EXPERIMENTAL STUDY OF THE INFLUENCE OF LATE HEAT TREATMENT ON THE RISK OF EXPANSION ASSOCIATED WITH DELAYED ETTRINGITE FORMATION

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Abstract

A long enough exposure to high enough temperature is a necessary condition to develop Delayed Ettringite Formation (DEF). Thermal conditions leading to DEF development have generally been investigated for concrete at early age. In this paper, the results of experimental laboratory investigations that aim to quantify the effect of a late thermal treatment on DEF characteristics (namely magnitude and kinetics of expansion) are presented. This study has confirmed the risk of a significant expansion associated to DEF for a late heat treatment on concrete. A pessimum effect with the heating duration is highlighted.

Keywords: concrete, DEF, late heat treatment, pessimum effect, expansion mechanism.

1 INTRODUCTION

Delayed Ettringite Formation (DEF) is an endogenous reaction, similar to Alkali Aggregate Reaction (AAR) in terms of structural effects, which can affect concretes heated at a temperature higher than about 65°C [1]. This phenomenon has been detected at early age in precast elements and massive concrete parts. Late heat treatments (which concern e.g. structures exposed to fire, radioactive waste depositories or parts of industrial structures like power plants) correspond to another situation that could induce expansion associated with DEF [2]. It may lead to concrete swelling, cracking of the structure, decrease of the mechanical properties of the affected materials and thus potential problems in terms of serviceability and structural safety of the affected structures.

This paper focuses on studying the effect of late heat treatments characterised by their maximum temperature and duration, on the risk of developing expansion. The experimental laboratory investigations were carried out on concrete specimens, using highly DEF-reactive cement, aiming to quantify the expansion magnitudes and kinetics due to different thermal histories and to identify the existence of an eventual pessimum effect regarding the thermal energy mentioned in the literature [3]. A number of heat treatments at 81 and 86°C were applied 100 days after casting, with duration 1-14 days. This article presents the results of expansion for the different thermal histories applied. The swelling characteristics (magnitude and kinetics) are quantified using a mathematical relation and analyzed as a function of the thermal history.

2 EFFECT OF A LATE HEAT TREATMENT ON DEF

Some studies in the literature have shown that not only a heat treatment at early age can induce expansion associated to DEF. Thus, as mentioned by [2-4], specimens heat-cured after a certain storage duration, or exposed to a second heat treatment can develop a significant expansion.

A late heat treatment leads to destabilization of ettringite present in the microstructure [2-4]. Moreover, Famy et al. (2002) [4] observed in SEM the formation of a lighter inner CSH rim between anhydrous grains and the darker CSH, formed before applying heat. These authors showed that this lighter inner CSH has a great affinity for sulphate and aluminium released from ettringite dissolution. However, only sulphates adsorbed in lighter inner CSH seem to participate in forming delayed ettringite. Aluminium ions are mobilized in CSH to contribute in CASH formation with the assumption that Al^{3+} substitutes to Si^{4+} [4].

From this study, sulphates mobilized in inner CSH, formed after a late heat treatment, constitute a reserve of reactants to form ettringite responsible for the development of expansions. However the aluminates source contributing to the formation of delayed ettringite in this case is still

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unidentified. [2] proposes that ettringite is formed from the AFm, with a dissolution/re-precipitation mechanism.

Authors of [2-4] have been interested mainly in the effect of a late heat treatment in the case of mortar, or the effect of a second heat treatment in the case of concrete. Therefore, in the present experimental study, we have been interested to quantify the effect of a late heat treatment (namely magnitude and kinetics of expansion) on concrete specimens that have not been formerly cured at high temperature at early age.

3 MATERIALS AND METHODS

Free expansion tests were performed on concrete specimens. The binder used is a CEM I 52.5 R CE CP2 NF which is a high early strength cement. It has relatively high sulfate, aluminate and alkali contents (respectively 3.46, 4.30 and 0.83%) which make it highly DEF-prone. However, to ensure optimum conditions for expansion to occur, KOH was added to mixing water up to a Na_2O_{eq} content of 1% of the cement content. The aggregates used are non-reactive regarding AAR [5]. Table 1 summarizes the concrete mix used in this study (with W/C=0.46).

