EFFECT OF TEMPERATURE AND CURING DURATION OF EARLY HEAT TREATMENTS ON THE RISK OF EXPANSION ASSOCIATED WITH DELAYED ETTRINGITE FORMATION

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Abstract

Delayed Ettringite formation (DEF) is an autogenous expansive reaction that can affect concrete. Exposure to high temperature is a necessary condition to develop DEF. The results of experimental laboratory investigations that aim to quantify the effect of thermal history on DEF characteristics (namely magnitude and kinetics of expansion) are presented. A temperature threshold for the concrete at early age, a pessimum effect with respect to the heating duration and a relation between effective thermal energy and swelling parameters (kinetics and magnitude) are highlighted.

Keywords: Concrete, expansion mechanism, DEF, Early age, Pessimum effect

1 INTRODUCTION

Delayed Ettringite Formation (DEF) is an internal swelling reaction that can affect concrete. Indeed, when the material has experienced high temperatures (typically above 65°C [1]) especially at early age (e.g. during precasting processes or in massive cast-in-place structures [2]), the ettringite turns unstable while the concrete is still plastic, and is dissolved. It forms again later after cooling in the hardened material and generates crystallization pressure leading to expansion of the material. This expansive process leads to macroscopic effects mainly consisting in material swelling, cracking and decrease of the mechanical properties which may cause large structural disorders due to unexpected deformations and additional stresses in concrete and reinforcement [3].

The objective of this study is to quantitatively predict the relation between thermal history and swelling characteristics (magnitude and kinetics) in order to adjust recommendations for prevention of DEF [4], since a critical and relatively easy-to-handle condition for avoiding the development of this reaction consists in limiting the temperature increase at early age.

The investigations carried out were focused on the effect of temperature and curing duration of early age heat treatments on the risk of developing DEF expansion [5]. The experiments were performed on concrete specimens, using a sulfate, aluminate and alkali-rich cement, submitted to different thermal histories. A number of heat treatments at 61, 66, 71 and 81°C were applied for durations ranging from 1 to 28 days. Monitoring of the specimens dimensions was performed with the final objective to identify a temperature threshold and confirm a pessimum effect with respect to the thermal curing duration [6].

This article presents the results of expansion tests obtained for different thermal histories applied at early age aiming at reproducing various curing conditions representative of massive structures. The swelling characteristics (magnitude and kinetics) are then quantified using a mathematical relation, and compared to thermal histories to determine the coupling between thermal history, swelling and kinetic parameters of the studied concrete mix. Finally, the swelling magnitude and kinetic parameters are discussed as functions of the thermal energy.

2 EFFECT OF TEMPERATURE ON DEF

According to several authors, a temperature above a threshold of about 65°C [1] is the necessary condition to develop DEF in a cementitious material. This increase of temperature could be due to the exothermic properties of cement hydration in the case of massive parts, where the temperature may exceed 70°C, leading to ettringite destabilization [1,7].

According to [8], maximum temperature influences expansion parameters (kinetics and magnitude). Thus, high temperature leads to faster kinetics and higher magnitudes of expansion. Namely, according to [7], temperature influences the stability of ettringite.

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As for the maximum temperature, heating duration has been identified as an important parameter for the development of DEF. [6] and [8] have shown that expansion increases with the heating duration for the same heating temperature. However, [6] demonstrated the existence of a pessimum effect: for a given heat treatment temperature and above a certain duration, the magnitude of expansion decreases. Subsequently the coupling between temperature and heating duration had to be considered in the definition of our experimental program.

In [9] and [10], swelling due to DEF was investigated with first exploration of the coupling effect of temperature and heating duration. These authors suggested a relationship based on experimental results using temperatures ranging from 71°C to 86°C and heating durations from 1 to 5 days. This relationship enabled to predict the swelling in the massive parts [11] by knowing their thermal history. The predictions of these coupling laws have to be compared with extended experimental results of this study to define their domain of validity.

3 MATERIALS AND METHODS

Table 1 presents the concrete mix studied (W/C=0.46). The cement used is a CEM I 52.5 R CE CP2 NF which has high aluminate, sulphate and alkali contents (respectively 3.46wt%, 4.30wt% and 0.83wt%) highly DEF-prone. The aggregates used are non-reactive regarding AAR (Alkali-Aggregate Reaction) [13].

After casting, prismatic specimens (110×110×220mm) were heated at different maximal temperatures (71°C and 81°C) during temperature plateaus of various duration (1 to 28 days) to check the validity domain of the coupling laws proposed by [9] and [10]. Heat treatments at 61°C and 66°C during 14 days have also been applied as possibly representative of mass concrete structures (like dams) subjected to lower but prolonged heating, and to determine the temperature threshold of DEF. Table 2 presents the heat treatments applied. The heat treatments were divided into four phases: a pre-treatment phase during 2 hours at 20°C, a heating phase at a rate of 5°C/h, a constant temperature plateau and a cooling phase at a rate of -5°C/h until 20°C. The device described in [12] used for the curing of the specimens consists of a water tank with temperature control according to the heating/cooling profile described in this paragraph.

