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# Stresses generated in expansive reactions of cementitious systems

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**Abstract**

The authors built an experimental assembly that enabled to measure the expansive stresses generated in cementitious systems in the course of hydration. The assembly was used to measure stresses generated in the hydration of pastes consisting of tricalcium silicate, acting as the cementitious matrix, and gypsum, in combination with CA, $C_3A$, $C_4A_3s$, $C_4AsH_{12}$ (AFm) and $Al_2(SO_4)_3 \cdot 18H_2O$, acting as the expansive component. Also measured were stresses generated in the hydration of hard-burnt CaO combined with tricalcium silicate. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Ettringite formation; CaO hydration; Expansive stresses

## 1. Introduction

A variety of reactions taking place in cementitious systems are known to be associated with an expansion of the material [1]. As long as such expansion is moderate, it may be considered useful and may be exploited to prevent crack formation in concrete structures, or even in the production of prestressed concrete elements. The latter is the case in "shrinkage compensated" or "prestressed" cements. If, however, the expansion is excessive, it may cause cracking and a permanent damage of the concrete structure. Expansive reactions most important, and thus most widely studied, are those associated with the formation of ettringite and that caused by the hydration of free calcium oxide. As the formation of both ettringite and calcium hydroxide is accompanied with a chemical shrinkage, special conditions must exist to bring about an expansion of the system. Different hypotheses forwarded to explain the mechanism of sulfate expansion were recently discussed by Brown and Taylor [2].

There are available only very few data on the magnitude of stresses generated by expansive reactions in cementitious systems. Mather [3] reported values in the order of 50,000 psi ( = 357 MPa) found in the hydration of restricted mixes made out of $C_4A_3s$, calcium sulfate and calcium oxide, whose stoichiometric compositions corresponded to ettringite. In experiments performed at the Bauakademie Weimar (Germany), expansive stresses of up to 60 MPa, associated with ettringite formation, were found in concrete samples [4].

The authors have developed a new method, which enabled measure expansive stresses in cementitious systems with great accuracy. The procedure and the found results are reported in this paper. The present work is an extension of our previous research, in which we studied the effect of the Al-source on the rate of ettringite formation and the extent of expansion [5].

## 2. Experimental

### 2.1. Apparatus

The core of the measuring assembly, developed in the laboratory of the authors, is a mold shown schematically in Fig. 1. It was made out of steel with a particularly high rigidity (steel C60 CK60 DIN 17200, Rm = 780–910 $N/mm^2$, Re = 490 $N/mm^2$). The mold contains a measuring cell to accommodate a test specimen $15 \times 15 \times 60$ $mm^3$, and has additional space for a measuring block, $25 \times 20 \times 15$ $mm^3$ in size, designated to measure the stresses generated by the specimen. The measuring block is made out of a low-rigidity steel (specialty steel X5 CrNi 189, DIN 17440), which exhibits a well-measurable elastic deformation, if

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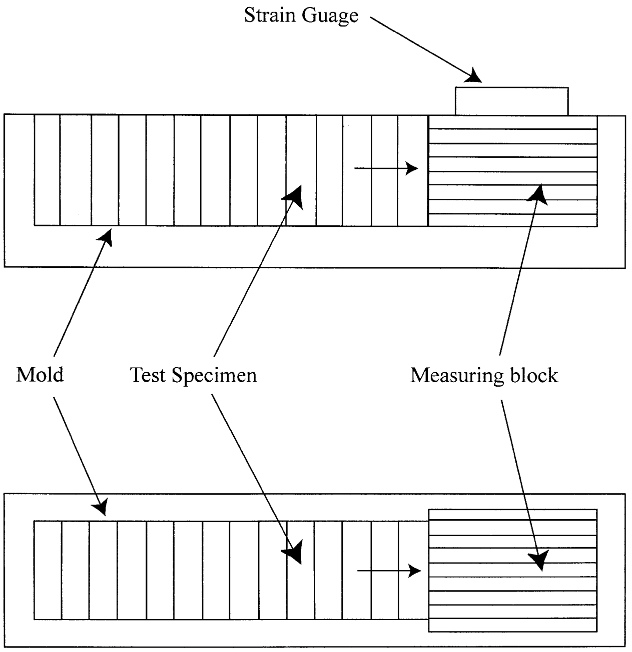

