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Delayed ettringite formation symptoms on mortars induced by high temperature due to cement heat of hydration or late thermal cycle

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Abstract

Cases of delayed ettringite formation (DEF) have mainly been detected on mortars or precast concretes steam-cured according to a predefined temperature cycle during hydration. The present study shows that other situations in which the material is submitted to a temperature cycle can induce DEF expansions. Mortar bars were made with three different cements (types 10, 20M, and 30). As a first heat treatment, the mortar bars were steam-cured to reproduce the temperature cycle they would undergo if they were at the center of a large mortar member. The dimensional variations of these specimens were studied for 1 year. After 1 year, half of the specimens were steam-cured for 1 month at 85 °C. The expansions were followed for two more years. The early-age steam-cure-induced expansions for mortar types 10 and 30. Late steam-curing induced expansions for the three cements tested. In one case (cement type 20M), the early-age steam cure has suppressed or delayed the expansion induced by the late steam cure. A scanning electron microscopy (SEM) study showed that typical DEF symptoms are associated with the expansions.

Keywords: Delayed ettringite formation; Heat of hydration; Thermal treatment

1. Introduction

Since the first cases of delayed ettringite formation (DEF) were reported on heat-cured mortars, DEF has been a subject of great concern [1–5]. As stated by Taylor et al. [5], DEF may be defined as "the formation of ettringite in a cementitious material by a process that begins after hardening is substantially complete and in which none of the sulfate comes from outside the cement paste." The issue whether ettringite is the cause of expansion is not definitively solved yet [6,7], but the necessity for the mortar to undergo a high temperature (above approximately 70 °C) during hydration is now well established [1–3]. The purpose of this experimental work was to determine if other curing conditions, during hydration or later, could lead to DEF.

The first issue of this work was to determine if a cementitious material could develop DEF from its own heat of hydration. A few field observations tend to demonstrate that DEF could be induced by an excessive rise of temperature because of the heat of hydration [4,8,9]. However, to our knowledge, no laboratory experiments have been carried out to validate this hypothesis. The first part of this work thus consisted in submitting different mortars to steam cures directly computed from their measured heats of hydration and in following their expansions with time. The length changes of the different mortars have been measured for 3 years.

The second issue of this work was to determine whether a concrete steam-cured long after its hydration could present DEF symptoms in the long term. Few data have been published about the evolution of hydrated mortars at high temperature in a saturated environment. The work of Paul and Glasser [10] followed the mineralogical and structural evolution of cement pastes kept at 85 °C for

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more than 8 years. Expansion was not the main issue of their work, but no length change could be observed after the warm moist cure, back to room temperature. However, pastes are known to present very long induction times before expanding and very low expansion rates [11]. In the present work, 1-year-old mortars have been submitted to a 1-month steam curing at 85 °C, and their expansions have been followed for two more years.

2. Experimental

2.1. Materials

Three different cements were used in this study: a type 10 cement (considered as an average Portland cement), a type 20M cement (low C3A content, low heat of hydration, low sulfate content), and a type 30 cement (high C3A content, high heat of hydration, high sulfate content). Types 10, 20M, and 30 refer to the Canadian Portland cements classification CAN/CSA-A5-98. The chemical and mineralogical compositions of the different cements provided by the manufacturer are given Tables 1 and 2.

No reliable relationship based on cement composition has been found yet to determine the DEF susceptibility of a cement [1,5]. However, considering a "classical" laboratory steam curing for precast mortar (for instance, 4 h precure, 12 h at 90 °C, and cooling [12], designed to cause DEF in a laboratory study), type 20M cement would be the least susceptible in developing DEF symptoms, whereas type 30 cement would be the best candidate for DEF.

Granitic, alkali–silicate reaction proof sand was used. Mortars were made according to the C305-82 ASTM standard procedure. The water/cement ratio was 0.4, and the sand/cement ratio was 2.1.

2.2. Definition of the hydration temperature cycle

Two distinct temperature cycles have been imposed on the mortars. The first temperature cycle reproduces the conditions at the center of a large concrete member having a very high cement content in which temperature rises because of the heat of hydration and low heat losses. It is called here "hydration temperature cycle".