Figure 1-a illustrates a heat treatment (called V_79), which has been inspired from thermal history at early age of a massive element. It has been applied as a realistic case to validate coupling laws of prediction. Figure 1-b shows the heat treatment applied in Martin's study [13], using the same material as the present study. The result of [13] has been used as a second validation case.

After heat treatment, the specimens were stored in a climatic chamber at 38°C under aluminium sealing for 12 hours in order to start monitoring of swelling in a stable thermal state (no thermal expansion is thus measured). After this phase, all specimens were stored in water at a 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: specimens are placed in a stainless steel structure allowing them to expand freely; continuous monitoring of expansion is made with digital displacement sensors. 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 axial strain response of the specimens can be quantified using a mathematical relation. In this work, Equation (1) proposed by [5] was used, 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. This relation is an alternative to Brunetaud's one [6] with better empirical agreement of the late phase. A parameter (ε_{hyd}) had been added to take into account an instantaneous hydric expansion during the first days of monitoring.

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

Figures 3 to 6 present the results of swelling as recorded 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, which turns out rather low. The parameters fitted on the experimental results are given in Table 3.

4.2 Temperature threshold

Figure 3 shows expansion of the specimens heated at 61°C during 14 days. After 550 days, the expansion is about 0.015% ℓ/ℓ, and unchanged from the first days of storage. It seems that, for this concrete, the threshold temperature of DEF is above 61°C. This has been confirmed with the case of thermal treatment with a temperature plateau equal to 66°C and duration of 14 days (Figure 3), which has developed an expansion higher than 0.16% after 200 days. Thus, the temperature threshold of DEF, for this concrete, is between 61°C and 66°C.

4.3 Effect of temperature plateau

Figure 4 shows expansions of specimens heated to 61, 66, 71 and 81°C during 14 days. For the same heating treatment duration, the expansions have a latency time shorter when the temperature plateau is higher.

A pessimum effect regarding the magnitude of expansion has been highlighted. For this 14 days temperature plateau duration, it lies between 71°C and 81°C.

4.4 Effect of heat treatment duration

Figures 5 and 6 present, respectively, the expansions of specimens heated at 71°C during 2, 7, 12, 14 and 28 days, and those treated at 81°C during 1, 3, 5, 7 and 14 days. Parameters of equation 1 fitted on the experimental results are given in Table 3.

From these results, the expansions have a latency time shorter when the duration of the heating, at a given maximum temperature, is longer. This coincides with results in the published literature [8].

A pessimum effect has been confirmed in relation with the heating duration (Figure 7). It is corresponding to the decrease of final expansion, for the case of heat treatment at 71°C for 28 days and heat treatment at 81°C for 5, 7 and 14 days, compared to the maximum obtained for each treatment temperature (i.e. 71°C_14 days and 81°C_3 days respectively).

5 DISCUSSION

5.1 Thermal energy

The studies of [9] and [10] have shown the need to take into account the temperature and heat duration as a couple to predict DEF expansions. Thus, expansion parameters (ε_∞, τ_L and τ_C), obtained in this study, were confronted to the supplied thermal energy during the different heat treatments applied. Firstly, it was assumed that total thermal energy (TTE), i.e. the integral of the temperature curve as a function of time above T = 20°C, is responsible of the development of DEF. Secondly, an effective thermal energy (ETE) was considered, with 65°C as a threshold temperature [Equation (2)]. ETE thus appears as a simplified quantitative index as compared to the integral value proposed by [9] and [10], with similar physical assumptions. In the second case, it is thus assumed that only the thermal energy supplied beyond the threshold temperature 65°C is responsible for DEF expansions. This assumption was chosen due to the result of section 4.2 (temperature threshold identified between 61°C and 66°C), and based on the information available in the literature [1].

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

5.2 Final expansion

The confrontation of the final expansion and the total thermal energy TTE shows that there is no satisfactory relationship between TTE and ε_∞ [5]. On the contrary, Figure 8 presents the final expansions as a function of the effective thermal energy ETE assumed to be responsible for the destabilization of ettringite at early age: there seems to be a master curve linking the effective thermal energy to the final expansion. Thus, the final expansion increases with the ETE applied, up to a certain value of about 2000°C.h beyond which expansions decrease. This could be due to the definitive aluminium substitution of silica in C-S-H gel (corresponding to the so-called CASH) eventually leading to the decrease of the quantity of ettringite precipitating and thus reducing the final expansion [14]:

- **below pessimum 0<ETE<~2000°C.h:** In this area, the amount of SO_4^{2-} adsorbed at the surface of CSH, and the formation of CASH increase with ETE [14]. In this range, increase of ETE induces a decrease of the Al/S fraction down to the stoichiometric 2/3 value. Thus, the amount of ettringite that can be formed at long-term increases, which corresponds to a decrease of the amount of monosulphoaluminates.
- **pessimum ETE~2000°C.h:** The maximum amount of delayed ettringite formed corresponds to ettringite stoichiometric availability of aluminate and sulphate (Al/S = 2/3). In this case, the definitive aluminium substitution of silica in C-S-H gel leads to form only ettringite.
- **above pessimum ETE>~2000°C.h:** The final expansion decreases with ETE. This may be related to the limitation of available aluminates. During the heating phase, aluminates may have been stabilized in other species like CASH [14].