Fig. 1. Schematical presentation of mold used in measuring expansive stresses.

exposed to external forces of a magnitude expected to be present in our experiments. An intimate contact between one end of the test specimen and the measuring block is ensured by the use of a screw mounted at the opposite side of the mold (not shown in Fig. 1). A strain gauge (type 3/120 LY11 by Hottinger) is mounted at the top of the measuring block to measure the strain generated by the pressure of the test specimen. The signal coming from the strain gauge is amplified by the amplifier Semmeg 9000, type 97202 and displayed by the registration unit Semmeg 9000, type 97302. Fig. 2 shows the complete testing assembly.

To calibrate the equipment, the relationship between the applied pressure and resultant strain of the measuring block was determined by the use of a hydraulic press.

In the described arrangement, any expansion of the test specimen will generate a deformation of the measuring block, which will be proportional to the force generated in the expansion process. The absolute magnitude of the expansion of the tested material will remain negligible even at relatively high expansive stresses, due to a significantly greater rigidity of the measuring block, as compared to the hardened cement pastes.

### 2.2. Materials

The following starting materials were used in the experiments.

Monocalcium aluminate ($CaO{\cdot}Al_2O_3$, abbreviated CA), tricalcium aluminate ($3CaO{\cdot}Al_2O_3$, abbreviated $C_3A$) and tetracalcium trialuminate sulfate ($4CaO{\cdot}3Al_2O_3{\cdot}SO_3$, abbreviated $C_4A_3s$) were synthesized by burning precompacted mixes of an appropriate composition made from $CaCO_3$, $Al_2O_3$ and $CaSO_4$ in an electric furnace at temperatures needed to reduce the free CaO content below 0.5 wt.%.

Monosulfate (AFm-phase, $4CaO{\cdot}Al_2O_3{\cdot}SO_3{\cdot}12H_2O$, abbreviated $C_4AsH_{12}$) was synthesized by shaking a water-suspension of $Al_2O_3$, $CaSO_4{\cdot}2H_2O$ and $Ca(OH)_2$ with a 1:1:3 molar ratio, in a closed container for 144 h at 110–120 °C. The obtained product was filtered, washed with methanol and dried in air at ambient temperature. The preparation contained approximately 77% monosulfate; the rest were small amounts of the starting materials and ettringite.

Calcium oxide (CaO, abbreviated C) was produced by burning $CaCO_3$ at a temperature of 1350 °C for 3 h, to obtain a CaO preparation of low reactivity. Such low-reactive form of calcium oxide was needed to prevent the hydration of this compound within the experimental mix prior to its setting and thus, to obtain a well-measurable expansion.

Tricalcium silicate ($3CaO{\cdot}SiO_2$, abbreviated $C_3S$) was synthesized by repeated burning of the pertinent $CaCO_3 + SiO_2$ blend to 1550 °C.

The used aluminum sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$, abbreviated $As_3H_{18}$) and gypsum ($CaSO_4{\cdot}2H_2O$, abbreviated $CsH_2$) were commercial products.

All materials, with the sole exception of monosulfate, which was formed in a highly dispersed form, were ground to a specific surface area of $300 \pm 10$ $m^2/kg$.

### 2.3. Testing procedure

Five experimental mixes were prepared by blending each of the Al-compounds together with gypsum in an $Al_2O_3/SO_3$ molar ratio of 1:3. The amounts of these constituents were selected to yield 30 wt.% of ettringite (related to the whole paste) upon complete hydration. The rest of the mix consisted of tricalcium silicate and water, which was added in an amount corresponding to a water–solid ratio of 0.40.

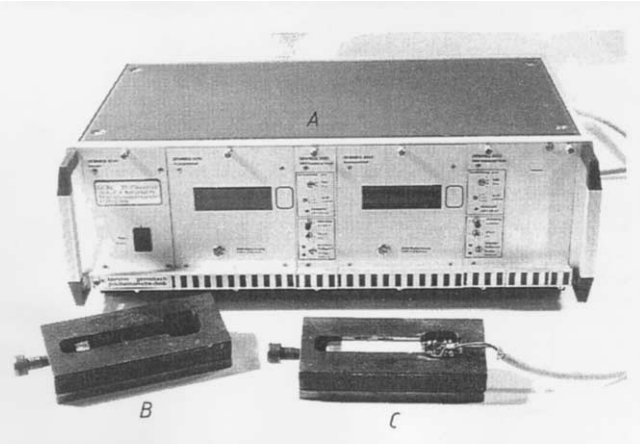

Fig. 2. Assembly for determination of expansive stresses in hardened cement pastes: (A) amplifier and registration unit, (B) mold — empty, (C) mold with test specimen, measuring block and strain gauge.

