pure gypsum, which achieved at the age of 1 day the same value of compressive strength (5.6 MPa) (1).

Scanning Electron Microscopy (SEM)

After the strength tests, specimens of 4-h-old GC and GCSF pastes were oven-dried at 50°C and their microstructure was observed with the help of SEM.

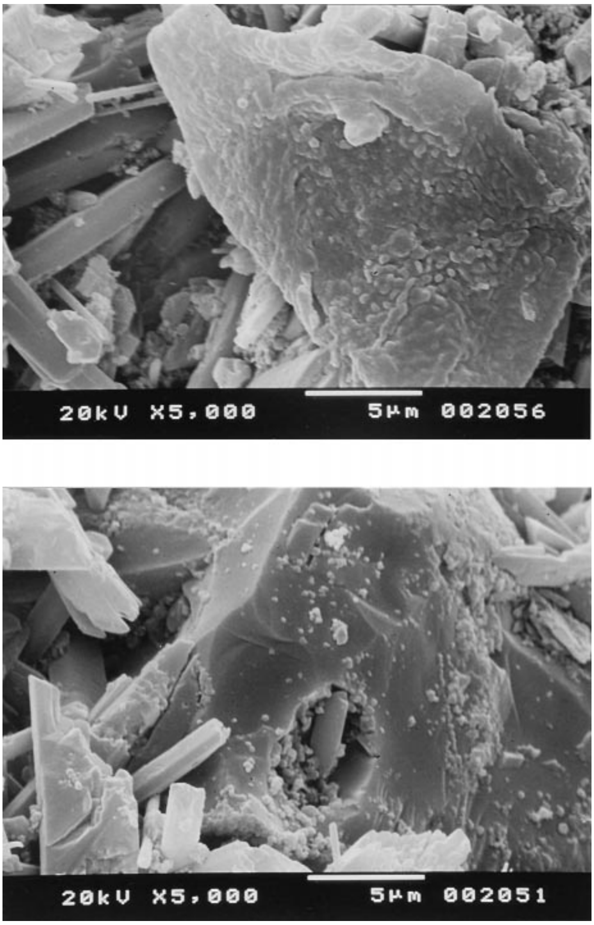

FIG. 8.
Micrographs of the microstructure of gypsum-Portland cement-silica fume paste at early age.

The microstructures of both mixes look similar. The separate cement grains are clearly seen in Figures 7 and 8; however, the products of cement hydration are almost not revealed in both of the pastes. The C-S-H gel formed, in GCSF mixes at old age as a result of pozzolanic reaction (1), is not observed here for these young pastes.

Small particles of silica fume are adsorbed on the surfaces of large crystals characteristic of gypsum (Fig. 8), but do not possess a microfiller property. The microstructure looks open and friable, like that of gypsum-cement (Fig. 7).

Conclusions

The rate of strength development of the GCSF blend in early age is similar to that of pure gypsum. This fact indicates the important point that the improved performance of such a blend at old age is not achieved as a result of mechanical behavior in early age.

The mechanical properties and microstructure of young gypsum-cement and of young gypsum-cement-silica fume pastes are very similar, because the strengthening role of silica fume as a pozzolanic component is not revealed within a period of a few hours. The early-age microstructures of both materials are very porous and no signs of C-S-H gel in between gypsum crystals are observed in the GSCF blends.

There were not found any signs of ettringite formation in the GCSF paste in early age. However, the question remains as to when ettringite starts to appear, and therefore this issue has to be investigated further.

The continuation of the work is of great importance, because it solves both theoretical and applied problems. The theoretical significance is for the understanding and explaining of the setting and hydration mechanisms of such a complicated system as gypsum-Portland cement-silica fume blend. The applied significance is for determining ways to improve water resistance of gypsum binders without any loss in the advantages of gypsum (early hardening, high early strength, enhanced workability, and fine finish).

Acknowledgments

The author kindly appreciates the valuable advice and help of Prof. Arnon Bentur during all the stages of the investigation, the assistance of Mr. Shimon Chermak and Ms. Rivi Eytan in carrying out the tests, and the help of Ms. Shirley Eagle in the paper preparation. The study was carried out by the invitation of the Ministry of Construction and Housing, State of Israel, and was supported by the fund for the promotion of research at the Technion-Israel Institute of Technology.

References

1. A. Bentur, K. Kovler, and A. Goldman, Adv. Cem. Res. 6, 109–116 (1994).
2. F. Alksnis, Hardening and Destruction of Gypsum-Cement Materials, Stroyizdat, Leningrad, 1988 (in Russian).
3. A. Volzhensky, V. Stambulko, and A. Ferronskaya, Gypsum-Cement-Pozzolana Binders, Concretes and Products, Stroyizdat, Moscow, 1971 (in Russian).
4. K. Kovler and A. Bentur, Differential Thermal Analysis of Hydration and Hardening in Gypsum-Portland Cement Systems, Proc. of Israel-Hungary Binat. Conf. on Thermal Analysis and Calorimetry of Materials, pp. 15–16, Ein-Bokek, Israel, 1996.
5. K. Kovler, Cem. Concr. Res. 28, 423–437 (1998).
6. E. Stav, In Situ Polymerization of Acrylamide and its Influences on the Mechanical Properties and Microstructure of Gypsum (dissertation), Technion-Israel Institute of Technology, 1993 (in Hebrew).