5.3 Latency time

The latency time of expansions has also been plotted as a function of the effective thermal energy. Figure 9 tends to prove existence of a master curve which links latency time to this effective thermal energy.

The development of DEF is faster when the effective energy supplied to destabilize ettringite increases. The ettringite formation depends on sulphate (SO_4^{2-}) and aluminate ($Al[OH]_4^-$) contents bound in CSH gel. These contents available to form ettringite depend on thermal history applied at early age. Thus, the amount of ettringite destabilized during heat treatment increases with ETE. This induces increase of sulphate and aluminium concentrations (due to the destabilization of the ettringite) in the pore solution. Therefore, the amount of sulphate and aluminium adsorbed in CSH gel increases with the concentration of both species [15, 16].

5.4 Characteristic time

Figure 10 illustrates the characteristic time of expansions as a function of the effective thermal energy. This figure shows the existence of a master curve which links characteristic time to this effective thermal energy. In fact, τ_c hardly varies beyond ETE~1000°C.h. This could be related to reactants limit contributing to the ettringite formation and/or to damage of the materials. Moreover, there is a no significant decrease of τ_c between 1500 and 4000 °C.h, and the possible parameter increase beyond ETE~4000°C.h is documented with only one case.

6 CONCLUSIONS

In this experimental study, the objective was to describe the effect of the thermal history at early age, for a concrete specimen, on the expansions due to DEF.

As mentioned in the literature, the swelling parameters have been confirmed to depend both on the temperature and the duration of heating.

A pessimum effect concerning final expansion regarding the heating duration has been confirmed: Above a given threshold of thermal energy, magnitude of expansion decreases.

The absence of expansion after about 550 days for the case 61°C_14 days, and the expansion higher than 0.16% after 200 days for the case 66°C_14 days, suggest that the threshold temperature of DEF, for the concrete mix investigated in this paper, lies between 61°C and 66°C.

The swelling parameters of the different expansion curves have been successfully linked to effective thermal energy (accounting for a temperature threshold of 65°C).

It has been established that magnitude and kinetics of expansion are linked to the ETE. Thus, the final expansion increases with ETE until about 2000°C.h, above which expansions decrease, thus describing the so-called pessimum effect. Latency and characteristic times decrease with ETE.

Chemical analyses and SEM observations are planned to confirm the assumptions associated with the chemical explanation of the pessimum effect. To validate the master curves concept highlighted, the confrontations of their predictions with results obtained on other concrete mixes are also scheduled. It is also planned to elaborate relationships between alpha and beta (see expansion model in section 4.1) as functions of the heat treatment applied, to more precisely describe an exponential evolution of the late phase of swelling.

7 Acknowledgments

This research programme falls within the framework of a partnership between IFSTTAR and EDF (Electricité de France). Therefore, the authors would like to thank A. Jeanpierre, E. Bourdarot and E. Grimal (EDF) for their participation in this work and for financial support.

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TABLE 1: Concrete mix (Kg/m^3) (NR = Non Reactive).

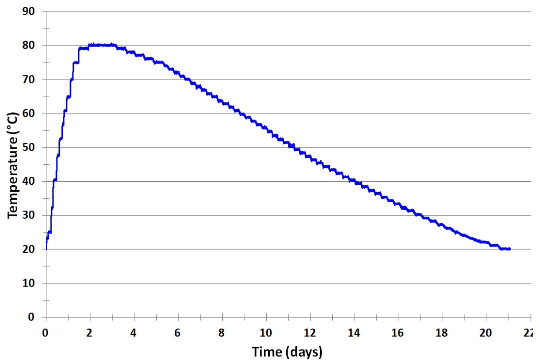
Cement	Water	Sand NR 0/2	Coarse aggregate NR 4/8	Coarse aggregate NR 8/12	KOH
410	188	854	100	829	1.745

TABLE 2: Heat treatments applied (plateau characteristics).

