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The impact of cement parameters on Delayed Ettringite Formation

A. Pavoine [a,*], X. Brunetaud [b], L. Divet [c]

[a] Laboratoire Eco-Matériaux, Centre d'Études Techniques de l'Équipement, Direction Régionale et Interdépartementale de l'Équipement et de l'Aménagement Île-de-France, 21–23 Rue Miollis, 75015 Paris, France
[b] Université d'Orléans, Centre de Recherche sur la Matière Divisée, CNRS, 1B rue de la Férollerie, 45071 Orléans cedex 2, France
[c] Institut français des sciences et technologies des transports, de l'aménagement et des réseaux, 58, boulevard Lefebvre, 75015 Paris, France

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ABSTRACT

Delayed Ettringite Formation (DEF) in concrete is likely to lead to swelling and cracking in structures which have undergone early age heating to a temperature of over 65 °C. Application of a method that accelerates this process has made it possible to study the impact of cement properties on DEF. For two temperatures reached by the concrete (75 °C or 85 °C), the study considers a domain defined by the sulphate content [2.6–3.6%], the alkali content [0.5–1%] and the Blaine specific area [3330–4635 cm^2/g] of the cement. The impact of these parameters and the interactions between them on swelling are discussed. Monitoring of the dynamic elastic modulus of the concretes shows that this property may be reduced by DEF, but that it may increase again once the swelling process has ceased, probably due to the gradual filling of voids by ettringite formed under conditions of limited supersaturation.

1. Introduction

Delayed Ettringite Formation (DEF) is a reaction that affects cementitious materials potentially causing them to swell and crack. DEF is a type of internal sulphate attack [1] that occurs when the constituents of concrete provide an initial source of sulphates as a result of inappropriate heating of the concrete to a temperature in excess of 65 °C. Delayed Ettringite Formation in concrete has been responsible for the premature deterioration of more than 50 structures in France. DEF can be encountered in large scale elements or precast elements. Because of the complexity of this swelling phenomenon, it never concerns the whole structure. This pathology is a worldwide problem and can be observed in certain circumstances if specific parameters are met simultaneously including concrete formula, temperature at which the concrete has been exposed and the presence of water. The diagnosis techniques, the impact of DEF on the properties of concrete and the conditions under which it develops are still subjects of much debate. Prior to the publication of a LCPC technical guide [2], there was no valid method for diagnosing swelling reactions in France. It is therefore likely that in France the number of structures affected by DEF on its own or in association with another swelling reaction has been under-estimated.

The results published in this paper are a supplement to the research carried out by Brunetaud et al. in order to identify the parameters responsible for the swelling reaction [3–5]. The first studies were concerned with heating (duration and temperature reached by the concrete) and concrete mix design (water to cement ratio, type of aggregate). The program described below relates to a parametric study whose purpose was to identify, within a defined domain, the relative impacts of temperature, certain characteristics of Portland cement (alkali content, sulphate content and fineness) on the swelling and the dynamic elastic modulus of the concrete.

1.1. The reaction mechanism and the parameters that play a role in DEF

DEF can occur in concretes that have undergone heating (to over 65–70 °C) when the mix design has certain characteristics and the material is exposed to a moist environment [6]. The early age heating of concrete alters the normal hydration process of Portland cement, according to a mechanism that has been thoroughly described by Taylor et al. [6]. In particular, the rise in temperature alters the conditions of sulphate equilibrium between the sulphate hydrates and the hydrated calcium silicates (C–S–H) by encouraging reversible ion adsorption onto the surface of the C–S–H [7]. This process is accentuated with rising pH and consequently the alkali content of the concrete. The formation of hydrated calcium monosulphoaluminate ($Ca_4Al_2(SO_4)(OH)_{12}(H_2O)_6$) within the concrete is favoured at high temperature and pH to

* Corresponding author.
E-mail addresses: alexandre.pavoine@developpement-durable.gouv.fr (A. Pavoine), Loic.divet@ifsttar.fr (L. Divet).

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the detriment of that of ettringite (hydrated calcium trisulphoaluminate $Ca_6Al_2(SO_4)_3(OH)_{12}(H_2O)_{26}$). When the concrete cools down, the calcium, the aluminates and the sulphates of the monosulphoaluminate react with the sulphates that are in solution leading to the formation of ettringite. Since this process occurs within the cement paste at the nanometric scale [6,8], it cannot be observed at the micrometric scale with a scanning electron microscopy (SEM). The crystallization of ettringite generates then considerable stresses in the material leading to microcracking which propagates in a complex manner due to the non-uniform nature of the composite matrix formed by the cement (which has undergone varying degrees of hydration), the voids and the granular inclusions of various sizes. As a consequence of Ostwald ripening [9], the small ettringite crystals tend to dissolve and reprecipitate in the cracks, forming larger crystals that are more stable [10].

