Experimental evidence for understanding DEF Sensitivity to early-age thermal history

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EXPERIMENTAL EVIDENCE FOR UNDERSTANDING DEF SENSITIVITY TO EARLY-AGE THERMAL HISTORY

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Abstract

Delayed Ettringite Formation (DEF) consists in an expansion of the affected concrete leading to a decrease of its mechanical properties and thus inducing problems in terms of serviceability and structural integrity. To manage the affected structures, re-assessment tools have to be provided. Such models have to include coupling laws taking into account the effects of influent parameters. Early-age temperature has a strong influence on DEF characteristics. Thus, its effects have to be finely understood. In this paper, a literature review is proposed to sum up the results available concerning this problem. Some explanations based on chemical processes are suggested. Then, the results of an experimental study that aims to quantify the couplings between thermal history and expansion characteristics are presented. Finally, coupling laws taking into account the effect of temperature are discussed. It appears that taking into account a DEF-increase rate lowered with the heat treatment duration could improve the predictions.

Résumé

La Réaction Sulfatique Interne (RSI) est une pathologie du béton qui conduit à son expansion. Cette dernière induit une diminution des performances mécaniques source de problèmes en termes de fonctionnalité en service et d'intégrité structurelle. Pour gérer les ouvrages atteints, il est nécessaire de disposer d'outils de re-calcul. Pour être précis, ceux-ci doivent prendre en compte les couplages entre les expansions et les paramètres influents. Dans cet article, les effets de la température au jeune âge sur les caractéristiques de la RSI sont étudiés. Une étude bibliographique synthétise les principaux résultats disponibles et propose des explications sur la bases des mécanismes chimiques. Le suivi de corps d'épreuve soumis à différents traitements thermiques a permis de quantifier les effets de la température sur les expansions. Ces résultats ont permis de calibrer une modélisation permettant de prédire l'expansion finale connaissant l'histoire thermique du matériau. Ainsi, la prise en compte d'une décroissance des effets thermiques avec le temps semble améliorer les prédictions.

1. INTRODUCTION

Delayed Ettringite Formation (DEF) is an autogenous swelling reaction that can affect concrete exposed to high temperature at early age, typically above 65°C [1]. Basically, this heating can occur either in precast elements [2] or in cast-in-place massive elements [3]. Due to the late formation of ettringite in the hardened concrete, this reaction leads to an expansion of the material inducing cracking and decrease of its mechanical properties [4]. Thus DEF implies severe concern in terms of serviceability and structural integrity [5-6].

On the one hand, to avoid DEF problems on newly built structures, technical recommendations have been published: the limitation of early-age temperature is recommended as one of the most efficient ways to avoid DEF expansions [7-9]. On the other hand, to deal with the affected structures, it is necessary to provide numerical tools to the structures owners and operators in order to re-assess and predict their structural behaviour [6;10]. Such models are based on coupling laws linking the mechanical effects of expansion and their influencing parameters. Regarding the effects of early-age temperature, some attempts have already been reported [11].

In this paper, the effects of early age temperature history regarding the DEF expansion are discussed. First, a brief literature review is proposed to illustrate the qualitative results available concerning the effects of temperature on DEF. Second, the results of an experimental study concerning the effect of temperature and duration of heat treatment on DEF expansion are analyzed. These results are then compared to the predictions of coupling laws linking the thermal history of the material to the potential DEF expansion.

2. EFFECT OF TEMPERATURE ON DEF: STATE OF THE ART

2.1 Basic mechanisms

DEF is defined as an internal sulphate attack induced by heating [12]. Consequently the thermal history of concrete has a strong influence on the features of a potential DEF expansion. In the field, for cast-in-place structures, this corresponds to the appearance of degradations in the most massive parts while the thinnest ones remain locally unaffected [6;10]: if the heat exchange area is small compared to the volume of the concrete element, the heat generated by hydration will significantly raise the inner temperature and thus induce a risk of DEF. To illustrate this, figure 1 represents the temperature monitoring in an abutment (length of 33.5m) after casting: the footing and the wall were cast separately. Though the concrete used was a CEM III with a low heat of hydration and despite a mild outer temperature, it can be seen that the massive wall experienced a temperature increase of more than 37°C in 24 hours (which was far from stabilization) while the thin footing showed much lower temperature elevations.