An additional mix consisted of a blend of 30 wt.% calcium oxide with tricalcium silicate, mixed with water at a water–solid ratio of 0.40. The role of tricalcium silicate was to produce test specimens strong enough for the measurements to be performed, and also to serve as source of $Ca^{2+}$ ions for the formation of ettringite, in some of the mixes. The exact composition of the mixes was given in our previous paper [5].

The experimental mixes were used for producing test specimens $15 \times 15 \times 60$ mm$^3$, which, after 24 h, i.e., after setting and prehardening, were transferred to the measuring chambre. The screw mounted at the opposite end of the chambre was used to produce an intimate contact between the test specimen and the measuring block. In one series of experiments the steel mold containing the test specimen was kept in a closed box with water at the bottom to maintain a high humidity of the air. In a parallel series, the test specimens were covered with a water-soaked sponge to assure their permanent contact with liquid water.

The deformation of the measuring block, and thus the stress generated by the test specimens, was measured for up to 25 days. To assess the reproducibility of the performed measurements, two parallel, independent runs were run with most of the mixes studied.

## 3. Results

Out of the five mixes that contained an Al-compound in combination with gypsum, only three, i.e., those made with CA, $C_4A_3s$ and $C_4AsH_{12}$ (Mixes No. 1, 3 and 4), produced measurable expansive stresses within the period of study, whereas the remaining two, i.e., those made with $C_3A$ and $As_3H_{18}$ (Mixes No. 2 and 5) did not. Figs. 3, 4 and 5 show the development of stresses in the former ones.

From the figures, it may be seen that the developed stresses were in all instances significantly higher in test specimens exposed to liquid water than in those cured in humid air. It is also apparent that in some mixes the attained stresses tended to decline after reaching a maximum value, to increase later again.

In water-cured specimens made with CA, the expansive stress attained a value of about 200 MPa within a few days and declined subsequently to a final value of about 80 MPa. In air-cured specimens of the same composition, the expansive stress did not exceed 40 MPa.

In specimens made with $C_4A_3s$, the maximum expansive stress was attained somewhat faster but its magnitude was distinctly lower, i.e., about 140 MPa. Subsequently, the expansive force dropped to a very low value, to increase again and to reach a final value of about 90 MPa. A similar fluctuation of the expansive stress was observed also in air-cured specimens, however, at a lower level.

Finally, in test specimens made with $C_4AsH_{12}$ (AFm), and cured under water, a measurable expansive stress started to develop only after an induction period of several days, to rise rapidly and to reach a value of about 180 MPa after 13 days. Subsequently, the stress value started to decline to a final value of about 100–120 MPa. Unlike in water-cured samples, in the air-cured specimens the expansive stress increased gradually, to reach a final value of 80 MPa after about 14 days.

Fig. 6 shows the development of the expansive stress in an air-cured mix made with calcium oxide. Here the stress increased steadily up to about 10 days of hydration and reached a final value of about 120 MPa. A decline of the stress value in the course of measurements, as seen in some