Prismatic specimens 11×11×22 cm were cured at ambient temperature for 100 days under aluminium sealing. Heat was applied to specimen immersed in water in a device described in [6], comprising four phases: a pre-treatment phase at 20°C during 100 days, followed by a heating phase at a rate of 5°C/h until a constant temperature plateau, and a subsequent cooling phase at a rate of -5°C/h. Plateau conditions varied from 81-86°C with durations ranging from 1 to 14 days. Treatment conditions are summarized in Table 2.

A realistic heat treatment (called V_79) corresponding to the case of thermal history, to which massive elements were submitted at early age was also applied to compare the expansion of this case with those obtained after simplified trapezoid shaped heat treatments Figure 1. It is intended to constitute a validation case.

After heat treatment, the specimens were stored under aluminium sealing in a climatic chamber at 38°C for 12 hours in order to start monitoring of swelling in a stable thermal state (no thermal expansion is thus measured afterwards). All specimens were stored in water containers, different for each case of thermal treatment applied, at constant temperature of 38°C to speed up the kinetics of DEF. Three identical samples were prepared to gather statistically representative data (average value of expansion and standard deviation). The swelling was monitored by digital device illustrated in Figure 2. In this paper, each sample is referred as TT_HD, where TT and HD are respectively the temperature (°C) and heating duration (days) of the plateau of the applied heat treatment.

4 RESULTS

4.1 Mathematical representation of the expansion curve

The expansion of the specimens can be quantified using a mathematical relation [Equation (1)], where ε_∞ is the final magnitude of expansion, τ_L and τ_C are respectively the latency and the characteristic times, and α and β are two parameters to take into account an exponential evolution of the late phase of swelling. The relation in [7] represents an alternative for Brunetaud's [3], with better empirical agreement of the late phase. A parameter (ε_{hyd}) has also been added to take into account an instantaneous hygric expansion during the first days of monitoring.

$$\begin{cases} \varepsilon(t) = \varepsilon_\infty . \dfrac{1 - e^{\left(\frac{-t}{\tau_C}\right)}}{1 + e^{\left(-\frac{t-\tau_L}{\tau_C}\right)}} . \left(1 - \beta . e^{\left(\frac{-t}{\alpha}\right)}\right) + \varepsilon_{hyd} \\ with : \alpha > 0 \; and \; 0 \leq \beta \leq 1 \end{cases} \quad (1)$$

Figure 3 presents the results of swelling monitoring for the different studied cases. Each curve corresponds to the average expansion of 3 prismatic specimens, and the error bars correspond to plus or minus the standard deviation. The parameters fitted on the experimental results are given in Table 3. It turns out that all specimens considered developed significant DEF-induced expansions, with rather low scatter and most of the potential expansion reached after 6 months.

4.2 Risk of DEF for concrete

The results of this experimental study (Figure 3) confirm the risk of a significant expansion associated with DEF in the case of a mature concrete submitted to a high temperature exposure after certain storage duration (100 days in this study).

4.3 Effect of heating duration

From Figure 3 presenting the expansions of specimens heated, after 100 days, at 81°C during 1, 3, 7 and 14 days, the latency time doesn't seem to be affected by the heat duration.

A pessimum effect is highlighted, for a late heat treatment, in relation with heating duration (Figure 4): the magnitude of expansions in the case of heat treatment at 81°C for 14 days is lower than the same parameter for the 81°C_7 days case.

5 DISCUSSION

5.1 Thermal energy

To study the influence of thermal history at different temperatures, expansion parameters (ε_∞, τ_L and τ_C) were compared to the supplied thermal energy during the various thermal treatments. At first, the total thermal energy (TTE) was considered, corresponding to the integral of the temperature curve as a function of time over T=20°C, which corresponds to the assumption that all thermal energy applied is responsible for the development of DEF. Then, an effective thermal energy (ETE) was considered, taking 65°C as a threshold temperature in the integral calculation [Equation (2)]. In this case it is assumed that only the thermal energy supplied beyond the threshold temperature 65°C is responsible for DEF expansions [1]. This may represent a simplified index with respect to original Baghdadi's [8] and Martin's [9] models.

$$Effective\ thermal\ energy = \begin{cases} \int (T(t) - 65)\, dt & if\ T(t) > 65°C \\ 0 & else \end{cases} \qquad (2)$$

5.2 Final expansion

Figure 5 presents the final expansion as a function of effective thermal energy ETE (temperature threshold of 65°C) assumed to be responsible for the destabilization of ettringite. There seems to be a relationship (master curve) linking the effective thermal energy to the final expansion as demonstrated in the case of early age heating [7]. Thus, the final expansion increases with ETE to a certain value of about 3 000°C.h beyond which the final expansion decreases.