Test methods have been developed to assess the risk of swelling in mortars or concretes [11–17]. Some specifications of published tests are summarised in Table 1. In contrast with the situation as regards to the alkali-aggregate reaction (AAR), for which it has been possible to develop rapid tests to assess the potential reactivity of aggregate particles [17], no rapid method exists for internal sulphate attack and it is necessary to monitor specimens for at least 1 year or even longer, in particular in the case of low water on cement (W/C) ratios [3]. In addition, most of the studies are performed on small specimens of mortar which may encourage alkalis leaching and reduce the amount of alkalis present in the interstitial solution of mortar (Table 1).

The reduction in pH that occurs as a consequence of alkalis leaching speeds up the reaction. It may also act as a trigger and should be avoided so it does not bias the analyses. The monitoring by Famy [24] of the alkali content of small mortar specimens (16 × 16 × 160 mm) immersed in water shows that more than 90% of the alkalis can be removed from the specimens after 160 days of immersion. To reduce this risk, the specimens may be kept in an almost saturated moist environment [18,25]. The method proposed by Pavoine et al. [13,14] differs from the others in two respects. First, it allows the evaluation of the risk of DEF on specimens defined by their thermal history at early age and their concrete mix design. The thermal history of the concrete refers to the temperature at the centre of a cast in place member or a precasted element. The test method therefore considers the mix design of the concrete and its use. The second difference involves the size of the specimens and the conservation conditions.

Table 1
Test conditions used for studying DEF.

Author	Temperature (°C)	Specimen	Test procedure
Zhang et al. [18,19]	1 cycle 6 h at 85 °C	Mortar bars (25 × 25 × 286 mm)	High humidity mortar bars suspended over water
Tosun [20]	Duggan test. Series of 3 wetting and drying cycles (respectively in deionized water and for 24, 24 and 72 h at 85 °C)	Mortar bars (25 × 25 × 285 mm)	Specimens stored in water at 20 °C
Escadeillas et al. 2007 [16], Aubert et al. [21]	1 cycle T_{max} = 80 °C for 8 h	Mortar prisms (40 × 40 × 160 mm)	Mortar stored in non renewed lime-saturated water at 20 °C or Nine wetting and drying cycles (respectively 5 days in water at 20 °C and 2 days in a drying oven at 40 °C) or Mortar stored in renewed deionized water at 20 °C
Brunetaud et al. [4]	1 cycle at 65 °C or 85 °C for 2/6 h or 2/10 days	Concrete cylinders (∅ 110 mm × 220 mm)	Concrete stored in water until 28 days Two wetting and drying cycles (respectively 7 days in water at 20 °C and 7 days at 38 °C) Concrete stored in non renewed water with a low water/concrete volume ratio (<1.5)
Fu et al. [22]	80 °C or 90 °C for 12 h	Mortar bars (25 × 25 × 160 mm)	Mortar bars stored in saturated lime water at 23 °C
Kelham [23]	70 °C or 80 °C for 12 h or 90 °C for 1 h	Mortar bars (16 × 16 × 160 mm)	Mortar bars stored in water at 20 °C
Pavoine et al. [13,14]	Reproduction of real temperature cycle of concrete element	Concrete cylinders (∅ 110 mm × 220 mm)	Two wetting and drying cycles (respectively 7 days in water at 20 °C and 7 days at 38 °C) Concrete stored in non renewed water with a low volumetric water/concrete ratio (<1.5)
Famy et al. [24]	12 h at 90 °C	Mortar bars (16 × 16 × 160 mm)	Mortar bars stored in water Mortar bars stored at 90–100% relative humidity Mortar bars stored in alkaline solution

Table 2
Impact of internal swelling reaction on compressive strength (Rc) and elastic modulus (E).

Author	AAR/DEF	Specimen	Expansion	Impact on Rc (MPa) Initial value/final value	Impact on E (GPa) Initial value/final value
Pavoine [26]	DEF	Concrete	1.6%	32.3/8.0	Undetermined
Zhang et al. [18,19]	DEF	Mortar	≈1.65%	Undetermined	≈38/≈23
Brunetaud [5]	DEF	Concrete	⩽0.1%	Slight increase	Dynamic elastic modulus Slight increase 35–45/40–50
			>0.1% with low expansion	No significant change	Dynamic elastic modulus No significant change
			>0.1% with rapid expansion	Large decrease	Dynamic elastic modulus Large decrease
			0.5%	40/30–34	
			0.9%	40/20–21	
			1.2%	40/14–16	
Larive 1997 [28]	AAR	Concrete	0.35%	45.8/52.2	
Multon [29]	AAR	Concrete	0.25% ± 0.06	38.4/46.7 in water	37.3/28.7 in water
			0.12% ± 0.02		37.3 ↘ 30.6 ↗ 34.6 in a sealed environment

In order to limit leaching by the immersion solution, the test specimens consist of concrete cylinders (∅ 110 mm, L 220 mm) or prisms (70 × 70 × 280 mm) that are immersed in a limited amount of water at 20 ± 2 °C. It should be explained that our previous work has shown that there is no significant difference between the behaviour of concrete that has been conserved in a saturated lime solution and concrete that has been conserved in water [26].