The heat experienced by concrete renders the primary ettringite unstable. Consequently, the corresponding aluminates and sulphates are available in the pore solution at early age. At this stage, sulphates are believed to be adsorbed by Calcium-Silicate-Hydrates (CSH) [13]. After cooling, the sulphates are released in the pore solution [14] to form ettringite inducing crystallisation pressure in the set concrete responsible of the expansion.

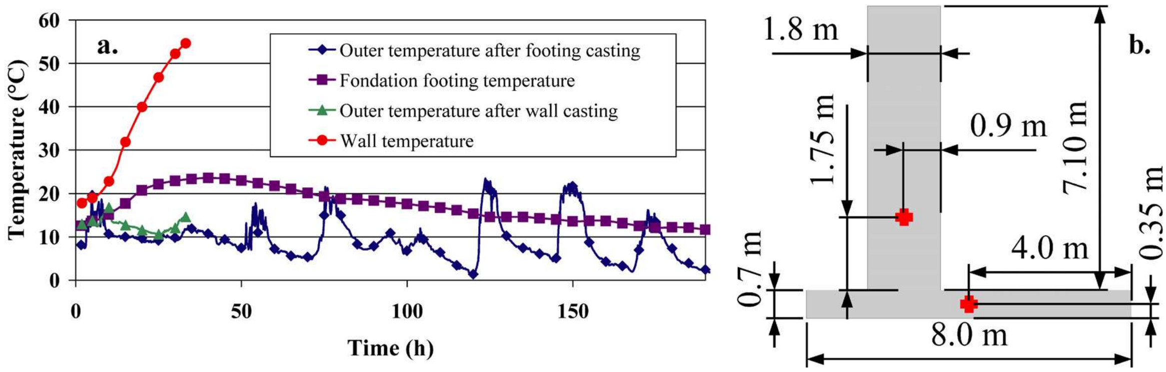

Figure 1 : Temperature monitoring (a) during the casting of an abutment (b) (location of the sensors marked by the crosses)

2.2 Effects of temperature and duration of a heat treatment

It is generally believed that an increase of the initial curing temperature leads to an increase of the magnitude of DEF expansion [15-16]. This result is however not systematic and some studies show a limited influence of temperature on the magnitude of expansion [17]. However, an agreement seems to exist concerning the acceleration of the onset and the rate of expansion while increasing the curing temperature [2;16-17].

The duration of heating seems to have a pessimum effect on DEF: for a given heat treatment temperature and below a “threshold” duration, the magnitude of expansion increases with the heating duration [11;18]; however, above this threshold, a decrease of the magnitude of expansion is observed [12;18-19].

To deal with these complex effects, the curing temperature and the corresponding duration should be considered as a couple [18-19]: the heat treatment is considered to bring a thermal energy initiating DEF. In this context, Baghdadi et al. [11] proposed an empiric relation based on a thermoactivated decomposition of ettringite according to a type of Arrhenius’ law [20].

2.3 Chemical considerations

Since temperature has an influence on many microscopic phenomena such as hydration of cement, composition of the pore solution, porosity, etc. [14;21-23], it has a very complex influence on ettringite nucleation (and thus DEF mechanism) which is believed to be highly dependent of the cement composition [24]. However, the thermal stability of ettringite has been widely studied: it appears that an increase of temperature is not prone to the precipitation of ettringite [25-26]. It delays the formation of the crystals until the system is cooled thus leading to the occurrence of internal crystallisation pressure and expansion. With the increase of temperature, monosulfate appears to be more stable than ettringite and could thus explain the delayed formation of the latter one after cooling [27]. Thus, in a first approach, the higher the temperature, the higher the amount of early ettringite decomposed during heating and the higher the expansion during late nucleation. However, for a high temperature and/or a long duration of heating, the formation of new products such as hydrogarnet trapping the reactants for ettringite such as aluminates and sulphates is believed to occur [22;27]. In this context, the late amount of ettringite that can precipitate in the hardened concrete decreases and lowers the potential expansion, thus explaining the pessimum effect.