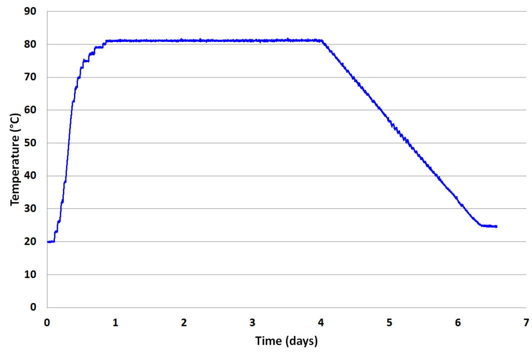
Mean temperature (°C)	Standard deviation of temperature (°C)	Heating duration (days)				
81.3°C	0.1	1	3	5	7	14
71.1°C	0.1	2	7	14	12	28
66.0°C	0.1	14	-	-	-	-
61.0°C	0.1	14	-	-	-	-

TABLE 3: Expansion parameters.

	ε_∞ (%)	τ_L (Days)	τ_C (Days)	α (Days)	β	ε_{Hyd} (%)	Quadratic error	ETE (°C.h)
71°C_2 days	0,49	181	39	200	0,52	0,010	6,36E-07	334
71°C_7 days	1,33	120	14	105	0,31	0,012	3,67E-06	1074
71°C_12 days	1,48	101	12	96	0,22	0,011	5,16E-06	1609
71°C_14 days	1,51	84	9	54	0,79	0,012	5,51E-06	2064
71°C_28 days	1,22	53	6	43	0,52	0,012	5,97E-06	4096
81°C_1 day	1,25	182	27	100	0,77	0,005	5,86E-06	454
81°C_3 days	1,74	115	14	61	0,92	0,012	5,70E-06	1231
81°C_5 days	1,66	95	13	62	1,00	0,012	5,96E-06	2001
81°C_7 days	1,45	64	12	62	0,71	0,010	3,09E-06	2794
81°C_14 days	0,89	55	15	98	1,00	0,001	1,66E-06	5518
V_79	1,47	111	12	29	0,58	0,003	1,09E-05	1435

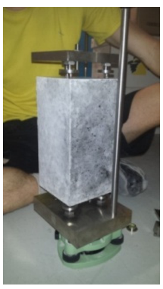


(a)

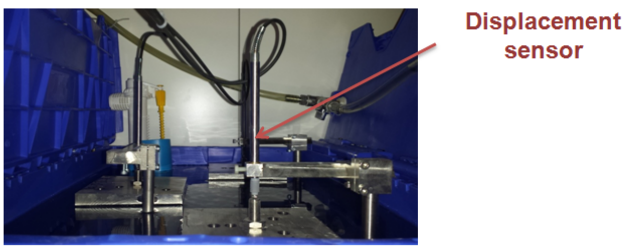


(b)

FIGURE 1: Heat treatments for the validation test:
(a): Realistic thermal history used for the validation test;
(b): Temperature profile applied in [13].



(a)



(b)

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

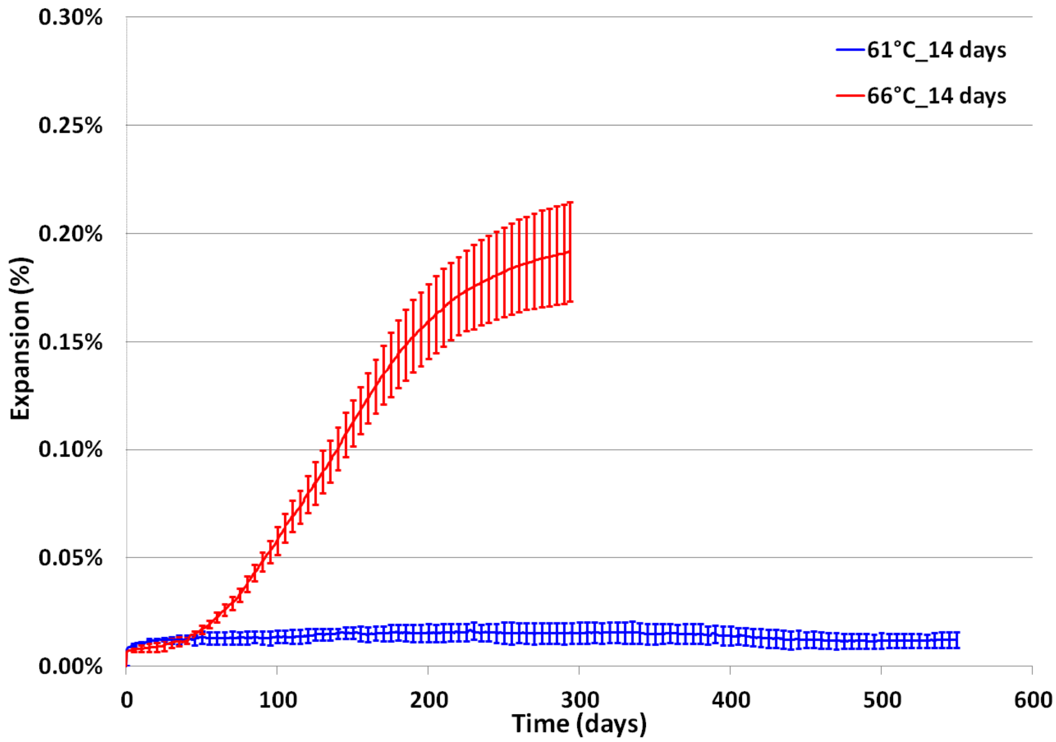


FIGURE 3: Expansion of specimens heated at 61°C and 66°C during 14 days.