Table 1
Chemical analyses of the cements used in this study (wt.%)

Cement	Type 10	Type 20M	Type 30
SiO_2	20.30	23.20	21.12
Al_2O_3	4.42	4.11	5.18
Fe_2O_3	3.00	4.09	2.73
CaO	62.60	63.13	63.25
MgO	2.74	0.98	1.26
SO_3	3.08	2.78	3.80
K_2O	0.82	0.60	1.08
Na_2O	0.29	0.07	0.10

Table 2
Mineralogical compositions of the cements used in this study determined by the Bogue calculation (wt.%)

Cement	Type 10	Type 20M	Type 30
C_3S	57.7	39.2	47.4
C_2S	14.6	36.9	24.8
C_3A	6.6	4.0	9.1
C_4AF	9.1	12.4	8.3

Calorimetric measurements during adiabatic hydration of the mortars described above yielded their total heat of hydration. The specific heat and the thermal conductivity of the different mortars were estimated (see Table 3).

Different simulations, using the software Quadrel [13], allowed to find a geometrical configuration for which the type 10 mortar, considered as the reference mortar, would reach 85 °C during hydration. This configuration consists of a 1-m wall of mortar. Of course, such a mortar wall (or concrete with such a high level of cement) would be exceedingly bad engineering and would never be cast since it would undergo thermal cracking. The experiment was actually designed to compare different cements in an autogenous heat curing. The type 10 mortar thus reaches 85 °C in about 24 h. Fig. 1(a) shows the different temperature cycles at the center of the hypothetic mortar wall during hydration, up to 7 days. After 7 days, the three curves are identical and reach 20 °C after 1 month.

These temperature cycles were adapted to be easily reproducible in the laboratory. The cycles were shortened to reach 20 °C in 1 week instead of 1 month. The maximum temperature of the type 30 cycle 4 was lowered by 5 °C in order not to reach 100 °C. These temperature cycles are represented Fig. 1(b). Mortar type 10 reaches 85 °C in 24 h, mortar type 20M reaches 75 °C in 36 h, and mortar type 30 reaches 95 °C in 18 h. Despite these modifications, these temperature cycles can still be considered as characteristic of what would undergo in the center of the 1-m wall described above. As it was designed, the experiment tests as much for heat of hydration as for inherent DEF susceptibility.

2.3. Specimens curing and conservation

Mortars were cast under the form of 35 × 35 × 200-mm bars in steel molds. For each mortar, half of the samples were thus readily steam-cured according to their hydration cycle (see Fig. 1(b)). The remaining specimens were left at room temperature (20 °C), 100% RH (samples left above a surface

Table 3
Calorimetric characteristics of the mortars used in this study

Cement	Type 10	Type 20M	Type 30
Total heat of hydration (kJ/kg)	331	302	380
Thermal conductivity (kJ/m h °C)	8.1	8.1	8.1
Specific heat (kJ/kg °C)	1.2	1.2	1.2

Total heat of hydration was measured and specific heat and thermal conductivity were estimated.

of water in sealed tanks) for reference samples. After steam curing, all samples were left at room temperature, 100% RH. After 1 year, half of the steam-cured samples and half of the samples cured at room temperature were submitted to a steam curing at 85 °C, for 1 month, to simulate a long period of heating due to the presence of exothermic waste. The rate of temperature rise was about 2 °C/h, slow enough not to generate thermal gradients in the prisms to avoid micro-cracking, and the samples were allowed to cool naturally at 100% RH after steam curing. These samples will be referred to as "01" (samples cured at room temperature and submitted to a late temperature cycle) and "11" (samples steam-cured during hydration and submitted to a second temperature cycle). The samples left at 20 °C will be referred to as "00" (samples left at 20 °C during the whole experiment) and "10" (samples steam-cured during hydration only).

All samples were left for two more years at room temperature, 100% RH. The four different temperature cycles combinations applied to the samples are schematized in Fig. 2.