It can be derived from the observations in the literature (section 2), that late heat treatment would have the effect of destabilizing the ettringite which has been formed during the storage phase before late heat treatment, and to form a lighter inner CSH having an ability to take up sulphate and aluminium. This layer of dense lighter inner CSH would be thicker when ETE applied gets higher, thus the sorption capacity of aluminium and sulphate gets higher with the increase of ETE. Therefore, the quantities of aluminium and sulphates adsorbed in lighter inner CSH increase with ETE. Thereafter, final expansion increase with the ETE.

The pessimum effect observed beyond about 3 000°C.h could be explained by a reduction of available aluminium because of a significant substitution potential of Si^{4+} by Al^{3+}[10], thus leading to the decrease of the amount of ettringite formed. However, the location of expansive ettringite in the case of late heat treatment is still unidentified.

5.3 Latency and characteristic times

The latency time of expansions has also been plotted as a function of the effective thermal energy (Figure 6). This figure shows that there is not a significant variation of latency time (which keeps in the order of 50 days) compared to the thermal history. The specimens cured at V_79 have a latency time relatively shorter than in the case of heat treatment at 81°C for 1, 3, 7 and 14 days. This could be attributed to the difference in cooling rate during heat treatment. In fact, heat treatment at 81°C and 86°C have the same cooling rate of -5°C/h, so the duration of the cooling phase until 20°C is, respectively, 12 hours and 13 hours. Conversely, duration of the cooling phase, in the case of heat treatment V_79 from 65°C to 20°C, is about 13 days. Therefore, it is possible to consider that this cooling phase in the case of V_79 is a part of the latency time, assuming that below the temperature threshold (65°C), ettringite can be formed. This may explain the relatively short latency time in the case V_79 as compared to the case of heat treatments at 81°C and 86°C.

Figure 7 illustrates the characteristic time as a function of ETE. As for the latency time, there is no significant variation (about 11 days (from 8 to 12) for most cases).

5.4 Comparison with the case of early age heat treatment

Figure 8 presents the comparison between the effect of early age and late heat treatment on the final expansion. Detailed results of the early-age heat treatment cases is described in [11]. It shows that the pessimum effect in the case of a late heat treatment occurs at a higher ETE (~3 000°C.h) compared to a heat treatment at early age (~2 000°C.h). The pessimum effect offset observed between the two cases could be explained by the light CSH content which has ability to take up sulphates and aluminium. This could influence the ETE which corresponds to a Al/S ratio of 2/3. Indeed, in the case of early age heat treatment, this value is about 2 000°C.h. For mature concrete, to mobilize the same Al/S ratio, it would be necessary to form denser CSH from anhydrous grains, which is equivalent to increase ETE (over 2 000°C.h). This could explain the offset pessimum.

For kinetics parameters, Figure 9 illustrates the comparison between latency time developed after early age and late heat treatment. For all studied cases, for the same thermal history, the specimens have developed expansions after a late heat treatment faster than at early age. Indeed, after heat treatment at early age, τ_L seems to converge to the one developed after late heat treatment. The characteristic time has also been compared after an early age and a late heat treatment [Figure 10]. The main difference between these two cases occurs for ETE below about 1 000°C.h. Therefore, τ_L and τ_C for a late heat treatment are shorter than for the case of heat treatment at early age.

6 CONCLUSIONS

In this experimental study, the risk of expansion associated with DEF in concrete has been confirmed for a concrete exposed to different thermal histories, after 100 days of maturation.

The final expansion depends on the temperature and the heating duration, as for the heat treatment at early age [7]. Moreover, a pessimum effect with the heating duration has been highlighted: for the same treatment temperature, there is a heating duration beyond which the magnitude of expansion decreases significantly. The final expansion increases with ETE until about 3000°C.h, above which expansions decrease. This result could be attributed to substitution of Si^{4+} by Al^{3+} in lighter inner CSH, leading to the decrease of the quantity of ettringite that can precipitate since less reactant is available.