A large number of laboratory test campaigns have been conducted to gain a better understanding of the parameters involved in DEF and to develop parametric models for evaluating the risk of swelling on an *a priori* basis [3,19,23,25,27]. Parametric studies have mainly investigated the sulphates, aluminates and alkalis in cement. Initially, limits for one or two parameters were proposed [25,27]. These simple criteria were rapidly shown to be insufficient to inhibit the development of DEF because of the need to take account of interactions between the parameters involved in DEF. Kelham [23] then Zhang et al. [19] have since proposed equations and limits for the evaluation of the risk of swelling based on the composition of the cement.

1.2. The impact of internal swelling reactions on the mechanical properties of concrete

Several studies have focused on the impact of internal swelling reactions on the mechanical properties of concrete (Table 2).

The unrestrained swelling potential of concrete affected by internal sulphate attack may exceed 1%, which is considerably more than the expansion observed in France in the case of concrete affected by the alkali-aggregate reaction. In the case of alkali-aggregate reaction, the maximum swelling is limited by the reactivity of the aggregate amongst other factors and is generally less than 0.3% [28,29]. This difference leads to a significantly different impact on the compressive strength of the concrete. The alkali-aggregate reaction does not lead to a systematic reduction in compressive strength. However, in the case of internal sulphate attack, a high level of swelling (>0.1%) leads to a reduction of between 60 and 75% of the initial compressive strength of the concrete [5,26].

Internal swelling reactions (DEF or AAR) lead to a reduction of the elastic modulus of the concrete. A reduction of between 20% (AAR) and 60% (DEF) may occur when swelling exceeds 0.1%. In both cases (DEF, AAR), the drop in the elastic modulus is generally followed by an increase in the modulus when the kinetic process of swelling becomes slower or stops. The final elastic modulus may consequently be fairly close to its initial value. Brunetaud's research has shown that no clear and direct relationship links the dynamic modulus and the expansion. One only relationship found was between the value of the modulus and the average rate of swelling when these are measured at the point of maximum rate of change [4].

2. Materials

The aim of this study is to identify the impact of various constituents of concrete on the risk of Delayed Ettringite Formation. The experimental studies carried out by Kelham followed by Zhang have shown that it is not only necessary to consider the impact of the individual constituents but also to take account of the interactions between each of the studied parameters. We therefore designed a full factorial experiment to characterise the impact of different parameters and the interactions between them on the performance of heat treated concrete. A 2^4 experimental design was used, which involved 16 tests. The selected parameters were the alkali content of cement, the sulphate content of cement, the heat treatment temperature of the concrete and the Blaine specific area of the cement. The range of values covered by the tests for sulphates, alkalis and the specific surface (Table 3) is consistent with the Portland cements available on the French market.

Table 3
Values and parameters studied with the factorial experimental design.

Parameters	Low value	High value
Alkalis	0.50%	1.00%
Sulphates (SO_3)	2.6%	3.6%
Blaine specific area	3330 cm^2/g	4635 cm^2/g
Temperature	75 °C	85 °C
Normalised value in models $Exp_{(490days)(s,a,b,t)}$ and $Exp_{(1700days)(s,a,b,t)}$	−1	+1

Table 4
Chemical composition of cement.

Chemical composition	(%)
SiO_2	19.0
Al_2O_3	4.1
Fe_2O_3	3.75
CaO	64.6
MgO	1.09
Na_2O	0.13
K_2O	0.56
Equivalent Na_2O	0.50
Total SO_3	3.36
Loss on ignition	1.48
Insoluble	1.14
Free lime	0.67
CO_2	0.96
Mineral composition	
C_3S bogue	69.0
C_2S bogue	2.35
C_3A bogue	4.45
C_4AF bogue	11.4

Table 5
Concrete mix design.

	Mixture proportion of concrete (kg/m^3)
Sand 0/0.315 mm	182.7
Sand 0.315/1 mm	133.7
Sand 1/4 mm	217.5
Sand 2/4 mm	232.0
Aggregate 4/8 mm	180.0
Aggregate 8/12.5 mm	842.4
Water (W)	191.9
Cement (C)	399.8

The experiments were carried out using Portland cement clinker (Table 4) with added gypsum. Sufficient gypsum was added to obtain a sulphate content of between 2.6% and 3.6% taking account of the fact that the clinker contained 0.6% of SO_3. The fineness of the cement was controlled by milling the clinker in one or two stages. The resulting specific surfaces were 3330 cm^2/g and 4635 cm^2/g. The lower alkali content (0.50%) was determined by the composition of the cement. The upper alkali content limit (1.00%) was obtained by adding potassium hydroxide to the mixing water.

The experiments were performed with a reference mix design using 400 kg/m^3 of cement with a W/C value of 0.48. French siliceous aggregates with six different granular ranges were used (Table 5). The initial slump is about 100 mm.

3. Experimental

The French test procedure [30] was applied to study the effect of DEF on the tested concretes. This test comprises four stages:

(1) Concrete mix design; (2) heat treatment; (3) drying and wetting cycles; and (4) immersion in water and monitoring.