Thus, despite some uncertainties, the qualitative role of temperature on DEF is well documented. However, very few predictive and quantitative relations exist in the literature despite they are needed for predictive models of the effect of DEF on structures. An experimental programme was thus launched for quantitative identification of these relations.

3. EXPERIMENTAL STUDY

3.1 Testing programme

The concrete mix designed for the test is given in Table 1 (W/C=0.49). The binder used is a CEM I 52.5 R CE CP2 NF which is a high early strength cement. It was chosen because of its high aluminate, sulphate and alkali contents (respectively 3.46, 4.30 and 0.83 wt. %) prone to DEF. However, to ensure optimum conditions for expansion to occur, K_2O was added to mixing water up to a Na_2O_{eq} content of 1% of the cement content.

Table 1: Concrete mix (kg/m^3)

Cement	Water	Sand 0/2 mm	Coarse aggregate 4/8 mm	Coarse aggregate 8/12 mm	K_2O
410	201	839	98	814	1.750

To study the influence of the thermal history, the specimens were heat treated right after casting at different temperatures with different durations. The heat treatments were performed in water in a specific device described in [28]. Figure 2 represents the monitoring of the temperature in the heating device. The heat treatment was divided into three phases: a heating phase, a constant temperature plateau and a cooling phase. Two hours after casting at 20°C, a heating phase was applied at a rate of 5°C/h up to the chosen temperature of the plateau. Three different temperatures of plateau were chosen (70, 80 and 85°C) and were applied during three days; concerning the 80°C-plateau, two other durations were considered: one day and five days. The durations were chosen to be representative of the thermal history of massive elements [3]. In this paper, each heat treatment is referred as xD_yC where x corresponds to the duration of the plateau and y to its temperature (e.g. 1D_80C corresponds to the plateau of one day at 80°C). Finally, a cooling phase (-5°C/h) was applied until 38°C.

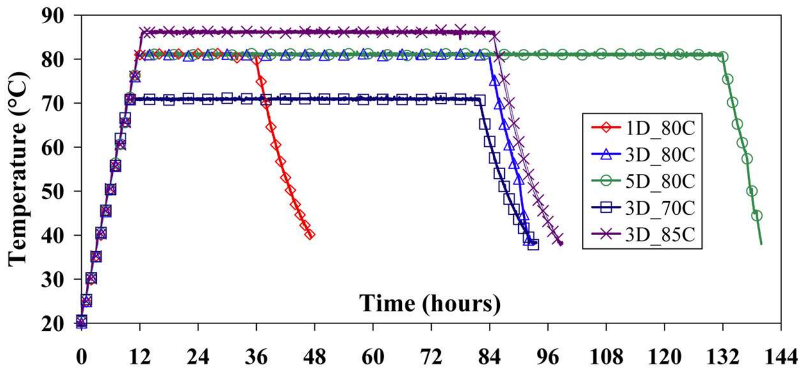

Figure 2: Temperature evolutions during the heat treatments

After heat treatment, all specimens were stored in water at constant temperature of 38°C for 900 days. The specimens are cylinders of 0.11m in diameter and 0.22m in height. For each heat treatment, three identical samples were prepared to gather statistically representative data. After casting, stainless steel pins were glued on three vertical locations placed at 120° from each other. The pins were used to set a digital extensometer in order to monitor the longitudinal expansion of the cylinders [29]. The water content of the specimens was monitored by weighing.