Furthermore, kinetics parameters (latency and characteristic time) do not exhibit a significant variation, and are shorter than in the case of heat treatment at early age [7]. More research is needed to better analyse this effect.

Finally, chemical analyses and SEM observations are necessary to explain the mechanisms of expansion (mainly the location of expansive ettringite) and the pessimum effect highlighted.

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TABLE 1: Concrete mix (kg/m3) (NR = Non Reactive).

Cement	Water	Sand NR 0/2	NR siliceous coarse aggregate 4/8	NR siliceous coarse aggregate 8/12	KOH
410	188	854	100	829	1.745

TABLE 2: Heat treatments applied (plateau characteristics).

Mean temperature (°C)	Standard deviation of temperature during the plateau (°C)	Heating duration (days)				
81.3°C	0.1	1 day	3 days	-	7 days	14 days
86.1°C	0.1	-	-	5 days	-	-

TABLE 3: Expansion parameters (ETE: effective thermal energy).

	ε_∞ (%)	τ_L (Days)	τ_C (Days)	α (Days)	β	ε_{Hyd} (%)	Quadratic error	ETE (°C.h)
81°C_1 day	0,74	47	12	43	1	0,005	1,98E-06	454
81°C_3 days	0,79	39	10	41	1	0,001	1,45E-06	1231
81°C_7 days	1,40	52	11	104	0,13	0,012	5,46E-06	2001
81°C_14 days	0,61	47	11	66	0,63	0,012	2,64E-06	5518
86°C_5 days	1,14	47	10	43	0,75	0,001	1,99E-06	2640
V_79	0,92	36	8	42	0,48	0,006	3,11E-06	1435

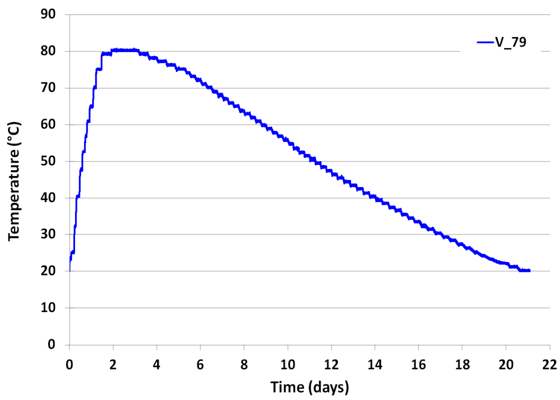

FIGURE 1: Heat treatment for the validation test: realistic thermal history used for the validation test.

(a) (b)

FIGURE 2: Measurement device:
(a): Leveling of instrument and specimens;
(b): Expansion monitoring of specimens 110×110×220mm.