– The dry materials were blended together for 30 s. The water (possibly containing alkalis in solution) was then added over 30 s. The concrete was mixed for 2 min 30 s. After mixing and placement in cylindrical moulds (∅ 110 mm × L 220 mm), the specimens were subjected to the heat treatment.
– The specimens were heat treated in a climatic chamber with a heat treatment that was representative of what occurs in a large concrete element but with an accelerated cooling phase. The specimens were initially cured for 3 h at 30 °C. The temperature was then increased to 75 or 85 °C at a rate of 25 °C per hour. The specimens were maintained at the high temperature for 2 days, after which the temperature was decreased to 20 °C at a rate of 25 °C per hour. The specimens were then removed from the moulds and stored at 20 °C and 100% relative humidity for 28 days.
– The specimens were exposed to two drying and wetting cycles in accordance with the French method. The objective of these was to increase the kinetics of the DEF reaction without changing its triggering conditions. The specimens were subjected to 2 cycles, each lasting 14 days. A cycle consisted of 7 days of drying at 38 °C and 30% relative humidity and 7 days of wetting in tap water at 20 °C. After two drying and wetting cycles, the ends of the specimens were sawn to provide parallel surfaces and three metal markers where then fixed to the specimen 100 mm apart.

Each specimen was subjected to measurements that consisted of determining the expansion, the elastic dynamic modulus and the mass. The expansion was measured with a Pfender ball extensometer distributed by Mohr and Federhaff whose measurement dispersion on the basis of three concrete specimens was less than 0.002%. The elastic dynamic modulus was obtained by a non destructive method based on a measurement of the first longitudinal oscillation frequency when the specimen was subjected to an impact at the centre of one of its bases. The self-oscillation frequency is linked to the dynamic modulus of the material by the following equation:

$$f_{\text{longi}} = \frac{1}{2L}\sqrt{\frac{E_{\text{dyn}}}{\rho}} \quad (1)$$

where f_{longi} is the longitudinal self-oscillation frequency (s^{-1}), L is the height of the specimen (m), E_{dyn} is the dynamic longitudinal elastic modulus (Pa) and ρ is the density of the specimen (kg m^{-3}).

4. Results

4.1. Expansion of the concretes

Expansion measurements were conducted at frequent intervals over a test period of 490 days (Fig. 1). The specimens were then stored in water at 20 ± 2 °C for more than 3 years and measured twice, after 1100 and 1700 days of immersion. The specimens were designated by their level, low (−) or high (+), with respect to the following factors: sulphates (S), alkalis (A), Blaine specific area (B) and the maximum temperature (T) attained during the heat treatment (75 °C or 85 °C).

The mean expansion of the three specimens after 490 days of monitoring and after 1700 days of monitoring is shown in Table 6. The final expansion of the concretes was between 0.01 and 0.78% and many of the concretes exhibited significant expansion (>0.04%). These results were used to perform variance analysis of the experimental design (Fig. 2). The significant factors were then used to obtain a model of swelling in the studied domain after 490 days ($\text{Exp}_{490\text{days}}$%) and after 1700 days ($\text{Exp}_{1700\text{days}}$%).

The standard deviation for the entire experimental program was 0.03% after 490 days of monitoring and 0.05% after 1700 days of monitoring. While the characteristic plots for the alkali-aggregate reaction exhibited an easily identifiable swelling plateau [28], in the case of internal sulphate attack, the sigmoid curves

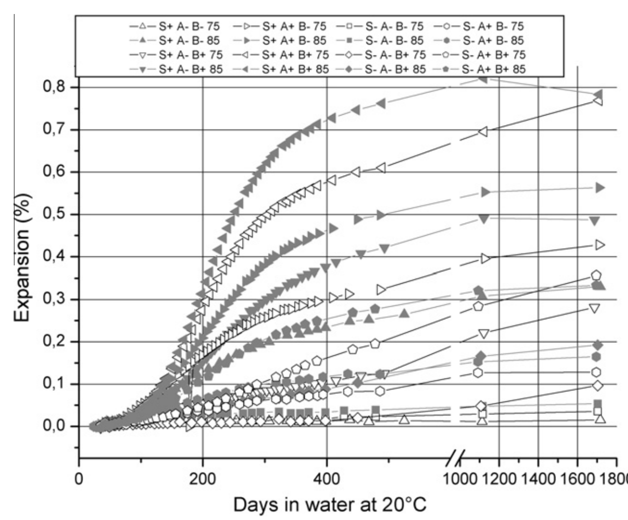

Fig. 1. Expansion of all the concrete specimens versus time.

Table 6
Concrete expansion after 490 or 1700 days immersion in water at 20 ± 2 °C.