3.2 Results and discussion

The expansion of DEF affected concretes can be quantified using equation 1 [10;18]. In this relation, ε_∞ corresponds to the final magnitude of expansion, τ_L and τ_C are the latency and the characteristic times respectively (corresponding to the duration before the onset of expansion and the duration to reach the final expansion after onset) and φ and δ are two parameters used to take into account a linear expansion at the end of the swelling process.

$$\varepsilon(t) = \varepsilon_\infty \cdot \frac{1 - e^{-\frac{t}{\tau_C}}}{1 - e^{-\frac{(t-\tau_L)}{\tau_C}}} \cdot \left(1 - \frac{\varphi}{\delta + t}\right) \text{ with } 0 \le \varphi \le \delta \tag{1}$$

The parameters fitted on the experimental results are given in Table 2. Figure 3 represents the monitoring of dimension and mass of the specimens. The dots represent the mean value of the considered parameter and the error bars correspond to plus/minus one time the standard deviation. The expansion appears to be strongly correlated with the water uptake. It has been associated to the formation of cracks during intense swelling acting as reservoirs [30].

Table 2: Parameters of the model describing the expansions

	3D_70C	1D_80C	3D_80C	5D_80C	3D_85C
ε_∞	0.66%	1.17%	1.58%	1.89%	1.54%
τ_C (days)	120	35	18	13	15
τ_L (days)	280	179	136	106	100
φ (days)	120	30	11	10	14
δ (days)	120	114	136	107	120

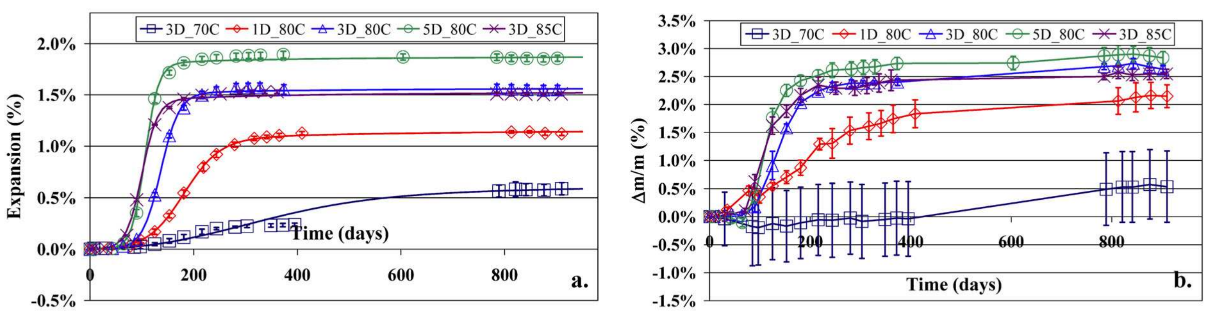

Figure 3: Expansion (a.) and mass monitoring (b.) of the specimens

Figure 4.a illustrates the influence of the duration of a 80°C-plateau on the expansion magnitude and kinetics relatively to the 1D_80C case. In the range of durations investigated in these tests, the higher the duration, the higher the magnitude and the more intense the kinetics. No pessimum effect could be clearly demonstrated with these results. Figure 4.b illustrates the influence of the temperature of a 3-days plateau on the characteristics of expansion. In general, both the magnitude and the kinetics of expansion increase with the temperature. However, a tendency to decrease the magnitude after three days at 85°C is observed and could be associated to a pessimum effect. Thus, for a given treatment duration of three days and for the specific concrete considered in these tests, the critical temperature threshold corresponding to a pessimum effect might be in the range of 80 to 85°C.

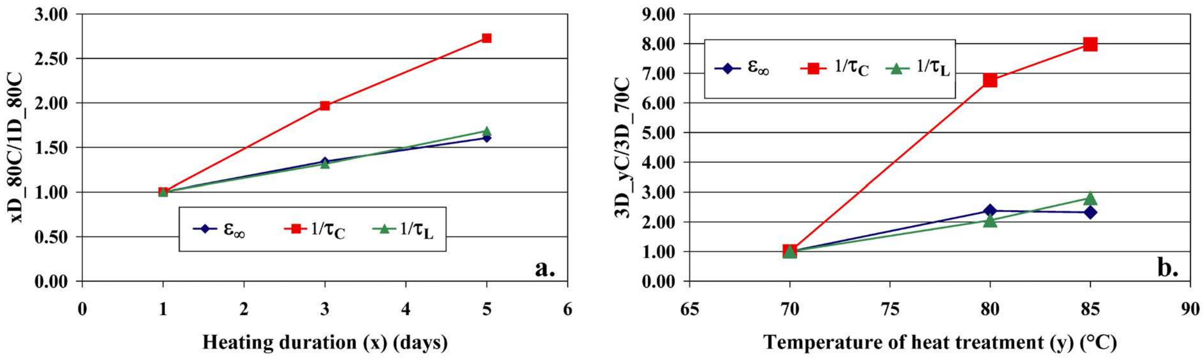

Figure 4: Effect of duration (a.) and temperature (b.) of the plateau of heat treatment on the magnitude and kinetics of expansion