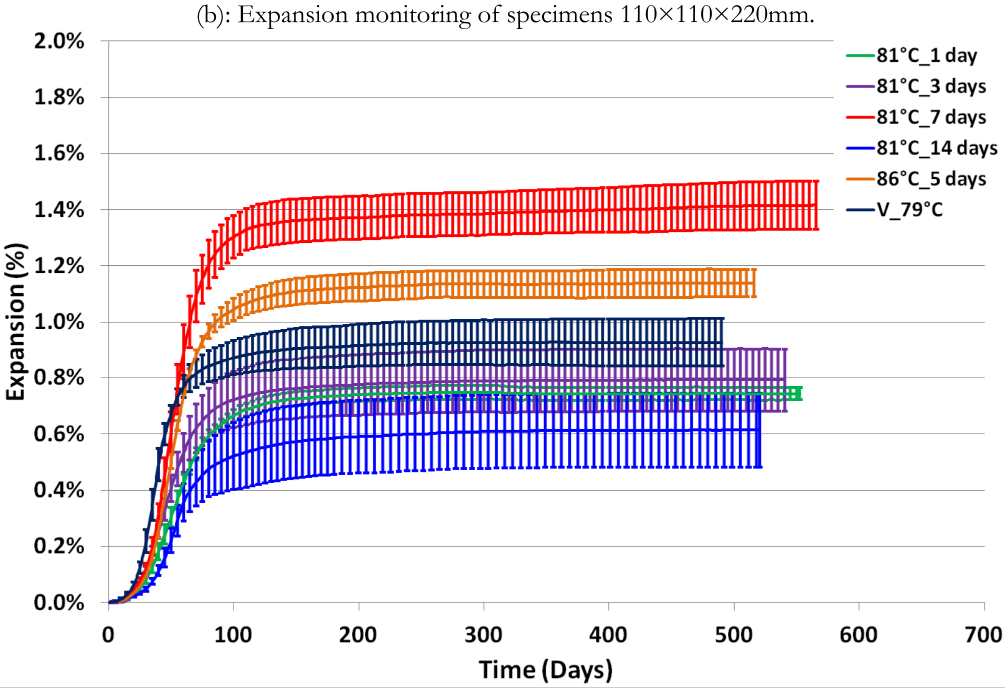

FIGURE 3: Expansion of specimens heated at 81°C during 1, 3, 7 and 14 days; heated at 86°C during 5 days; and submitted to V_79 thermal treatment.

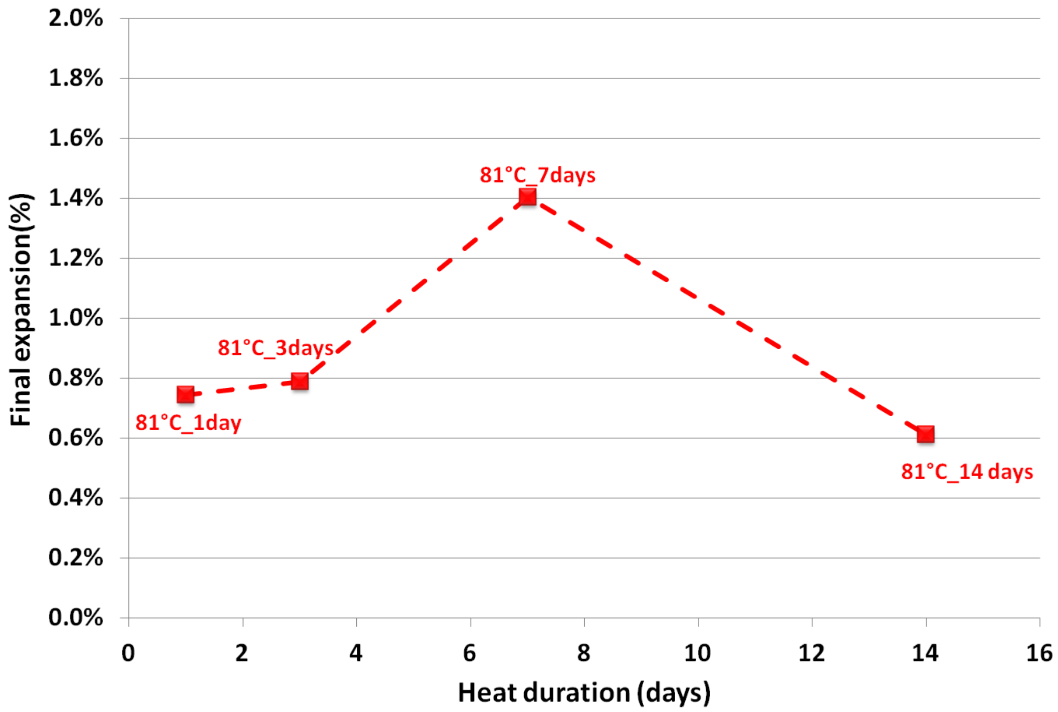

FIGURE 4: Effect of the duration of the heat treatment plateau on magnitude of expansion (for temperature plateau of 81°C).