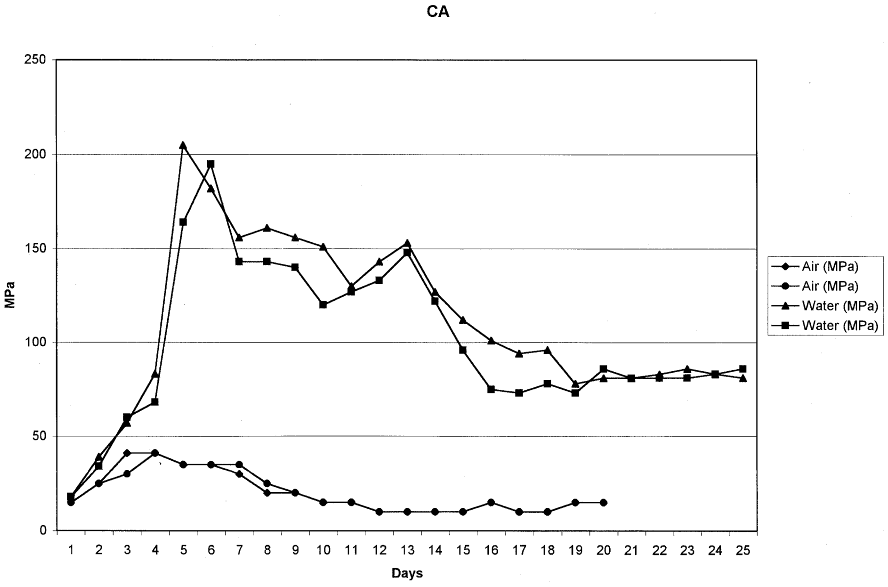

Fig. 3. Expansive stress as function of time — Mix No. 1 (CA).

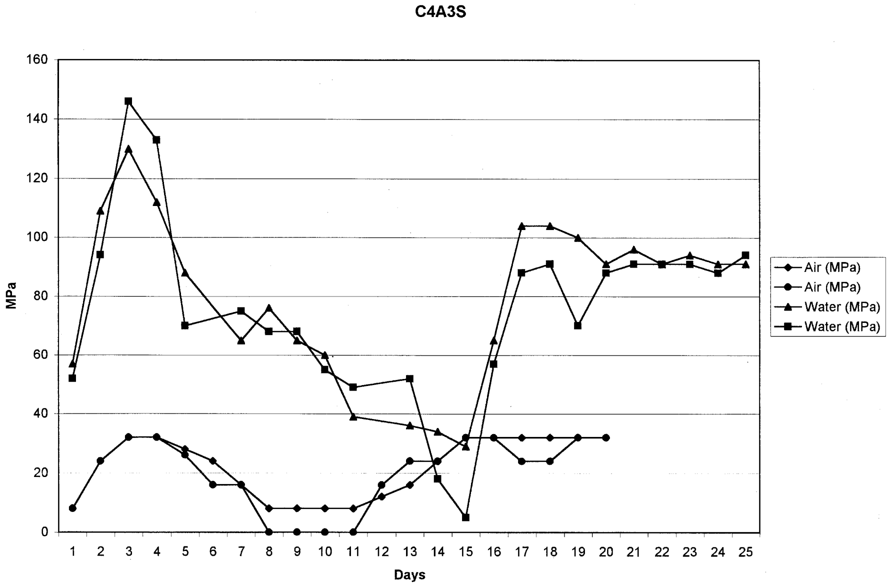

Fig. 4. Expansive stress as function of time — Mix No. 3 ($C_4A_3s$).

mixes made with Al-compounds in combination with gypsum, was not observed.

## 4. Discussion

The results of our experiments indicate that some, but not all mixes that contained an Al-compound in combination with calcium sulfate, exhibited a significant expansive stress development within the time span of our measurements. Table 1 shows the maximum expansive stress produced by the individual mixes and the time since the start of the measurement at which a stress of such magnitude was attained. In addition, the table shows also the amount of ettringite formed by that time, as well as the expansion of the same mixes, if allowed to hydrate spatially unrestricted for the same period of time.

Not surprisingly, mixes that did not produce measurable expansive stresses exhibited also no, or only a barely noticeable expansion, if allowed to hydrate unrestricted. As to the amount of formed ettringite, it may be seen that one of the nonexpanding mixes (Mix No. 2, made with $C_3A$) contained only very small amounts of it in the initial days of hydration. It may be assumed that in this mix the absence of expansion and expansive stress generation was due to the formation of insufficient amounts