Reference	Expansion (%) at 490 days			Expansion (%) at 1700 days		
	Exp. 1	Exp. 2	Exp. 3	Exp. 1	Exp. 2	Exp. 3
S + A − B − 75	0.015	0.013	0.013	0.018	0.013	0.016
S + A − B − 85	0.281	0.308	0.205	0.346	0.376	0.268
S + A − B + 75	0.077	0.083	0.216	0.181	0.223	0.441
S + A − B + 85	0.437	0.405	0.422	0.489	0.491	0.483
S + A + B − 75	0.359	0.338	0.272	0.439	0.458	0.387
S + A + B − 85	0.508	0.470	0.515	0.567	0.530	0.592
S + A + B + 75	0.603	0.613	0.613	0.703	0.870	0.734
S + A + B + 85	0.722	0.750	0.814	0.677	0.809	0.863
S − A − B − 75	0.026	0.021	0.022	0.042	0.032	0.033
S − A − B − 85	0.037	0.041	0.040	0.049	0.060	0.054
S − A − B + 75	0.020	0.022	0.018	0.081	0.111	0.097
S − A − B + 85	0.108	0.109	0.092	0.202	0.196	0.179
S − A + B − 75	0.086	0.096	0.068	0.125	0.147	0.112
S − A + B − 85	0.108	0.132	0.130	0.151	0.174	0.169
S − A + B + 75	0.175	0.216	0.194	0.335	0.376	0.358
S − A + B + 85	0.273	0.265	0.293	0.325	0.318	0.357

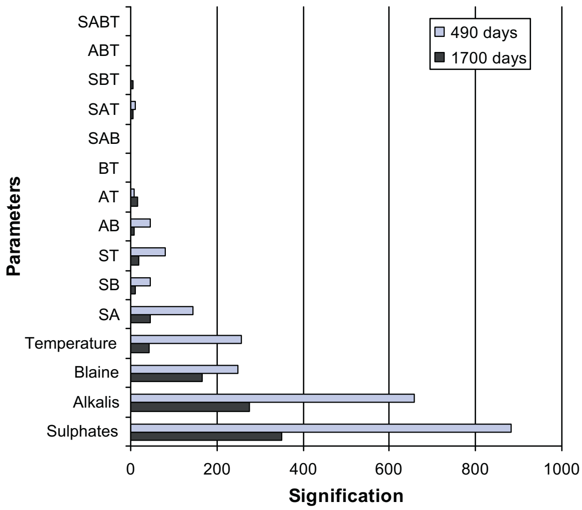

Fig. 2. Variance analysis. Signification of parameters with regard to expansion after 490 and 1700 days in water at 20 ± 2 °C. The limit of signification is about 4 for *F*(0.05; 1; 45). S for sulphates, A for alkalis, B for Blaine specific area, *T* for temperature.

for swelling ended with a continuation of slow swelling. The equation proposed by Larive (Eq. (2), Table 7) to describe the process must therefore be corrected to take account of the continuation of slow swelling in the case of internal sulphate attack (Eq. (3), Table 7) [5].

The expansion of concrete can be written for a chosen duration of immersion in water. The experimental plan is designed with two levels for each factor. That conducts to a linear model. As an example, two models ($Exp_{490days}$ and $Exp_{1700days}$) are proposed below for 490 days of immersion and 1700 days of immersion.

- $Exp_{(490days)(s,a,b,t)} = 0.243 + 0.135s + 0.116a + 0.072b + 0.068t + 0.055sa + 0.031sb + 0.041st + 0.031ab - 0.012at - 0.015sat$ (%).
- $Exp_{(1700days)(s,a,b,t)} = 0.314 + 0.144s + 0.127a + 0.099b + 0.050t + 0.052sa + 0.024sb + 0.034st + 0.021ab - 0.030at - 0.017sat$ (%).

In these two models, the terms «*s*», «*a*», «*b*» and «*t*» refer to normalised values in a range of −1 to +1 for the sulphates, the alkalis, the Blaine specific area and the temperature (Table 3). The constant is the mean expansion at 490 or 1700 days. The use of normalised values allows the comparison of the relative impact of each factor or interactions between the factors. These models can only be used in the experimental field defined for this factorial experience plan (Table 3).

In the case of both models, the first order parameters are the gypsum content and the alkali content. The interactions between the parameters have a second order impact, with the most important interaction being between the factors with a first order impact.

The concretes that did not swell during the test were those that had undergone heat treatment at 75 °C and which were made with cement with a sulphate content of 2.6%. This result backs up the French recommendations [31] which advocate the use of cement with the ES label [32], amongst other possibilities, in order to achieve the Bs, Cs and Ds prevention levels. A prevention level is defined as a function of both, the kind of structure (or concrete element in the structure) and, the level of humidity to which the concrete is exposed (three levels are defined between dry environment and presence of liquid water). The levels Bs, Cs and Ds refer to concrete elements exposed to water (drying and wetting cycles or permanent water) where the development of internal swelling reaction is little acceptable or not acceptable. The only concrete mix design that did not swell and which was made with cement with a sulphate content of 3.6% was that for which all the other parameters exhibited the low value of the studied domain. We can observe that changing from an "S + A − B − 75" combination to an "S + A − B + 75" combination resulted in swelling of the concrete. The increase of the specific area of the cement in this mix design encouraged DEF. One hypothesis to explain this result is that an activation of the least reactive aluminate phases (C_4AF) leads to an increase in the aluminates that can be remobilized during Delayed Ettringite Formation.