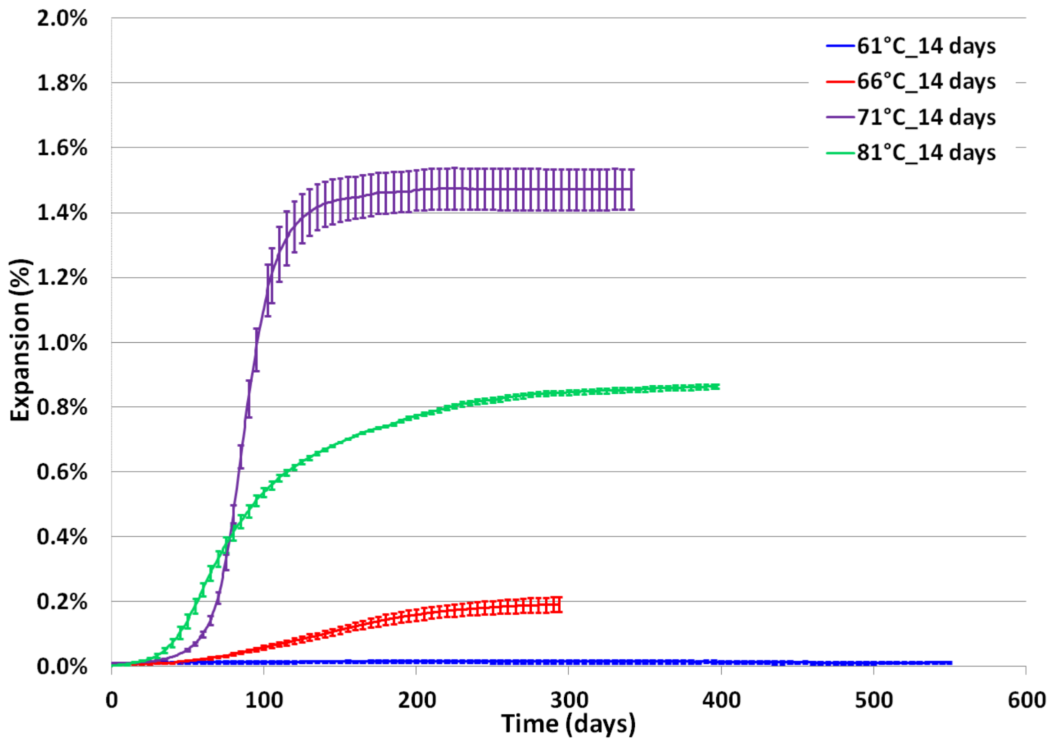


FIGURE 4: Expansion of specimens heated at 61°C, 66°C, 71°C and 81°C during 14 days.