4. MODELLING THE COUPLING BETWEEN THERMAL HISTORY AND EXPANSION

4.1 Calibration of Baghdadi's law

To set up reliable numerical tools to re-assess the DEF-affected structures, it is necessary to provide predictive relations concerning the chemically-induced expansions. Baghdadi et al. suggested equation 2 inspired from an Arrhenius' law to assess the magnitude of expansion knowing the early-age thermal history [11]. In this relation, α is a constant depending on the concrete mix, E_a is the activation energy, T_0 is the temperature threshold above which the DEF potential is believed to increase, t_m is the mature time of concrete, R is the gas constant and T(t) is the concrete temperature at time t. Table 3 gives an estimation of the parameters of equation 2 for the tests presented in this paper. The quadratic error is about 0.35%.

$$\varepsilon_\infty = \alpha \cdot \int_0^{t_m} \begin{Bmatrix} 0 & \text{if } T(t) < T_0 \\ \exp\left(-\dfrac{E_a}{R} \cdot \dfrac{1}{T(t)-T_0}\right) & \text{else} \end{Bmatrix} \cdot dt \qquad (2)$$

Table 3: Parameters of Baghdadi's model

α (h^{-1})	E_a (J/mol)	T_0 (°C)
6.90E-04	438.50	43.30

Figure 5 compares the prediction of the model to the measured magnitudes of expansion. The experimental results are qualitatively fairly well reproduced with an increase of expansion with the duration of the plateau for a given temperature, or with the temperature for a given duration of the heating plateau. However, contrarily to all other estimations, the 1D_80C prediction is significantly underestimated. This implies that the effect of low temperatures applied for a long duration are overestimated compared to those of higher temperatures associated with a short duration.

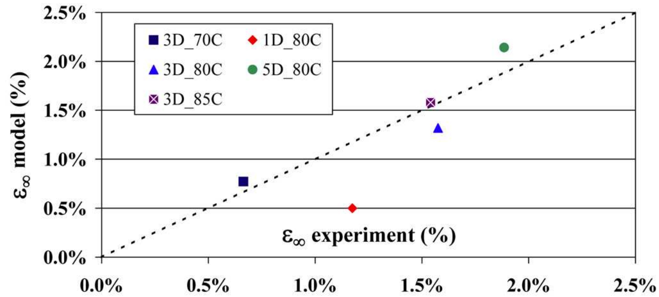

Figure 5: Comparison of the measured and predicted magnitudes of expansion according to equation 2

4.2 Consideration of a decreasing impact of temperature with the exposure duration

To reduce the deviations emphasized in the previous section, equation 3 is proposed. In this relation, λ and β are two constants which are believed to be material characteristics and $t_{exp}(t)$ is the exposure time, that is the period during which the temperature of the material $T(t)$ is above the temperature threshold T_0. Table 4 gives an estimation of the parameters. Case 1 is using the same activation energy and temperature threshold as those determined for Baghdadi's law (see section 4.1) to assess the effect of λ and β compared to α. In case 2, all parameters are considered to be variable for the calibration in order to lower as much as possible the quadratic error. Figure 6 compares the prediction of the model with equation 3 to the measured expansions according to cases 1 and 2.