The decision to study a narrow temperature domain [75–85 °C] limits the impact of variations of this parameter. Except in the case of some concretes for which no significant swelling was measured (when no alkali was added), the principal effect of increasing the temperature to between 75 and 85 °C was to increase the rate of swelling. In this range of temperature, the continuation of swelling between 490 and 1700 days did not significantly change the model. The main impact of the variation in the studied factors remained the same, except for the temperature, whose impact diminished because of the continuation of swelling between 490 and 1700 days in some concretes that had been heat treated at 75 °C.

4.2. Change in the mass of the concretes

To illustrate the variation of the expansion versus the mass, the results for specimens with gypsum content of 3.6% are given in

Table 7
Modelling of the swelling plots.

Alkali aggregate reaction	Internal sulphate attack
$\varepsilon(t) = \varepsilon_\infty \dfrac{1 - e^{\frac{t}{\tau_{car}}}}{1 + e^{-\frac{t-\tau_{lat}}{\tau_{car}}}}$ (2)	$\varepsilon(t) = \varepsilon_{sig} \dfrac{1 - e^{\frac{t-t_0}{\tau_{car}}}}{1 + e^{-\frac{t-t_0-\tau_{lat}}{\tau_{car}}}} \left(1 + \dfrac{\tau_{car}}{\tau_{lat}} \alpha_{(W/C)} \dfrac{\beta\tau_{lat}}{\beta\tau_{lat} + t - t_0}\right)$ (3)

With
$\varepsilon(t)$: expansion at the time (t) (%).
ε_∞: maximum expansion (%).
ε_{sig}: expansion at the inflection point (%).
τ_{lat}: latency time at the inflection point (days).
τ_{car}: characteristic time that defines the swelling kinetic (days).
$\alpha_{(W/C)}$: correction term. $\alpha(0.48) = 0.0065$ and $\alpha(0.35) = 0.0160$ [3].
β: correction term. $\beta = 3$ [3].
t_0: age of the concrete on the day of immersion (days).
t: age of the concrete (days).

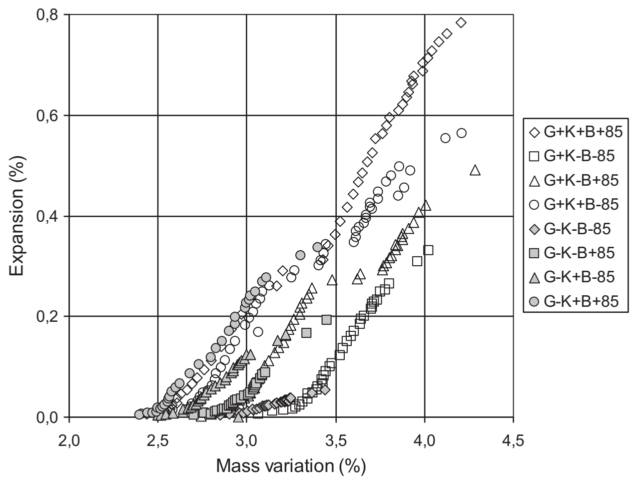

Fig. 3. Expansion versus mass variation of the concrete specimens heat treated at 85 °C.

Fig. 3. The results show, as already published in the literature, the absence of a single relationship between the expansion of the concrete and its change in mass during the test. However, in the case of considerable degrees of swelling (>0.1%), the mass of the concrete increased in proportion to its swelling. From an experimental standpoint, once the relationship between mass and expansion has been established for a given concrete, it may be possible to increase the frequency of mass measurements and reduce the frequency of swelling measurements.

4.3. Dynamic elastic modulus

In the case of a given concrete, the dynamic elastic modulus is linked to the static modulus. As this link is dependent on the degree of saturation, all the tests were conducted on specimens that were in totally saturated state. Monitoring the dynamic elastic modulus of the immersed concretes therefore has the benefit of allowing us to characterise the static elastic modulus with a non destructive method. The results of 1700 days of monitoring are illustrated in Fig. 4 for gypsum content of 2.6% and Fig. 5 for gypsum content of 3.6%. The swelling of the concretes does not systematically lead to a decrease in the elastic modulus. After a very long period (1700 days), an increase of the elastic modulus is clearly apparent,

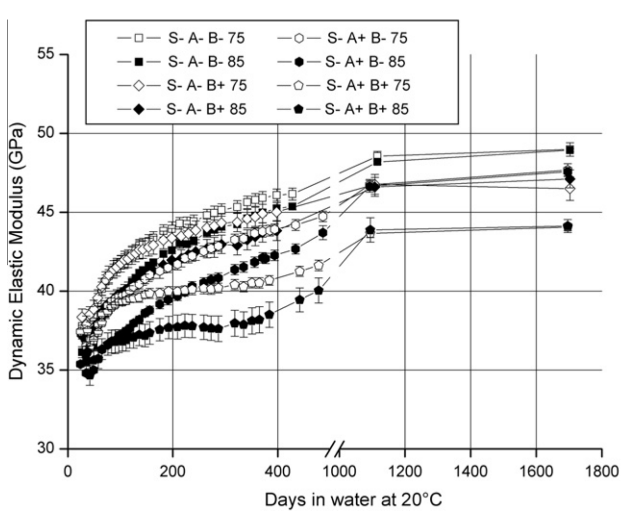

Fig. 4. Dynamic elastic modulus versus time of the concrete specimens with gypsum content of 2.6%.