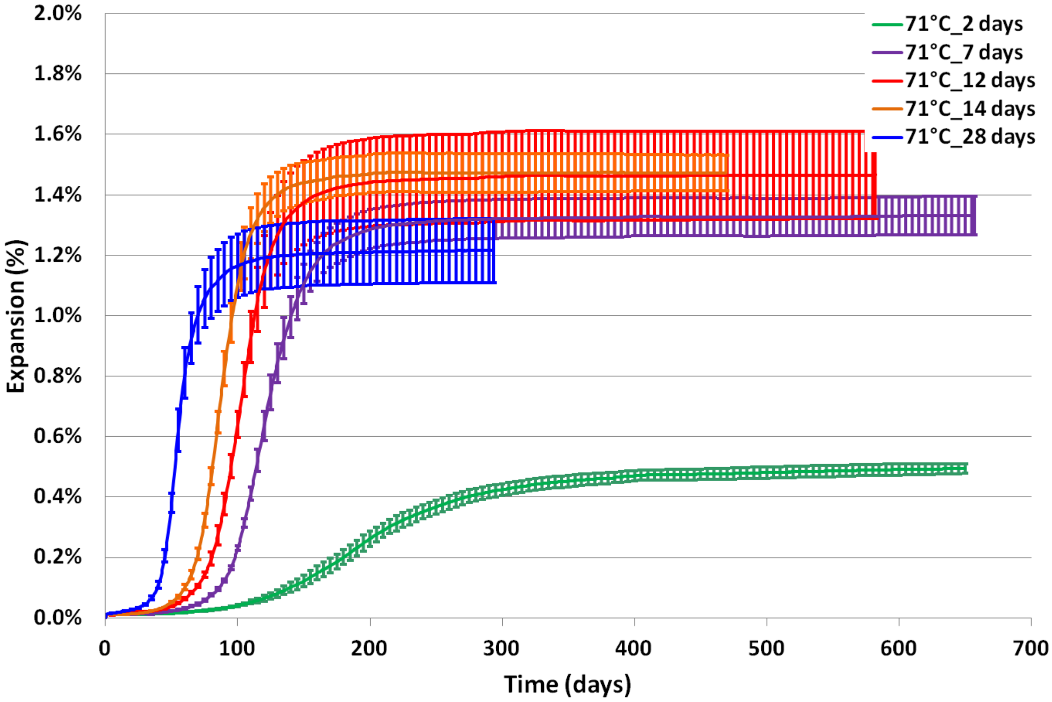


FIGURE 5: Expansion of specimens heated at 71°C during 2, 7, 12, 14 and 28 days.

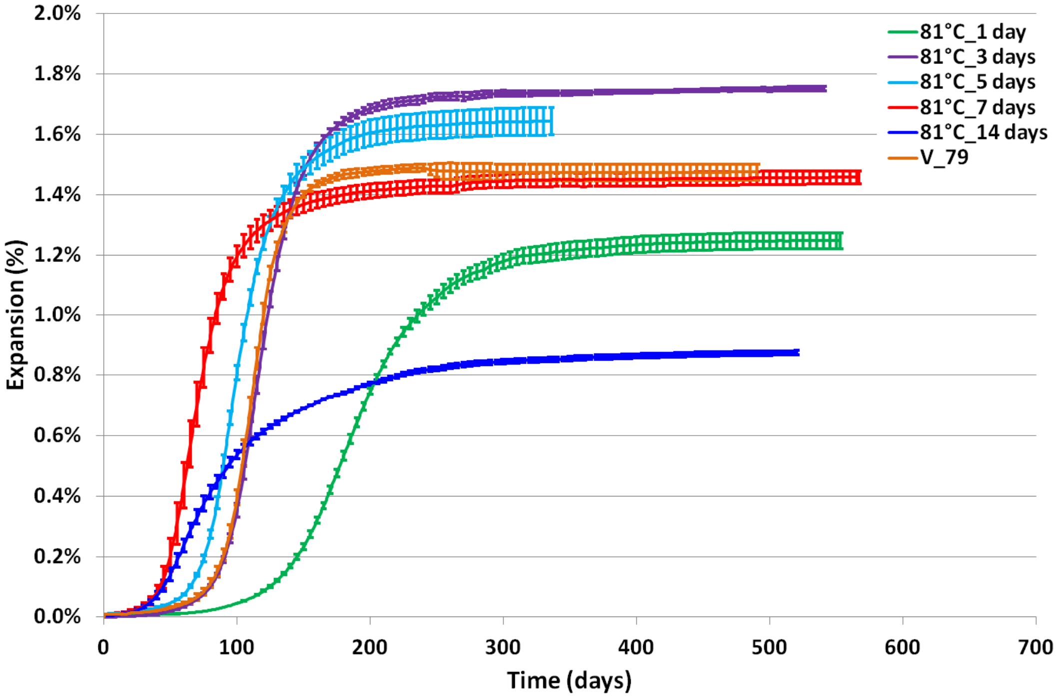


FIGURE 6: Expansion of specimens heated at 81°C during 1, 3, 5, 7 and 14 days.