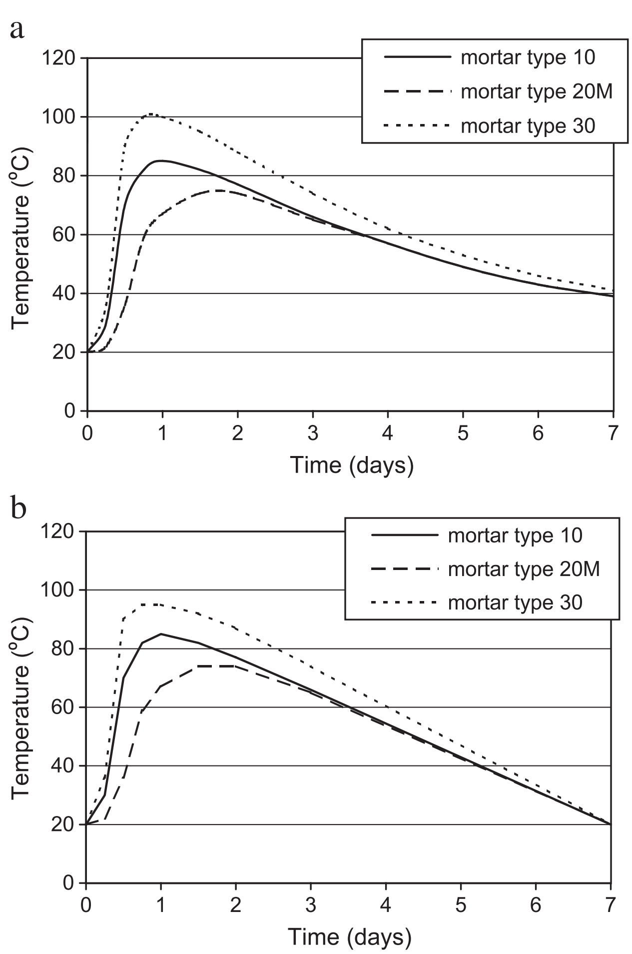

Fig. 1. Comparison of the temperature cycles at the center of a 1-m wall of mortar and the cycles imposed to the mortar prisms. (a) Temperature at the center of the 1-m wall depending on the mortars, simulated from calorimetric measurements. (b) Temperature cycles imposed to the three different mortars during hydration.

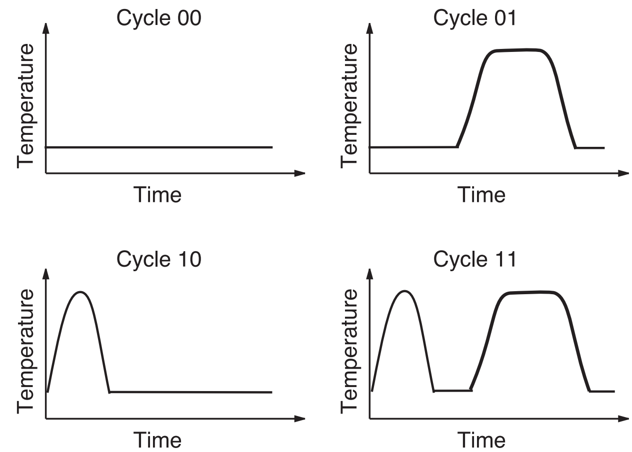

Fig. 2. Different temperature cycles imposed to each mortar. Every mortar undergoes four types of testing conditions: hydration at room temperature (cycles 00 and 01) or steam curing (cycles 10 and 11) for 1 week; second steam curing at 85 °C (cycles 01 and 11; or not: cycles 00 and 10) for 1 month after 1 year of hydration at 100% RH.

2.4. Measurements and analyses

Length changes of the specimens were recorded for 3 years. For each mortar and curing condition, average expansion was computed from four different samples. Scanning electron microscope (SEM) observations were performed on fractured samples.

3. Results

3.1. Effect of a high temperature due to heat of hydration

This part deals with the expansion of the samples submitted or not to the temperature cycle during hydration and that have not undergone a second cycle of temperature (cycles 00 and 10). It thus deals with the possibility of DEF induced by the heat of hydration of the cement itself.

Fig. 3 shows the length changes of the samples of mortar types 30, 10, and 20M which have been steam-cured or not during hydration.