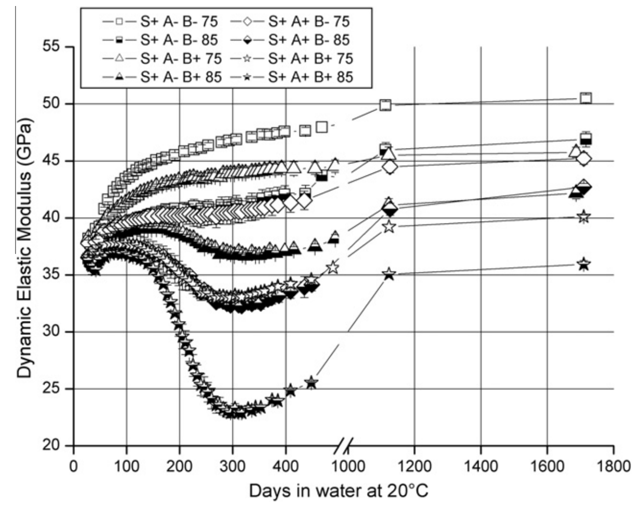

Fig. 5. Dynamic elastic modulus versus time of the concrete specimens with gypsum content of 3.6%.

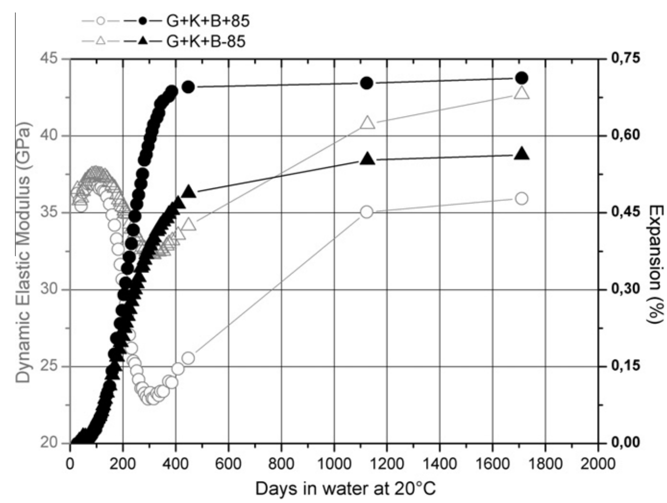

Fig. 6. Longitudinal expansion and variation in dynamic elastic modulus versus time for two concretes exhibiting a large modulus drop.

even if the swelling process has stabilized. This increase is particularly marked in the case of the most severely damaged concretes (Fig. 6). This can be explained by a reduction of the porosity related to the crack network of the concrete due to the formation of large ettringite crystals (due to Ostwald ripening). These crystals fill the cracks but do not exert enough crystallization pressure to cause further damage. Microscopic examination of the concrete (S + B + A + 85) by SEM shows that the concretes that have been kept in water for more than 1700 days are relatively compact due to massive ettringite filling their cracks and voids.

An increase in the elastic modulus after a large drop also occurs in the case of the alkali-aggregate reaction [29]. With concretes whose swelling attained a level of 0.25%, a 20% drop in Young's modulus was measured after 1 year of monitoring. During the year that followed, swelling stabilized and ceased to change, while the Young's modulus of the concrete increased to a value that was only 7% below its initial value.

5. Discussion

As the DEF index as defined by Zhang et al. [19] for these concretes is less than 1 in all cases, this criterion would not enable

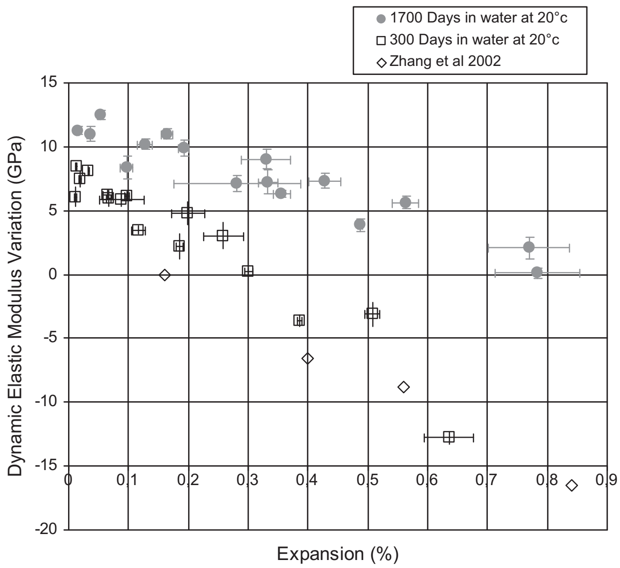

Fig. 7. Dynamic elastic modulus variation versus expansion after 300 or 1700 days in water at 20 ± 2 °C.