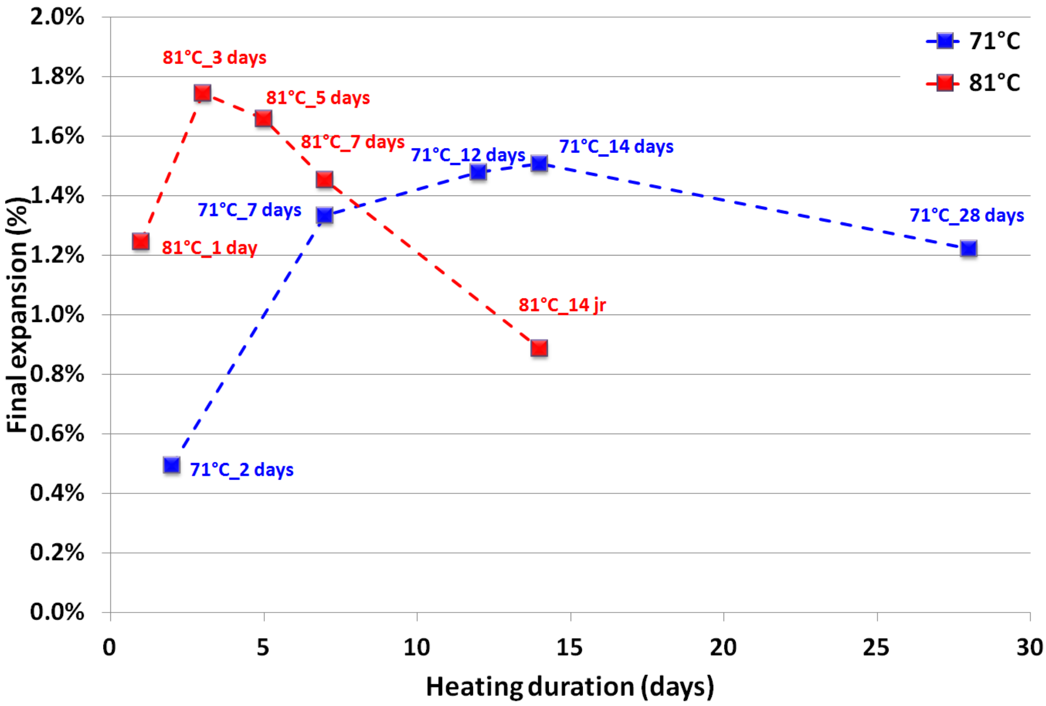


FIGURE 7: Effect of temperature and duration of heat treatment on magnitude of expansion.

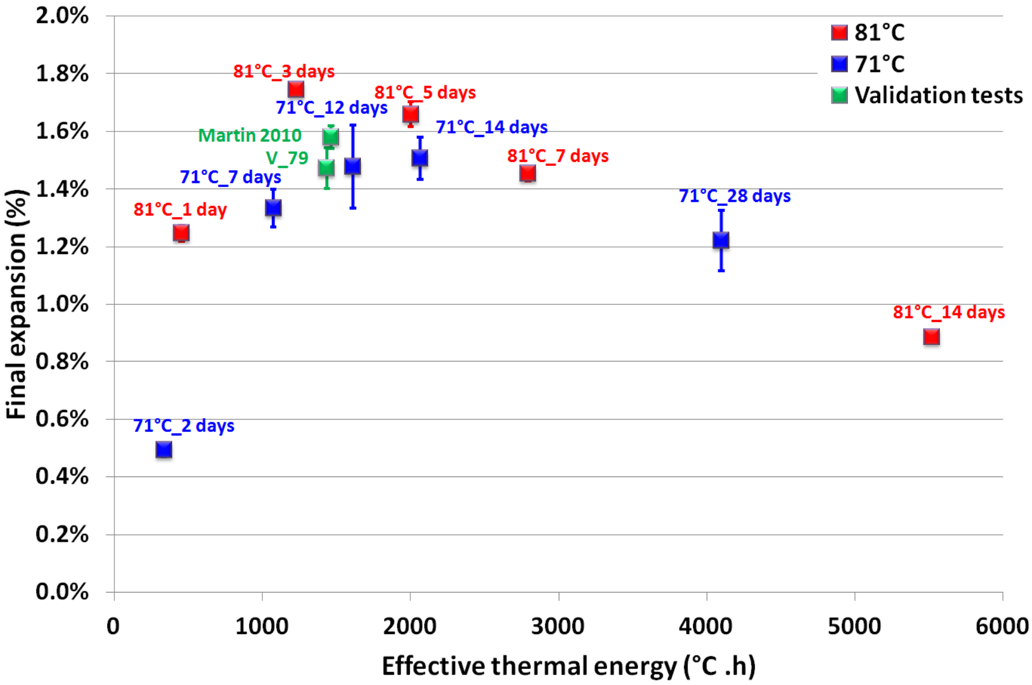


FIGURE 8: Effect of effective thermal energy on magnitude of expansion.