Mortars type 10 and 30 which have been steam-cured during hydration (cycle 10), present high levels of expansion (up to 2.2% for mortar type 30; see Fig. 3(a); and 1.7% for mortar type 10; see Fig. 3(b)) after an induction period of about 100 days. After 3 years, mortar type 20M shows no sign of expansion. None of the mortars that have been hydrated at room temperature (cycle 00) present significant expansion (Fig. 3(a–c)). SEM studies on these mortars revealed no alkali–silicate reaction features, such as siliceous gel. DEF features, such as ettringite deposits around aggregates and in air voids, are detected on the two mortars that have expanded (see Fig. 4). These artifacts are not believed to be the cause of expansion [3,5] but are systematically observed on mortars suffering from DEF. Similar secondary ettringite formation in voids (e.g., by Ostwald ripening) is often observed in mature

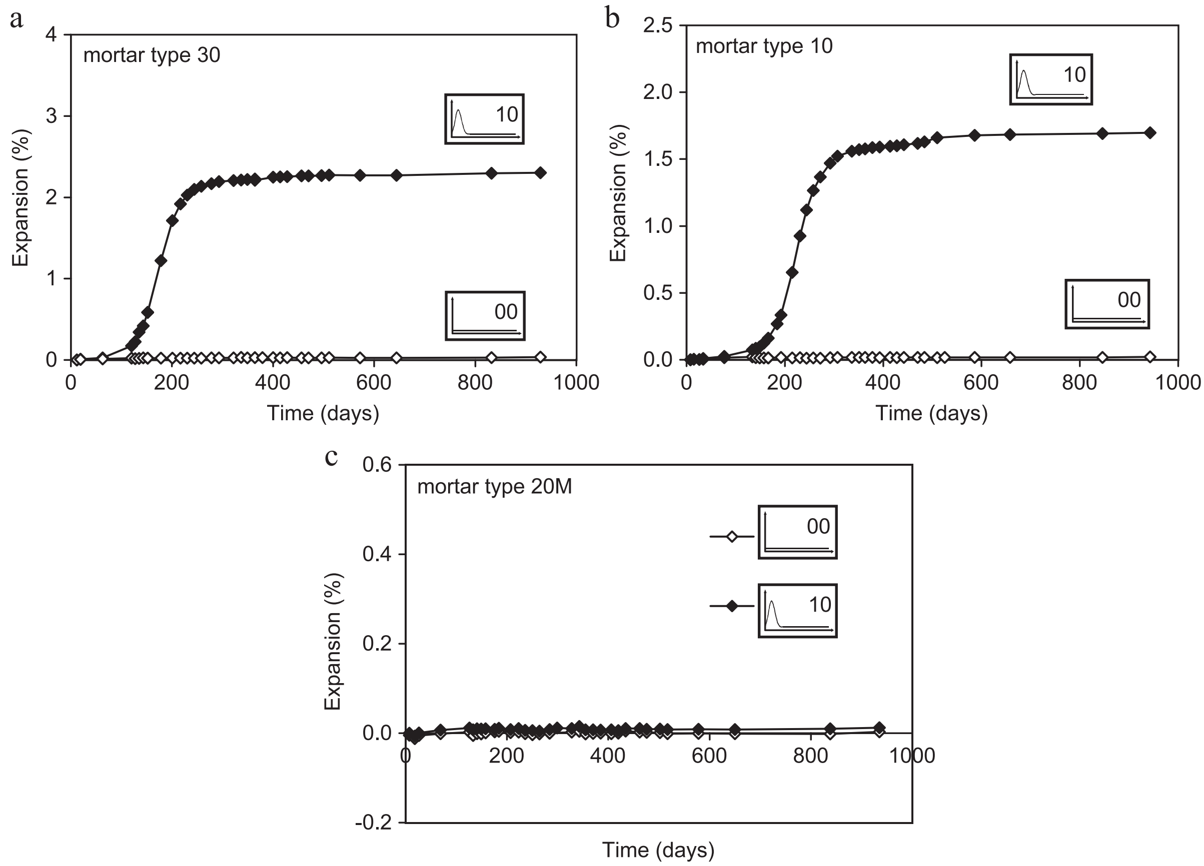

Fig. 3. Expansions of the three different mortars submitted or not to steam curing during hydration (cycles 00 and 10). (a) Expansion of type 30 mortar (cycle 00 and 10). (b) Expansion of type 10 mortar (cycle 00 and 10). (c) Expansion of type 20M mortar (cycles 00 and 10).

concretes, but none of these artifacts could be found in the mortars that did not expand.