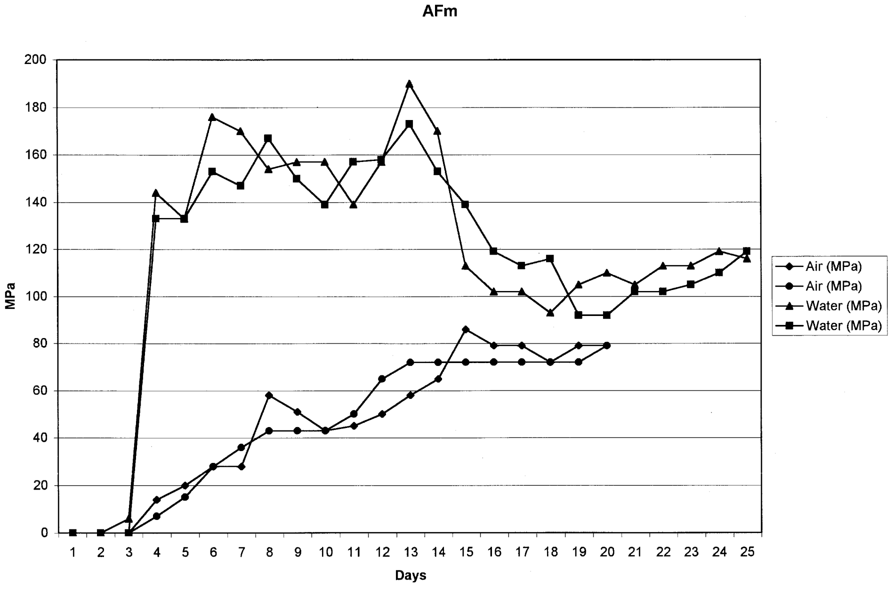

Fig. 5. Expansive stress as function of time — Mix No. 4 ($C_4AsH_{12}$).