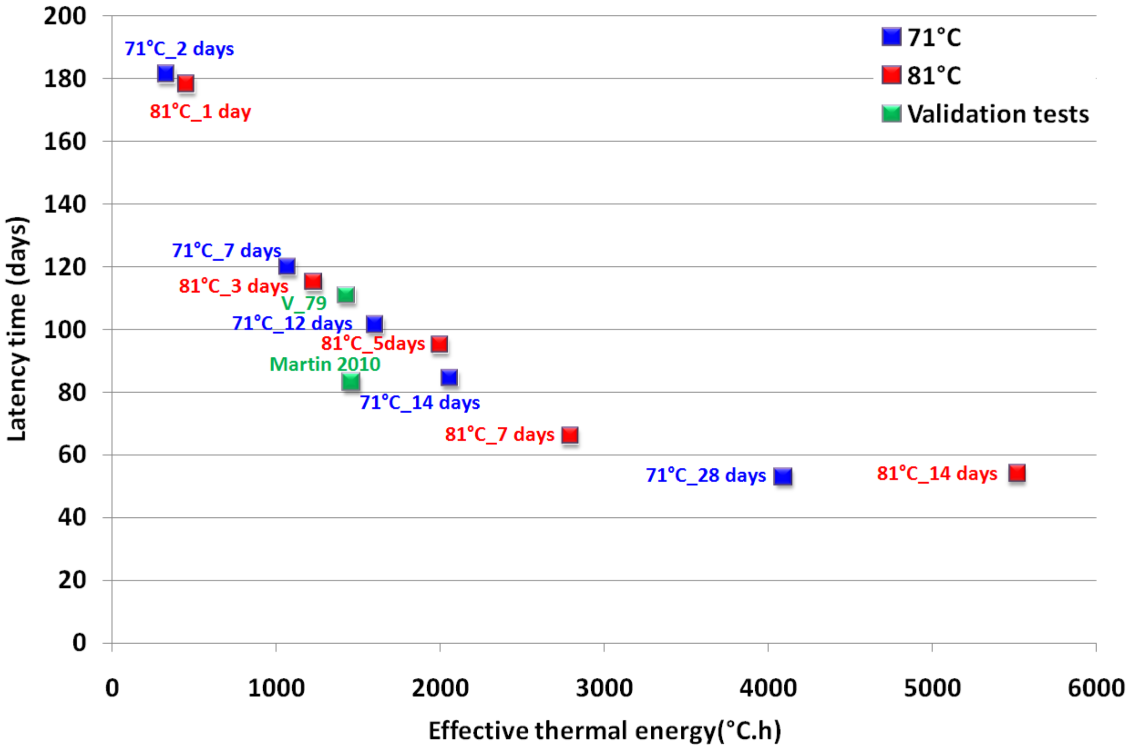


FIGURE 9: Effect of effective thermal energy on latency time.

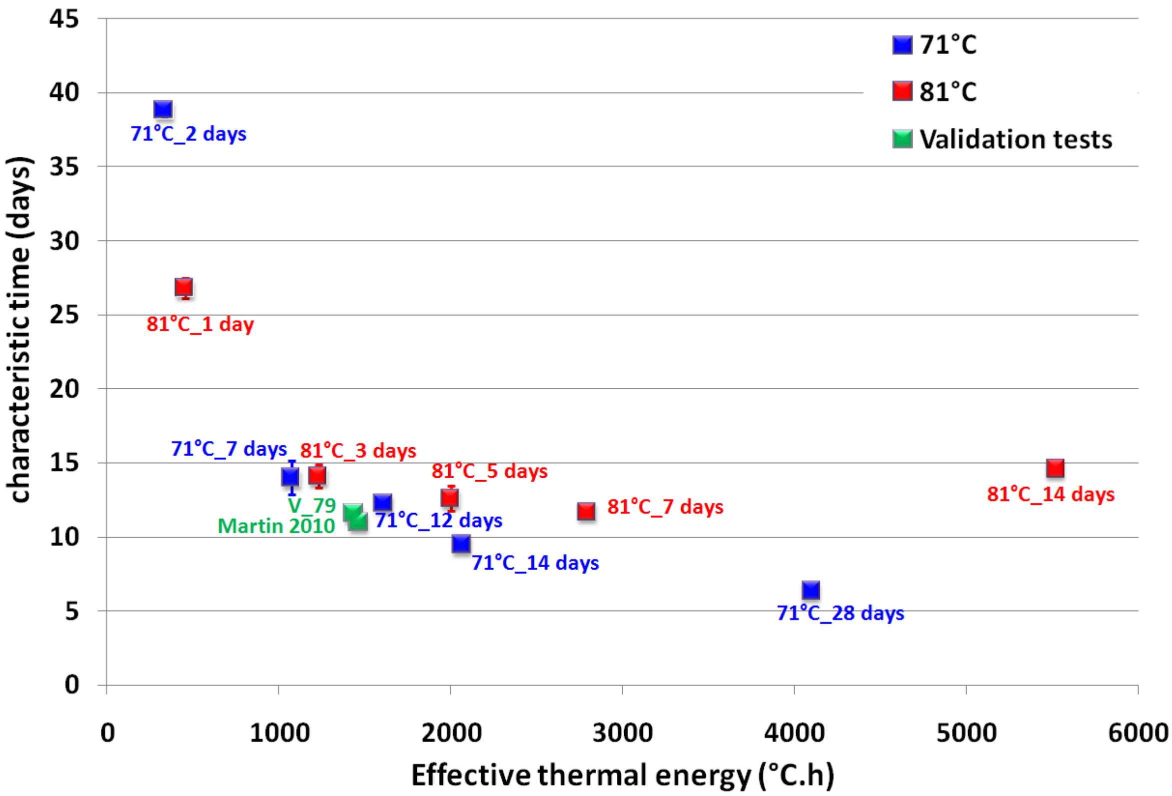


FIGURE 10: Effect of effective thermal energy on characteristic time.