These results are in accordance with what is expected for such mortars if they had been steam-cured according to a laboratory precast mortar steam cycle: a higher temperature of cure leads to higher levels of expansion [1,3,14] and mortars made with cements with a high level of sulfate (types 10 and 30, as compared to type 20M) are more liable to expand because of DEF [1,3,15–18].

The absence of expansion of mortar type 20M does not show that this mortar would not expand if it was subjected to a "standard" laboratory steam curing, since the maximum temperature reached by this mortar is about 75 °C, which is close to the threshold temperature 70 °C often considered as the minimum temperature to trigger DEF [5].

The main finding of these first results is that the core of a large concrete member that would undergo conditions similar to those applied to the mortars of the present study may

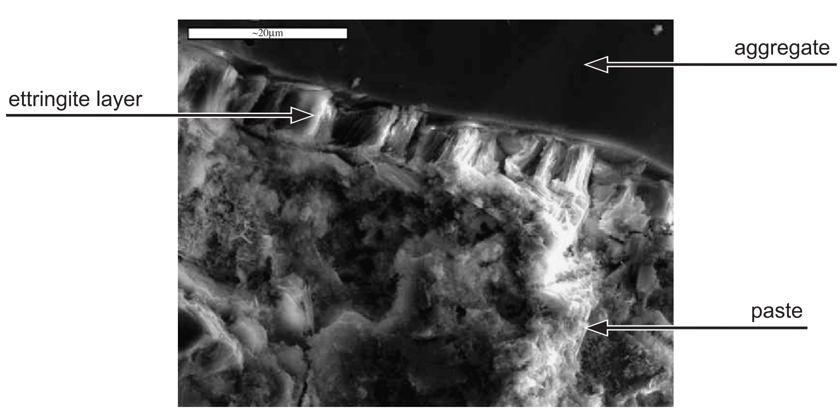

Fig. 4. Ettringite deposits around an aggregate of mortar type 10 steam-cured during hydration. Such deposits are not an evidence for DEF, but are systematically found on mortars suffering from DEF.

expand if the cement is DEF-prone. However, such a thermal profile would hardly be obtained, even in the worst scenario (large concrete section, excess of cement, high external temperature). The results of this study could help in understanding the few field cases reported in the scientific documentation [4,8,9]. The conditions under which the mortar may or may not expand are still to be found, since this work gives no information on the effect of different parameters, which have been studied for more classical steam-curing cycles. These questions are, considering a temperature cycle due to the heat of hydration, the following:

– What would happen if the geometrical configuration would lead to higher/lower temperatures?
– What would happen if the mortar would stay a shorter/longer time at high temperature?
– What would happen if the rates of temperature rise and fall would differ, due to a different geometry of the concrete member?
– Water availability and alkali release have been found to be an important parameter altering the rate of expansion and the final expansion [5,12]. Since high temperatures due to heat of hydration can only be obtained in very large concrete members, are the water availability and the alkali release significant enough to allow DEF or will they delay expansion indefinitely?

3.2. Effect of a long steam-curing cycle on 1-year-old mortars

This section deals with the effect of a temperature cycle (85 °C steam curing for 1 month) on mature mortars that have or have not been steam-cured during hydration (cycles 01 and 11). Fig. 5 shows the length changes of the samples of mortars type 30, 10, and 20M before and after the second temperature cycle.

Mortar type 30 presents very significant expansion after having been steam-cured at 85 °C for 1 month. Whether the mortar had been steam-cured during hydration, the type 30 mortar expands by more than 1% (1.6% for cycle 01, 1.2% for cycle 11). The maximum rates of expansion are similar in both cases and similar to the expansion after the first steam curing. The main difference between the two behaviors is that the expansion of the mortar that had been steam-cured during hydration does not present the 100-day induction time of cycle 01. Whether the origin of this behavior is mechanical (an already cracked paste is more susceptible of undergoing expansion) or microstructural (the presence of C_3S hydrated