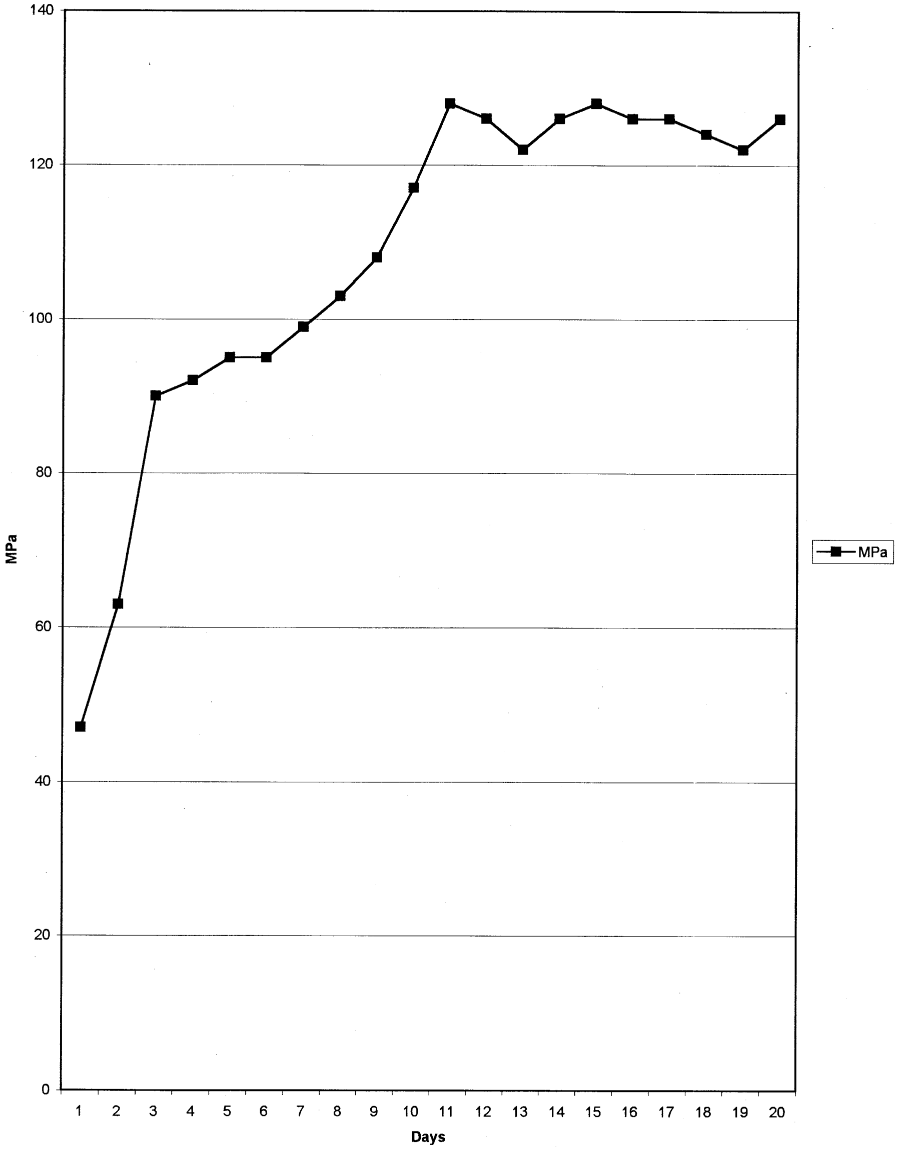

Fig. 6. Expansive stress as function of time — Mix No. 6 (CaO).

of this phase within the time period in which the experiment was run. It must be noted, however, that in a separate experiment, a mix of the same composition exhibited a distinct expansion if allowed to hydrate for several months [5].

Unlike in Mix No. 2, in Mix No. 5 the introduced aluminum sulfate became almost completely converted to ettringite within 1 day. We assume that in this mix the absence of expansion and stress generation was due to the fact that virtually all the ettringite was formed at a stage at which the mix was still plastic and thus unable to develop expansive stresses.

A comparison of data found in samples cured in air and in those that were in contact with liquid water shows great differences in the magnitude of developed stresses. These findings appear to indicate that swelling phenomena contribute to a significant degree to the development of expansive stresses associated with ettringite formation.

All three water-cured mixes that developed measurable expansive stresses associated with ettringite formation exhibited a decline of the stress value after reaching a maximum within a few days, to stabilize ultimately at a significantly lower level. The decrease of the stress value took place despite the formation of additional amounts of ettringite in the paste. The origin of this phenomenon is not obvious. We assume that it may be caused by a closer not specified restructuring of the texture of the cement paste as it undergoes further hydration.

Unlike in pastes yielding ettringite as a product of the hydration process, the paste made with calcium oxide did not exhibit a decline of the developed expansive stress as the hydration progressed. Thus, a restructuring of the hardened

Table 1
Maximum stress in restricted test specimens, ettringite content at maximum stress, and expansion of unrestricted test specimens at hydration times corresponding to maximum stress

| Mix No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Al-source | CA | $C_3A$ | $C_4A_3s$ | $C_4AsH_{12}$ | $As_3H_{18}$ |
| *Air-cured samples* | | | | | |
| Maximum stress (MPa/day) | 40/4 | – | 30/3 | 80/14 | – |
| Ettringite (%) | 8 | 7 days: 3, 28 days: 4 | 8 | 8 | 1 day: 25 |
| Expansion (mm/m) | 15 | 7 days: < 2, 28 days: 8 | 8 | 50 | 28 days: < 2 |
| *Water-cured samples* | | | | | |
| Maximum stress (MPa/day) | 200/5 | – | 140/3 | 180/12 | – |
| Ettringite (%) | 10 | 7 days: 4, 28 days: 5 | 10 | 12 | 1 day: 28 |
| Expansion (mm/m) | 20 | 7 days: < 2, 28 days: 13 | 30 | 70 | 28 days: < 2 |

paste in the course of hydration, associated with a decline of the generated expansive stress, appears not to take place in this system.

In assessing the obtained results, it must be pointed out that the absolute magnitude of the expansive stresses generated in a cementitious system will depend on a number of factors. Thus, in mixes of other composition and/or hydrating under different conditions, the measured expansive stresses may be higher or lower than that found in our own experiments.

## 5. Conclusions

Some but not all pastes made from tricalcium silicate in combination with appropriate amounts of gypsum and an aluminate compound — if mixed in the ratio $Al_2O_3/SO_3 = 1:3$ — exhibit an expansion if unrestricted, or a development of expansive stresses if allowed to hydrate under restriction. The magnitude of the attained stresses is significantly higher in pastes hydrating under water than in those hydrating just in humid air. Both the expansion and stress development are consequences of ettringite formation in the system. After reaching a maximum value within a few days, the magnitude of the existing stress tends to decline, despite the formation of additional amounts of ettringite, to stabilize ultimately at a lower level. Contrary to pastes whose expansion is associated with ettringite formation, the hydration of hard-burnt calcium oxide causes a development of expansive stresses, which remain constant after reaching a maximum value.

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