to identify the mix designs that presented a risk. The equation proposed by Kelham [23] does not allow us to interpret the results of this study either. There are major differences between these test programs (the temperature of heat treatment, the size of the specimens, the conservation conditions, proportioning, etc.) which cannot be covered by a single model. However, we can point out that both Kelham's model and that obtained in our study highlight the importance of the interaction between the alkali content and the sulphate content: the risk of swelling increases when these two factors increase, as long as the sulphate content remains below 4%. In our study, the ettringite that can be formed in the concretes accounted for between 14% (SO_3 = 2.6%) and 20% (SO_3 = 3.6%) of the volume of the hydrated cement paste. The amount of ettringite in the paste is therefore close to, if not higher than, the amount of ettringite that is required to exert a hydrostatic pressure of more than 2 MPa irrespective of the shape of the pores in which it precipitates [8].

Referring to Brunetaud's classification [4], we did not observe any negligible swelling in this test program (i.e. expansion bellow 0.04%). Weak swellings, which are defined as linear expansions whose final amplitude lies between 0.04% and 0.2%, were observed for seven types of specimens. In these low-expansion cases, there was no significant impact on the dynamic elastic modulus evolution. Large swellings, which are defined as sigmoid expansions whose final amplitude exceeds 0.4%, were observed for the other nine types of specimens. These high-expansion cases experienced a significant drop in dynamic modulus, which begins towards an expansion of 0.1%, immediately followed by an acceleration of the expansion. The drop in dynamic modulus reached 33% for the specimen with the highest rate of expansion. During the phase of stabilisation of the large swellings, the dynamic modulus turned from decrease to significant increase, due to a progressive filling of the previously-opened cracks by ettringite. For almost every case, this long run healing made it possible to recover the initial value of the dynamic modulus.

Fig. 7 shows the variation in the dynamic elastic modulus between the first measurements made during the first month of monitoring and the measurements made after 300 days or 1700 days as a function of the expansion achieved by the concretes at these times. The period of 300 days generally speaking corresponds to the largest modulus reduction in the test program. The specimens that had undergone considerable swelling at this time were those that had sustained the most damage, which concurs with Zhang's observations [18]. The same analysis conducted after 1700 days of monitoring shows that there is still an association between damage and expansion in the case of this batch of specimens, but there is no single relationship that connects these two parameters. In addition, an analysis of damage as a function of the kinetic of swelling at the inflexion point leads to the same conclusion. These findings do not therefore contradict those of Brunetaud et al. [4]. The expansion exhibited by the concretes during this study is in general proportional to the maximum rate of swelling, which leads to a good correlation between the drop in the elastic modulus and expansion on one hand and the drop in the elastic modulus and the maximum rate of expansion on the other.

6. Conclusion and outlook

Parametric modelling of the impact of a swelling reaction on concretes has enabled us to identify the relative impact of the studied parameters within a clearly defined study domain. Our study was conducted for sulphate contents of [2.6–3.6%], alkali contents of [0.50–1.00%] and a range of Blaine specific areas that is representative of French cements [3330–4635 cm^2/g]. Calculation of coefficients of both models and their respective ranking shows that coupling effects are essential on DEF-related expansions. Only factorial design of experiments method can highlight the relevant interactions between parameters. Most coefficients of the models obtained with the factorial plan of experiments are very significant. The empirical models allow to interpolate the behaviour of the concretes within the covered experimental field. Apart from this experimental field, these models cannot substitute for realistic tests performed on concrete. The variance analysis shows the major role of the sulphate content, the alkali content and the combined effect of both on the swelling potential when concrete temperature is maintained during 10 h between 75 °C and 85 °C at early ages on DEF-related expansions. In this experimental field, the concrete heat treatment during 10 h at 85 °C leads to DEF whatever are the cement parameters. However, if the temperature reached by the concrete is limited to 75 °C the risk of DEF can be limited by reducing the amount of sulphate, the alkali content and the Blaine specific area.

The French recommendations that set out to protect against the risk of internal sulphate attack in new concrete constructions have taken these results into account by giving particular importance to the alkali content of concrete and the sulphate content of cement [31]. In the case of concrete containing 400 kg/m^3 of cement and that has not undergone heating to over 75 °C, these tests confirm the absence of swelling when sulphate and alkali contents remain low.

The impact of a swelling reaction on the elastic modulus has been confirmed by a study that lasted for several years. As has been observed elsewhere in the case of the alkali-aggregate reaction, the dynamic elastic modulus can drop (by 37%) in the course of internal sulphate attack. However, the loss of elastic modulus is compensated by its gradual increase in the long term when the expansion phenomenon is slowing down. This late increase of elastic modulus is probably due to a later formation of ettringite in the voids.

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