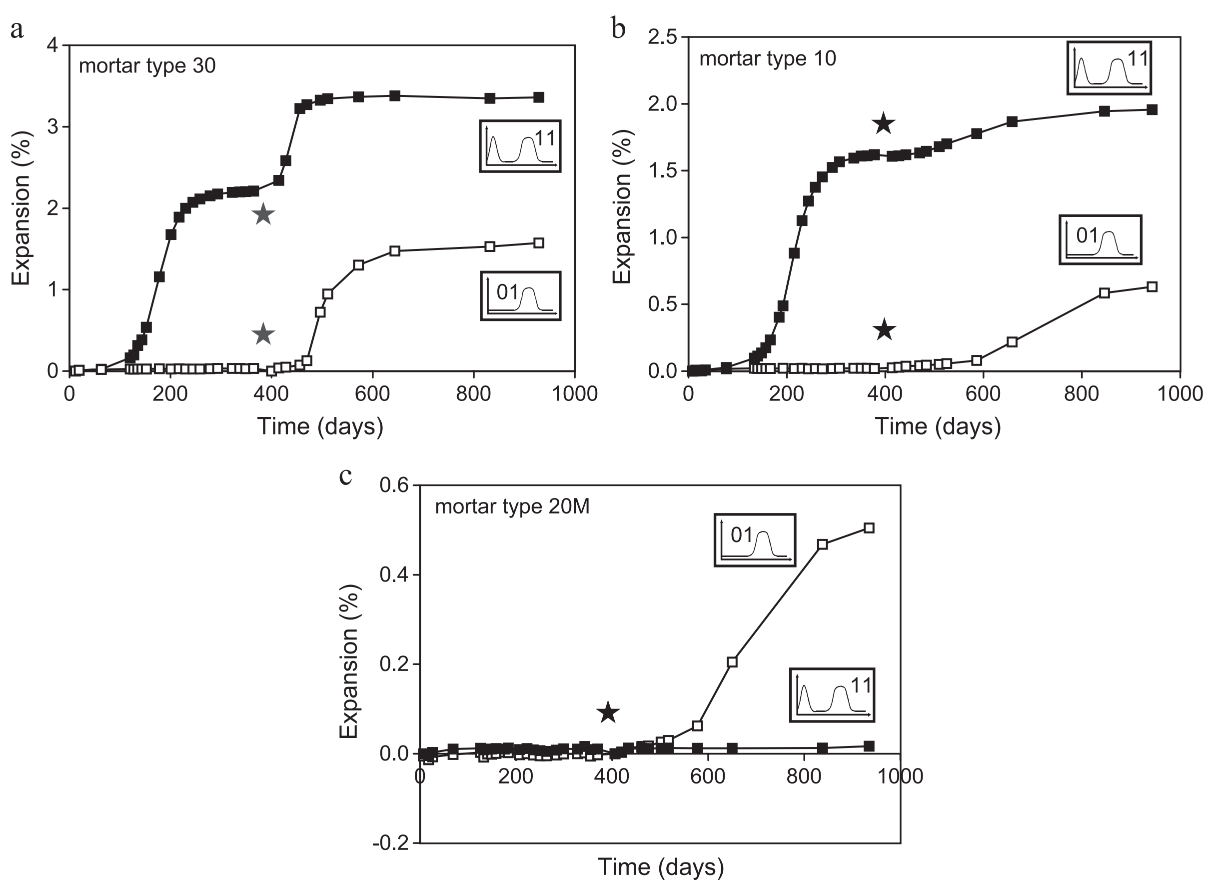

Fig. 5. Expansions of the three different mortars steam-cured 1 year after hydration (cycles 01 and 11, second cycle represented by symbol ★). (a) Expansion of type 30 mortar (cycles 01 and 11). (b) Expansion of type 10 mortar (cycles 01 and 11). (c) Expansion of type 20M mortar (cycles 01 and 11).

at high temperature during hydration could play a predominant role in the expansion mechanism [5]) is not determined.

Mortar type 10 presents similar behaviors, but the expansion rates are slower than when induced by a steam cure during hydration and the incremental expansions are smaller (0.65% cycle 01, 0.35% cycle 11). The induction period after the second steam curing is a bit shorter for the mortar that has been steam-cured during hydration.