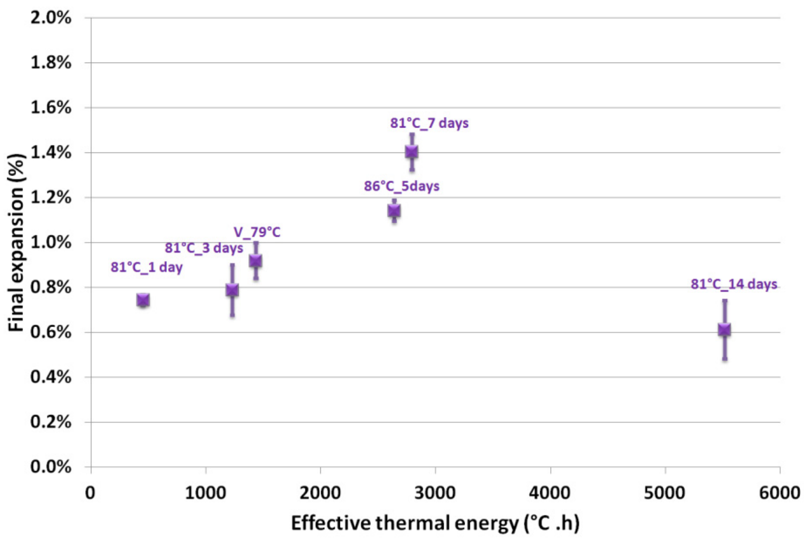

FIGURE 5: Effect of effective thermal energy on magnitude of expansion.

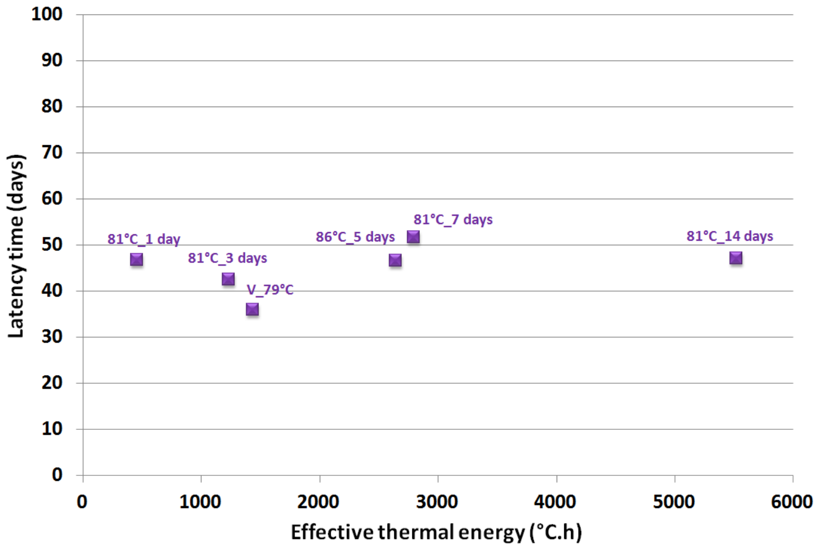

FIGURE 6: Effect of effective thermal energy on latency time.

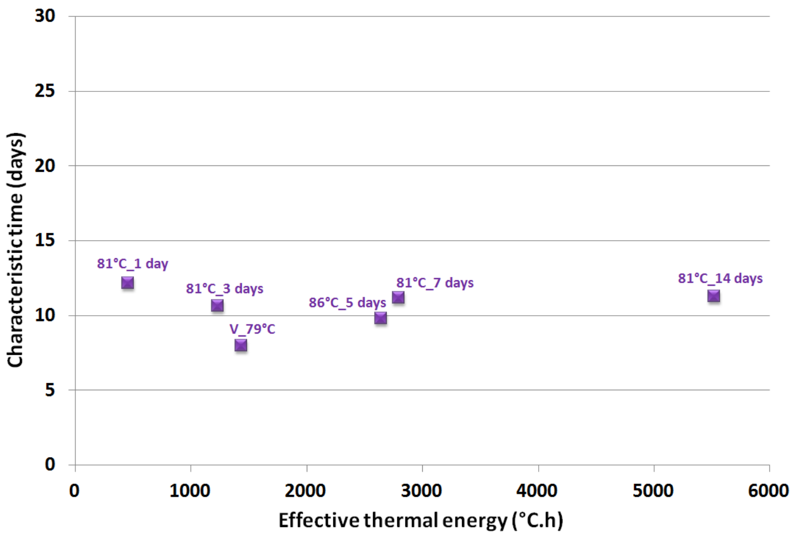

FIGURE 7: Effect of effective thermal energy on characteristic time.