$$\begin{cases} \varepsilon_\infty = \int_0^{t_m} \alpha(t) \cdot \begin{Bmatrix} 0 & \text{if } T(t) < T_0 \\ \exp\left(-\dfrac{E_a}{R} \cdot \dfrac{1}{T(t) - T_0}\right) & \text{else} \end{Bmatrix} \cdot dt \\ \text{with} \begin{cases} \alpha(t) = \lambda \cdot \beta \cdot t_{exp}(t)^{\beta-1} \; ; \lambda > 0 \; ; \beta \in \left]0;1\right[\\ t_{exp}(t) = \int_0^t \begin{Bmatrix} 0 & \text{if } T(u) < T_0 \\ 1 & \text{else} \end{Bmatrix} \cdot du \end{cases} \end{cases} \tag{3}$$

Table 4: Parameters of the proposed model

	λ (h^{-2})	β (-)	E (J/mol)	T_0 (°C)	Quadratic error
Case 1	3.93E-01	4.63E-02	438.50	43.30	0.18%
Case 2	8.79E-01	2.57E-02	438.50	48.00	0.16%

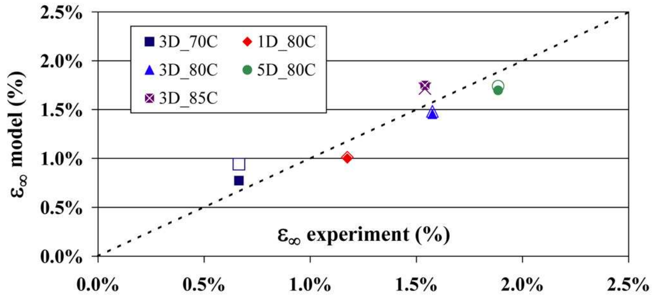

Figure 6: Comparison of the measured and predicted magnitudes of expansion according to equation 3 (hollow marks = case 1; plain marks = case 2)

Figure 7 illustrates the evolution of the α parameters in equations 2 and 3. To take into account the deviations emphasized in Baghdadi's law, the α(t) function gives a higher weight to the effects of temperature at the beginning of the exposure duration than at the end. This could be interpreted as a decrease of the ability of CSH to trap the sulphates. Indeed, CSH are believed to have a certain adsorption capacity due to their chemical structure [31]: at the beginning of heat treatment, since CSH are "sulphate-free", the sulphates are adsorbed very fast, thus corresponding to a fast increase of the DEF potential magnitude. Then, since the number of slots available for adsorption decreases with the exposure duration, the capacity of the CSH to trap sulphates decreases.

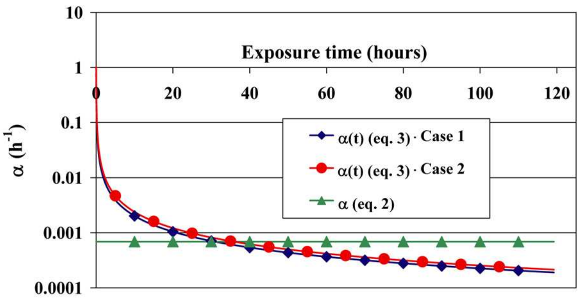

Figure 7: Evolution of the α parameters in equations 2 and 3

5. CONCLUSION

Early-age thermal history of concrete is critical for potential DEF expansion. The literature review has shown qualitatively the effects of temperature on expansion: below a threshold in duration and/or a threshold in temperature (i.e. below a certain thermal energy), both kinetics and magnitude of DEF expansion increase; above these thresholds, the magnitude might decrease. This pessimum effect could be explained by the formation of new hydrates trapping ettringite reactants.

The presented experimental study has quantitatively confirmed these effects: concrete cylinders exposed to different heat treatments at early age have been monitored in terms of dimension and mass during 900 days. The expansions have been characterized both in terms of magnitude and kinetics and correlated to the corresponding thermal history.

Finally, some attempts of prediction of the potential DEF expansion have been performed. Baghdadi's model has been improved by taking into account the evolution of the ability of the

CSH to bind ettringite reactants such as sulphates. However, the proposed model does not take into account a similar effect of the maximum temperature of heat treatment. These first results should be confirmed by testing the model on other early-age thermal histories.

The present results emphasize the critical issue consisting in controlling the temperature in mass concrete at early age regarding potential DEF expansion. In the end, the proposed model could be used to assess a risk of expansion from the temperature monitoring and the composition of concrete.

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