The behavior of mortar type 20M is drastically different. It has been seen earlier that this mortar did not expand even if steam-cured up to about 75 °C during hydration (cycles 00 and 10, Fig. 3(c)). As for mortar types 30 and 10, mortar type 20M subjected to a steam curing at 85 °C for 1 month a year after hydration (cycle 01) begins to expand significantly (0.5% at 950 days) after a short induction period of about 100 days. On the contrary, mortar type 20M, which has been steam-cured during hydration, presents no sign of expansion 450 days after the 85 °C steam curing. For unknown reasons, expansion might be delayed, or inhibited, by the steam cure during hydration.

4. Discussion

4.1. Concordance of these results with proposed mechanisms for DEF

The experimental results of this work seem to broaden the conditions needed to initiating DEF symptoms on mortars, since the temperature generated by the heat of cement hydration can trigger DEF. However, it seems that the conditions that must be met by the mortar are the same as for a classical steam-cured mortar:

- None of the samples kept at room temperature expanded. This result is in accordance with the fact that mortars that have not been submitted to temperatures above ≈ 70 °C do not develop DEF.
- The cements that are more DEF-prone (in this work, types 10 and 30 cements) develop DEF more easily than other cements (cement type 20M for the present work) and present higher rates of expansion and higher final expansions.

The results of this study show that DEF can develop after long steam curing on mature mortars. This consideration excludes a few DEF mechanisms that have been proposed before. First, DEF is not only a hydration-related phenomenon, and the high sulfate concentrations in solution during hydration are not required to trigger DEF. High temperature may be sufficient to explain the higher sulfate concentrations of sulfate in solution. Secondly, DEF has been explained by the positive volume change from unhydrated cement aluminum-bearing phases to hydrated ettringite in the cement paste. In 1-year-old mortars, all C_3A is hydrated, so the expansions cannot result from conversion of C_3A to ettringite. These considerations favor, in the case of DEF induced by a late thermal cycle, the hypothesis of the conversion from hydrated sulfoaluminate (probably calcium monosulfoaluminate, stable at high temperature) to ettringite.

4.2. Possible objections to the relevance of these results

These results seem to show that large concrete members, reaching high temperatures because of the heat of hydration of the cement, may suffer DEF with time. However, the laboratory experimental conditions applied in this work differ slightly from what would happen in the bulk of a large concrete volume. The main differences are the result of the small dimension of the mortar samples used in this study:

- The temperature cycles during hydration were shortened as compared to what was given by simulations. Longer curing times might have suppressed expansion, as reported [1,3]. However, long curing at 85 °C (1 month after 1 year of hydration) does produce expansion in at least one testing condition for the three mortars tested.
- Alkali leaching, which controls expansion due to DEF [12], is very fast on small laboratory samples. This leaching of Na^+ and K^+ ions would be much slower on larger concrete members. This might delay, or even inhibit, expansion of large concrete members. Water ingress would also be slower on large sections.
- Apart from alkali leaching, mechanical dimensional effects might affect the way a large structure reacts as compared with a small sample.
- CO_2 has been suspected of being a triggering agent for DEF [19]. During steam curing and conservation, the samples are in contact with CO_2 of the air. This CO_2 can diffuse deeply in the samples because of their small dimensions, and interact with ettringite or simply change the chemical equilibrium of the system. This might happen much slower on large concrete members.

5. Conclusions

The main conclusions of this 3-year study are the following:

- Some mortars, when exposed to a temperature cycle simulating the temperature induced by the heat of cement hydration, can expand after an induction period. Final expansions can reach a few percents after 1 year. From these results, one can imagine that under certain conditions, large concrete members may suffer DEF because of the high temperature reached at the core of the concrete member during hydration. More work is necessary to confirm this conclusion and evaluate the possible impact of the size of the structure on the phenomena—for instance, the effective temperature in the structure during hydration, the water ingress in the structure, or the rate of alkali leaching.

– One-year-old mortars, when subjected to a 1-month steam curing at 85 °C, can expand with similar features as DEF-affected mortars. Mortars that have previously expanded because of DEF expand again. Mortars that have not suffered from DEF or that have been hydrated at room temperature can expand as well. No such result has been reported before and allows to conclude that DEF is not a phenomenon only related to a high temperature during hydration. It also appears that an early mild heat treatment can suppress (or delay significantly) expansion due to heating at later age. The conditions of success of this process are to be determined. More work is needed to determine the exact mechanisms of DEF. The results of the present study should help develop new tests and models for the study of the occurrence and mechanisms of DEF.

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