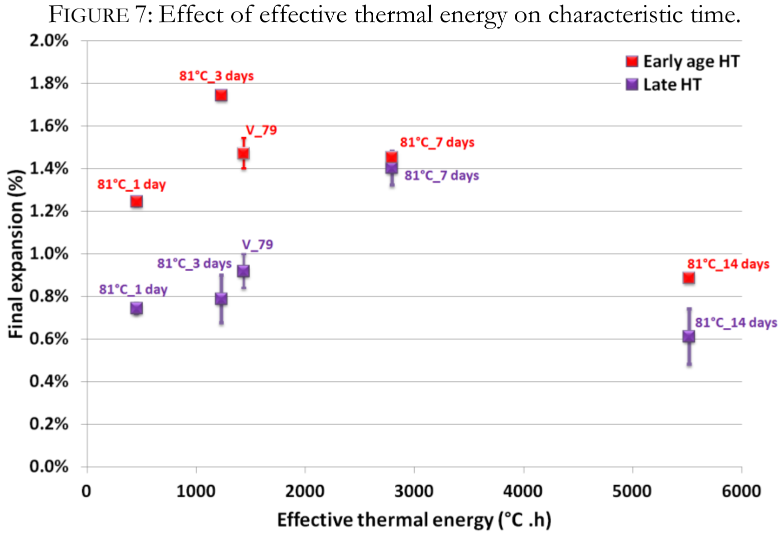

FIGURE 8: Comparison of final expansion, as a function of ETE, for early age and late heat treatment.

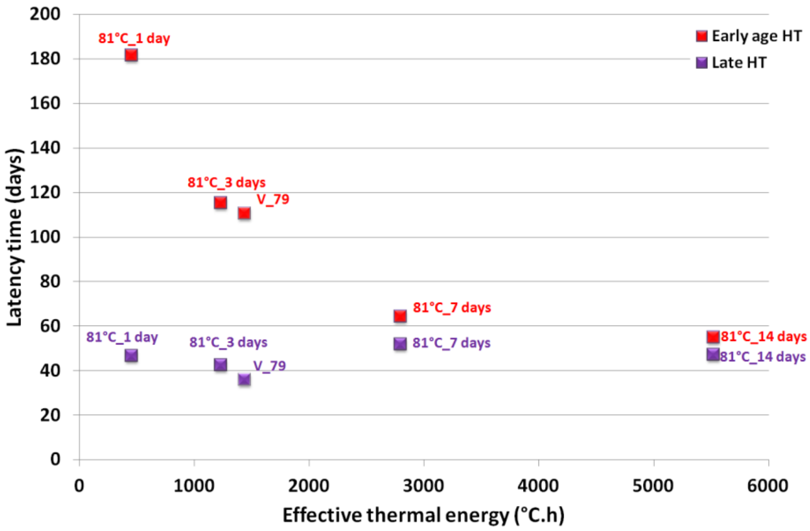

FIGURE 9: Comparison of Latency time, as a function of ETE, for early age and late heat treatment.

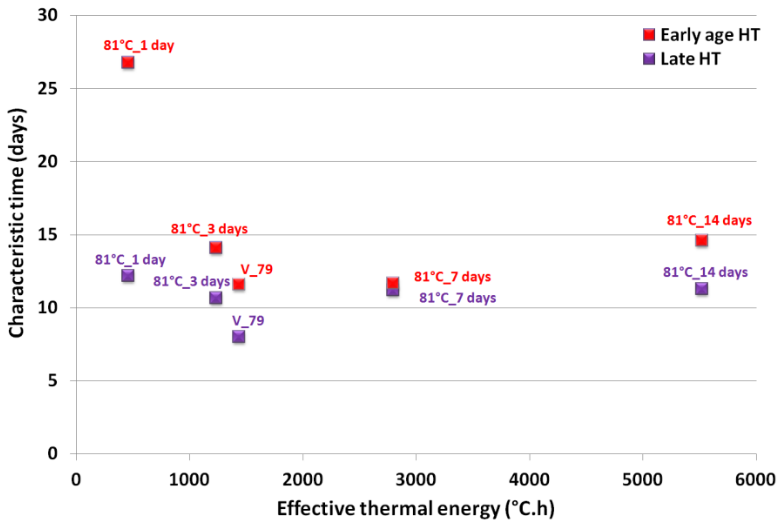

FIGURE 10: Comparison of characteristic time, as a function of ETE, for early age and late heat treatment.